Thermodynamics I

For an introduction to basic thermodynamics at the right level, see chapter 2 of Wang and Ricardo, volume 2. For more detail, see chapters 1–9, 19, and 20 of Blundell and Blundell. For interesting discussion, see chapters I-39 through I-43 of the Feynman lectures. There is a total of **78** points.

1 Ideal Gases and Heat Engines

Questions about ideal gas heat engines are straightforward. They were very common on the USAPhO a decade ago, though problems today tend to require a deeper understanding of thermodynamics. Nonetheless, it's fundamental material that you should know.

Idea 1

The ideal gas law comes in a few common forms,

$$PV = nRT = Nk_BT, \quad P = \frac{\rho RT}{\mu} = \frac{\rho k_B T}{m}.$$

Here, Avogadro's number is $N_A = N/n$, so that $R = N_A k_B$, m is the mass of a gas molecule, and $\mu = N_A m$ is the molar mass. The first law of thermodynamics says

$$dU = dW + dQ, \quad dW = -P\,dV.$$

The heat capacity at constant volume is defined so that $dU = nC_V\,dT$ at constant volume. As a result, if we define $C_P = C_V + R$, we have

$$Q = \begin{cases} nC_V \Delta T & \text{at constant volume} \\ nC_P \Delta T & \text{at constant pressure} \end{cases} \quad C_V = \begin{cases} 3R/2 & \text{monatomic} \\ 5R/2 & \text{diatomic} \\ 3R & \text{polyatomic} \end{cases}.$$

Using the first law, we can derive the results

$$W = -nRT \log \frac{V_f}{V_i} \text{ for isothermal expansion}$$

and

$$PV^\gamma = \text{constant for adiabatic expansion}, \quad \gamma = C_P/C_V,$$

both of which you should easily be able to rederive.

Idea 2

For a cyclic process that takes in heat Q_{in} from a hot reservoir at temperature T_H and outputs heat Q_{out} to a cold reservoir at temperature T_C, the work done is $W = Q_{\text{in}} - Q_{\text{out}}$. The efficiency $\eta = W/Q_{\text{in}}$ is maximized by the Carnot engine, for which $\eta = 1 - T_C/T_H$.

Remark

The study of thermodynamics arose from efforts in the early 19th century to understand the efficiency of steam engines. However, Carnot's ideal reversible engine doesn't resemble practical engines, since the isothermal steps take place at zero temperature difference, and therefore take infinite time. Suppose the isothermal steps take place at temperature $T_1 < T_H$ and $T_2 > T_C$, and that the rate of heat flow is proportional to the temperature difference. This engine isn't reversible, but it does yield a nonzero average power. When T_1 and T_2 are set to maximize the average power, it turns out the efficiency is simply $1 - \sqrt{T_C/T_H}$, and this expression more closely matches the efficiencies of real engines.

[2] **Problem 1.** Derive the Carnot efficiency using the fact that (a) the engine is reversible, so a complete cycle leaves the entropy of the universe unchanged, or (b) directly from idea 1.

Remark

The most common mistake students make in this problem set is forgetting to account for the work done by the atmosphere.

[3] **Problem 2.** 🕓 USAPhO 2009, problem A4.

[3] **Problem 3.** 🕓 USAPhO 2011, problem A1.

If you want further practice, see USAPhO 1998 A1, 2008 A2, and 2010 A3. This kind of routine question should be easy. Some competitions try to make them harder by making the cycles more complicated (some truly crazy ones have been considered in the literature), but this is contrived and doesn't really require much insight. Instead, we'll move on to slightly subtler problems.

Example 1

A cold room is initially at temperature T. The heater is turned on, raising the temperature to $T + \Delta T$. Assuming the thermal insulation is ideal, at most what fraction of the energy released by the heater stays in the room?

Solution

As long as the room has any contact with the outside at all, air will leak out to set the pressure equal to atmospheric pressure. Its volume also stays the same, so by the ideal gas law, Nk_BT stays the same, but this is proportional to the internal energy of the air. Thus, at most 0% of the energy released by the heater stays in the room; the increase in average energy per molecule is exactly compensated by the decrease in the number of molecules. If there are thermal losses, the total internal energy of the air in the room actually decreases.

Example 2

A thermally isolated cylinder is divided into two compartments by a thermally conductive piston. Initially, the piston divides the cylinder into two compartments, A and B, of equal volume $V/2$ and temperature T_0. One mole of monatomic gas is in each compartment. An external agent slowly moves the piston to the side until the volumes are $V/3$ and $2V/3$. Throughout this process, the temperature remains uniform. What is the final temperature?

Solution

The tricky thing about this problem is that the pressures in the two compartments aren't equal; this is possible because the external agent is holding the piston. Instead, the temperatures are made equal by heat conduction. The work done by the agent is

$$dW = -p_A\,dV_A - p_B\,dV_B = -RT\left(\frac{dV_A}{V_A} + \frac{dV_B}{V_B}\right).$$

On the other hand, this is also equal to the increase in energy,

$$dW = dU = \frac{3}{2}nR\,dT = 3R\,dT.$$

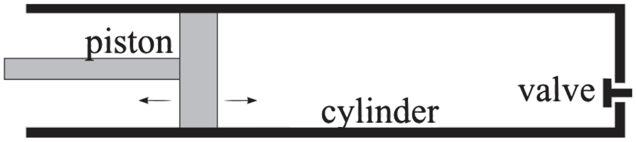
Combining the two gives a differential equation,

$$3\int\frac{dT}{T} = -\int\frac{dV_A}{V_A} - \int\frac{dV_B}{V_B}$$

which means the final temperature T_f obeys

$$3\log\frac{T_F}{T_0} = -\log\frac{2}{3} - \log\frac{4}{3} = \log\frac{9}{8}, \quad T_F = \frac{3^{2/3}}{2}T_0.$$

[3] **Problem 4** (EstPhO 2002)**.** In this problem we consider the combustion cycle of a car engine. Model the engine as a cylinder with a piston on the left and a valve on the right.



The steps of the process are as follows.

1. Gas entry: the piston moves from the rightmost position to the leftmost; fresh air comes in through the valve and fills the cylinder.
2. Pressure increase: the valve closes, and the piston quickly moves back to the rightmost position.
3. Work: fuel is injected in the cylinder and is ignited; you may model this process as occurring instantaneously. Then the gas starts expanding and pushes the piston to the leftmost position.
4. Gas disposal: the valve is opened. The piston is pushed to the right at constant pressure until it reaches its rightmost position, and the process then repeats.

Neglect friction and heat conduction, suppose the number of fuel molecules is negligible compared to the number of air molecules, and treat air as a diatomic ideal gas. Let k be the ratio of the maximum and minimum volumes of the cylinder. Draw the cycle on a PV diagram and find its efficiency.

[3] **Problem 5** (IZhO 2022). A quasistatic process is carried out with one mole of an ideal monatomic gas, as a result of which its initial volume $V_0 = 1\,\mathrm{m}^3$ increases four times, and the initial pressure $P_0 = 10^5\,\mathrm{Pa}$ decreases two times. For each small section of the quasistatic process, the ratio of work to the change in internal energy is the same. Find the total work done by the gas in this process.

[3] **Problem 6.** ⏲ USAPhO 2018, problem A3.

2 Dynamic Ideal Gases

Idea 3

Problems involving ideal gases can be mechanics questions. For example, the first law of thermodynamics becomes conservation of energy, where the energy includes the internal energy of the gas in addition to the usual kinetic and potential energy. You may also have to use the principles of hydrostatic equilibrium and Bernoulli's principle from **M7**.

Example 3

A space station is a large cylinder of radius R_0 filled with air molecules of mass m. The cylinder spins about its axis at an angular velocity ω, and the air rotates along with it. If the temperature T is constant inside the station, what is the ratio of the air pressure at the center of the station to the pressure at the rim?

Solution

If we work in a frame rotating with the space station, this is a fluid statics problem. By considering force balance on a thin parcel of air of radial thickness dr and area A, we have

$$A\,dP = \rho g_{\mathrm{eff}} A\,dr$$

where $g_{\mathrm{eff}} = \omega^2 r$ is the centrifugal acceleration. Applying the ideal gas law,

$$\frac{dP}{P} = \frac{m g_{\mathrm{eff}}}{k_B T}\,dr$$

which integrates to give

$$\frac{P(r=0)}{P(r=R_0)} = e^{-m\omega^2 r^2/2k_B T}.$$

[5] **Problem 7.** In this problem we'll make a simple model for the atmosphere.

(a) Assume the atmosphere to be an ideal gas at constant temperature T in mechanical equilibrium, with gas molecules of mass m. Show that the pressure depends on height as

$$P(h) = P_0\, e^{-mgh/k_B T}$$

by demanding that small parcels of gas be in mechanical equilibrium.

(b) The assumption of constant temperature is not very accurate. Sunlight warms air near the ground, causing large parcels of it to slowly rise; simultaneously other parcels of air slowly fall. This results in a well-mixed atmosphere and, since heat conduction in air is poor, the rising and falling processes are approximately adiabatic, not isothermal. Assuming the air molecules are diatomic with mass m, show that the temperature varies linearly with height. Does the atmosphere get colder or hotter with increasing height?

(c) Estimate the rate of temperature change with height numerically; is your result reasonable?

(d) Now ignoring the mixing effect of the sun, argue that an atmosphere with a temperature gradient or larger or smaller magnitude than the result you found in part (c) will be unstable or stable against spontaneous convection, respectively. (Hint: see idea 4.)

(e) $\star$ More generally, one might wonder how the total energy of the atmosphere, summed over all molecules, is divided into kinetic (i.e. thermal) and potential (i.e. gravitational) energy. Show that for *any* configuration in mechanical equilibrium (i.e. not necessarily adiabatic or isothermal), $E_{\text{grav}}/E_{\text{kin}}$ has the same value, and find this value.

When "thermal inversion" occurs, the temperature gradient has the opposite sign to the natural one you found in part (b), causing the atmosphere to be very stable against convection. Such events can cause very high air pollution in cities, since the pollutants can't escape. For more about atmospheric physics, see chapter 37 of Blundell.

[3] **Problem 8.** ⏲ USAPhO 1997, problem B2.

Remark

A Foehn is a hot, dry wind that comes down from a mountain range. This occurs in three steps. First, warm air rises adiabatically up the opposite side of the mountain range. As the air rises, it cools, causing the water vapor to condense and fall as rain. The now dry air then falls adiabatically down the mountain range. Since the heat capacity is now lower, the falling air heats up more than the rising air cooled down, becoming hot and dry at the bottom.

Idea 4

Consider an ideal gas in a container. In simple heat engine problems, we assume the gas stays in equilibrium, meaning that it has a single, well-defined pressure and temperature throughout. But in almost all real-world applications, there will be some deviations from equilibrium.

For example, suppose you started to heat the bottom of the container. Then the gas would no longer be in thermal equilibrium, because it doesn't have a uniform temperature, and if the heating is sufficiently sudden, it wouldn't be in mechanical equilibrium, because it wouldn't have a uniform pressure either. For a human-scale container, mechanical equilibrium is usually reestablished quickly, by a readjustment of the density. Thermal equilibrium is reestablished on a longer timescale, as energy spreads out through heat transfer.

In this simple example, we were able to talk about the temperature of individual parts of the gas, even though the gas as a whole wasn't in thermal equilibrium. That's because each piece of the gas is in thermal equilibrium with itself, so temperature can be defined locally.

In more violent situations, even that might not be possible.

In general, conservation laws are quite useful for nonequilibrium problems, because following the detailed dynamics may be impossible.

Example 4

A thermally insulated chamber contains a vacuum; it is connected to the outside by a small valve. The valve is opened until the air inside the chamber reaches atmospheric pressure, then closed. The temperature of the air outside the chamber is T_0. Treating the air as diatomic, what is the temperature T of the air inside the chamber?

Solution

Let the chamber have a volume V, and let the atmospheric pressure be p_0. As our system, consider the set of all air that eventually makes it inside the chamber, and suppose this air has volume V_0 before it enters the chamber. The work done on this air by the entire rest of the atmosphere, as it enters the chamber, is $p_0 V_0$. The final internal energy of the air is

$$E = \frac{5}{2} nRT_0 + p_0 V_0 = \frac{7}{2} nRT_0.$$

On the other hand, we also have $E = nC_V T = (5/2)nRT$, which gives

$$T = \frac{7}{5} T_0.$$

At that point, the flow stops because the pressure is equalized, even though the temperature isn't. This is an example of mechanical equilibrium being attained before thermal equilibrium. (In the long run, the temperature will equality too, by heat transfer through the walls.)

You might suspect this violates energy conservation. Where does the extra thermal energy of the gas come from? It's taken from the air behind it pushing it into the chamber. But on a deeper level, the energy is ultimately gravitational: the entire atmosphere shrinks down toward the Earth a bit once the volume V_0 of air is removed from it, and this decrease in gravitational potential energy is the same as the increase in thermal energy of this system.

You might also suspect this violates the second law of thermodynamics. We started with everything at temperature T_0, and got a part of the system to a higher temperature than the rest. Using this temperature difference, you could then run a heat engine, which apparently allows you to get work for free. The problem with this reasoning is that heating isn't the *only* thing that happens; the initially empty chamber also gets filled up. After running the heat engine, you would have to pump the air out to reset the system to its original state, which takes work. Another way of thinking about it is that the entropy actually doesn't decrease when the air goes into the chamber. The thermal energy is less evenly distributed, decreasing entropy, but the air now has more volume to occupy, increasing entropy.

[2] **Problem 9.** Consider two cylinders A and B of equal volume V, connected by a thin valve. The

cylinders are thermally insulated from the environment, but conduct heat well between each other. Cylinder A is equipped with a piston that can compress the gas inside. Initially, the valve is sealed, cylinder A contains an ideal monatomic gas at temperature T, and cylinder B contains a vacuum.

Now suppose the valve is opened, and the piston is slowly pushed inward so that the pressure in cylinder A remains constant, until it cannot go any further. What is the final temperature of the gas, and what is the final volume of cylinder A?

[4] **Problem 10.** Consider a cylinder of gas with cross-sectional area A and volume V. Assume all surfaces are frictionless and thermally insulating. A piston of mass m is placed snugly on top, and the entire setup is inside an atmosphere with pressure P_{atm}.

(a) First suppose the system is in equilibrium, so that the pressure of the gas inside is $P_{\text{atm}} + mg/A$. The piston is then given a slight downward displacement. Find the angular frequency of small oscillations by assuming the ideal gas law always holds for the gas as a whole. This setup is known as the Ruchardt experiment, and can be used to determine γ.

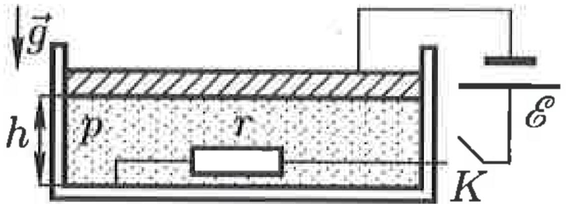
(b) Under what circumstances is the result of part (a) a good approximation?

(c) Now suppose that instead, the piston is initially suspended from a thread carrying tension mg, so that the pressure of the gas is just P_{atm}. Suddenly, the thread is cut. The piston falls down the cylinder and bounces up and down several times before eventually coming to rest. Explain why the equation $PV^\gamma = \text{const}$ cannot be used to determine the final state.

(d) Assuming the final downward displacement of the piston is d, find the net work done on the gas, assuming that *all* of the energy dissipated goes into the gas.

(e) Find d and the final temperature of the gas, assuming the gas is monatomic.

[3] **Problem 11** (Russia 2008)**.** A cylinder with a metal bottom and insulating walls is underneath a thin massive metal piston located at a height h, which is much smaller than the cylinder diameter. A resistor of resistance r is placed inside and connected to an electric circuit with an emf $\mathcal{E}$.



The circuit is connected to the piston and cylinder bottom with light flexible wires. Initially, the switch is open, the cylinder is filled with helium at a pressure $p \gg \epsilon_0 \mathcal{E}^2/h^2$, which you can treat as a monatomic ideal gas with a dielectric constant of 1. The system is thermally insulated, placed in vacuum, and at thermal and mechanical equilibrium. Then the switch K is closed. Find the height H of the piston after a long time.

[4] **Problem 12** (Cahn)**.** A long, cylindrical tank of length L and radius R is placed on a carriage that can slide without friction on rails. The mass of the empty tank and carriage is M. Initially, the tank is filled with an ideal gas of total mass $m \ll M$ at pressure P_0 and temperature T_0. The left end of the tank is heated to a fixed temperature T_1, while the right end of the tank has its temperature fixed at T_0, where $T_1 - T_0 \ll T_0$.

In this problem, you need only work to first order in $(T_1 - T_0)/T_0$. Suppose that the temperatures have been maintained for long enough for the gas to enter a steady state.

(a) Argue that the temperature $T(x)$ of the gas in the tank is a linear function of position.

(b) Find the density of the gas in the tank as a function of position.

(c) Find the distance the carriage has moved.

(d) In order for the carriage to have moved, a horizontal force had to have acted on it. Where did this force come from?

[4] **Problem 13.** APhO 2010, problem 3B. A mathematical problem on a collapsing bubble.

Remark

Students often get stuck on problem 14, which is about a chimney above a furnace, because they forget that the base of the furnace is open to the air, and so its pressure is equal to the atmospheric pressure. Indeed, in real life it is very hard to produce air pressures substantially above atmospheric pressure. You need to either tightly seal a container (which applies to the engines of the problems above, or to pressure cookers), or make the air move very quickly (which occurs in jet engines, covered in **T3**, or in specialized "blast" furnaces).

[4] **Problem 14.** IPhO 2010, problem 2. A neat, tricky problem about how chimneys work.

3 Statistical Mechanics

There are fundamentally two approaches to describing systems of many interacting particles: bottom-up and top-down. In the top-down approach of thermodynamics, we try to roughly describe the behavior of the whole system in terms of a few macroscopically measurable observables, such as pressure and temperature, and hope this is enough information to extract what we want. In the bottom-up approach, we start by analyzing the behavior of individual molecules, governed by Newtonian mechanics. Of course, we can't do this exactly, but it turns out to be possible to make probabilistic statements about individual molecules. This is the approach of statistical mechanics.

Idea 5: Boltzmann Distribution

The probability distribution for the states of a particle in a system of temperature T is proportional to $e^{-E/k_B T}$. Specifically:

- For quantum systems, where the energy levels are discrete, the probability of being in a state n with energy E_n is proportional to $e^{-E_n/k_B T}$.
- For a single classical particle, the state is instead specified by (x, p), the position and the momentum, and the probability density in this space, called phase space, is proportional to $e^{-E(x,p)/k_B T}$.

It isn't possible to derive the Boltzmann distribution from anything we've already covered, but you'll see in **T2** how it emerges from a simpler postulate.

Example 5: Isothermal Atmosphere

Do problem 7 using statistical mechanics.

Solution

The energy is

$$E(\mathbf{x}, \mathbf{p}) = mgz + \frac{p^2}{2m}.$$

The probability distribution for height z is found by integrating over all the other quantities,

$$p(z) \propto \int dx \int dy \int d^3\mathbf{p}\, e^{-E(\mathbf{x},\mathbf{p})/k_BT} = e^{-mgz/k_BT} \int dx \int dy \int d^3\mathbf{p}\, e^{-p^2/2m}.$$

However, the remaining integrals are just constants independent of z, so we just get

$$p(z) \propto e^{-mgz/k_BT}.$$

Since the particles are assumed independent (since we have an ideal gas), the probability for a particle to be at a point is proportional to the density of gas at that point. We see the density falls exponentially with height, so by the ideal gas law, the pressure does too.

[1] **Problem 15.** Do example 3 using statistical mechanics.

[3] **Problem 16.** Some basic computations for ideal gases.

(a) For an ideal gas in a box, show that the probability distribution of speeds obeys

$$p(v) \propto v^2 e^{-mv^2/2k_BT}$$

at any point in the box, regardless of the shape of the box.

(b) Compute the most probable speed, i.e. the location of the peak of this probability distribution.

(c) Show that the average kinetic energy is $\langle mv^2/2 \rangle = 3k_BT/2$. This is a special case of the equipartition theorem, shown below. (Hint: you will have to do a somewhat tricky integral. See the example below and the examples in **P1** for guidance.)

Remark: Deriving the Maxwell Velocity Distribution

Statistical mechanics implies that the velocity distribution in an ideal gas is

$$p(\mathbf{v}) \propto e^{-mv^2/k_BT}$$

which is a three-dimensional Gaussian. This result was first derived by Maxwell, long before statistical mechanics was understood, using an ingenious argument.

Suppose the ideal gas is inside a rectangular box, so that collisions with its left and right sides determine v_x, the front and back sides determine v_y, and the top and bottom sides determine v_z. The distributions of velocities in each direction should therefore be independent, and identical by rotational symmetry, so that we can write

$$p(\mathbf{v}) = f(v_x)f(v_y)f(v_z)$$

for some function f. Moreover, by rotational symmetry, $p(\mathbf{v})$ can only depend on v^2. Taking the logarithm of both sides and defining $g = \log f$, we have

$$\log p = g(v_x) + g(v_y) + g(v_z)$$

and the right-hand side only depends on v^2. This is only possible if $g(x) = -\alpha x^2$ for a constant α, which yields $p(\mathbf{v}) \propto e^{-\alpha v^2}$. The value of α can be determined by demanding the pressure match the ideal gas law (see example 7).

However, assuming independence of the components of velocity v_i is a one-off trick, which doesn't work in general. For example, when relativistic effects are important, the v_i are *not* independent – if v_x is near c, then v_y and v_z must be small. (Concretely, if a collision with a wall in the yz plane applies a relativistic impulse Δp_x, then it also changes v_y and v_z since $\mathbf{p} = \gamma m \mathbf{v}$.) The v_i also aren't independent if quantum statistics matters. For example, if the gas particles are fermions, as discussed in **X1**, then no two can be in the same state, so some final $\mathbf{v}$'s are forbidden. So in modern statistical mechanics, we usually use a different derivation, which is equally slick but generalizes better.

The idea is that in thermodynamic equilibrium, time reversal symmetry implies every reaction is in "detailed balance". Specifically, suppose that when two gas molecules collide elastically, with velocities $(\mathbf{v}_1, \mathbf{v}_2)$, they exit with velocities $(\mathbf{v}_1', \mathbf{v}_2')$. Then the rate at which this happens must be equal to the rate at which gas molecules with velocities $(\mathbf{v}_1', \mathbf{v}_2')$ collide, which causes them to exit with velocities $(\mathbf{v}_1, \mathbf{v}_2)$. (Otherwise, you could distinguish a video of the molecules' dynamics from the same video played in reverse.) Therefore,

$$p(\mathbf{v}_1)p(\mathbf{v}_2)\,|\mathbf{v}_1 - \mathbf{v}_2| = p(\mathbf{v}_1')p(\mathbf{v}_2')\,|\mathbf{v}_1' - \mathbf{v}_2'|$$

where the relative velocity factor is present because a larger relative velocity gives more opportunities for collision. However, for elastic collisions, the initial and final relative velocities are the same, so this factor just cancels out.

Now, by rotational symmetry we have $p(\mathbf{v}) = f(v^2)$ for some function f, so

$$f(v_1^2)f(v_2^2) = f(v_1'^2)f(v_2'^2)$$

Furthermore, by energy conservation we have $v_1^2 + v_2^2 = v_1'^2 + v_2'^2$. Then the above equation can only be satisfied if f is an exponential, $f(x) \propto e^{-\alpha x}$, which again gives $p(\mathbf{v}) \propto e^{-\alpha v^2}$.

Idea 6: Equipartition Theorem

Suppose some degree of freedom in phase space contributes to the energy by a power law,

$$E \propto p^n \text{ or } H \propto x^n.$$

Then in thermal equilibrium, there is an average energy of $k_B T/n$ in this degree of freedom. The proof of this is just a straightforward generalization of the reasoning in problem 16(c). Note that the proof of the equipartition theorem is entirely classical, i.e. it holds when a system is adequately described by classical mechanics. It does a good job of describing the heat capacities of simple gases near room temperature, as you can see here.

Here are a few important examples of the equipartition theorem.

- A mass on a spring in one dimension has
$$E = \frac{p^2}{2m} + \frac{kx^2}{2}.$$
This involves two degrees of freedom in phase space, each with $n = 2$, so the average energy is $2(k_BT/2) = k_BT$.

- In problem 7 you considered a system with a linear potential energy, $E(h) = mgh$. This is a degree of freedom with $n = 1$, and accordingly, the average potential energy of each molecule is k_BT.

- An atom in a solid can be thought of as attached to its neighbors by springs. Since the atom is in three dimensions, this yields three copies of the first example, and hence an average thermal energy of $3k_BT$. This implies that the specific heat per atom in a solid is $3k_B$ (or equivalently $3R$ per mole), which is called the Dulong–Petit law.

Incidentally, because systems in thermal equilibrium are also in long-term mechanical equilibrium, the virial theorem from **M6** applies, and tells us the ratio between the average kinetic and potential energy; of course, it matches the result of the equipartition theorem. You'll investigate some more key examples in the problems below.

Example 6

A free particle in one dimension, $H = p^2/2m$, has energy levels $E_n = n^2 E_0$ for $n = 0, 1, 2, \ldots$, as we will show in **X1**. Show that the average energy at high temperatures is consistent with the equipartition theorem.

Solution

The probability of being in energy level n is proportional to $e^{-n^2E_0/k_BT}$. Therefore, by normalizing the probability distribution, the probability itself is
$$p_n = \frac{e^{-n^2E_0/k_BT}}{\sum_{m=0}^\infty e^{-m^2E_0/k_BT}}.$$
Therefore, the average value of the energy is
$$\langle E \rangle = \sum_{n=0}^\infty n^2 E_0 \, p_n = \frac{\sum_{n=0}^\infty n^2 E_0 e^{-n^2E_0/k_BT}}{\sum_{n=0}^\infty e^{-n^2E_0/k_BT}}.$$
At high temperatures, this quantum result should reduce to the classical result of the equipartition theorem. Note that at such temperatures, the typical values of n will be very high. Therefore, we can treat the sums over n as continuous integrals,
$$\langle E \rangle \approx \frac{\int_0^\infty dn \, n^2 E_0 e^{-n^2E_0/k_BT}}{\int_0^\infty dn \, e^{-n^2E_0/k_BT}} = \frac{\int_0^\infty x^2 e^{-x^2} \, dx}{\int_0^\infty e^{-x^2} \, dx} \, k_BT$$

where we switched to the dimensionless variable $x = \sqrt{n^2 E_0 / k_B T}$. Evaluating either of these integrals is tricky, but we can relate them using integration by parts,

$$\int_0^\infty x^2 e^{-x^2} \, dx = \int_0^\infty (2xe^{-x^2} \, dx) \, \frac{x}{2} = \frac{1}{2} \int_0^\infty e^{-x^2} \, dx.$$

Therefore, the ratio of integrals is $1/2$, giving an average energy of $k_B T/2$ as expected.

[3] **Problem 17.** The energy of a photon is $E = pc$.

(a) Treating the photon classically, compute the average energy of a photon moving in one dimension, assuming it obeys the Boltzmann distribution with temperature T. Check that the result obeys the equipartition theorem.

(b) Generalize this result to three dimensions to compute γ for a 3D photon gas.

[3] **Problem 18.** A one-dimensional quantum harmonic oscillator has energy levels $E_n = nE_0$ for $n \geq 0$, as you will show in **X1**.

(a) Compute the average energy of the system at temperature T.

(b) Show that at high temperatures, the average energy obeys the equipartition theorem.

(c) Show that the energy at low temperatures is instead exponentially suppressed. This is why some modes are said to "freeze out", so they do not contribute to C_V.

The phenomenon of "freezing out" was one of the greatest puzzles of classical physics in the 19th century, though nobody anticipated the resolution would be as strange as quantum mechanics.

[3] **Problem 19.** The Boltzmann distribution can be normalized to a probability distribution by dividing by the so-called partition function $Z = \sum_n e^{-E_n/k_B T}$.

(a) For a quantum harmonic oscillator, compute the probability of occupancy of the ground state (i.e. the lowest energy state) at temperature T.

(b) Do the same for the hydrogen atom, where $E_n = -E_0/n^2$ for $n \geq 1$. You should get a rather strange answer. Does it make physical sense?

[3] **Problem 20.** To model paramagnetism, consider a set of N independent magnetic dipoles in a vertical magnetic field B and temperature T. Each dipole has two possible quantum states, spin up and spin down, with energies $\boldsymbol{\mu} \cdot \mathbf{B}$ and magnetic dipole moment $\mu_z = \pm e\hbar/2m$.

(a) Defining the magnetization M as the total magnetic moment, find the average magnetization of the magnet as a function of T.

(b) Show that $M \propto 1/T$ in the limit of high T. This result is called Curie's law.

Remark

In principle, all of our results about statistical mechanics can be derived by following the microscopic dynamics, e.g. the collisions of atoms with each other for a gas. It's just very hard to do so in practice.

However, you can still get a bit of insight in simple cases. For example, consider a one-dimensional ideal gas in a uniform gravitational field, $E = p^2/2m + mgh$. Since the kinetic energy is a quadratic degree of freedom, and the potential energy is a linear degree of freedom, the average potential energy must be twice the average kinetic energy. Furthermore, this should be true no matter how rarely collisions happen; less frequent collisions simply mean it takes longer to get to thermal equilibrium, without changing what that equilibrium is.

Therefore, we have the concrete, classical mechanical prediction that a mass bouncing elastically on the ground, suffering no collisions at all, will have an average potential energy equal to twice its average kinetic energy, which you can verify directly from Newton's laws.

Here's a more subtle puzzle. In our analysis of the isothermal atmosphere, we found that the distribution of speeds is the same everywhere. But if you look at any one particle, it will clearly pick up speed as it falls down. How is this self-consistent? Wouldn't this tend to increase the temperature at lower heights?

Again, it's easiest to think about this situation in the limit of a very thin gas, where collisions are rare. Indeed, each particle that starts at the top of the atmosphere will pick up a lot of speed as it falls down. But why are there any particles at the top at all? Because at the bottom of the atmosphere, which is much more dense, particles occasionally get a lot of energy through collisions, which propels them to the top. In equilibrium, the particles going down *do* arrive at the bottom with unusually high speed, but they're balanced out by the unusually fast particles going the other way. Keeping track of the details here can be quite complex, especially when collisions are frequent, but miraculously the Boltzmann distribution takes care of it all for us!

4 Kinetic Theory

Idea 7

Kinetic theory is the branch of statistical mechanics that focuses on the motion of individual molecules in a gas. It can get quite mathematically involved, since one must consider the effects of molecular collisions, which is why the subject is usually reserved for graduate school. However, in some simple situations, collisions can be neglected, effectively making the molecules independent.

Example 7: Ideal Gas Law

Derive the ideal gas law using kinetic theory.

Solution

Without loss of generality, we consider a cubical container of gas of side length L and N gas molecules. Consider the pressure exerted on a wall aligned with the yz plane. A given gas molecule will hit this wall with period $2L/v_x$, transferring a momentum of $2p_x$. Then the pressure on the wall is

$$P = \frac{F}{A} = \frac{1}{L^2}\frac{N\langle p_x v_x\rangle}{L}.$$

This can be written as

$$P = \frac{N}{V}\langle p_x v_x\rangle = \frac{N}{V}\frac{\langle \mathbf{p}\cdot\mathbf{v}\rangle}{3} = \frac{N}{3V}\langle mv^2\rangle = \frac{Nk_BT}{V}$$

where we used rotational symmetry and the equipartition theorem.

Of course, this calculation was doable because we neglected interactions between different gas molecules. However, this doesn't matter as much as one might think. We assumed molecules can cross the whole container without colliding, but if they do, the derivation still basically works because they just transfer their momentum to another molecule. As long as the molecules are moving freely most of the time, the answer above is approximately right.

In **T2**, we'll see how an attractive interaction lowers the pressure. In **T3**, we'll see that when the gas gets very dense, this leads to a dramatic effect: the gas condenses into a liquid.

[2] **Problem 21.** Use kinetic theory to find the pressure of a photon gas (i.e. an ideal gas of massless particles, which satisfy $E = pc$) in terms of its total internal energy U and volume V. Use this result to find γ for a photon gas, where γ is defined so that PV^γ is constant in an adiabatic process.

Example 8

An astronaut of mass M stranded in outer space makes a primitive rocket as follows. They take a piece of dry ice of mass $m \ll M$ and molar mass μ and put it in a long, thin glass held at temperature T. The dry ice sublimates, and the astronaut points the opening of the glass in the opposite of the direction they want to go. Estimate, within an order of magnitude, how fast the astronaut is going after all the dry ice is gone.

Solution

Let m' be the mass of a molecule of dry ice. By the equipartition theorem, the molecules have speed

$$v \sim \sqrt{\frac{kT}{m'}} = \sqrt{\frac{NkT}{Nm'}} = \sqrt{\frac{RT}{\mu}}.$$

The molecules exit the glass traveling more or less in the same direction, so by momentum conservation the final speed of the astronaut is on the order of

$$\frac{m}{M}v = \frac{m}{M}\sqrt{\frac{RT}{\mu}}.$$

We have implicitly assumed that the glass is long enough that the molecules get into thermal equilibrium with the glass before they leave it. For a short glass, the answer would instead depend on the typical speeds of molecules at the moment they sublimate.

Example 9

A container of volume V is filled with a gas of uniform temperature T, and placed in a vacuum. If a small hole is punched in the container and gas slowly leaks out, how does the temperature in the container change over time?

Solution

The mean free path λ is the average distance a gas molecule moves before it hits another one. Let d be the width of the hole. There are two important limiting cases.

If $\lambda \ll d$, then molecules can't make it out of the hole without undergoing many collisions. Thus, if the gas has some average flow velocity, its molecules will be carried along with it. We can thus treat the gas like a continuous fluid, and the logic of example 4 applies. The gas inside the container does $P\,dV$ work on the gas exiting and hence loses energy. Thus, the remaining gas cools down, so the temperature of the container decreases over time. (Doing this problem quantitatively requires the analogue of Bernoulli's principle for gases, which we derive in **T3**.)

If $d \ll \lambda$, then molecules fly out of the hole without encountering any others at all; this is the regime of "effusion". Therefore, we shouldn't think in terms of an average gas pressure or flow velocity, but rather just consider each molecule on its own. An individual molecule has a greater chance of escaping through the hole if it's moving faster. Thus, the molecules that come out will on average be higher energy than the ones that stay in the container. So just as in the opposite limit, the remaining gas cools down, but for a totally different reason. (This case is treated quantitatively in problem 2.24 of Wang and Ricardo, volume 2.)

Remark

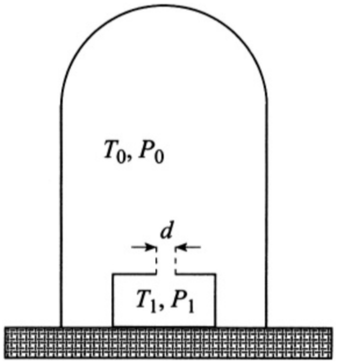
The previous example implies that a gas of uniform temperature can turn into a hot gas and a cold gas without needing any external work, which seems to directly contradict the second law of thermodynamics! To phrase it another way, you can use the free temperature difference to run a heat engine, which seemingly allows perpetual motion.

Of course, the resolution is that the total entropy of the gas is still going up. The kinetic energy is getting less spread out, but the positions of the atoms are getting more spread out, since some can now be outside the container. Thus, the "perpetual motion" only works as long as the gas is still leaking out of the container; it stops once the density becomes uniform. The lesson here is that, while most setups extract work from a temperature difference, more generally you can extract it from any potential increase in entropy; in this case, it comes from an initial difference in densities.

[2] **Problem 22** (Kalda)**.** Natural uranium consists of mainly two isotopes, ^{238}U and ^{235}U, and the relative concentration of the latter is 0.7%. Uranium is enriched by a multi-stage process, where

at each stage, evaporated UF_6 is led through a porous wall. The porous wall is a thin film with microscopic holes, much smaller than the mean free path of the molecules, but larger than the dimension of the molecules. How many stages are needed to increase the $^{235}\mathrm{U}$ content to 1.4%? The molar mass of fluoride is $19\,\mathrm{g/mol}$.

[2] **Problem 23** (Cahn)**.** A small vessel with a tiny hole of diameter d is placed inside a chamber, where the pressure is so low that the mean free path is $\lambda \gg d$. The temperature of the gas in the chamber is T_0, and the pressure is P_0. The temperature in the vessel is kept at a constant $T_1 = 4T_0$.



What is the pressure inside the vessel when steady state is reached?

[5] **Problem 24.** In this problem, we consider a simple kinetic theory model for "transport" in a sparse gas. Two parallel plates are at a distance L from each other. The space between the plates is filled with a gas of density ρ, with molecule of mass m. Assume that the gas density is low enough to neglect collisions between gas molecules, and that all radiation effects can be neglected.

(a) Suppose the two plates are held at temperatures $T + \Delta T$ and T, where $\Delta T \ll T$. Assume that when gas molecules bounce from a plate, they instantly obtain the plate's temperature. Estimate the heat flux per area P/A (in units of $\mathrm{W/m^2}$) between the plates. (This determines the thermal conductivity, to be defined in **T2**.)

(b) Suppose the top plate moves with a transverse speed $v_\parallel$ parallel to itself, while the bottom plate is still, and $mv_\parallel^2 \ll k_B T$. Assume that when gas molecules bounce from a plate, they obtain that plate's transverse speed. Estimate the force per area F/A on each plate. (This determines the viscosity, as defined in **M7**.)

Both the thermal conductivity and viscosity are associated with the transport of conserved quantities (energy and transverse momentum, respectively) through the gas. Now, above we have neglected collisions entirely, which is unrealistic for most gases unless they are extremely sparse. However, it's possible to get some rough estimates for what happens in the presence of collisions.

(c) Let σ be the cross-sectional area of a gas molecule. Estimate the mean free path d of a gas molecule.

(d) Our previous analysis held when $L \ll d$. Now suppose, more realistically, that $L \gg d$. Estimate P/A and F/A in the steady state. (Hint: consider a set of imaginary planes that are spaced by a distance d, and consider the heat/momentum flow between pairs of adjacent planes; for such pairs, collisions can be neglected.)

(e) Suppose a gas molecule begins at the top plate, and both plates have temperature T. Again assuming that $L \gg d$, estimate the typical time it takes before the gas molecule hits the bottom plate. (Hint: model the position of the particle as a sum of random steps, and recall the facts about variance in **P2**.)

For a clear discussion of the ideas of this problem, see sections 7.3 and 7.4 of The Art of Insight.

[5] **Problem 25.** ⏱ EuPhO 2017, problem 2. A nice problem using many of the above ideas.

Example 10

A box of mass M contains an ideal gas consisting of many particles, with total mass M_g. Find $\langle V_x^2 \rangle$, the average mean-square velocity of the box along the x-axis.

Solution

This problem illustrates how kinetic theory can get very subtle, even when we don't have to keep track of the detailed collision dynamics. First, note that if each gas molecule has mass m, then each one has $\langle v_x^2 \rangle = k_B T/m$ by equipartition. Now there are two simple arguments that give different answers.

1. If we apply equipartition of energy to the box itself, we get $\langle V_x^2 \rangle = k_B T/M$.
2. The total momentum of the box and gas together is zero, so

$$MV_x = -m \sum_{i=1}^{N} v_{x,i}.$$

On the other hand, by the rules of error propagation introduced in **P1**,

$$\left\langle \left(m \sum_{i=1}^{N} v_{x,i} \right)^2 \right\rangle = m^2 \, N \, \frac{k_B T}{m} = k_B T M_g$$

which implies

$$\langle V_x^2 \rangle = \frac{M_g}{M^2} k_B T.$$

What's going on? It actually turns out that both of these arguments are wrong in general, but each one is correct in different limiting cases.

The problem with the first argument is that the derivation of equipartition of energy assumes that each degree of freedom is independent of the others, i.e. it ignores the fact that when the box picks up momentum, the gas must have a compensating opposite total momentum. The problem with the second argument is that it assumes the velocities of the molecules are independent of each other, which is also not quite true.

Note that the energy and momentum of the box are related by $E = P^2/2M$. Now, if the box is heavy, $M \gg M_g$, it can store lots of momentum even when it has very little energy, and conversely when it has a decent amount of energy it must have an enormous momentum. The latter implies that the first argument fails. But the second argument works, because the box serves as a "sink" for momentum. For example, the gas molecules could all be moving to the right, and that would be easily compensated by the box moving slightly to the left.

If the box is light, $M \ll M_g$, then it can have lots of energy even having negligible momentum. In this case, the first argument works, because the box doesn't ever have enough momentum to substantially affect the gas's behavior. But the second argument fails, because if the box can't carry much momentum, then the gas molecules' momenta must almost entirely cancel out among themselves by momentum conservation, meaning that they are not independent.

The general solution can be found with a simple trick. The problem with the equipartition argument is essentially that we treat the box velocity V_x as independent of the center of mass velocity of the gas, $\overline{v}_x$. We can therefore switch to the variables

$$v_{\mathrm{CM}} = \frac{M_g \overline{v}_x + M V_x}{M_g + M}, \quad v_{x,\mathrm{rel}} = V_x - \overline{v}_x.$$

These two new variables are independent, because the momentum conservation constraint just says the former is always equal to zero. Thus, we can safely apply equipartition of energy to v_{rel}. Recalling the reduced mass idea from **M6**, we have

$$E \supset \frac{1}{2} \mu v_{x,\mathrm{rel}}^2, \quad \mu = \frac{M M_g}{M + M_g}.$$

By equipartition we have

$$\langle v_{x,\mathrm{rel}}^2 \rangle = \frac{k_B T}{\mu}$$

and by momentum conservation we conclude

$$\langle V_x^2 \rangle = \left(\frac{M_g}{M + M_g} \right)^2 \langle v_{x,\mathrm{rel}}^2 \rangle = \frac{k_B T}{M} \frac{M_g}{M + M_g}$$

which reduces to the two answers found above in the appropriate limits. This problem turns out to be relevant to astrophysics, where it is a toy model for the dynamics of a supermassive black hole in a galaxy. For a complete analysis which starts from the postulates of kinetic theory, see this paper.

Remark

Above, we discussed the distinction between "bottom-up" and "top-down" approaches, but there are also bridges between the subjects. For example, suppose you had a large volume of gas, where the mean free path is much smaller than the container's size. Here, the gas can come into equilibrium *locally*, at which point we may describe its state with a temperature field $T(\mathbf{x}, t)$, along with other fields, such as pressure, density, and velocity. This leads to the subject of hydrodynamics, which can be derived from kinetic theory. We started on this subject in **M7**, but there we neglected any thermal properties; we will return to it in **T3**.

On the other hand, suppose an entire macroscopic system is already in thermal equilibrium. The system is homogeneous, so there's no need for hydrodynamics, but it can still be difficult to infer the macroscopic behavior of the system. For example, if you had water molecules at a given temperature and pressure, it's still hard to calculate what phase they're in! In physics, our best tool for this kind of problem is the renormalization group, which bridges the gap by considering a series of "coarse-graining" operations that gradually zoom out. This is a deep subject, typically reserved for graduate courses.

Thermodynamics I

For an introduction to basic thermodynamics at the right level, see chapter 2 of Wang and Ricardo, volume 2. For more detail, see chapters 1–9, 19, and 20 of Blundell and Blundell. For interesting discussion, see chapters I-39 through I-43 of the Feynman lectures. There is a total of **78** points.

1 Ideal Gases and Heat Engines

Questions about ideal gas heat engines are straightforward. They were very common on the USAPhO a decade ago, though problems today tend to require a deeper understanding of thermodynamics. Nonetheless, it's fundamental material that you should know.

Idea 1

The ideal gas law comes in a few common forms,

$$PV = nRT = Nk_BT, \quad P = \frac{\rho RT}{\mu} = \frac{\rho k_B T}{m}.$$

Here, Avogadro's number is $N_A = N/n$, so that $R = N_A k_B$, m is the mass of a gas molecule, and $\mu = N_A m$ is the molar mass. The first law of thermodynamics says

$$dU = dW + dQ, \quad dW = -P\,dV.$$

The heat capacity at constant volume is defined so that $dU = nC_V\,dT$ at constant volume. As a result, if we define $C_P = C_V + R$, we have

$$Q = \begin{cases} nC_V\Delta T & \text{at constant volume} \\ nC_P\Delta T & \text{at constant pressure} \end{cases} \quad C_V = \begin{cases} 3R/2 & \text{monatomic} \\ 5R/2 & \text{diatomic} \\ 3R & \text{polyatomic} \end{cases}.$$

Using the first law, we can derive the results

$$W = -nRT \log \frac{V_f}{V_i} \text{ for isothermal expansion}$$

and

$$PV^\gamma = \text{constant for adiabatic expansion}, \quad \gamma = C_P/C_V,$$

both of which you should easily be able to rederive.

Idea 2

For a cyclic process that takes in heat Q_{in} from a hot reservoir at temperature T_H and outputs heat Q_{out} to a cold reservoir at temperature T_C, the work done is $W = Q_{\text{in}} - Q_{\text{out}}$. The efficiency $\eta = W/Q_{\text{in}}$ is maximized by the Carnot engine, for which $\eta = 1 - T_C/T_H$.

Remark

The study of thermodynamics arose from efforts in the early 19th century to understand the efficiency of steam engines. However, Carnot's ideal reversible engine doesn't resemble practical engines, since the isothermal steps take place at zero temperature difference, and therefore take infinite time. Suppose the isothermal steps take place at temperature $T_1 < T_H$ and $T_2 > T_C$, and that the rate of heat flow is proportional to the temperature difference. This engine isn't reversible, but it does yield a nonzero average power. When T_1 and T_2 are set to maximize the average power, it turns out the efficiency is simply $1 - \sqrt{T_C/T_H}$, and this expression more closely matches the efficiencies of real engines.

[2] **Problem 1.** Derive the Carnot efficiency using the fact that (a) the engine is reversible, so a complete cycle leaves the entropy of the universe unchanged, or (b) directly from idea 1.

Solution. (a) At the end of a heat engine cycle, the working fluid comes back to its original state, so its entropy is unchanged. When an engine is reversible, it also leaves the entropy of the surroundings unchanged, so that the total entropy of the universe doesn't go up. (If it did go up, then we wouldn't be able to reverse the cycle, by the second law of thermodynamics.)

The increase in entropy of the cold reservoir is Q_{out}/T_C, while the decrease in entropy of the hot reservoir is Q_{in}/T_H. Setting these equal to each other, we find

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_C}{T_H}$$

as desired.

(b) There are a lot of ways to do this, but we'll show one that will be useful later. Note that during the heating and cooling steps, we have

$$dQ = dU - dW = nC_V\,dT + P\,dV.$$

Using the ideal gas law, we have

$$dT = \frac{1}{nR}(P\,dV + V\,dP)$$

and plugging this in gives

$$dQ = \frac{C_P}{R}P\,dV + \frac{C_V}{R}V\,dP.$$

Dividing by T and using the ideal gas law again, we have

$$\frac{dQ}{T} = nC_P\frac{dV}{V} + nC_V\frac{dP}{P} = nC_V\frac{d(PV^\gamma)}{PV^\gamma}.$$

Therefore, the quantity $\Delta Q/T$ for the heating and cooling steps only depends on the change of the quantity PV^γ. This is equal and opposite for those steps, since PV^γ stays the same in the adiabatic steps, which means $Q_{\text{in}}/T_H = Q_{\text{out}}/T_C$. The derivation then continues as in part (a). (Of course, what we've done here is essentially just deriving the expression for the entropy, up to constants, without explicitly calling it that. This will be explored in more detail in **T2**.)

Remark

The most common mistake students make in this problem set is forgetting to account for the work done by the atmosphere.

[3] **Problem 2.** 🕒 USAPhO 2009, problem A4.

[3] **Problem 3.** 🕒 USAPhO 2011, problem A1.

If you want further practice, see USAPhO 1998 A1, 2008 A2, and 2010 A3. This kind of routine question should be easy. Some competitions try to make them harder by making the cycles more complicated (some truly crazy ones have been considered in the literature), but this is contrived and doesn't really require much insight. Instead, we'll move on to slightly subtler problems.

Example 1

A cold room is initially at temperature T. The heater is turned on, raising the temperature to $T + \Delta T$. Assuming the thermal insulation is ideal, at most what fraction of the energy released by the heater stays in the room?

Solution

As long as the room has any contact with the outside at all, air will leak out to set the pressure equal to atmospheric pressure. Its volume also stays the same, so by the ideal gas law, $N k_B T$ stays the same, but this is proportional to the internal energy of the air. Thus, at most 0% of the energy released by the heater stays in the room; the increase in average energy per molecule is exactly compensated by the decrease in the number of molecules. If there are thermal losses, the total internal energy of the air in the room actually decreases.

Example 2

A thermally isolated cylinder is divided into two compartments by a thermally conductive piston. Initially, the piston divides the cylinder into two compartments, A and B, of equal volume $V/2$ and temperature T_0. One mole of monatomic gas is in each compartment. An external agent slowly moves the piston to the side until the volumes are $V/3$ and $2V/3$. Throughout this process, the temperature remains uniform. What is the final temperature?

Solution

The tricky thing about this problem is that the pressures in the two compartments aren't equal; this is possible because the external agent is holding the piston. Instead, the temperatures are made equal by heat conduction. The work done by the agent is

$$dW = -p_A \, dV_A - p_B \, dV_B = -RT \left(\frac{dV_A}{V_A} + \frac{dV_B}{V_B} \right).$$

On the other hand, this is also equal to the increase in energy,

$$dW = dU = \frac{3}{2} n R \, dT = 3R \, dT.$$

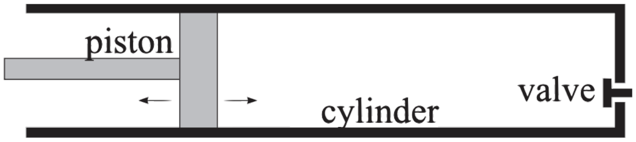
Combining the two gives a differential equation,

$$3\int \frac{dT}{T} = -\int \frac{dV_A}{V_A} - \int \frac{dV_B}{V_B}$$

which means the final temperature T_f obeys

$$3\log\frac{T_F}{T_0} = -\log\frac{2}{3} - \log\frac{4}{3} = \log\frac{9}{8}, \quad T_F = \frac{3^{2/3}}{2}T_0.$$

[3] **Problem 4** (EstPhO 2002)**.** In this problem we consider the combustion cycle of a car engine. Model the engine as a cylinder with a piston on the left and a valve on the right.



The steps of the process are as follows.

1. Gas entry: the piston moves from the rightmost position to the leftmost; fresh air comes in through the valve and fills the cylinder.
2. Pressure increase: the valve closes, and the piston quickly moves back to the rightmost position.
3. Work: fuel is injected in the cylinder and is ignited; you may model this process as occurring instantaneously. Then the gas starts expanding and pushes the piston to the leftmost position.
4. Gas disposal: the valve is opened. The piston is pushed to the right at constant pressure until it reaches its rightmost position, and the process then repeats.

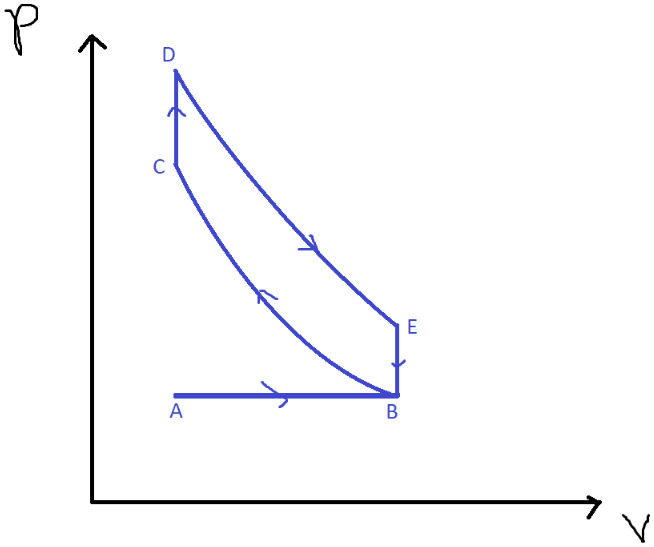
Neglect friction and heat conduction, suppose the number of fuel molecules is negligible compared to the number of air molecules, and treat air as a diatomic ideal gas. Let k be the ratio of the maximum and minimum volumes of the cylinder. Draw the cycle on a PV diagram and find its efficiency.

Solution. This problem is a bit trickier because it's less clear how to treat the steps. Of course, the second step is just an adiabatic compression, but the third is subtle. Since the number of fuel molecules is negligible, burning the fuel essentially just rapidly deposits energy into the system, raising its temperature. Thus, the first half of the third step is an isochoric (constant volume) heating; the second half of the third step is an adiabatic expansion.

Finally, the fourth and first steps should be regarded as one unit. When the valve is opened, the gas in the cylinder quickly falls to atmospheric pressure, as it freely expands out. Then the piston moves to the right, doing work $P_{\text{atm}}\Delta V$. In the first step, the piston moves to the left, pulling in fresh air and doing work $-P_{\text{atm}}\Delta V$. So the first half of the fourth step has an isochoric pressure decrease. The second half of the fourth step, and the first step, do no net work, and function solely to pull in fresh air.

This tells us what's going on, but where are the heat reservoirs? The heating step occurs when the fuel is burned, so the burnt fuel itself is effectively the hot reservoir. The gas is cooled by letting it leave and replacing it with new gas, so in some sense the atmosphere is the cold reservoir. But unlike the other examples of heat engines above, we use a different set of gas every cycle.

The PV diagram is shown below.



The first, second, third, fourth bullet steps correspond to AB, BC, CD+DE, and EB+BA respectively. Since BC and DE are adiabats ($P_E V_B^\gamma = P_D V_A^\gamma$ and $P_C V_A^\gamma = P_B V_B^\gamma$), the net work is

$$W = \oint p\,dV = \frac{P_D V_A - P_E V_B}{\gamma - 1} + \frac{P_B V_B - P_C V_A}{\gamma - 1}.$$

The heat from the fuel, Q, can be found with the internal energy change from C to D:

$$Q = C_V n(T_D - T_C) = \frac{C_V}{R} V_A (P_D - P_C) = \frac{(P_D - P_C)V_A}{\gamma - 1}.$$

Thus the efficiency can be found with $\epsilon = W/Q$ and $P_E = P_D k^{-\gamma}$, $P_B = P_C k^{-\gamma}$,

$$\epsilon = \frac{W}{Q} = \frac{(P_D - P_C)V_A - (P_E - P_B)V_B}{(P_D - P_C)V_A} = 1 - k^{1-\gamma}.$$

For diatomic gas, $\gamma = 7/5$, so $\epsilon = 1 - 1/k^{2/5}$.

[3] **Problem 5** (IZhO 2022)**.** A quasistatic process is carried out with one mole of an ideal monatomic gas, as a result of which its initial volume $V_0 = 1\,\mathrm{m}^3$ increases four times, and the initial pressure $P_0 = 10^5\,\mathrm{Pa}$ decreases two times. For each small section of the quasistatic process, the ratio of work to the change in internal energy is the same. Find the total work done by the gas in this process.

Solution. This problem is good practice for working with the laws of thermodynamics directly. Let $\eta = dW/dU$ be the constant ratio of work to internal energy change. By combining the results $dW = P\,dV$, $dU = (3/2)R\,dT$, and $PV = RT$, and following essentially the same derivation as that for an adiabatic process, we find

$$-\frac{dP}{P} = \left(1 - \frac{2}{3\eta}\right)\frac{dV}{V}$$

which implies

$$P \propto V^{(2/3\eta)-1}.$$

In other words, this is like an adiabatic process, but with a different effective value of γ. Using the given initial and final conditions, we have $\eta = 4/3$, so that $P \propto V^{-1/2}$. Thus,

$$W = \int P\, dV = \int_{V_0}^{4V_0} P_0 \left(\frac{V_0}{V}\right)^{1/2} dV = 2P_0V_0 = 2 \times 10^5\,\mathrm{J}.$$

This problem might look contrived, but "polytropic" processes where PV^β is constant, for a general value of β, are commonly considered in engineering thermodynamics.

In physics we often assume processes are adiabatic, $\beta = \gamma$, but in real life nothing is ever an ideal adiabatic process. Instead, engineers parametrize this by allowing β to be general, and measuring its value. As a simple concrete example, if the chamber containing the gas also contains some dirt, in thermal equilibrium of the gas, that dirt contributes to the system's heat capacities C_V and C_P. It therefore shifts the effective value of γ away from its ideal gas value.

[3] **Problem 6.** 🕓 USAPhO 2018, problem A3.

2 Dynamic Ideal Gases

Idea 3

Problems involving ideal gases can be mechanics questions. For example, the first law of thermodynamics becomes conservation of energy, where the energy includes the internal energy of the gas in addition to the usual kinetic and potential energy. You may also have to use the principles of hydrostatic equilibrium and Bernoulli's principle from **M7**.

Example 3

A space station is a large cylinder of radius R_0 filled with air molecules of mass m. The cylinder spins about its axis at an angular velocity ω, and the air rotates along with it. If the temperature T is constant inside the station, what is the ratio of the air pressure at the center of the station to the pressure at the rim?

Solution

If we work in a frame rotating with the space station, this is a fluid statics problem. By considering force balance on a thin parcel of air of radial thickness dr and area A, we have

$$A\, dP = \rho g_{\text{eff}} A\, dr$$

where $g_{\text{eff}} = \omega^2 r$ is the centrifugal acceleration. Applying the ideal gas law,

$$\frac{dP}{P} = \frac{m g_{\text{eff}}}{k_B T}\, dr$$

which integrates to give

$$\frac{P(r=0)}{P(r=R_0)} = e^{-m\omega^2 r^2/2k_BT}.$$

[5] **Problem 7.** In this problem we'll make a simple model for the atmosphere.

(a) Assume the atmosphere to be an ideal gas at constant temperature T in mechanical equilibrium, with gas molecules of mass m. Show that the pressure depends on height as

$$P(h) = P_0 \, e^{-mgh/k_B T}$$

by demanding that small parcels of gas be in mechanical equilibrium.

(b) The assumption of constant temperature is not very accurate. Sunlight warms air near the ground, causing large parcels of it to slowly rise; simultaneously other parcels of air slowly fall. This results in a well-mixed atmosphere and, since heat conduction in air is poor, the rising and falling processes are approximately adiabatic, not isothermal. Assuming the air molecules are diatomic with mass m, show that the temperature varies linearly with height. Does the atmosphere get colder or hotter with increasing height?

(c) Estimate the rate of temperature change with height numerically; is your result reasonable?

(d) Now ignoring the mixing effect of the sun, argue that an atmosphere with a temperature gradient or larger or smaller magnitude than the result you found in part (c) will be unstable or stable against spontaneous convection, respectively. (Hint: see idea 4.)

(e) $\star$ More generally, one might wonder how the total energy of the atmosphere, summed over all molecules, is divided into kinetic (i.e. thermal) and potential (i.e. gravitational) energy. Show that for *any* configuration in mechanical equilibrium (i.e. not necessarily adiabatic or isothermal), $E_{\text{grav}}/E_{\text{kin}}$ has the same value, and find this value.

When "thermal inversion" occurs, the temperature gradient has the opposite sign to the natural one you found in part (b), causing the atmosphere to be very stable against convection. Such events can cause very high air pollution in cities, since the pollutants can't escape. For more about atmospheric physics, see chapter 37 of Blundell.

Solution. (a) The ideal gas law becomes $PV = Nk_BT$, and the density is $\rho = Nm/V$, so $Pm = \rho k_B T$. By considering forces on a parcel of height dh and cross sectional area A, we see

$$A \, dP = -\rho g A \, dh$$

which implies

$$\frac{dP}{P} = -\frac{mg}{k_B T} dh.$$

Integrating yields the desired result.

(b) Since the expansion is adiabatic, $T^\gamma P^{1-\gamma}$ is constant, so $T \propto P^{1-1/\gamma}$. This implies

$$\frac{dT}{T} = \frac{dP}{P}(1 - 1/\gamma).$$

Since the motion of the parcels of air is slow, hydrostatic equilibrium remains approximately true. Using the equation derived in part (a) gives

$$\frac{dT}{T} = -\frac{mg}{k_B T}(1 - 1/\gamma) \, dh$$

which simply rearranges to

$$\frac{dT}{dh} = -\frac{mg}{k_B}(1 - 1/\gamma)$$

which is a linear decrease as desired.

(c) We have that

$$\frac{dT}{dh} = -\frac{mg}{k_B}\frac{2}{7} \approx -\frac{2}{7}\frac{(30\,{}^{\mathrm{g}}\!/\!_{\mathrm{mol}})(9.8\,{}^{\mathrm{m}}\!/\!_{\mathrm{s}^2})}{(8.314\,{}^{\mathrm{kg\,m}^2}\!/\!_{\mathrm{s}^{-2}\mathrm{K}^{-2}\mathrm{mol}^{-1}})} \approx -10\,\mathrm{K/km}$$

which is reasonable. One reason it's a bit unrealistically high is because air typically contains water vapor, which increases the heat capacity.

(d) Suppose the temperature gradient is smaller in magnitude than the gradient we found above. Consider a packet of air that is perturbed and moves upward. As it moves upward, it expands adiabatically, lowering its temperature; since the existing temperature gradient is less than in the well-mixed adiabatic atmosphere, the packet will end up colder than its surroundings. However, it is also at the same pressure because mechanical equilibrium is quickly reached, so since $P \propto \rho T$, the density is higher and it falls back down. Hence the situation is stable. The same reasoning occurs in reverse for a larger temperature gradient.

(e) In mechanical equilibrium, the pressure differential should balance the gravitational pull.

$$dP = -\rho g\, dh$$

The thermal energy for an ideal gas is $E_{\text{kin}} = \int \beta k_B T\, dN$ where $\beta = C_V/R$. The potential energy of the molecule is $E_{\text{grav}} = \int gh\, dM$, where N represents number of molecules and M as the cumulative mass of the atmosphere (so $dM = m\, dN$, and $dM = \rho A\, dh$). The differential forms are

$$dE_{\text{kin}} = \beta k_B T\, dM/m, \qquad dE_g = gh\, dM.$$

Since $\rho = mP/k_B T$ from ideal gas law and substituting in $dM = \rho A\, dh$, we have

$$dE_{\text{kin}} = \beta P A\, dh \qquad dE_g = \rho g h A\, dh$$

We can find the total kinetic energy by integrating by parts. Let the atmosphere end at height H (where we could also take $H \to \infty$).

$$E_{\text{kin}} = \beta A \int_0^H P\, dh = \beta \left(A P(H) H - 0 - \int_0^H hA\, dP \right).$$

Since at the top of the atmosphere, it supports nothing, $P(H) = 0$. We also have $dP = -\rho g\, dh$ for mechanical equilibrium:

$$E_{\text{kin}} = \beta \int_0^H \rho g h A\, dh = \beta E_{\text{grav}}.$$

Thus, we conclude that

$$\boxed{\frac{E_{\text{grav}}}{E_{\text{kin}}} = \frac{R}{C_V}}.$$

For monatomic gases, this ratio is 2/3, while for diatomic gases like air, it's 2/5.

By the way, this result is actually a corollary of the virial theorem, which we met in **M6**. The virial theorem states that for particles interacting by a power law potential $V \propto r^n$ in long-term mechanical equilibrium, we have $\langle K \rangle = \frac{n}{2}\langle V \rangle$ on average. In this case, the particles are the gas molecules and the Earth, which interact with $n = 1$, so that we expect $\langle V \rangle / \langle K \rangle = 2$.

Here, $\langle V \rangle$ corresponds to what we've called E_{grav}, but we need to be careful with $\langle K \rangle$. The proof of the virial theorem doesn't account for the energy of any degrees of freedom that aren't acted on by the force, which here includes the internal degrees of freedom of the gas, and the horizontal translational degrees of freedom. We should therefore single out the vertical translational kinetic energy, $\langle K \rangle = E_{\text{kin}}(R/2C_V)$, giving the expected result. (We also should add on the vertical kinetic energy of the Earth, but this is negligible.) Thus, you could also have solved this problem in one step using the virial theorem, which illustrates its power.

[3] **Problem 8.** ⏲ USAPhO 1997, problem B2.

Remark

A Foehn is a hot, dry wind that comes down from a mountain range. This occurs in three steps. First, warm air rises adiabatically up the opposite side of the mountain range. As the air rises, it cools, causing the water vapor to condense and fall as rain. The now dry air then falls adiabatically down the mountain range. Since the heat capacity is now lower, the falling air heats up more than the rising air cooled down, becoming hot and dry at the bottom.

Idea 4

Consider an ideal gas in a container. In simple heat engine problems, we assume the gas stays in equilibrium, meaning that it has a single, well-defined pressure and temperature throughout. But in almost all real-world applications, there will be some deviations from equilibrium.

For example, suppose you started to heat the bottom of the container. Then the gas would no longer be in thermal equilibrium, because it doesn't have a uniform temperature, and if the heating is sufficiently sudden, it wouldn't be in mechanical equilibrium, because it wouldn't have a uniform pressure either. For a human-scale container, mechanical equilibrium is usually reestablished quickly, by a readjustment of the density. Thermal equilibrium is reestablished on a longer timescale, as energy spreads out through heat transfer.

In this simple example, we were able to talk about the temperature of individual parts of the gas, even though the gas as a whole wasn't in thermal equilibrium. That's because each piece of the gas is in thermal equilibrium with itself, so temperature can be defined locally. In more violent situations, even that might not be possible.

In general, conservation laws are quite useful for nonequilibrium problems, because following the detailed dynamics may be impossible.

Example 4

A thermally insulated chamber contains a vacuum; it is connected to the outside by a small valve. The valve is opened until the air inside the chamber reaches atmospheric pressure, then closed. The temperature of the air outside the chamber is T_0. Treating the air as diatomic, what is the temperature T of the air inside the chamber?

Solution

Let the chamber have a volume V, and let the atmospheric pressure be p_0. As our system, consider the set of all air that eventually makes it inside the chamber, and suppose this air has volume V_0 before it enters the chamber. The work done on this air by the entire rest of the atmosphere, as it enters the chamber, is p_0V_0. The final internal energy of the air is

$$E = \frac{5}{2}nRT_0 + p_0V_0 = \frac{7}{2}nRT_0.$$

On the other hand, we also have $E = nC_VT = (5/2)nRT$, which gives

$$T = \frac{7}{5}T_0.$$

At that point, the flow stops because the pressure is equalized, even though the temperature isn't. This is an example of mechanical equilibrium being attained before thermal equilibrium. (In the long run, the temperature will equality too, by heat transfer through the walls.)

You might suspect this violates energy conservation. Where does the extra thermal energy of the gas come from? It's taken from the air behind it pushing it into the chamber. But on a deeper level, the energy is ultimately gravitational: the entire atmosphere shrinks down toward the Earth a bit once the volume V_0 of air is removed from it, and this decrease in gravitational potential energy is the same as the increase in thermal energy of this system.

You might also suspect this violates the second law of thermodynamics. We started with everything at temperature T_0, and got a part of the system to a higher temperature than the rest. Using this temperature difference, you could then run a heat engine, which apparently allows you to get work for free. The problem with this reasoning is that heating isn't the *only* thing that happens; the initially empty chamber also gets filled up. After running the heat engine, you would have to pump the air out to reset the system to its original state, which takes work. Another way of thinking about it is that the entropy actually doesn't decrease when the air goes into the chamber. The thermal energy is less evenly distributed, decreasing entropy, but the air now has more volume to occupy, increasing entropy.

[2] **Problem 9.** Consider two cylinders A and B of equal volume V, connected by a thin valve. The cylinders are thermally insulated from the environment, but conduct heat well between each other. Cylinder A is equipped with a piston that can compress the gas inside. Initially, the valve is sealed, cylinder A contains an ideal monatomic gas at temperature T, and cylinder B contains a vacuum.

Now suppose the valve is opened, and the piston is slowly pushed inward so that the pressure in cylinder A remains constant, until it cannot go any further. What is the final temperature of the gas, and what is the final volume of cylinder A?

Solution. Suppose the pressure in cylinder A is always P. Suppose the final volume of A is V', and suppose the final temperature is T'. Then, the energy of the system before the compression is $E_i = \frac{3}{2}n_0RT$ where n_0 is the total number of moles of gas. The energy after the compression is $E_f = \frac{3}{2}n_0RT'$. We have that $E_f - E_i = P(V - V')$. The piston stops once the pressure in B is equal to P, so $PV' = nRT'$ and $PV = (n_0 - n)RT'$, so $P(V + V') = n_0RT'$. Therefore,

$$2n_0RT = 2PV = P(V - V') + P(V + V') = \frac{3}{2}n_0R(T' - T) + n_0RT',$$

so

$$2T = \frac{3}{2}(T' - T) + T' \implies 4T = 3T' - 3T + 2T' \implies \boxed{T' = \frac{7}{5}T}.$$

We see that

$$2PV' = P(V + V') - P(V - V') = n_0RT' - \frac{3}{2}n_0R(T' - T) = \frac{4}{5}n_0RT,$$

so $2\frac{V'}{V}n_0RT = \frac{4}{5}n_0RT$, so $\boxed{V' = 2V/5}$.

[4] **Problem 10.** Consider a cylinder of gas with cross-sectional area A and volume V. Assume all surfaces are frictionless and thermally insulating. A piston of mass m is placed snugly on top, and the entire setup is inside an atmosphere with pressure P_{atm}.

(a) First suppose the system is in equilibrium, so that the pressure of the gas inside is $P_{\text{atm}} + mg/A$. The piston is then given a slight downward displacement. Find the angular frequency of small oscillations by assuming the ideal gas law always holds for the gas as a whole. This setup is known as the Ruchardt experiment, and can be used to determine γ.

(b) Under what circumstances is the result of part (a) a good approximation?

(c) Now suppose that instead, the piston is initially suspended from a thread carrying tension mg, so that the pressure of the gas is just P_{atm}. Suddenly, the thread is cut. The piston falls down the cylinder and bounces up and down several times before eventually coming to rest. Explain why the equation $PV^\gamma = \text{const}$ cannot be used to determine the final state.

(d) Assuming the final downward displacement of the piston is d, find the net work done on the gas, assuming that *all* of the energy dissipated goes into the gas.

(e) Find d and the final temperature of the gas, assuming the gas is monatomic.

Solution. (a) When the mass has a displacement of x, let the gas pressure be P_x. Then

$$PV^\gamma = P_x(V - Ax)^\gamma$$

so

$$P_x = P\left(\frac{V}{V - Ax}\right)^\gamma \approx p\left(1 + \gamma\frac{Ax}{V}\right).$$

Thus, the force on the mass is

$$F = -(P_x - P)A \approx -P\gamma\frac{Ax}{V}A$$

so

$$\ddot{x} \approx -\frac{\gamma PA^2}{mV}x, \quad \omega = \sqrt{\frac{\gamma PA^2}{mV}}.$$

(b) First, we've treated the gas as always having the pressure of a *static* ideal gas. That means the piston needs to move slowly enough for the gas to have time to adjust to this pressure, i.e. the piston should always be moving much slower than the speed of sound in the gas. This happens automatically, as long as the amplitude is small enough.

Second, as mentioned in **M6**, even in the case where the piston is moving arbitrarily slowly, it has effective extra inertia because it needs to move the gas in front of it out of the way. That is, in the language of **M4**, the Lagrangian for the system should contain both the kinetic energy of the piston and the gas, and the latter contributes an effective extra inertia, lowering the frequency. This extra term is negligible as long as the density of the gas is much lower than the density of the piston.

For reasonable experimental setups, both of these conditions are easily satisfied. In real life, the hardest part of getting this to work is probably making the piston oscillate with low friction, while still being airtight.

(c) It depends on how you derive $PV^\gamma = \text{const}$. One way to derive it, which you saw in problem 1, is to write down basic results like $dW = -P\,dV$, $dU = nC_V\,dT$, and $PV = nRT$, and combine them. What could possibly go wrong with that? The problem is that during this process, the gas does not even have a uniform pressure or temperature; there is no such thing as a single P or T.

Another way to derive it, as we'll show in **T2**, is to argue that the entropy is constant. (Then we can ignore all the complicated stuff that happens in the middle, because entropy is a state function.) The entropy turns out to be a function of PV^γ, which implies PV^γ is constant. The reason this argument fails is because entropy *isn't* constant. As the piston's motion damps out, kinetic energy is dissipated to heat, increasing the entropy.

(d) The work done on the gas is

$$W = mgd + P_{\text{atm}}Ad$$

where we counted the work done by the weight of the piston, and the atmospheric work.

How does this energy get into the gas? As the piston bounces up and down, it creates sound waves in the gas. These eventually fall apart and turn into ordinary thermal energy, i.e. random motion of the gas molecules; this is what damps the motion of the piston even though it doesn't have any friction. However, sound waves are excited in the atmosphere during this processes as well, and this also carries energy away. We expect most of the energy to end up in the gas if the pressure variations in the gas are larger, e.g. with a very heavy weight. We assume that all of it ends up in the gas just for simplicity, since there's no reasonable way to compute the relative contributions.

(e) By conservation of energy,

$$W = \frac{3}{2}nR\Delta T.$$

On the other hand, by the ideal gas law,

$$\Delta(PV) = nR\Delta T$$

which means we have

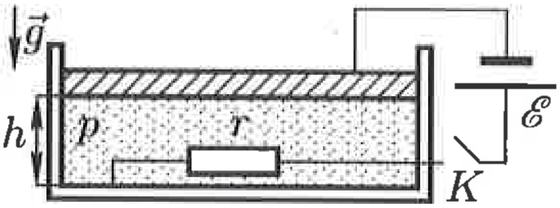
$$mgd + P_{\text{atm}}Ad = \frac{3}{2}\left(\left(P_{\text{atm}} + \frac{mg}{A}\right)(V - Ad) - PV\right).$$

Solving for d, we have

$$d = \frac{3}{5}\frac{mgV}{A(mg + P_{\text{atm}}A)}.$$

Interestingly, this approaches only 3/5 of the total height when mg goes to infinity.

[3] **Problem 11** (Russia 2008)**.** A cylinder with a metal bottom and insulating walls is underneath a thin massive metal piston located at a height h, which is much smaller than the cylinder diameter. A resistor of resistance r is placed inside and connected to an electric circuit with an emf $\mathcal{E}$.



The circuit is connected to the piston and cylinder bottom with light flexible wires. Initially, the switch is open, the cylinder is filled with helium at a pressure $p \gg \epsilon_0 \mathcal{E}^2/h^2$, which you can treat as a monatomic ideal gas with a dielectric constant of 1. The system is thermally insulated, placed in vacuum, and at thermal and mechanical equilibrium. Then the switch K is closed. Find the height H of the piston after a long time.

Solution. Several things happen at once. Energy is dissipated in the resistor, causing the gas to warm up and increase in pressure. At the same time, charge accumulates on the top and bottom plates, which form a parallel plate capacitor, causing them to attract each other. And when the piston moves, energy is exchanged between the gas and the capacitor. Keeping track of the detailed time evolution of the gas, piston, and RC circuit would be very complicated, but since we only care about the final state, we can use energy conservation instead.

The total energy added to the system is the work done by the battery, $\mathcal{E}q$, where q is the final charge on the capacitor plates, so energy conservation gives

$$\frac{3}{2}p_1V_1 + mgh + \mathcal{E}q = \frac{3}{2}p_2V_2 + mgH + \frac{q^2}{2C}.$$

We also know that in the final state,

$$q = C\mathcal{E} = \frac{\epsilon_0 A\mathcal{E}}{H}$$

where A is the surface area of the top and bottom plates. The attractive force between the plates is

$$F = \frac{q^2}{2\epsilon_0 A} = \frac{\epsilon_0 A\mathcal{E}^2}{2H^2}$$

which means the final pressure is

$$p_2 = p_1 + \frac{F}{A} = p_1 + \frac{\epsilon_0\mathcal{E}^2}{2H^2}.$$

Of course, we also have $V_1 = Ah$, $V_2 = AH$, $p_1 = p$, and force balance in the initial state implies $mgh = p_1V_1$. Carefully plugging all of this in and writing everything in terms of H/h and the small ratio $\epsilon_0\mathcal{E}^2/h^2p$ yields the result

$$\left(\frac{H}{h}\right)^2 - \frac{H}{h} = -\frac{\epsilon_0\mathcal{E}^2}{10h^2p}$$

and solving the quadratic gives

$$H = h\left(\frac{1}{2} + \sqrt{\frac{1}{4} - \frac{\epsilon_0\mathcal{E}^2}{10h^2p}}\right) \approx h - \frac{\epsilon_0\mathcal{E}^2}{10hp}.$$

[4] **Problem 12** (Cahn). A long, cylindrical tank of length L and radius R is placed on a carriage that can slide without friction on rails. The mass of the empty tank and carriage is M. Initially, the tank is filled with an ideal gas of total mass $m \ll M$ at pressure P_0 and temperature T_0. The left end of the tank is heated to a fixed temperature T_1, while the right end of the tank has its temperature fixed at T_0, where $T_1 - T_0 \ll T_0$.

In this problem, you need only work to first order in $(T_1 - T_0)/T_0$. Suppose that the temperatures have been maintained for long enough for the gas to enter a steady state.

(a) Argue that the temperature $T(x)$ of the gas in the tank is a linear function of position.

(b) Find the density of the gas in the tank as a function of position.

(c) Find the distance the carriage has moved.

(d) In order for the carriage to have moved, a horizontal force had to have acted on it. Where did this force come from?

Solution. (a) At steady state, the temperature of the gas at each location will be constant. Thus considering a thin cross section of thickness dx perpendicular to the cylinder's axis, the power going through it is $P = \kappa A dT/dx$ where κ and $A = \pi R^2$ are thermal conductivity and cross sectional area, respectively. In steady state, no net heat will enter/exit the gas, so P is constant, and with $T_1 - T_0 \ll T_0$, κ is constant. Thus dT/dx is constant (giving a linear $T(x) = T_1 - x(T_1 - T_0)/L$) with $x = 0$ and $x = L$ being the left and right ends respectively.

(b) The pressure is constant since horizontal pressure gradients would cause movements, and $\rho(x) = \frac{\mu P}{RT(x)}$, and a Taylor expansion gives us

$$\rho(x) \approx \frac{\mu P}{RT_1}\left(1 + \frac{x(T_1 - T_0)}{LT_1}\right).$$

Thus density is a linear function too, so the average density is $\rho_0 = \rho(L/2)$. Thus $\rho(L/2)\pi R^2 L = m$. From our $\rho(x)$ equation and taking first order approximations (uniform temperature), we get that

$$\frac{d\rho}{dx} = \frac{\mu P}{RT_1}\frac{T_1 - T_0}{LT_1} \approx \frac{\rho_0(T_1 - T_0)}{T_0 L}.$$

Thus

$$\rho(x) = \frac{m}{\pi R^2 L}\left(1 + \frac{T_1 - T_0}{T_0}\frac{x - L/2}{L}\right)$$

(c) The center of mass of the gas is at position

$$x_{\text{cm}} = \frac{1}{m}\int_0^L x\rho(x)\pi R^2\,dx = \frac{1}{L}\int_0^L \left(1 + \frac{T_1 - T_0}{T_0}\frac{x - L/2}{L}\right) x\,dx$$

$$x_{\text{cm}} = L\left(\frac{1}{2} + \frac{T_1 - T_0}{12T_0}\right)$$

Thus it was displaced to a distance $\Delta x = L(T_1 - T_0)/(12T_0)$ to the right with respect to the carriage.

Since there's no net force on the system, the center of mass of the entire system must stay stationary. Thus the displacement of the carriage D satisfies

$$MD + m(D + \Delta x) = 0$$

$$D = -L\frac{m}{M+m}\left(\frac{T_1 - T_0}{12T_0}\right)$$

The lowest order approximation yields

$$D = -L\,\frac{m}{M}\,\frac{T_1 - T_0}{12T_0}.$$

(d) When a gas molecule bounces off a hotter wall, it picks up kinetic energy in the collision; in other words, it bounces off faster than it came in. (This is the microscopic way heat is transferred through conduction.) That means that the pressure the gas molecules exert on a hot wall is actually *greater* than the pressure of the gas itself. (Similarly, the pressure on a cold wall is lower.) So even though the pressure of the gas was initially uniform, an unbalanced force was exerted on the walls, pushing the entire carriages in the direction of the hot wall.

[4] **Problem 13.** APhO 2010, problem 3B. A mathematical problem on a collapsing bubble.

Remark

Students often get stuck on problem 14, which is about a chimney above a furnace, because they forget that the base of the furnace is open to the air, and so its pressure is equal to the atmospheric pressure. Indeed, in real life it is very hard to produce air pressures substantially above atmospheric pressure. You need to either tightly seal a container (which applies to the engines of the problems above, or to pressure cookers), or make the air move very quickly (which occurs in jet engines, covered in **T3**, or in specialized "blast" furnaces).

[4] **Problem 14.** IPhO 2010, problem 2. A neat, tricky problem about how chimneys work.

3 Statistical Mechanics

There are fundamentally two approaches to describing systems of many interacting particles: bottom-up and top-down. In the top-down approach of thermodynamics, we try to roughly describe the behavior of the whole system in terms of a few macroscopically measurable observables, such as pressure and temperature, and hope this is enough information to extract what we want. In the bottom-up approach, we start by analyzing the behavior of individual molecules, governed by Newtonian mechanics. Of course, we can't do this exactly, but it turns out to be possible to make probabilistic statements about individual molecules. This is the approach of statistical mechanics.

Idea 5: Boltzmann Distribution

The probability distribution for the states of a particle in a system of temperature T is proportional to e^{-E/k_BT}. Specifically:

- For quantum systems, where the energy levels are discrete, the probability of being in a state n with energy E_n is proportional to e^{-E_n/k_BT}.

- For a single classical particle, the state is instead specified by (x, p), the position and the momentum, and the probability density in this space, called phase space, is proportional to $e^{-E(x,p)/k_BT}$.

It isn't possible to derive the Boltzmann distribution from anything we've already covered, but you'll see in **T2** how it emerges from a simpler postulate.

Example 5: Isothermal Atmosphere

Do problem 7 using statistical mechanics.

Solution

The energy is

$$E(\mathbf{x}, \mathbf{p}) = mgz + \frac{p^2}{2m}.$$

The probability distribution for height z is found by integrating over all the other quantities,

$$p(z) \propto \int dx \int dy \int d^3\mathbf{p}\, e^{-E(\mathbf{x},\mathbf{p})/k_BT} = e^{-mgz/k_BT} \int dx \int dy \int d^3\mathbf{p}\, e^{-p^2/2m}.$$

However, the remaining integrals are just constants independent of z, so we just get

$$p(z) \propto e^{-mgz/k_BT}.$$

Since the particles are assumed independent (since we have an ideal gas), the probability for a particle to be at a point is proportional to the density of gas at that point. We see the density falls exponentially with height, so by the ideal gas law, the pressure does too.

[1] **Problem 15.** Do example 3 using statistical mechanics.

Solution. Working again in the rotating frame of reference, integrating the centrifugal force gives a potential energy $U(r) = -m\omega^2 r^2/2$. Therefore, the radial probability distribution is

$$p(r) \propto e^{m\omega^2 r^2/2k_BT}.$$

By the definition of density, we have $\rho(r) \propto p(r)$, and at fixed temperature, the pressure $P(r)$ is prportional to the density by the ideal gas law. Thus, the pressure obeys

$$\frac{P(r=0)}{P(r=R_0)} = e^{-m\omega^2 r^2/2k_BT}.$$

exactly as found earlier.

[3] **Problem 16.** Some basic computations for ideal gases.

(a) For an ideal gas in a box, show that the probability distribution of speeds obeys

$$p(v) \propto v^2 e^{-mv^2/2k_BT}$$

at any point in the box, regardless of the shape of the box.

(b) Compute the most probable speed, i.e. the location of the peak of this probability distribution.

(c) Show that the average kinetic energy is $\langle mv^2/2 \rangle = 3k_BT/2$. This is a special case of the equipartition theorem, shown below. (Hint: you will have to do a somewhat tricky integral. See the example below and the examples in **P1** for guidance.)

Solution. (a) Note that the probability that a particle has velocity (v_x, v_y, v_z) is given by $f(v_x, v_y, v_z) dv_x dv_y dv_z$ where $f(v_x, v_y, v_z) \propto e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)}$. Then, we see that

$$p(v)\, dv \propto (4\pi v^2 dv) e^{-\frac{m}{2k_BT}v^2},$$

so $p(v) \propto v^2 e^{-mv^2/2k_BT}$.

(b) We set $p'(v) = 0$, so

$$v^2(-mv/k_BT)e^{-mv^2/2k_BT} = -2ve^{-mv^2/2k_BT} \implies v = \sqrt{\frac{2k_BT}{m}}.$$

(c) Using the result of part (a),

$$\langle mv^2/2 \rangle = \frac{\int_0^\infty \left(\frac{1}{2}mv^2\right) v^2 e^{-mv^2/2k_BT}\, dv}{\int_0^\infty v^2 e^{-mv^2/2k_BT}\, dv} = \frac{k_BT}{2} \frac{\int_0^\infty x^4 e^{-x^2/2}\, dx}{\int_0^\infty x^2 e^{-x^2/2}\, dx}$$

where we nondimensionalized the integral. To evaluate it, note that by integration by parts,

$$\int_0^\infty (x^3)(xe^{-x^2/2}\, dx) = 3\int_0^\infty x^2 e^{-x^2/2}\, dx.$$

Then the ratio of integrals is just 3, giving

$$\langle mv^2/2 \rangle = \frac{3}{2}k_BT$$

as desired.

Remark: Deriving the Maxwell Velocity Distribution

Statistical mechanics implies that the velocity distribution in an ideal gas is

$$p(\mathbf{v}) \propto e^{-mv^2/k_BT}$$

which is a three-dimensional Gaussian. This result was first derived by Maxwell, long before statistical mechanics was understood, using an ingenious argument.

Suppose the ideal gas is inside a rectangular box, so that collisions with its left and right sides determine v_x, the front and back sides determine v_y, and the top and bottom sides determine v_z. The distributions of velocities in each direction should therefore be independent, and identical by rotational symmetry, so that we can write

$$p(\mathbf{v}) = f(v_x)f(v_y)f(v_z)$$

for some function f. Moreover, by rotational symmetry, $p(\mathbf{v})$ can only depend on v^2. Taking the logarithm of both sides and defining $g = \log f$, we have

$$\log p = g(v_x) + g(v_y) + g(v_z)$$

and the right-hand side only depends on v^2. This is only possible if $g(x) = -\alpha x^2$ for a constant α, which yields $p(\mathbf{v}) \propto e^{-\alpha v^2}$. The value of α can be determined by demanding the pressure match the ideal gas law (see example 7).

However, assuming independence of the components of velocity v_i is a one-off trick, which doesn't work in general. For example, when relativistic effects are important, the v_i are *not* independent – if v_x is near c, then v_y and v_z must be small. (Concretely, if a collision with a wall in the yz plane applies a relativistic impulse Δp_x, then it also changes v_y and v_z since $\mathbf{p} = \gamma m \mathbf{v}$.) The v_i also aren't independent if quantum statistics matters. For example, if the gas particles are fermions, as discussed in **X1**, then no two can be in the same state, so some final $\mathbf{v}$'s are forbidden. So in modern statistical mechanics, we usually use a different derivation, which is equally slick but generalizes better.

The idea is that in thermodynamic equilibrium, time reversal symmetry implies every reaction is in "detailed balance". Specifically, suppose that when two gas molecules collide elastically, with velocities $(\mathbf{v}_1, \mathbf{v}_2)$, they exit with velocities $(\mathbf{v}_1', \mathbf{v}_2')$. Then the rate at which this happens must be equal to the rate at which gas molecules with velocities $(\mathbf{v}_1', \mathbf{v}_2')$ collide, which causes them to exit with velocities $(\mathbf{v}_1, \mathbf{v}_2)$. (Otherwise, you could distinguish a video of the molecules' dynamics from the same video played in reverse.) Therefore,

$$p(\mathbf{v}_1)p(\mathbf{v}_2)\,|\mathbf{v}_1 - \mathbf{v}_2| = p(\mathbf{v}_1')p(\mathbf{v}_2')\,|\mathbf{v}_1' - \mathbf{v}_2'|$$

where the relative velocity factor is present because a larger relative velocity gives more opportunities for collision. However, for elastic collisions, the initial and final relative velocities are the same, so this factor just cancels out.

Now, by rotational symmetry we have $p(\mathbf{v}) = f(v^2)$ for some function f, so

$$f(v_1^2)f(v_2^2) = f(v_1'^2)f(v_2'^2)$$

Furthermore, by energy conservation we have $v_1^2 + v_2^2 = v_1'^2 + v_2'^2$. Then the above equation can only be satisfied if f is an exponential, $f(x) \propto e^{-\alpha x}$, which again gives $p(\mathbf{v}) \propto e^{-\alpha v^2}$.

Idea 6: Equipartition Theorem

Suppose some degree of freedom in phase space contributes to the energy by a power law,

$$E \propto p^n \text{ or } H \propto x^n.$$

Then in thermal equilibrium, there is an average energy of $k_B T/n$ in this degree of freedom. The proof of this is just a straightforward generalization of the reasoning in problem 16(c). Note that the proof of the equipartition theorem is entirely classical, i.e. it holds when a system is adequately described by classical mechanics. It does a good job of describing the heat capacities of simple gases near room temperature, as you can see here.

Here are a few important examples of the equipartition theorem.

- A mass on a spring in one dimension has
$$E = \frac{p^2}{2m} + \frac{kx^2}{2}.$$
This involves two degrees of freedom in phase space, each with $n = 2$, so the average energy is $2(k_BT/2) = k_BT$.
- In problem 7 you considered a system with a linear potential energy, $E(h) = mgh$. This is a degree of freedom with $n = 1$, and accordingly, the average potential energy of each molecule is k_BT.
- An atom in a solid can be thought of as attached to its neighbors by springs. Since the atom is in three dimensions, this yields three copies of the first example, and hence an average thermal energy of $3k_BT$. This implies that the specific heat per atom in a solid is $3k_B$ (or equivalently $3R$ per mole), which is called the Dulong–Petit law.

Incidentally, because systems in thermal equilibrium are also in long-term mechanical equilibrium, the virial theorem from **M6** applies, and tells us the ratio between the average kinetic and potential energy; of course, it matches the result of the equipartition theorem. You'll investigate some more key examples in the problems below.

Example 6

A free particle in one dimension, $H = p^2/2m$, has energy levels $E_n = n^2 E_0$ for $n = 0, 1, 2, \ldots$, as we will show in **X1**. Show that the average energy at high temperatures is consistent with the equipartition theorem.

Solution

The probability of being in energy level n is proportional to $e^{-n^2E_0/k_BT}$. Therefore, by normalizing the probability distribution, the probability itself is
$$p_n = \frac{e^{-n^2E_0/k_BT}}{\sum_{m=0}^{\infty} e^{-m^2E_0/k_BT}}.$$

Therefore, the average value of the energy is
$$\langle E \rangle = \sum_{n=0}^{\infty} n^2 E_0 \, p_n = \frac{\sum_{n=0}^{\infty} n^2 E_0 e^{-n^2E_0/k_BT}}{\sum_{n=0}^{\infty} e^{-n^2E_0/k_BT}}.$$

At high temperatures, this quantum result should reduce to the classical result of the equipartition theorem. Note that at such temperatures, the typical values of n will be very high.

Therefore, we can treat the sums over n as continuous integrals,

$$\langle E\rangle \approx \frac{\int_0^\infty dn\, n^2 E_0 e^{-n^2 E_0/k_B T}}{\int_0^\infty dn\, e^{-n^2 E_0/k_B T}} = \frac{\int_0^\infty x^2 e^{-x^2}\, dx}{\int_0^\infty e^{-x^2}\, dx}\, k_B T$$

where we switched to the dimensionless variable $x = \sqrt{n^2 E_0/k_B T}$. Evaluating either of these integrals is tricky, but we can relate them using integration by parts,

$$\int_0^\infty x^2 e^{-x^2}\, dx = \int_0^\infty (2xe^{-x^2}\, dx)\, \frac{x}{2} = \frac{1}{2}\int_0^\infty e^{-x^2}\, dx.$$

Therefore, the ratio of integrals is $1/2$, giving an average energy of $k_B T/2$ as expected.

[3] **Problem 17.** The energy of a photon is $E = pc$.

(a) Treating the photon classically, compute the average energy of a photon moving in one dimension, assuming it obeys the Boltzmann distribution with temperature T. Check that the result obeys the equipartition theorem.

(b) Generalize this result to three dimensions to compute γ for a 3D photon gas.

Solution. Since we're talking about both momenta p and probabilities p here, let's temporarily rename the probability distribution function to f.

(a) Using the Boltzmann distribution and $E = pc$,

$$f(p) \propto e^{-pc/k_B T}.$$

Then the expected energy is

$$\langle E\rangle = \langle pc\rangle = \frac{\int_0^\infty (pc) e^{-pc/k_B T}\, dp}{\int_0^\infty e^{-pc/k_B T}\, dp} = k_B T\, \frac{\int_0^\infty x e^{-x}\, dx}{\int_0^\infty e^{-x}\, dx}.$$

Note that the numerator can be related to the denominator using integration by parts,

$$\int_0^\infty x e^{-x}\, dx = \int_0^\infty e^{-x}\, dx.$$

Then the fraction is just 1, so

$$\langle E\rangle = k_B T.$$

Evidently, every degree of freedom where the energy is *linear* in the momentum contributes energy $k_B T$. This is just as we expect by the equipartition theorem, since there's one degree of freedom with $n = 1$.

(b) The reasoning is very similar, but now

$$f(\mathbf{p}) \propto e^{-|p|c/k_B T}.$$

The expected energy is then, using spherical coordinates,

$$\langle E\rangle = \langle pc\rangle = \frac{\int_0^\infty (pc) e^{-pc/k_B T} (4\pi p^2)\, dp}{\int_0^\infty e^{-pc/k_B T} (4\pi p^2)\, dp} = k_B T\, \frac{\int_0^\infty x^3 e^{-x}\, dx}{\int_0^\infty x^2 e^{-x}\, dx}.$$

Again the numerator can be related to the denominator using integration by parts,

$$\int_0^\infty x^3 e^{-x}\,dx = 3\int_0^\infty x^2 e^{-x}\,dx.$$

Then the fraction is 3, so $\langle pc\rangle = 3k_BT$, which is just what we expected since there are three linear degrees of freedom. Hence we have $\gamma = 4/3$.

[3] **Problem 18.** A one-dimensional quantum harmonic oscillator has energy levels $E_n = nE_0$ for $n \geq 0$, as you will show in **X1**.

(a) Compute the average energy of the system at temperature T.

(b) Show that at high temperatures, the average energy obeys the equipartition theorem.

(c) Show that the energy at low temperatures is instead exponentially suppressed. This is why some modes are said to "freeze out", so they do not contribute to C_V.

The phenomenon of "freezing out" was one of the greatest puzzles of classical physics in the 19th century, though nobody anticipated the resolution would be as strange as quantum mechanics.

Solution. (a) The average energy is

$$\langle E\rangle = \frac{\sum_{n\geq 0} nE_0 e^{-nE_0/k_BT}}{\sum_{n\geq 0} e^{-nE_0/k_BT}}.$$

Let

$$f(x) = \sum_{n\geq 0} e^{-nx} = \frac{1}{1-e^{-x}},$$

so

$$\sum_{n\geq 0} ne^{-nx} = -f'(x) = \frac{e^{-x}}{(1-e^{-x})^2}.$$

Thus,

$$\langle E\rangle = \boxed{E_0\frac{e^{-E_0/k_BT}}{1-e^{-E_0/k_BT}}}.$$

(b) Note that if $k_BT \gg E_0$, then $e^{-E_0/k_BT} \approx 1 - E_0/k_BT$, so plugging into the formula, we get that $\langle E\rangle \approx k_BT$, as desired.

(c) For low temperatures, we have $e^{-E_0/k_BT} \ll 1$, which gives $\langle E\rangle \approx E_0 e^{-E_0/k_BT}$.

[3] **Problem 19.** The Boltzmann distribution can be normalized to a probability distribution by dividing by the so-called partition function $Z = \sum_n e^{-E_n/k_BT}$.

(a) For a quantum harmonic oscillator, compute the probability of occupancy of the ground state (i.e. the lowest energy state) at temperature T.

(b) Do the same for the hydrogen atom, where $E_n = -E_0/n^2$ for $n \geq 1$. You should get a rather strange answer. Does it make physical sense?

Solution. (a) The probability is

$$p_0 = \frac{e^{-(0)E_0/k_BT}}{Z} = \frac{1}{Z}$$

where the partition function is

$$Z = \frac{1}{1 - e^{-E_0/k_BT}}$$

by summing a geometric series, so the answer is

$$p_0 = 1 - e^{-E_0/k_BT}.$$

(b) The problem here is that there are an infinite number of energy levels that have similar energy. So the sum used to define Z diverges, which means that the probability of occupying any given state is *zero*! This seems to be a paradox.

The resolution is that this really is the correct answer, if you have *true* thermal equilibrium in an infinite volume. The electron simply has a huge volume it could wander around to, so as the volume goes to infinity, that means the chance it'll be near the proton falls to zero. This can happen even if the electron begins in the ground state and the temperature is extremely low; it just takes a long time. After some number of aeons, the random thermal radiation at some moment will just happen to be enough to pop the electron free, and then it'll wander away, probably never to return.

So the answer is formally true, but it's not realistic, because in everyday life and in physics labs we perform experiments with finite volumes and finite times. This can be accounted for by hand by just cutting off the sum at some high n, say

$$Z = \sum_{n=0}^{10^6} e^{-E_n/k_BT}.$$

Such a cutoff corresponds to only allowing atomic orbitals that fit in a typical room, which is reasonable, and using this value of Z gives reasonable results, as would any sufficiently high but finite cutoff. For more on this point, see this paper.

[3] **Problem 20.** To model paramagnetism, consider a set of N independent magnetic dipoles in a vertical magnetic field B and temperature T. Each dipole has two possible quantum states, spin up and spin down, with energies $\boldsymbol{\mu} \cdot \mathbf{B}$ and magnetic dipole moment $\mu_z = \pm e\hbar/2m$.

(a) Defining the magnetization M as the total magnetic moment, find the average magnetization of the magnet as a function of T.

(b) Show that $M \propto 1/T$ in the limit of high T. This result is called Curie's law.

Solution. (a) Since the dipoles are completely independent, we can treat them separately, giving

$$M = N \frac{\frac{e\hbar}{2m} e^{\frac{e\hbar B}{2mk_BT}} - \frac{e\hbar}{2m} e^{-\frac{e\hbar B}{2mk_BT}}}{e^{\frac{e\hbar B}{2mk_BT}} + e^{-\frac{e\hbar B}{2mk_BT}}} = \frac{Ne\hbar}{2m} \tanh \frac{e\hbar B}{2mk_BT}.$$

(b) Note that $\tanh x \approx x$ for $x \ll 1$, so $M \propto 1/T$ in limit of high T as desired.

Remark

In principle, all of our results about statistical mechanics can be derived by following the microscopic dynamics, e.g. the collisions of atoms with each other for a gas. It's just very hard to do so in practice.

However, you can still get a bit of insight in simple cases. For example, consider a one-dimensional ideal gas in a uniform gravitational field, $E = p^2/2m + mgh$. Since the kinetic energy is a quadratic degree of freedom, and the potential energy is a linear degree of freedom, the average potential energy must be twice the average kinetic energy. Furthermore, this should be true no matter how rarely collisions happen; less frequent collisions simply mean it takes longer to get to thermal equilibrium, without changing what that equilibrium is.

Therefore, we have the concrete, classical mechanical prediction that a mass bouncing elastically on the ground, suffering no collisions at all, will have an average potential energy equal to twice its average kinetic energy, which you can verify directly from Newton's laws.

Here's a more subtle puzzle. In our analysis of the isothermal atmosphere, we found that the distribution of speeds is the same everywhere. But if you look at any one particle, it will clearly pick up speed as it falls down. How is this self-consistent? Wouldn't this tend to increase the temperature at lower heights?

Again, it's easiest to think about this situation in the limit of a very thin gas, where collisions are rare. Indeed, each particle that starts at the top of the atmosphere will pick up a lot of speed as it falls down. But why are there any particles at the top at all? Because at the bottom of the atmosphere, which is much more dense, particles occasionally get a lot of energy through collisions, which propels them to the top. In equilibrium, the particles going down *do* arrive at the bottom with unusually high speed, but they're balanced out by the unusually fast particles going the other way. Keeping track of the details here can be quite complex, especially when collisions are frequent, but miraculously the Boltzmann distribution takes care of it all for us!

4 Kinetic Theory

Idea 7

Kinetic theory is the branch of statistical mechanics that focuses on the motion of individual molecules in a gas. It can get quite mathematically involved, since one must consider the effects of molecular collisions, which is why the subject is usually reserved for graduate school. However, in some simple situations, collisions can be neglected, effectively making the molecules independent.

Example 7: Ideal Gas Law

Derive the ideal gas law using kinetic theory.

Solution

Without loss of generality, we consider a cubical container of gas of side length L and N gas molecules. Consider the pressure exerted on a wall aligned with the yz plane. A given gas molecule will hit this wall with period $2L/v_x$, transferring a momentum of $2p_x$. Then the pressure on the wall is

$$P = \frac{F}{A} = \frac{1}{L^2} \frac{N \langle p_x v_x \rangle}{L}.$$

This can be written as

$$P = \frac{N}{V} \langle p_x v_x \rangle = \frac{N}{V} \frac{\langle \mathbf{p} \cdot \mathbf{v} \rangle}{3} = \frac{N}{3V} \langle m v^2 \rangle = \frac{N k_B T}{V}$$

where we used rotational symmetry and the equipartition theorem.

Of course, this calculation was doable because we neglected interactions between different gas molecules. However, this doesn't matter as much as one might think. We assumed molecules can cross the whole container without colliding, but if they do, the derivation still basically works because they just transfer their momentum to another molecule. As long as the molecules are moving freely most of the time, the answer above is approximately right.

In **T2**, we'll see how an attractive interaction lowers the pressure. In **T3**, we'll see that when the gas gets very dense, this leads to a dramatic effect: the gas condenses into a liquid.

[2] **Problem 21.** Use kinetic theory to find the pressure of a photon gas (i.e. an ideal gas of massless particles, which satisfy $E = pc$) in terms of its total internal energy U and volume V. Use this result to find γ for a photon gas, where γ is defined so that PV^γ is constant in an adiabatic process.

Solution. By the exact same reasoning as in the example,

$$P = \frac{N}{V} \langle p_x v_x \rangle = \frac{1}{3} \frac{N}{V} \langle \mathbf{p} \cdot \mathbf{v} \rangle.$$

However, for photons we have $pv = pc = E$, so

$$P = \frac{1}{3} \frac{N}{V} \langle E \rangle = \frac{U}{3V}.$$

In other words, the pressure is always one third of the energy density. Notice that the number of photons cancelled out, as it must have because it wasn't specified anywhere in the problem. As you'll see in **T2**, the number of photons is determined by the volume and temperature; it isn't an independent parameter like it is for the ideal gas. As you heat or cool a photon gas, photons can be freely emitted and absorbed by the walls, changing the total number to reach equilibrium.

Starting from $U = 3PV$ and taking the differential of both sides, in an adiabatic process we have

$$dU = đW = -P\, dV, \quad dU = 3(P\, dV + V\, dP).$$

Simplifying gives

$$-\frac{4}{3} \frac{dV}{V} = \frac{dP}{P}$$

which is equivalent to $PV^{4/3}$ being constant, so $\gamma = 4/3$.

Example 8

An astronaut of mass M stranded in outer space makes a primitive rocket as follows. They take a piece of dry ice of mass $m \ll M$ and molar mass μ and put it in a long, thin glass held at temperature T. The dry ice sublimates, and the astronaut points the opening of the glass in the opposite of the direction they want to go. Estimate, within an order of magnitude, how fast the astronaut is going after all the dry ice is gone.

Solution

Let m' be the mass of a molecule of dry ice. By the equipartition theorem, the molecules have speed

$$v \sim \sqrt{\frac{kT}{m'}} = \sqrt{\frac{NkT}{Nm'}} = \sqrt{\frac{RT}{\mu}}.$$

The molecules exit the glass traveling more or less in the same direction, so by momentum conservation the final speed of the astronaut is on the order of

$$\frac{m}{M} v = \frac{m}{M}\sqrt{\frac{RT}{\mu}}.$$

We have implicitly assumed that the glass is long enough that the molecules get into thermal equilibrium with the glass before they leave it. For a short glass, the answer would instead depend on the typical speeds of molecules at the moment they sublimate.

Example 9

A container of volume V is filled with a gas of uniform temperature T, and placed in a vacuum. If a small hole is punched in the container and gas slowly leaks out, how does the temperature in the container change over time?

Solution

The mean free path λ is the average distance a gas molecule moves before it hits another one. Let d be the width of the hole. There are two important limiting cases.

If $\lambda \ll d$, then molecules can't make it out of the hole without undergoing many collisions. Thus, if the gas has some average flow velocity, its molecules will be carried along with it. We can thus treat the gas like a continuous fluid, and the logic of example 4 applies. The gas inside the container does $P\,dV$ work on the gas exiting and hence loses energy. Thus, the remaining gas cools down, so the temperature of the container decreases over time. (Doing this problem quantitatively requires the analogue of Bernoulli's principle for gases, which we derive in **T3**.)

If $d \ll \lambda$, then molecules fly out of the hole without encountering any others at all; this is the regime of "effusion". Therefore, we shouldn't think in terms of an average gas pressure or flow velocity, but rather just consider each molecule on its own. An individual molecule has a greater chance of escaping through the hole if it's moving faster. Thus, the molecules that come out will on average be higher energy than the ones that stay in the container. So just as in the opposite limit, the remaining gas cools down, but for a totally different reason. (This case is treated quantitatively in problem 2.24 of Wang and Ricardo, volume 2.)

Remark

The previous example implies that a gas of uniform temperature can turn into a hot gas and a cold gas without needing any external work, which seems to directly contradict the second law of thermodynamics! To phrase it another way, you can use the free temperature difference to run a heat engine, which seemingly allows perpetual motion.

Of course, the resolution is that the total entropy of the gas is still going up. The kinetic energy is getting less spread out, but the positions of the atoms are getting more spread out, since some can now be outside the container. Thus, the "perpetual motion" only works as long as the gas is still leaking out of the container; it stops once the density becomes uniform. The lesson here is that, while most setups extract work from a temperature difference, more generally you can extract it from any potential increase in entropy; in this case, it comes from an initial difference in densities.

[2] **Problem 22** (Kalda)**.** Natural uranium consists of mainly two isotopes, ^{238}U and ^{235}U, and the relative concentration of the latter is 0.7%. Uranium is enriched by a multi-stage process, where at each stage, evaporated UF_6 is led through a porous wall. The porous wall is a thin film with microscopic holes, much smaller than the mean free path of the molecules, but larger than the dimension of the molecules. How many stages are needed to increase the ^{235}U content to 1.4%? The molar mass of fluoride is 19 g/mol.

Solution. Say the two different versions of UF_6 have molecular masses M_1, M_2. The key idea here is that the average kinetic energy of each one is the same (namely $\frac{3}{2}k_BT$), so $\frac{1}{2}M_1v_1^2 = \frac{1}{2}M_2v_2^2$. This means that $v_1/v_2 = \sqrt{M_2/M_1}$, so the rate that M_1 leaves divided by the rate that M_2 leaves is $\sqrt{M_2/M_1}$. Thus, the rate at which 238 leaves divided by the rate that 235 leaves is

$$r = \sqrt{(235 + 6 \cdot 19)/(238 + 6 \cdot 19)} = 0.9957\ldots.$$

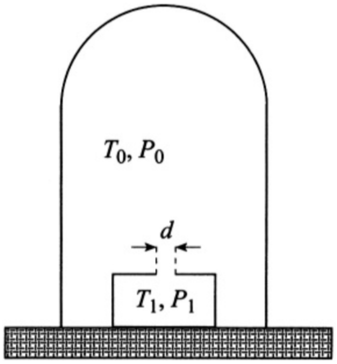
Throughout the process, almost all of the uranium is ^{238}U, so the proportion of it falls by approximately r per stage. Therefore, the number of stages N obeys

$$0.9957^N \approx 1/2$$

which has solution $N \approx 160$.

This problem assumed a large mean free path, in which case the molecules escaped by effusion. In the opposite limit, where the mean free path is small, we would instead describe the gas using fluid flow equations, such as Bernoulli's principle. However, in that limit the two isotopes would just get carried along with the flow in the same way, leading to no enrichment.

[2] **Problem 23** (Cahn)**.** A small vessel with a tiny hole of diameter d is placed inside a chamber, where the pressure is so low that the mean free path is $\lambda \gg d$. The temperature of the gas in the chamber is T_0, and the pressure is P_0. The temperature in the vessel is kept at a constant $T_1 = 4T_0$.



What is the pressure inside the vessel when steady state is reached?

Solution. Since the chamber is much larger than the vessel, gas entering the vessel and leaving from the vessel won't affect the pressure or temperature of the chamber. Now, it is very easy to fall into the following trap. One may argue that steady state is reached when the pressures in the vessel and chamber are the same. After all, isn't that what happens when two gases come in equilibrium?

The problem is that we are in the effusive regime $\lambda \gg d$. Thus, if a particle is near the hole and heading towards it, it's likely to just pass through without hitting anything at all; it doesn't "know" that it's entered a region of higher pressure, so there's no reason for the pressures to equalize. Instead, equilibrium just occurs whenever the rate of particles going from the chamber to the vessel is the same as the rate of particles going from the vessel to the chamber. This rate is proportional to the number density times the average speed, so in equilibrium,

$$n_0 \langle v_0 \rangle = n_1 \langle v_1 \rangle.$$

We also know that $\langle v_i \rangle \propto \sqrt{T_i}$ by equipartition. Therefore, $n_1 = n_0/2$, and the ideal gas law says $p \propto nT$, so $p_1 = 2p_0$.

If you think the step where we asserted $n_i \langle v_i \rangle$ matched on both sides was not rigorous enough, here's a more formal derivation. (The result of this derivation will also be used in **T2**.)

Lemma. Given a box with an (ideal) gas of particle mass m, temperature T, and number density n (number of particles per unit volume), the number of particles leaving a small hole of area A per unit time is

$$\frac{nA}{4} \langle v \rangle = \frac{nA}{4} \sqrt{\frac{8k_B T}{\pi m}}$$

assuming that $\sqrt{A} \ll \lambda$.

Proof. Let $f(v)$ be the distribution of velocities of the particles. What this means is that the probability that a particle has velocity in $[v_x, v_x + dv_x] \times [v_y, v_y + dv_y] \times [v_z, v_z + dv_z]$ is

$$f\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) dv_x dv_y dv_z.$$

Set up spherical coordinates with origin at the hole. We will now count the number of particles that hit the hole in a time dt using a funny double counting argument, where we start by counting the number of particles that hit the hole with a certain velocity and then integrate over all velocities.

We will start by counting the number of particles that move with speed v (technically speed in $[v, v + dv]$, but from now on we'll be lazy about this) and spherical coordinate angles (θ, ϕ). Here $\theta = 0$ means pointing toward the hole, and $\theta = \pi/2$ is parallel to the plane of the hole (the spherical coordinates for the velocity are flipped compared to those for space, since the $\theta = 0$ rays are anti-parallel). In a given volume dV, the number of particles with this velocity is just

$$(ndV) \cdot f(v) \cdot v^2 \sin\theta \, dv \, d\theta \, d\phi.$$

For this given velocity, the volume in space that will allow such particles to hit the hole is a tilted cone object with base A, slant θ, slant height vdt, and aligned in the proper ϕ direction. In particular, its volume is $A(vdt)\cos\theta$, so the number of particles with velocity (v, θ, ϕ) hitting the hole in time dt is

$$(nAdt) \cdot f(v) \cdot v^3 \sin\theta \cos\theta \, dv \, d\theta \, d\phi.$$

Thus, the rate of particles leaving is

$$\alpha = nA \int_0^\infty v^3 f(v) \, dv \int_0^{\pi/2} \sin\theta\cos\theta \, d\theta \int_0^{2\pi} d\phi = \pi n A \int_0^\infty v^3 f(v) \, dv.$$

On the other hand, note that the average speed is

$$\langle v \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} v \cdot f(v) \cdot v^2 \sin\theta \, dv \, d\theta \, d\phi = 4\pi \int_0^\infty v^3 f(v) \, dv,$$

which tells us that

$$\alpha = \frac{nA}{4} \langle v \rangle,$$

as desired. Note that this derivation didn't depend on the particular form of $f(v)$. For instance, it would work just as well for a relativistic particle, or even photons, as we'll see in **T2**.

[5] **Problem 24.** In this problem, we consider a simple kinetic theory model for "transport" in a sparse gas. Two parallel plates are at a distance L from each other. The space between the plates is filled with a gas of density ρ, with molecule of mass m. Assume that the gas density is low enough to neglect collisions between gas molecules, and that all radiation effects can be neglected.

(a) Suppose the two plates are held at temperatures $T + \Delta T$ and T, where $\Delta T \ll T$. Assume that when gas molecules bounce from a plate, they instantly obtain the plate's temperature. Estimate the heat flux per area P/A (in units of W/m^2) between the plates. (This determines the thermal conductivity, to be defined in **T2**.)

(b) Suppose the top plate moves with a transverse speed $v_\parallel$ parallel to itself, while the bottom plate is still, and $mv_\parallel^2 \ll k_B T$. Assume that when gas molecules bounce from a plate, they obtain that plate's transverse speed. Estimate the force per area F/A on each plate. (This determines the viscosity, as defined in **M7**.)

Both the thermal conductivity and viscosity are associated with the transport of conserved quantities (energy and transverse momentum, respectively) through the gas. Now, above we have neglected collisions entirely, which is unrealistic for most gases unless they are extremely sparse. However, it's possible to get some rough estimates for what happens in the presence of collisions.

(c) Let σ be the cross-sectional area of a gas molecule. Estimate the mean free path d of a gas molecule.

(d) Our previous analysis held when $L \ll d$. Now suppose, more realistically, that $L \gg d$. Estimate P/A and F/A in the steady state. (Hint: consider a set of imaginary planes that are spaced by a distance d, and consider the heat/momentum flow between pairs of adjacent planes; for such pairs, collisions can be neglected.)

(e) Suppose a gas molecule begins at the top plate, and both plates have temperature T. Again assuming that $L \gg d$, estimate the typical time it takes before the gas molecule hits the bottom plate. (Hint: model the position of the particle as a sum of random steps, and recall the facts about variance in **P2**.)

For a clear discussion of the ideas of this problem, see sections 7.3 and 7.4 of The Art of Insight.

Solution. (a) The gas molecules have speed $v \sim \sqrt{k_B T/m}$, and they hit the plates every time $t \sim L/v$. Each time a plate is hit, an energy $\Delta E \sim k_B \Delta T$ is deposited or taken away. So the average energy flow rate for one atom is

$$P_{\text{atom}} = \frac{\Delta E}{t} \sim \frac{k_B \Delta T}{L} \sqrt{\frac{k_B T}{m}}.$$

The number of atoms per unit area of the plate is $L\rho/m$, which gives

$$\frac{P}{A} \sim k_B \Delta T \, \frac{\rho}{m} \sqrt{\frac{k_B T}{m}}.$$

(b) This is rather similar, except that instead of an energy ΔE deposited every impact, a momentum $\Delta p_\parallel = m v_\parallel$ is deposited per impact. Then by the exact same logic,

$$\frac{F}{A} \sim m v_\parallel \, \frac{\rho}{m} \sqrt{\frac{k_B T}{m}}.$$

Notice that the result of this problem depends explicitly on the molecular mass m. This is very important, because in the early days of kinetic theory, the quantity m canceled out of almost every calculation. This led people to believe that atoms were unobservable in principle; they were just a fictitious calculational tool used to approximate continuous matter. One of Einstein's most famous discoveries was showing that macroscopically observable properties of Brownian motion did depend on m, hence giving a way to indirectly observe the reality of atoms; you will do this calculation in **XRev**.

(c) If a molecule moves a distance x, it'll sweep out a volume of σx. The number density is ρ/m, so the molecule should expect $\rho \sigma x/m$ collisions. The mean free path d is when you would expect 1 collision:

$$d = \frac{m}{\sigma \rho}.$$

(d) The results for when collisions can be neglected,

$$\frac{P}{A} \sim k_B \delta T \, \frac{\rho}{m} \sqrt{\frac{k_B T}{m}} \qquad \frac{F}{A} \sim m \delta v \, \frac{\rho}{m} \sqrt{\frac{k_B T}{m}}$$

can still give us the heat/momentum flow between adjacent planes separated by distance d (so a total of L/d of these planes). Thus $\Delta T = \frac{L}{d} \delta T$ and $v = \frac{L}{d} \delta v$. This transfer will be the same throughout in steady state, and plugging in the previously obtained $d = m/\sigma\rho$ yields

$$\frac{P}{A} \sim \frac{k_B \Delta T}{\sigma L} \sqrt{\frac{k_B T}{m}} \qquad \frac{F}{A} \sim \frac{m v}{\sigma L} \sqrt{\frac{k_B T}{m}}.$$

Remarkably, the density ρ has completely dropped out! This was one of the most surprising early predictions of kinetic theory, which was confirmed by Maxwell. For higher densities, more molecules are available to carry energy or momentum, but they can't go as far before colliding.

(e) The molecule will be moving at velocity $v \sim \sqrt{k_B T/m}$, so it takes time $t \sim d/v$ to go between planes of separation d. However, after this point the molecule's velocity will be randomized, so its next step might go in any direction. This is a description of a random walk.

Each step of time t changes the displacement from the original plate by approximately $\pm d$, and the steps are independent. Then the standard deviation of the displacement adds in quadrature, as covered in **P2**. The typical time to hit is when we get a standard deviation of order L,

$$t_{\text{hit}} \sim \left(\frac{L}{d}\right)^2 \frac{d}{v} \sim \frac{L^2}{d}\sqrt{\frac{m}{k_B T}}.$$

[5] **Problem 25.** ⏱ EuPhO 2017, problem 2. A nice problem using many of the above ideas.

Solution. See the official solution here.

Example 10

A box of mass M contains an ideal gas consisting of many particles, with total mass M_g. Find $\langle V_x^2 \rangle$, the average mean-square velocity of the box along the x-axis.

Solution

This problem illustrates how kinetic theory can get very subtle, even when we don't have to keep track of the detailed collision dynamics. First, note that if each gas molecule has mass m, then each one has $\langle v_x^2 \rangle = k_B T/m$ by equipartition. Now there are two simple arguments that give different answers.

1. If we apply equipartition of energy to the box itself, we get $\langle V_x^2 \rangle = k_B T/M$.
2. The total momentum of the box and gas together is zero, so

$$M V_x = -m \sum_{i=1}^{N} v_{x,i}.$$

On the other hand, by the rules of error propagation introduced in **P1**,

$$\left\langle \left(m \sum_{i=1}^{N} v_{x,i} \right)^2 \right\rangle = m^2 N \frac{k_B T}{m} = k_B T M_g$$

which implies

$$\langle V_x^2 \rangle = \frac{M_g}{M^2} k_B T.$$

What's going on? It actually turns out that both of these arguments are wrong in general, but each one is correct in different limiting cases.

The problem with the first argument is that the derivation of equipartition of energy assumes that each degree of freedom is independent of the others, i.e. it ignores the fact that when the box picks up momentum, the gas must have a compensating opposite total momentum. The problem with the second argument is that it assumes the velocities of the molecules are independent of each other, which is also not quite true.

Note that the energy and momentum of the box are related by $E = P^2/2M$. Now, if the box is heavy, $M \gg M_g$, it can store lots of momentum even when it has very little energy, and conversely when it has a decent amount of energy it must have an enormous momentum. The latter implies that the first argument fails. But the second argument works, because the box serves as a “sink” for momentum. For example, the gas molecules could all be moving to the right, and that would be easily compensated by the box moving slightly to the left.

If the box is light, $M \ll M_g$, then it can have lots of energy even having negligible momentum. In this case, the first argument works, because the box doesn't ever have enough momentum to substantially affect the gas's behavior. But the second argument fails, because if the box can't carry much momentum, then the gas molecules' momenta must almost entirely cancel out among themselves by momentum conservation, meaning that they are not independent.

The general solution can be found with a simple trick. The problem with the equipartition argument is essentially that we treat the box velocity V_x as independent of the center of mass velocity of the gas, $\overline{v}_x$. We can therefore switch to the variables

$$v_{\text{CM}} = \frac{M_g \overline{v}_x + M V_x}{M_g + M}, \quad v_{x,\text{rel}} = V_x - \overline{v}_x.$$

These two new variables are independent, because the momentum conservation constraint just says the former is always equal to zero. Thus, we can safely apply equipartition of energy to v_{rel}. Recalling the reduced mass idea from **M6**, we have

$$E \supset \frac{1}{2} \mu v_{x,\text{rel}}^2, \quad \mu = \frac{M M_g}{M + M_g}.$$

By equipartition we have

$$\langle v_{x,\text{rel}}^2 \rangle = \frac{k_B T}{\mu}$$

and by momentum conservation we conclude

$$\langle V_x^2 \rangle = \left(\frac{M_g}{M + M_g} \right)^2 \langle v_{x,\text{rel}}^2 \rangle = \frac{k_B T}{M} \frac{M_g}{M + M_g}$$

which reduces to the two answers found above in the appropriate limits. This problem turns out to be relevant to astrophysics, where it is a toy model for the dynamics of a supermassive black hole in a galaxy. For a complete analysis which starts from the postulates of kinetic theory, see this paper.

Remark

Above, we discussed the distinction between "bottom-up" and "top-down" approaches, but there are also bridges between the subjects. For example, suppose you had a large volume of gas, where the mean free path is much smaller than the container's size. Here, the gas can come into equilibrium *locally*, at which point we may describe its state with a temperature field $T(\mathbf{x}, t)$, along with other fields, such as pressure, density, and velocity. This leads to the subject of hydrodynamics, which can be derived from kinetic theory. We started on this subject in **M7**, but there we neglected any thermal properties; we will return to it in **T3**.

On the other hand, suppose an entire macroscopic system is already in thermal equilibrium. The system is homogeneous, so there's no need for hydrodynamics, but it can still be difficult to infer the macroscopic behavior of the system. For example, if you had water molecules at a given temperature and pressure, it's still hard to calculate what phase they're in! In physics, our best tool for this kind of problem is the renormalization group, which bridges the gap by considering a series of "coarse-graining" operations that gradually zoom out. This is a deep subject, typically reserved for graduate courses.

Thermodynamics II

Chapters 3 and 4.1–4.4 of Wang and Ricardo, volume 2 cover the topics of this problem set at an appropriate level. For more detail, see chapters 10–16, 18, 21, and 23 of Blundell and Blundell. For interesting discussion, see chapters I-44 through I-46 of the Feynman lectures. There is a total of **83** points.

1 [A] The First Law

We started **T1** with basic thermodynamics; here we will treat it more thoroughly, using partial derivatives. Partial derivatives don't appear on the IPhO and APhO, and only rarely appear on the INPhO. However, they're a useful way to organize your thinking in more complex problems.

Idea 1

The first law states that

$$\Delta U = \Delta Q + \Delta W$$

where ΔU is the change in internal energy, ΔQ is the heat given to the system, and ΔW is the work done on the system. Only U is an intrinsic property of the system itself, i.e. a state function, we make this distinction explicit by writing the differential version as

$$dU = đQ + đW.$$

Idea 2

For a gas, the state of the system is specified by the pressure P, volume V, and temperature T, and the three are related by the ideal gas law. The infinitesimal work done is

$$đW = -P\,dV.$$

Similarly, many simple thermodynamic systems can be described by a temperature and a pair of "conjugate variables". For example, a bubble has surface tension γ, area A, and temperature T, where

$$đW = \gamma\,dA.$$

A rubber band, is described by its tension F, length L, and temperature T, with

$$đW = F\,dL.$$

In all of these simple examples, we have three variables and one "equation of state" which relates them, which means two parameters are required to describe the system's state. That's why, for example, you can't speak of a "heat capacity" dU/dT. There's more than one way to change the temperature: if we do it at constant volume, we get the heat capacity C_V, and if we do it at constant pressure, we get C_P. In **T1**, we just made these distinctions verbally, but this quickly gets confusing as you do more complex calculations. A more rigorous and powerful approach is to use partial derivatives, which explicitly specify what quantity is being held constant as another is changed.

Example 1

Consider describing a plane with Cartesian coordinates (x, y) and polar coordinates (r, θ). Calculate the partial derivatives $(\partial x/\partial r)|_\theta$ and $(\partial x/\partial r)|_y$.

Solution

To evaluate the first partial derivative, we need to write x as a function of r and θ. This is done by $x = r\cos\theta$. Differentiating with respect to r and treating θ as a constant, we have

$$\left.\frac{\partial x}{\partial r}\right|_\theta = \cos\theta.$$

To evaluate the second, we should write x in terms of r and y. This is done starting with

$$r^2 = x^2 + y^2.$$

We could solve for x here. However, it's quicker to use the usual trick of implicit differentiation: note that differentiating both sides with respect to r, at fixed y, gives

$$2r = 2x\left.\frac{\partial x}{\partial r}\right|_y + 0$$

which yields the answer,

$$\left.\frac{\partial x}{\partial r}\right|_y = \frac{r}{x} = \frac{1}{\cos\theta}.$$

These two results are different: changing what you keep constant changes the derivative. You can see this geometrically by evaluating the two versions of $\partial x/\partial r$ at a few points.

Idea 3: Multivariable Differential

The change of a function $f(x, y)$ upon independent changes in x and y is

$$df = \left.\frac{\partial f}{\partial x}\right|_y dx + \left.\frac{\partial f}{\partial y}\right|_x dy$$

which you can recognize as an alternative form of the multivariable chain rule from **P1**. We can also use this equation to describe increments of quantities that aren't state functions, in which case we'll write the left-hand side as $đf$.

Example 2: Heat Capacities

The heat capacities at constant volume and constant pressure are defined as

$$C_V = \left.\frac{\partial Q}{\partial T}\right|_V, \quad C_P = \left.\frac{\partial Q}{\partial T}\right|_P.$$

Find a formula for $C_P - C_V$ in terms of the variables P, V, T, and the internal energy U.

Solution

First off, to avoid any confusion, note that the definitions above does not imply that Q can be written as a function of T and V, or T and P. It can't, because Q isn't a state function. We simply mean that in a process that changes the variables P, V, and T by some infinitesimal amount, we pick up an increment of heat transfer $đQ$ that can be written as a linear combination of those differentials. That is, we may write

$$đQ = C_V\,dT + \left.\frac{\partial Q}{\partial V}\right|_T dV = C_P\,dT + \left.\frac{\partial Q}{\partial P}\right|_T dP.$$

Now we massage the first expression into one containing only dT and dP. Since V, T, and P are all related by the equation of state, we can write V as a function of T and P, so

$$dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP.$$

Plugging this into the first expression, we have

$$đQ = C_V\,dT + \left.\frac{\partial Q}{\partial V}\right|_T \left(\left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP \right)$$

from which we see, by identifying the coefficient of dT, that

$$C_P - C_V = \left.\frac{\partial Q}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P.$$

We're not done, because we don't have a nice expression for $(\partial Q/\partial V)_T$. To finish up, we can use the first law of thermodynamics, along with $đW = -P\,dV$, to show that

$$\left.\frac{\partial Q}{\partial V}\right|_T = \left.\frac{\partial U}{\partial V}\right|_T + P.$$

We thus conclude that

$$C_P - C_V = \left(\left.\frac{\partial U}{\partial V}\right|_T + P \right) \left.\frac{\partial V}{\partial T}\right|_P.$$

This is actually quite intuitive. The extra heat we have to put in at constant pressure, when we allow the volume to change, comes from two sources. First, we have to make up for the energy lost to $P\,dV$ work. Second, we have to make up for the energy intrinsically needed to expand the gas, by doing work against the attractive intermolecular forces between the gas molecules. (That second term is zero for an ideal gas by definition.) However, trying to show this result without the organizing framework of partial derivatives would be prone to error.

Remark

The partial derivative satisfies a few more important identities. First off, if you always hold the *same* variable constant, then all two-variable functions effectively turn into one-variable functions, which means we recover the basic rules from **P1**,

$$\left.\frac{\partial w}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = \left.\frac{\partial w}{\partial x}\right|_z, \quad \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1$$

where the second identity is just the first in the special case $w = x$. For example, the first identity ensures the coefficients of dP in the two expressions for $đQ$ above are equal. In addition, partial derivatives commute and satisfy the triple product rule,

$$\left.\frac{\partial}{\partial y}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = \left.\frac{\partial}{\partial x}\right|_y \left.\frac{\partial z}{\partial y}\right|_x, \quad \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1.$$

You won't need to use any of these identities in the problem sets. However, it might be reassuring to know that these are *all* the rules you'll ever need for partial derivatives.

[1] **Problem 1.** For an monatomic ideal gas, we have $U = (3/2)nRT$ and the equation of state $PV = nRT$. Evaluate C_V and C_P using the results above.

[3] **Problem 2.** In this problem we modify the ideal gas to account for a short-ranged attractive intermolecular force. This attraction yields a negative contribution to the energy, so that

$$U = \frac{3}{2}nRT - \frac{an^2}{V}.$$

(a) Explain why the change in energy is proportional to n^2/V.

(b) Argue that because of this extra term, the pressure is an^2/V^2 less than it would be for an ideal gas. Hence conclude the equation of state is

$$\left(P + \frac{an^2}{V^2}\right)V = nRT.$$

(c) Show that the heat capacities are

$$C_V = \frac{3}{2}nR, \quad C_P - C_V = nR + \frac{2an^2}{TV} + O(n^3)$$

in the limit where the gas is dilute.

In **T3**, we will combine this pressure correction with a "volume exclusion factor" to yield the van der Waals gas, which is useful for modeling the liquid-gas phase transition.

2 The Second Law

Idea 4: Entropy

The increase in entropy of a body at temperature T that receives heat $đQ$ is

$$dS = \frac{đQ}{T}$$

if the process is reversible; moreover, entropy is a state function.

Idea 5: Second Law

The second law of thermodynamics takes several equivalent forms, which are all useful.

- For an isolated system, $dS > 0$ for any spontaneous process.
- Clausius: no process is possible whose sole result is the transfer of heat from a colder to a hotter body.
- Kelvin: no process is possible whose sole result is the complete conversion of heat into work.
- Carnot: of all heat engines working between two given temperatures, none is more efficient than a Carnot engine.

Example 3: Mixing Entropy

A container of volume V is divided in half by a partition. The two halves contain pure nitrogen and oxygen gas, respectively, both at pressure P and temperature T. The partition is removed and the gases are allowed to mix. How much does the entropy increase?

Solution

We cannot apply the formula $dS = đQ/T$, because the gas is not in equilibrium during the process. However, because entropy is a state function, we can calculate its change by considering a path that only goes through equilibrium states.

Suppose we introduce a piston at one end of the container, which is magically transparent to oxygen atoms, and slowly and isothermally move it to the center of the container. This puts the nitrogen back where it started. The change in entropy of the nitrogen is

$$\Delta S_{\mathrm{N}} = \frac{Q}{T} = -\frac{W}{T} = nR \log \frac{V_i}{V_f} = -nR \log 2 = -N k_B \log 2$$

where N is the number of nitrogen molecules, which is also the number of oxygen molecules. If we do the same for the oxygen with another piston, introduced from the other side, we get another, equal decrease in the entropy. This takes us back to the original state, so since entropy is a state function, the increase in entropy when we allowed the gases to mix was

$$\Delta S = -2\Delta S_{\mathrm{N}} = 2N k_B \log 2.$$

[3] **Problem 3.** Some basic conceptual questions about the second law.

(a) Verify explicitly that the second law of thermodynamics allows heat to flow from a hot body to a cold one, but not vice versa.

(b) Derive the efficiency of a Carnot engine operating between reservoirs of temperatures $T_H > T_C$ by using the fact that the Carnot cycle is reversible, i.e. that after a complete Carnot cycle the entropy of the universe is unchanged.

(c) Let's suppose that in addition to reservoirs at temperatures T_H and T_C, you had a reservoir at temperature $(T_H + T_C)/2$. Is the Carnot cycle between the extreme reservoirs still the most efficient option? If not, what's the maximum possible efficiency?

(d) Consider the free expansion of an ideal gas. No work is done, and the internal energy U does not change. However, the entropy increases since the process is irreversible. On the other hand, the first law states

$$dU = T\,dS + đW$$

so there appears to be a contradiction. What is wrong with this argument?

[3] **Problem 4.** Most thermodynamic systems have positive heat capacities, but a gravitationally bound system of particles has a negative heat capacity by the virial theorem, as does a black hole. Suppose a system with negative heat capacity C_1 is placed in thermal contact with a slightly cooler system with positive heat capacity C_2.

(a) What happens in the long run if $|C_1| > |C_2|$?

(b) What happens in the long run if $|C_1| < |C_2|$?

(c) Some systems, such as lasers, have a negative temperature and a positive heat capacity. (You'll see another example of negative temperature in problem 11.) What happens if such a system is placed in thermal contact with a system with positive temperature and heat capacity?

[3] **Problem 5** (Kardar)**.** The solar system originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

(a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law?

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?

(c) The evolution of life and intelligence requires even further levels of organization. Why does this not violate the second law?

For a nice discussion of these issues, see section 36.7 of Blundell and Blundell.

[4] **Problem 6.** We can find an expression for entropy of an ideal gas using pure thermodynamics. Consider n moles of an ideal gas with adiabatic index γ, initially at pressure P and volume V.

(a) Suppose the gas is heated at constant volume to pressure P'. Compute the change in entropy.

(b) Suppose the gas is instead expanded at constant pressure to volume V'. Compute the change in entropy.

(c) By combining your two results, show that the entropy $S(P, V)$ of the ideal gas is

$$S = nC_V \log(PV^\gamma) + \text{constant}$$

when n is constant. The constant can't be found using classical thermodynamics alone, since it only can determine changes in entropy.

(d) Now consider the case where the ideal gas is allowed to freely expand into a vacuum, reaching a final volume V'. This is an example of a nonequilibrium process that changes the entropy, despite no work or heat transfer. Find the resulting change in entropy.

(e) So far, we don't know anything about how S depends on n, because we only considered processes that kept n constant. However, the entropy should be extensive, meaning that if the pressure and temperature are kept the same, then S is proportional to n. Thus, if in general

$$S/n = C_V \log(PV^\gamma f(n)) + \text{constant}$$

then the right-hand side must be independent of n. Using this, find $f(n)$.

[3] **Problem 7.** 🕓 USAPhO 2014, problem A2.

[3] **Problem 8.** 🕓 USAPhO 2017, problem A2. A simple but tricky problem. (For a more involved problem based on the same fundamental idea, see Physics Cup 2019, problem 2.)

[3] **Problem 9.** 🕛 USAPhO 2020, problem B3. An advanced problem which shows you how to compute corrections for a slightly nonideal gas. (Note that you can use the quantity T in any of the parts, not just (e) and (f).)

3 Quantum Statistical Mechanics and the Third Law

Idea 6: Third Law

The entropy of any thermodynamic system approaches zero as the temperature goes to zero.

The third law of thermodynamics is a bit of a black sheep. Unlike the other laws, it is inherently quantum mechanical, and comes from the statistical definition of entropy, as described below.

[2] **Problem 10.** Show that the third law requires the specific heat C to approach zero as the temperature approaches zero. (Since this isn't true for a classical ideal gas, the ideal gas law *must* break down in quantum mechanics, at low temperatures. You can also see this from your result for the entropy in problem 6, which diverges at low temperatures; there's no way to add a constant to it to make it go to zero at zero temperature.)

Idea 7: Microcanonical Ensemble

If a large isolated system in thermodynamic equilibrium is in one of Ω quantum states, then we assume all of the states are equally likely, and the entropy is

$$S = k_B \log \Omega.$$

This is the fundamental definition of entropy; in fact the equation $dS = đQ/T$ does not define entropy, but rather defines temperature! The third law follows from this result because at temperature $T = 0$, all systems settle into their ground state, so $\Omega = 1$ and $S = 0$.

Remark

The assumption that all states are equally likely may sound a bit confusing, because in **T1** we used the Boltzmann distribution, which stated that higher-energy states were less likely to be occupied. The difference is that for the Boltzmann distribution, we assumed the system was inside an environment at temperature T. In fact, all quantum states of the system and environment together remain equally likely in this context, but lower-energy states of the system correspond to more energy in the environment, and hence (usually) more possible environment states. Thus, accounting for the number of possible environment states, lower-energy states of the system are more likely. You will make all this precise in problem 11, where you will use it to derive the Boltzmann distribution.

Example 4: Mixing Entropy

Repeat example 3 using statistical mechanics.

Solution

In statistical mechanics, we can compute S directly using $S = k_B \log \Omega$. Focusing on a single oxygen or nitrogen molecule, let Ω_i be the initial number of possible states. When the partition is removed, the possible position space for the particle doubles, and since quantum states all have the same volume in phase space, the number of states available doubles. So for one particle,

$$\Delta S_{\text{part}} = k_B \log(2\Omega_i) - k_B \log \Omega_i = k_B \log 2.$$

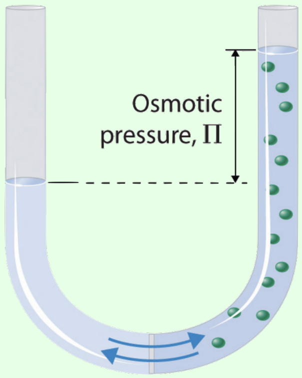
Since the $2N$ particles are independent,

$$\Delta S = 2N \Delta S_{\text{part}} = 2N k_B \log 2$$

in agreement with the result from thermodynamics.

Example 5: Osmotic Pressure

A water-filled tube is divided by a membrane which only allows water molecules through. When a substance is dissolved in one half of the tube, forming N ions, the water level on that side is observed to go up, as shown.



Explain why, and calculate the height difference, neglecting interactions between different ions, and between the ions and the water.

Solution

Osmotic pressure is an example of an entropic force. Suppose that the water level on one of the tube goes up. The water is otherwise unchanged, since it's just translated along the tube, so its entropy has not changed. But its energy is higher, and this energy must have come via heat transfer from the environment. Hence the entropy of the environment has decreased.

If there were no dissolved ions, this would show why water levels don't spontaneously go up: it is forbidden by the second law. But here, increasing the water in the section with the ions increases the ions' entropy, since they now have more positions they could be in. Since the number of available quantum states is proportional to the available volume, we have

$$S_{\text{ion}} = N k_B \log V$$

up to an additive constant, which means that

$$dS_{\text{ion}} = \frac{N k_B}{V} \, dV.$$

In equilibrium, let there be an osmotic pressure difference P across the membrane. Then moving a volume dV of water across it costs energy $P \, dV$, so

$$dS_{\text{env}} = -\frac{đQ}{T} = -\frac{P}{T} \, dV.$$

In thermodynamic equilibrium the total entropy is maximized, giving

$$dS_{\text{ion}} + dS_{\text{env}} = 0.$$

Solving for the osmotic pressure gives

$$PV = N k_B T.$$

The height difference is simply found using hydrostatic pressure,

$$h = \frac{P}{\rho g} = \frac{N k_B T}{\rho V g}.$$

The appearance of a pressure here in response to an opportunity for decreasing entropy is generally called an "entropic force". In fact, you might have already seen this result in chemistry class, but in rather different notation. In chemistry textbooks, you'll typically see

$$\Pi = iMRT$$

where Π is the osmotic pressure, M is the molarity of solute, and the van 't Hoff factor i is the number of moles of ions per mole of solute. This is perfectly equivalent to what we found.

Remark

Why does the expression for osmotic pressure bear a suspicious resemblance to the ideal gas law? The reason is that, by completely neglecting interactions between the solute and solvent, we have effectively treated the solute ions like an ideal gas, from the standpoint of entropy. This gives an additional contribution to the pressure, which can be derived just like the pressure of an ideal gas is in **T1**. (Using this reasoning backwards, one can conclude that the pressure of an ideal gas can also be described as an entropic force, using the same reasoning as above.)

The reason that this kinetic theory connection to the ideal gas law is not emphasized in chemistry classes is that the solute particles don't actually behave like an ideal gas at all. They are part of a liquid, and hence are constantly bumping into the solvent particles. The thermodynamic reasoning we used above is more general, because it only requires that the interaction between the solvent and solute doesn't significantly change the solute's entropy.

By the way, if you're wondering precisely whan an entropic force *is*, rest assured that nothing magical is going on here. In the end, there are no forces at play except for the ordinary forces you're familiar with. It's just that often, calculating what those forces do in aggregate in thermodynamically large systems is very hard. An entropic force simply means a force whose value we can calculate most easily using the tool of entropy.

[5] **Problem 11.** This is a long problem, but a really useful one that ties a lot of things together. Consider a set of N atoms, each of which may be in the ground state, with zero energy, or in an excited state with energy E_0. Suppose it is only known that the total energy of the system is $\alpha N E_0$.

(a) For large N, Stirling's approximation states that

$$\log N! \approx N \log N - N.$$

Derive this expression by writing $\log N!$ as a sum, and approximating the sum with an integral.

(b) Using Stirling's approximation, show that the entropy of the system is

$$S = N k_B \left(\alpha \log \frac{1}{\alpha} + (1 - \alpha) \log \frac{1}{1 - \alpha} \right).$$

Sketch the entropy as a function of α.

(c) Using the definition of temperature, $dS = đQ/T$, show that the system has a temperature of

$$T = \frac{E_0}{k_B} \frac{1}{\log(1 - \alpha) - \log \alpha}.$$

Sketch the temperature as a function of α. In particular, what temperature do you need to get $\alpha = 1/2$? How about $\alpha = 1$?

(d) Show that the third law is satisfied.

(e) Now consider just a single one of the N atoms, where the total energy of the system is $\alpha N E_0$ as before. Show that the probability it is excited obeys the Boltzmann distribution.

[5] **Problem 12.** This long problem illustrates some important features of free energy. A rubber molecule can be modeled in one dimension as a chain consisting of a series of $N = N_+ + N_- \gg 1$ links of length a, where N_+ point in the $+z$ direction and N_- point in the $-z$ direction. The orientations of each of the links are independent, and it costs no energy to rotate a link. Thus all configurations are equally likely at any temperature.

(a) Find the length L of the chain in terms of N_+ and N_-.

(b) Using Stirling's approximation,

$$\log N! \approx N \log N - N$$

and assuming that $L \ll Na$, show that

$$S = Nk_B \left(\log 2 - \frac{L^2}{2N^2a^2} \right)$$

and hence show that the entropy decreases as L increases. This model is very basic; for instance, it tells us nothing about the tension in the chain, but the sign here is correct. (Hint: notice that the changes in entropy are of order L^2/N, and hence are very small. You will have to be careful with your approximations to avoid dropping an important contribution.)

(c) Note that the entropy doesn't depend on temperature, because all configurations have the same energy. In a more realistic model, the total entropy of the molecule would be the sum of the entropy computed above, plus the entropy due to additional thermal motions, such as vibrations of the links. Given this, if a rubber band is quickly stretched, does it feel warm or cold to the touch? (You can check your answer experimentally!)

(d) Now suppose a mass m is hung from the bottom of the chain. Find the average length of the chain at temperature T, using the Boltzmann distribution. Do not assume $L \ll Na$. (The force that raises this mass is another example of an entropic force.)

(e) It turns out that you can also arrive at this answer by maximizing the entropy of the entire universe S_{univ}. Argue in general that S_{univ} is maximized when the Helmholtz free energy

$$F = U - TS$$

is minimized, where U is the total energy of the rubber band and mass, and T is the temperature of the system and its surroundings. (Hint: use the expression for dS_{univ}, along with conservation of energy.)

(f) Show that in the limit $L \ll Na$, F is indeed minimized at the equilibrium length.

Remark: Heat vs. Work

What is the difference between work and heat? If we have a gas in a cylinder with a piston, moving the piston counts as work. Clearly, if we split the piston into two halves and moved them independently, this would still be work. But we can keep splitting the piston until we are down to individual atoms of the piston. These can transfer energy to gas particles because they can slam into them as the gas particles are bouncing off, like a batter hitting a baseball. But as mentioned in **T1**, this is precisely how a hot wall transfers energy to a gas! So when did we transition from doing work to supplying heat?

The point is that there is no sharp distinction. There's just energy transfer; work is the subset of energy transfers that we keep track of detail, and heat is the subset we don't. Entropy quantifies our ignorance of the precise state a system is in. That's why supplying heat changes the entropy and doing work doesn't.

Remark: Is Entropy Subjective?

Our definition of entropy involved the number of states the system "could" be in, but of course in reality the system is actually in just one state. We really mean the number of states the system could be in given the information you know. For example, for an ideal gas we usually know the temperature, pressure, and volume.

You might find this disturbing because it implies the entropy is subjective, depending on what each person personally knows. But the entropy determines things like F, and hence the amount of work that can be extracted from the system, so how could it differ?

In fact, there is no contradiction between these two things. For example, suppose that besides the usual properties, particles in an ideal gas can be slightly bigger or smaller. If you happen to somehow know that all of the big particles are on the left side of a box and all the small particles are on the right side, then the entropy you assign to the box is lower than somebody who doesn't know about this, and accordingly you can extract more work from the box. For instance, you can put a filter that only allows small particles through in the middle, then collect energy as small particles move from right to left.

On the other hand, if you are hit on the head and forget that the particles are sorted by size, your entropy for the gas goes up. And accordingly, you can now extract less work, because you wouldn't know it made sense to put in such a filter in the first place!

While this example may seem contrived, it's actually exactly the same as our earlier mixing entropy example! If you don't have any equipment that can distinguish between oxygen and nitrogen molecules, then the "unmixed" state already has just as much entropy as the mixed state. In this case, the entropy doesn't change at all when you allow the gases to mix.

What this example shows is that you don't have to know everything about a system to use thermodynamics. Even if you are wrong about how the system behaves microscopically, you can still use the theory to describe what *you* can do with the system, using *your* knowledge. That's the core reason for the longevity of thermodynamics. As a recent paper put it:

> If physical theories were people, thermodynamics would be the village witch. Over the course of three centuries, she smiled quietly as other theories rose and withered, surviving major revolutions in physics, like the advent of general relativity and quantum mechanics. The other theories find her somewhat odd, somehow different in nature from the rest, yet everyone comes to her for advice, and no one dares

to contradict her.

For more about this perspective, see the insightful articles by E.T. Jaynes, *The Gibbs Paradox* and *Information Theory and Statistical Mechanics*. (But don't read too much of his later work, since he got pretty cranky with age.)

4 Blackbody Radiation

Idea 8: Planck's Law

As we will show in **X1**, the radiation power per unit area from an object at temperature T at frequency f, per unit frequency, is

$$I(f) = \frac{2\pi h f^3}{c^2} \frac{1}{e^{hf/k_B T} - 1} e(f)$$

where $e(f)$ is called the emissivity. For an ideal blackbody, $e(f) = 1$. By integrating over all frequencies, one finds that the total power per unit area from an ideal blackbody is

$$J = \int_0^\infty I(f)\, df = \sigma T^4, \quad \sigma = \frac{2\pi^5 k_B^4}{15 c^2 h^3}.$$

This is the Stefan–Boltzmann law, which can also be derived with dimensional analysis. It's a compact and useful result, which means it comes up quite often in Olympiads.

[2] **Problem 13.** Some basic manipulations with Planck's law.

(a) Show that $J \propto T^4$ by nondimensionalizing the integral, as explained in **P1**.

(b) Prove Wien's displacement law, which states that the maximum of $I(f)$ for an ideal blackbody occurs at a frequency which is proportional to T.

Example 6

At high temperatures, the resistivities of many temperatures scale approximately linearly with temperature. Suppose that a light bulb supplies total radiation power P when connected across an AC voltage V. How does P scale with V?

Solution

The total power dissipated in the resistor scales as V^2/R, and $R \propto \rho \propto T$. This power must equal the blackbody radiation power emitted, so by the Stefan–Boltzmann law,

$$P \propto T^4 \propto \frac{V^2}{T}$$

from which we conclude that $T \propto V^{2/5}$, so $P \propto V^{8/5}$.

Example 7

A nonideal blackbody absorbs a fraction $a(f)$ of incident radiation of frequency f. (For an ideal blackbody, $a(f) = 1$.) Show that the second law implies Kirchoff's law, $e(f) = a(f)$.

Solution

First let's consider the case where $a(f)$ and $e(f)$ are constants, which don't depend on f. If we place two blackbodies of temperature T right next to each other, then the rate at which the first heats the second is proportional to $e_1 a_2$, while the rate the second heats the first is proportional to $e_2 a_1$. By the second law, these must be equal, which implies $e_1/a_1 = e_2/a_2$. Hence the ratio is constant. But for a perfect blackbody, $e = a$, so the two are equal.

More generally, suppose we place in between the two blackbodies a filter that only lets light of frequency f through, and blocks everything else. Then the same reasoning gives $e_1(f)/a_1(f) = e_2(f)/a_2(f)$, so $e(f) = a(f)$. Thermodynamics forces good absorbers to also be good emitters. It's possible to derive this microscopically, by considering how individual atoms behave; in that context Kirchoff's law follows from time reversal symmetry.

You might wonder what would happen if we placed a "one-way" filter which only let light through in one direction. Such a filter would act like Maxwell's demons for photons: if you used one to divide a room full of photons, it would start directing photons of certain frequencies to one side or the other, decreasing the entropy. So thermodynamics also forbids the existence of one-way filters; again, microscopically this is a result of time reversal symmetry.

Example 8

A satellite contains a nuclear reactor at its core, fixed at temperature T_H. Suppose the exterior of the satellite is somehow fixed at temperature T_C, and the satellite runs an ideal heat engine, using the core and exterior as hot and cold reservoirs. Treat the exterior as an ideal blackbody, and neglect the temperature of outer space. What value of T_C maximizes the rate of work extracted?

Solution

One might think that T_C should be as low as possible, to increase the efficiency of the cycle. However, a lower T_C means a lower rate of heat emission $\dot{Q}_{\text{out}}$, since we are limited by emission of blackbody radiation, which lowers the rate of work done $\dot{W}$.

The rate of heat emitted from the satellite is

$$\dot{Q}_{\text{out}} = \sigma A T_C^4 \propto T_C^4.$$

Therefore, the rate of work done is

$$\dot{W} = \eta \dot{Q}_{\text{in}} = \eta \frac{T_H}{T_C} \dot{Q}_{\text{out}} \propto \left(1 - \frac{T_C}{T_H}\right) \frac{T_H}{T_C} T_C^4 = T_H T_C^3 - T_C^4.$$

This is maximized when $T_C = (3/4) T_H$, at which point the efficiency is $1/4$.

[2] **Problem 14.** Consider two adjacent blackbodies with similar temperatures, exchanging energy by radiation. Show that the rate of change of the temperature difference is approximately proportional to the temperature difference itself. This is an example of Newton's law of cooling, which implies the temperature difference decays exponentially. How does the time scale for cooling depend on the average temperature of the blackbodies?

[3] **Problem 15** (IPhO 1992)**.** A satellite is a sphere of diameter D orbiting about the Earth.

(a) First suppose the satellite is perfectly black. Ignoring the effect of the Earth, find its temperature T in terms of the temperature $T_\odot$ of the Sun, the radius $R_\odot$ of the Sun, and the radius R of Earth's orbit.

(b) How does the answer change if the satellite has a uniform emissivity $e(f) = e_0 < 1$?

(c) If an engineer wishes to make T as small as possible using a special paint, which can have an arbitrary $e(f)$, sketch how the function $e(f)$ should look.

[3] **Problem 16** (IPhO 1996)**.** Two perfectly black surfaces of temperatures T_h and T_ℓ are parallel to each other in vacuum, and the net heat flux from the hotter surface to the colder one is P.

Now suppose that N parallel, thermally insulating, perfectly black plates are placed in between them. This shielding reduces the heat flux to P'. Find P' in terms of P.

Example 9

In problem 16 you considered some ideally black surfaces, but things get more complicated when the surfaces have general emissivity. For simplicity, consider two walls facing each other, with emissivities e_1 and e_2. Verify that when both walls have temperature T, there is no net energy flow from one to the other.

Solution

Let $I_0 = \sigma T^4$. The second wall emits radiation of intensity $e_2 I_0$, so in equilibrium it must absorb this amount as well. Verifying this takes a little work.

The first wall emits radiation of intensity $e_1 I_0$, and a fraction e_2 of it gets absorbed by the second wall. The rest bounces back to the first wall, and if it doesn't get absorbed by the first wall, then it comes back to the second wall again for another chance to get absorbed. The total intensity transferred from the first wall to the second is the sum of an infinite series,

$$I_{1\to 2} = (e_1 I_0)\,(e_2 + (1-e_2)(1-e_1)e_2 + \ldots) = \frac{e_1 e_2 I_0}{e_1 + e_2 - e_1 e_2}.$$

This isn't the expected result, because there's another contribution. When the second wall emits radiation, it can reflect off the first wall and then get reabsorbed by the second wall.

So the second wall absorbs a total radiation intensity due to its own emission, of

$$I_{2\to 2} = (e_2 I_0)\left((1-e_1)e_2 + (1-e_1)(1-e_2)(1-e_1)e_2 + \ldots\right) = \frac{(1-e_1)e_2^2 I_0}{e_1+e_2-e_1e_2}.$$

When you sum these contributions, you get $e_2 I_0$ as expected. This is a typical example of the power of thermodynamics: it is often easy to tell what the answer has to be, but the way that answer comes about can be a bit complicated.

Example 10

Suppose a black sphere of radius r is placed inside a large container of arbitrary shape, whose walls are a blackbody with temperature T. In the steady state, what is the rate of power absorbed by the sphere from the walls?

Solution

Radiation is continually emitted from all points on the walls in all directions, so it would seem that we have to do a complicated integral to find how much hits the sphere, which would be hard even if we were given the container's shape. But the problem is actually trivial due to the second law of thermodynamics!

Let's suppose the sphere itself is also at temperature T. Then it sends power $(4\pi r^2)\sigma T^4$ to the walls, since all radiation that exits the sphere hits the walls. But if the sphere and walls are at the same temperature, a temperature difference cannot spontaneously appear. Therefore, the power going from the walls to the sphere must also be $(4\pi r^2)\sigma T^4$. And since this quantity can also be expressed as a geometric integral, it can't depend on the temperature of the sphere, so it must be true for any sphere temperature.

For a tough problem which uses a variant of this idea, see EFPhO 2010, problem 2.

[2] **Problem 17.** ◷ USAPhO 2011, problem A3.

[3] **Problem 18.** ◷ USAPhO 2006, problem B2. The graphs are hard to read, but do your best!

[3] **Problem 19.** ◷ USAPhO 2019, problem A2. An elegant, tricky radiation problem. (This is essentially the same problem as Physics Cup 2022, problem 5.)

[3] **Problem 20.** Planck's law can be used to understand atomic physics, as Einstein showed and as you will now show. Suppose we have a collection of two-state atoms encased inside a cavity, whose walls are blackbodies with temperature T. In equilibrium, there will be N_1 atoms in the ground state and N_2 atoms in the excited state, bathed in a photon gas of temperature T. Three physical processes can occur:

1. Atoms in the excited state can each spontaneously decay with rate A.
2. Atoms in the ground state can absorb a photon. For each atom, the rate of this process is $B\rho(f)$ where $\rho(f)$ is the energy density of radiation at frequency f.

3. Atoms in the excited state can undergo stimulated emission when interacting with a photon, in the process $e + \gamma \to g + \gamma + \gamma$. For each atom, the rate of this process is $B'\rho(f)$.

These three "Einstein coefficients" depend on the frequency, but not on the temperature.

(a) Argue that $\rho(f)$ is proportional to $I(f)$ in Planck's law. In fact,

$$I(f) = \frac{c}{4}\rho(f)$$

though you do not have to show this.

(b) Write down an expression for dN_2/dt.

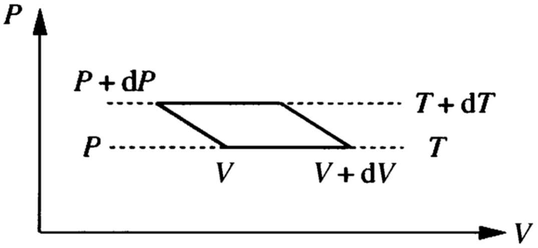
(c) In the steady state, for any temperature, N_2/N_1 must be given by the Boltzmann distribution. Using this, find A and B' in terms of B.

This is an extraordinary result: one might have expected a difficult calculation to find each of A, B, and B', but if you know one, then by thermodynamics you know them all. In particular, thermodynamics *requires* spontaneous emission to be possible, $A \neq 0$.

[3] **Problem 21.** In **T1**, we derived some properties of photon gases using basic kinetic theory. Here, we'll derive some more properties, starting from Planck's law and then sticking with pure thermodynamics. As in problem 20, we assume there is a photon gas at temperature T, with pressure P within a cavity of volume V, whose walls are perfect blackbodies. (Note that since photons can be absorbed and emitted by the walls, it doesn't make sense to talk about N as for an ideal gas. Instead, N is determined by the other parameters. This actually makes things simpler, since there's one less variable to worry about.)

(a) It turns out that the pressure of the photon gas is $P = AT^4$ where A is a constant. Explain why the pressure depends only on the temperature. (Harder, optional task: explain why $P \propto T^4$ starting from Planck's law.)

(b) Our next goal is to compute $U(T, V)$. Consider an infinitesimal Carnot cycle, shown below.



By equating the efficiency of this cycle to the Carnot efficiency, find $(\partial U/\partial V)|_T$.

(c) By integrating this result, and using $U(T, 0) = 0$, find $U(T, V)$.

(d) We can now use these results to find $S(T, V)$, just as we did for an ideal gas in problem 6, i.e. by considering the change of entropy during some infinitesimal process and then integrating the result. Do this in any way you like. Can the third law be satisfied?

[5] **Problem 22.** Physics Cup 2018, problem 9.

5 Heat Conduction

Idea 9: Fourier's Law

In **T1**, you investigated heat conduction from the standpoint of kinetic theory. Now we revisit the subject from the standpoint of hydrodynamics. The flux of heat (i.e. the power per unit area) due to thermal conduction is proportional to the temperature gradient,

$$J = -\kappa \frac{dT}{dx}.$$

By considering the net heat flowing in and out of a slab of width dx, we have

$$\frac{du}{dt} = -\frac{dJ}{dx} = \kappa \frac{d^2T}{dx^2}.$$

where u is the energy density. Intuitively, this shows how heat conduction works to smooth out temperature gradients. For example, if the temperature had a local minimum, then du/dt would be positive at that point, as heat flows in from all directions.

Example 11

Find the steady state heat flow through a rectangular slab of area A and thickness d, whose left and right ends are held at temperature T and $T + \Delta T$.

Solution

By the argument in the above idea, in the steady state the energy density within the slab is constant, so $d^2T/dx^2 = 0$ and the temperature gradient is uniform. In this steady state, heat simply flows uniformly through the slab, without accumulating anywhere in it, just like current flows uniformly through a resistor. (Since this "internal" steady state is often reached quickly, in many problems it is just assumed to hold, without being explicitly stated.)

Therefore, the temperature gradient is just $\Delta T/d$ everywhere in the slab, so

$$P = JA = \frac{\kappa A \Delta T}{d}.$$

This is single most important equation for heat conduction problems.

Remark: Continuity Equations

We can generalize the results above to three dimensions. In this case, the flux of heat is described by a vector,

$$\mathbf{J} = -\kappa \nabla T.$$

The conservation of energy equation becomes

$$\frac{du}{dt} = -\nabla \cdot \mathbf{J} = \kappa \nabla^2 T.$$

The first equality here is known as a continuity equation, and it is the general way that the density of a conserved quantity is related to a flow. For example, the continuity equation for fluids, which we saw in one-dimensional form in **M7**, is written in three dimensions as

$$\frac{d\rho}{dt} = -\nabla \cdot (\rho \mathbf{v})$$

and expresses conservation of mass. The continuity equation for charge, which we'll see in **E4**, is very similar,

$$\frac{d\rho}{dt} = -\nabla \cdot \mathbf{J}$$

where ρ is a charge density and $\mathbf{J}$ is a current density.

[2] **Problem 23.** Supposing that it takes five minutes to boil an egg. Estimate how long it takes to boil an ostrich egg, which has three times the diameter.

[2] **Problem 24** (Cahn)**.** Estimate how long it will take for a small pond of depth $D = 0.5\,\mathrm{m}$ to freeze completely in a very cold winter. Take the thermal conductivity of the ice to be $\kappa = 2.2\,\mathrm{W/m\,K}$, the latent heat of fusion $L = 3.4 \times 10^5\,\mathrm{J/kg}$, and the density $\rho = 0.9 \times 10^3\,\mathrm{kg/m^3}$. Take the outside temperature to be a constant $T_0 \approx -10\,^\circ\mathrm{C}$, and for simplicity, suppose the entire pond starts at a uniform temperature $0\,^\circ\mathrm{C}$.

Example 12

Model a brick pizza oven as a sphere with inner radius R_1, outer radius R_2, and thermal conductivity κ. The inside of the oven is held at temperature T_1 and the outside of the oven is held at temperature T_2. In equilibrium, find $T(r)$, and the power needed to keep the inside of the oven at temperature T_1.

Solution

Consider a shell of radius r and thickness dr. The outward heat flow through it is

$$P(r) = -\kappa(4\pi r^2)\,\frac{dT}{dr}.$$

In addition, because the shells have constant temperature, there can be no net heat accumulating in any shell. Thus, $P(r)$ must actually be independent of r. Renaming it to P, we can integrate the resulting differential equation to find

$$\int_{T_1}^{T(r)} dT = -\int_{R_1}^{r} \frac{P}{4\pi\kappa r^2}\,dr$$

which gives the solution

$$T(r) = T_1 + (T_2 - T_1)\frac{r - R_1}{r}\frac{R_2}{R_2 - R_1}.$$

Now that we know $T(r)$, we can evaluate dT/dr at any radius to find the total power, using the first equation. Another slicker way, which doesn't even require knowing $T(r)$, is to integrate the first equation all the way from the inside of the oven to the outside,

$$\int_{T_1}^{T_2} dT = -\int_{R_1}^{R_2} \frac{P}{4\pi\kappa r^2}\,dr.$$

This gives an expression for the power in terms of the other parameters, yielding

$$P = 4\pi\kappa(T_1 - T_2)\frac{R_1 R_2}{R_2 - R_1}.$$

[2] **Problem 25.** Consider a sphere of a radioactive rock, which constantly produces heat σ per unit volume. The outside of the sphere is held at temperature T_0, the sphere's radius is R, and its thermal conductivity is κ. Find the temperature at the center of the sphere.

[3] **Problem 26.** 🕔 USAPhO 2016, problem A4. A practical conduction question.

[3] **Problem 27.** 🕔 USAPhO 2013, problem A1. An elegant conduction question.

[4] **Problem 28.** 🕛 EuPhO 2023, problem 1. A cute problem on thermal lensing.

Thermodynamics II

Chapters 3 and 4.1–4.4 of Wang and Ricardo, volume 2 cover the topics of this problem set at an appropriate level. For more detail, see chapters 10–16, 18, 21, and 23 of Blundell and Blundell. For interesting discussion, see chapters I-44 through I-46 of the Feynman lectures. There is a total of **83** points.

1 [A] The First Law

We started **T1** with basic thermodynamics; here we will treat it more thoroughly, using partial derivatives. Partial derivatives don't appear on the IPhO and APhO, and only rarely appear on the INPhO. However, they're a useful way to organize your thinking in more complex problems.

Idea 1

The first law states that

$$\Delta U = \Delta Q + \Delta W$$

where ΔU is the change in internal energy, ΔQ is the heat given to the system, and ΔW is the work done on the system. Only U is an intrinsic property of the system itself, i.e. a state function, we make this distinction explicit by writing the differential version as

$$dU = đQ + đW.$$

Idea 2

For a gas, the state of the system is specified by the pressure P, volume V, and temperature T, and the three are related by the ideal gas law. The infinitesimal work done is

$$đW = -P\,dV.$$

Similarly, many simple thermodynamic systems can be described by a temperature and a pair of "conjugate variables". For example, a bubble has surface tension γ, area A, and temperature T, where

$$đW = \gamma\,dA.$$

A rubber band, is described by its tension F, length L, and temperature T, with

$$đW = F\,dL.$$

In all of these simple examples, we have three variables and one "equation of state" which relates them, which means two parameters are required to describe the system's state. That's why, for example, you can't speak of a "heat capacity" dU/dT. There's more than one way to change the temperature: if we do it at constant volume, we get the heat capacity C_V, and if we do it at constant pressure, we get C_P. In **T1**, we just made these distinctions verbally, but this quickly gets confusing as you do more complex calculations. A more rigorous and powerful approach is to use partial derivatives, which explicitly specify what quantity is being held constant as another is changed.

Example 1

Consider describing a plane with Cartesian coordinates (x, y) and polar coordinates (r, θ). Calculate the partial derivatives $(\partial x/\partial r)|_\theta$ and $(\partial x/\partial r)|_y$.

Solution

To evaluate the first partial derivative, we need to write x as a function of r and θ. This is done by $x = r\cos\theta$. Differentiating with respect to r and treating θ as a constant, we have

$$\left.\frac{\partial x}{\partial r}\right|_\theta = \cos\theta.$$

To evaluate the second, we should write x in terms of r and y. This is done starting with

$$r^2 = x^2 + y^2.$$

We could solve for x here. However, it's quicker to use the usual trick of implicit differentiation: note that differentiating both sides with respect to r, at fixed y, gives

$$2r = 2x\left.\frac{\partial x}{\partial r}\right|_y + 0$$

which yields the answer,

$$\left.\frac{\partial x}{\partial r}\right|_y = \frac{r}{x} = \frac{1}{\cos\theta}.$$

These two results are different: changing what you keep constant changes the derivative. You can see this geometrically by evaluating the two versions of $\partial x/\partial r$ at a few points.

Idea 3: Multivariable Differential

The change of a function $f(x, y)$ upon independent changes in x and y is

$$df = \left.\frac{\partial f}{\partial x}\right|_y dx + \left.\frac{\partial f}{\partial y}\right|_x dy$$

which you can recognize as an alternative form of the multivariable chain rule from **P1**. We can also use this equation to describe increments of quantities that aren't state functions, in which case we'll write the left-hand side as $đf$.

Example 2: Heat Capacities

The heat capacities at constant volume and constant pressure are defined as

$$C_V = \left.\frac{\partial Q}{\partial T}\right|_V, \quad C_P = \left.\frac{\partial Q}{\partial T}\right|_P.$$

Find a formula for $C_P - C_V$ in terms of the variables P, V, T, and the internal energy U.

Solution

First off, to avoid any confusion, note that the definitions above does not imply that Q can be written as a function of T and V, or T and P. It can't, because Q isn't a state function. We simply mean that in a process that changes the variables P, V, and T by some infinitesimal amount, we pick up an increment of heat transfer $đQ$ that can be written as a linear combination of those differentials. That is, we may write

$$đQ = C_V \, dT + \left.\frac{\partial Q}{\partial V}\right|_T dV = C_P \, dT + \left.\frac{\partial Q}{\partial P}\right|_T dP.$$

Now we massage the first expression into one containing only dT and dP. Since V, T, and P are all related by the equation of state, we can write V as a function of T and P, so

$$dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP.$$

Plugging this into the first expression, we have

$$đQ = C_V \, dT + \left.\frac{\partial Q}{\partial V}\right|_T \left(\left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP \right)$$

from which we see, by identifying the coefficient of dT, that

$$C_P - C_V = \left.\frac{\partial Q}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P.$$

We're not done, because we don't have a nice expression for $(\partial Q/\partial V)_T$. To finish up, we can use the first law of thermodynamics, along with $đW = -P \, dV$, to show that

$$\left.\frac{\partial Q}{\partial V}\right|_T = \left.\frac{\partial U}{\partial V}\right|_T + P.$$

We thus conclude that

$$C_P - C_V = \left(\left.\frac{\partial U}{\partial V}\right|_T + P \right) \left.\frac{\partial V}{\partial T}\right|_P.$$

This is actually quite intuitive. The extra heat we have to put in at constant pressure, when we allow the volume to change, comes from two sources. First, we have to make up for the energy lost to $P \, dV$ work. Second, we have to make up for the energy intrinsically needed to expand the gas, by doing work against the attractive intermolecular forces between the gas molecules. (That second term is zero for an ideal gas by definition.) However, trying to show this result without the organizing framework of partial derivatives would be prone to error.

Remark

The partial derivative satisfies a few more important identities. First off, if you always hold the *same* variable constant, then all two-variable functions effectively turn into one-variable functions, which means we recover the basic rules from **P1**,

$$\left.\frac{\partial w}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = \left.\frac{\partial w}{\partial x}\right|_z, \quad \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1$$

where the second identity is just the first in the special case $w = x$. For example, the first identity ensures the coefficients of dP in the two expressions for $đQ$ above are equal. In addition, partial derivatives commute and satisfy the triple product rule,

$$\left.\frac{\partial}{\partial y}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = \left.\frac{\partial}{\partial x}\right|_y \left.\frac{\partial z}{\partial y}\right|_x, \quad \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1.$$

You won't need to use any of these identities in the problem sets. However, it might be reassuring to know that these are *all* the rules you'll ever need for partial derivatives.

[1] **Problem 1.** For an monatomic ideal gas, we have $U = (3/2)nRT$ and the equation of state $PV = nRT$. Evaluate C_V and C_P using the results above.

Solution. Note that

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \frac{3}{2}nR,$$

and

$$C_P - C_V = \left(\left.\frac{\partial U}{\partial V}\right|_T + P\right)\left.\frac{\partial V}{\partial T}\right|_P = P\frac{nR}{P} = nR.$$

Thus, we see $C_P = (5/2)nR$ as expected.

[3] **Problem 2.** In this problem we modify the ideal gas to account for a short-ranged attractive intermolecular force. This attraction yields a negative contribution to the energy, so that

$$U = \frac{3}{2}nRT - \frac{an^2}{V}.$$

(a) Explain why the change in energy is proportional to n^2/V.

(b) Argue that because of this extra term, the pressure is an^2/V^2 less than it would be for an ideal gas. Hence conclude the equation of state is

$$\left(P + \frac{an^2}{V^2}\right)V = nRT.$$

(c) Show that the heat capacities are

$$C_V = \frac{3}{2}nR, \quad C_P - C_V = nR + \frac{2an^2}{TV} + O(n^3)$$

in the limit where the gas is dilute.

In **T3**, we will combine this pressure correction with a "volume exclusion factor" to yield the van der Waals gas, which is useful for modeling the liquid-gas phase transition.

Solution. (a) Since the interaction is short-ranged, the energy associated with bonds to a single given molecule is proportional to the density, n/V. We pick up another factor of n from the total number of molecules.

(b) The differential of this energy is $dU = (an^2/V^2)dV$, which behaves just like a negative contribution to the pressure, $\Delta P = -an^2/V^2$.

(c) The first result is just from the definition of the heat capacity. Next,

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\bigg|_T + P \right) \frac{\partial V}{\partial T}\bigg|_P = \left(P + \frac{an^2}{V^2} \right) \frac{\partial V}{\partial T}\bigg|_P .$$

To get $\partial V/\partial T|_P$, differentiate the equation of state with respect to T at constant P,

$$nR = \left(P + \frac{an^2}{V^2} - \frac{2an^2}{V^2} \right) \frac{\partial V}{\partial T}\bigg|_P .$$

Plugging this result in and expanding to lowest order in a, which requires using the equation of state again, gives the result.

2 The Second Law

Idea 4: Entropy

The increase in entropy of a body at temperature T that receives heat $đQ$ is

$$dS = \frac{đQ}{T}$$

if the process is reversible; moreover, entropy is a state function.

Idea 5: Second Law

The second law of thermodynamics takes several equivalent forms, which are all useful.

- For an isolated system, $dS > 0$ for any spontaneous process.
- Clausius: no process is possible whose sole result is the transfer of heat from a colder to a hotter body.
- Kelvin: no process is possible whose sole result is the complete conversion of heat into work.
- Carnot: of all heat engines working between two given temperatures, none is more efficient than a Carnot engine.

Example 3: Mixing Entropy

A container of volume V is divided in half by a partition. The two halves contain pure nitrogen and oxygen gas, respectively, both at pressure P and temperature T. The partition is removed and the gases are allowed to mix. How much does the entropy increase?

Solution

We cannot apply the formula $dS = đQ/T$, because the gas is not in equilibrium during the process. However, because entropy is a state function, we can calculate its change by considering a path that only goes through equilibrium states.

Suppose we introduce a piston at one end of the container, which is magically transparent to oxygen atoms, and slowly and isothermally move it to the center of the container. This puts the nitrogen back where it started. The change in entropy of the nitrogen is

$$\Delta S_{\mathrm{N}} = \frac{Q}{T} = -\frac{W}{T} = nR \log \frac{V_i}{V_f} = -nR \log 2 = -N k_B \log 2$$

where N is the number of nitrogen molecules, which is also the number of oxygen molecules. If we do the same for the oxygen with another piston, introduced from the other side, we get another, equal decrease in the entropy. This takes us back to the original state, so since entropy is a state function, the increase in entropy when we allowed the gases to mix was

$$\Delta S = -2\Delta S_{\mathrm{N}} = 2Nk_B \log 2.$$

[3] **Problem 3.** Some basic conceptual questions about the second law.

(a) Verify explicitly that the second law of thermodynamics allows heat to flow from a hot body to a cold one, but not vice versa.

(b) Derive the efficiency of a Carnot engine operating between reservoirs of temperatures $T_H > T_C$ by using the fact that the Carnot cycle is reversible, i.e. that after a complete Carnot cycle the entropy of the universe is unchanged.

(c) Let's suppose that in addition to reservoirs at temperatures T_H and T_C, you had a reservoir at temperature $(T_H + T_C)/2$. Is the Carnot cycle between the extreme reservoirs still the most efficient option? If not, what's the maximum possible efficiency?

(d) Consider the free expansion of an ideal gas. No work is done, and the internal energy U does not change. However, the entropy increases since the process is irreversible. On the other hand, the first law states

$$dU = T\,dS + đW$$

so there appears to be a contradiction. What is wrong with this argument?

Solution. (a) If $đQ$ of heat flows from T_1 to T_2 with $T_1 > T_2$, the total change in entropy is

$$-đQ/T_1 + đQ/T_2 > 0,$$

so $đQ > 0$ as desired.

(b) The change in entropy of the engine itself is zero, because it just ends up at its original state. The only other contribution is the change in entropy of the reservoirs,

$$\Delta S_{\text{univ}} = \frac{Q_C}{T_C} - \frac{Q_H}{T_H}.$$

Setting this to zero gives $Q_C/T_C = Q_H/T_C$. The efficiency is then

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_C}{T_H}.$$

(c) The Carnot engine is still the most efficient option. There are several ways to see this, but one way is to note that from the standpoint of entropy changes in part (b), any reversible engine is just a combination of a Carnot engine operating between the extreme reservoirs, and a Carnot engine operating between the hottest reservoir and the middle one. The overall efficiency is a weighted average of the two, and hence cannot be greater than the efficiency of a Carnot engine operating between the extreme reservoirs alone.

(d) The problem is that $đQ \neq T\,dS$ for irreversible processes. For example, in free expansion the entropy goes up, even though no heat is added.

[3] **Problem 4.** Most thermodynamic systems have positive heat capacities, but a gravitationally bound system of particles has a negative heat capacity by the virial theorem, as does a black hole. Suppose a system with negative heat capacity C_1 is placed in thermal contact with a slightly cooler system with positive heat capacity C_2.

(a) What happens in the long run if $|C_1| > |C_2|$?

(b) What happens in the long run if $|C_1| < |C_2|$?

(c) Some systems, such as lasers, have a negative temperature and a positive heat capacity. (You'll see another example of negative temperature in problem 11.) What happens if such a system is placed in thermal contact with a system with positive temperature and heat capacity?

Solution. (a) Since heat will be transferred from the hotter system (with negative heat capacity) to the cooler system (with positive heat capacity), *both* systems will get hotter! If $|C_1| > |C_2|$, then the initially cooler system with positive heat capacity "catches up" in temperature, and equilibrium is reached.

(b) If $|C_1| < |C_2|$, the cooler system never catches up in temperature. The heat transfer goes on indefinitely, with both systems continually becoming hotter, until something about this description breaks down.

This sounds crazy; can it really happen? Consider a system of many particles interacting under gravity, with an initially uniform temperature T. The particles near the middle of the system are dominated by gravitational potential energy; this dense "core" region has negative heat capacity. The particles in the "halo", which extends further outward, are dominated by kinetic energy, and have positive heat capacity like a standard ideal gas.

If the core becomes slightly hotter, then the exact situation described in this problem occurs, and heat flows from the core to the halo. If the core is dense enough relative to the halo, then $|C_1| < |C_2|$ and there is a runaway, known as the "gravothermal catastrophe." In the long run, the particles in the halo are ejected as they reach escape velocity, while the particles in the core collapse into a black hole. This is possibly the (very) long-term fate of our galaxy. If you think about it, a similar process has already happened in our solar system, which started as a disk of dust; the end result was the formation of the Sun and planets, with much of the rest of the dust blown away.

(c) By the second law, heat should leave the negative temperature system and go into the positive temperature system, that way $dS = đQ/T$ is positive for both systems. Thus the negative temperature system will get more negative, and the positive temperature system will get hotter. This will continue until the negative temperature system goes back to a positive temperature (and the temperatures meet at equilibrium), as seen by moving to the left on the graph in problem 10.

[3] **Problem 5** (Kardar)**.** The solar system originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

(a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law?

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?

(c) The evolution of life and intelligence requires even further levels of organization. Why does this not violate the second law?

For a nice discussion of these issues, see section 36.7 of Blundell and Blundell.

Solution. (a) When the dust cloud gravitationally contracted, it heated up and then released its energy by radiation. Thus, the entropy of the interstellar space around the solar system went up.

(b) Again, the process releases a lot of heat, which then increases the entropy of the Sun itself. Or, if you consider the long run, waiting until the Sun dies, then radiation is emitted from the surface of the Sun, increasing the entropy of the surrounding universe.

(c) Earth receives energy at high temperature (about 6000 K) from the Sun, then radiates this energy back to outer space at low temperature (about room temperature). This process increases the total entropy of the Earth's surroundings, which means life can exploit this to decrease its own entropy, by letting this energy pass through it.

[4] **Problem 6.** We can find an expression for entropy of an ideal gas using pure thermodynamics. Consider n moles of an ideal gas with adiabatic index γ, initially at pressure P and volume V.

(a) Suppose the gas is heated at constant volume to pressure P'. Compute the change in entropy.

(b) Suppose the gas is instead expanded at constant pressure to volume V'. Compute the change in entropy.

(c) By combining your two results, show that the entropy $S(P, V)$ of the ideal gas is

$$S = nC_V \log(PV^\gamma) + \text{constant}$$

when n is constant. The constant can't be found using classical thermodynamics alone, since it only can determine changes in entropy.

(d) Now consider the case where the ideal gas is allowed to freely expand into a vacuum, reaching a final volume V'. This is an example of a nonequilibrium process that changes the entropy, despite no work or heat transfer. Find the resulting change in entropy.

(e) So far, we don't know anything about how S depends on n, because we only considered processes that kept n constant. However, the entropy should be extensive, meaning that if the pressure and temperature are kept the same, then S is proportional to n. Thus, if in general

$$S/n = C_V \log(PV^\gamma f(n)) + \text{constant}$$

then the right-hand side must be independent of n. Using this, find $f(n)$.

Solution. (a) For heating at constant volume, we have

$$\Delta S = \int \frac{\text{đ}Q}{T} = nC_V \log \frac{T'}{T} = nC_V \log \frac{P'}{P}.$$

(b) For heating at constant pressure, we have

$$\Delta S = \int \frac{\text{đ}Q}{T} = nC_P \log \frac{T'}{T} = nC_P \log \frac{V'}{V}.$$

(c) Suppose we start at some fixed pressure and volume P_0 and V_0, and use the above two steps to get to pressure and volume P and V. Then

$$S(P,V) = S(P_0,V_0) + nC_V \log \frac{P'}{P} + nC_P \log \frac{V'}{V} = S(P_0,V_0) + nC_V \log \frac{P'}{P} + nC_V \log \frac{V'^\gamma}{V^\gamma}.$$

Since P_0 and V_0 and $S(P_0,V_0)$ are all fixed constants, we hence have

$$S(P,V) = nC_V \log(PV^\gamma) + \text{constant}$$

as desired.

(d) Since no work or heat transfer occurred, the internal energy must stay the same. Thus the temperature stayed the same. Using our previously obtained result, we get

$$\Delta S = nC_V \log\left(\frac{TV'^{\gamma-1}}{TV^{\gamma-1}}\right) = nR \log\left(\frac{V'}{V}\right).$$

This can also be found by considering an isothermal process to get to the final state and finding the entropy change using $dS = dQ/T$. Since entropy is a state function, the final changes in entropy are equivalent.

(e) Use the ideal gas law to substitute $V = nRT/P$, giving

$$S/n = C_V \log\left(P\frac{n^\gamma R^\gamma T^\gamma}{P^\gamma} f(n)\right) + \text{constant}.$$

For constant P and T, the argument of the logarithm is independent of n when

$$f(n) = n^{-\gamma}.$$

The resulting general expression for the entropy of an ideal gas, up to the remaining constant (which can't be found without using quantum statistical mechanics) is called the Sackur–Tetrode equation.

[3] **Problem 7.** USAPhO 2014, problem A2.

[3] **Problem 8.** USAPhO 2017, problem A2. A simple but tricky problem. (For a more involved problem based on the same fundamental idea, see Physics Cup 2019, problem 2.)

[3] **Problem 9.** USAPhO 2020, problem B3. An advanced problem which shows you how to compute corrections for a slightly nonideal gas. (Note that you can use the quantity T in any of the parts, not just (e) and (f).)

3 Quantum Statistical Mechanics and the Third Law

Idea 6: Third Law

The entropy of any thermodynamic system approaches zero as the temperature goes to zero.

The third law of thermodynamics is a bit of a black sheep. Unlike the other laws, it is inherently quantum mechanical, and comes from the statistical definition of entropy, as described below.

[2] **Problem 10.** Show that the third law requires the specific heat C to approach zero as the temperature approaches zero. (Since this isn't true for a classical ideal gas, the ideal gas law *must* break down in quantum mechanics, at low temperatures. You can also see this from your result for the entropy in problem 6, which diverges at low temperatures; there's no way to add a constant to it to make it go to zero at zero temperature.)

Solution. We have

$$dS = \frac{đQ}{T} = \frac{C(T)\,dT}{T}.$$

Therefore, for a small temperature T_0, we have

$$S(T_0) = \int_0^{T_0} dT\, \frac{C(T)}{T}$$

and the right-hand side must go to zero as T_0 goes to zero. But if $C(T)$ doesn't go to zero as T does, instead approaching a nonzero limit, then the right-hand side is instead infinite.

Idea 7: Microcanonical Ensemble

If a large isolated system in thermodynamic equilibrium is in one of Ω quantum states, then we assume all of the states are equally likely, and the entropy is

$$S = k_B \log \Omega.$$

This is the fundamental definition of entropy; in fact the equation $dS = đQ/T$ does not define entropy, but rather defines temperature! The third law follows from this result because at temperature $T = 0$, all systems settle into their ground state, so $\Omega = 1$ and $S = 0$.

Remark

The assumption that all states are equally likely may sound a bit confusing, because in **T1** we used the Boltzmann distribution, which stated that higher-energy states were less likely to be occupied. The difference is that for the Boltzmann distribution, we assumed the system was inside an environment at temperature T. In fact, all quantum states of the system and environment together remain equally likely in this context, but lower-energy states of the system correspond to more energy in the environment, and hence (usually) more possible environment states. Thus, accounting for the number of possible environment states, lower-energy states of the system are more likely. You will make all this precise in problem 11, where you will use it to derive the Boltzmann distribution.

Example 4: Mixing Entropy

Repeat example 3 using statistical mechanics.

Solution

In statistical mechanics, we can compute S directly using $S = k_B \log \Omega$. Focusing on a single oxygen or nitrogen molecule, let Ω_i be the initial number of possible states. When the partition is removed, the possible position space for the particle doubles, and since quantum states all have the same volume in phase space, the number of states available doubles. So for one particle,

$$\Delta S_{\text{part}} = k_B \log(2\Omega_i) - k_B \log \Omega_i = k_B \log 2.$$

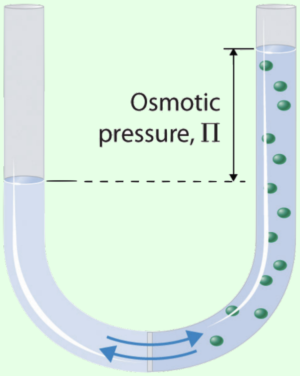
Since the $2N$ particles are independent,

$$\Delta S = 2N \Delta S_{\text{part}} = 2N k_B \log 2$$

in agreement with the result from thermodynamics.

Example 5: Osmotic Pressure

A water-filled tube is divided by a membrane which only allows water molecules through. When a substance is dissolved in one half of the tube, forming N ions, the water level on that side is observed to go up, as shown.



Explain why, and calculate the height difference, neglecting interactions between different ions, and between the ions and the water.

Solution

Osmotic pressure is an example of an entropic force. Suppose that the water level on one of the tube goes up. The water is otherwise unchanged, since it's just translated along the tube, so its entropy has not changed. But its energy is higher, and this energy must have come via heat transfer from the environment. Hence the entropy of the environment has decreased.

If there were no dissolved ions, this would show why water levels don't spontaneously go up: it is forbidden by the second law. But here, increasing the water in the section with the ions increases the ions' entropy, since they now have more positions they could be in. Since the number of available quantum states is proportional to the available volume, we have

$$S_{\text{ion}} = N k_B \log V$$

up to an additive constant, which means that

$$dS_{\text{ion}} = \frac{N k_B}{V} \, dV.$$

In equilibrium, let there be an osmotic pressure difference P across the membrane. Then moving a volume dV of water across it costs energy $P \, dV$, so

$$dS_{\text{env}} = -\frac{đQ}{T} = -\frac{P}{T} \, dV.$$

In thermodynamic equilibrium the total entropy is maximized, giving

$$dS_{\text{ion}} + dS_{\text{env}} = 0.$$

Solving for the osmotic pressure gives

$$PV = N k_B T.$$

The height difference is simply found using hydrostatic pressure,

$$h = \frac{P}{\rho g} = \frac{N k_B T}{\rho V g}.$$

The appearance of a pressure here in response to an opportunity for decreasing entropy is generally called an "entropic force". In fact, you might have already seen this result in chemistry class, but in rather different notation. In chemistry textbooks, you'll typically see

$$\Pi = iMRT$$

where Π is the osmotic pressure, M is the molarity of solute, and the van 't Hoff factor i is the number of moles of ions per mole of solute. This is perfectly equivalent to what we found.

Remark

Why does the expression for osmotic pressure bear a suspicious resemblance to the ideal gas law? The reason is that, by completely neglecting interactions between the solute and solvent, we have effectively treated the solute ions like an ideal gas, from the standpoint of entropy. This gives an additional contribution to the pressure, which can be derived just like the pressure of an ideal gas is in **T1**. (Using this reasoning backwards, one can conclude that the pressure of an ideal gas can also be described as an entropic force, using the same reasoning as above.)

The reason that this kinetic theory connection to the ideal gas law is not emphasized in chemistry classes is that the solute particles don't actually behave like an ideal gas at all. They are part of a liquid, and hence are constantly bumping into the solvent particles. The thermodynamic reasoning we used above is more general, because it only requires that the interaction between the solvent and solute doesn't significantly change the solute's entropy.

By the way, if you're wondering precisely whan an entropic force *is*, rest assured that nothing magical is going on here. In the end, there are no forces at play except for the ordinary forces you're familiar with. It's just that often, calculating what those forces do in aggregate in thermodynamically large systems is very hard. An entropic force simply means a force whose value we can calculate most easily using the tool of entropy.

[5] **Problem 11.** This is a long problem, but a really useful one that ties a lot of things together. Consider a set of N atoms, each of which may be in the ground state, with zero energy, or in an excited state with energy E_0. Suppose it is only known that the total energy of the system is $\alpha N E_0$.

(a) For large N, Stirling's approximation states that

$$\log N! \approx N \log N - N.$$

Derive this expression by writing $\log N!$ as a sum, and approximating the sum with an integral.

(b) Using Stirling's approximation, show that the entropy of the system is

$$S = N k_B \left(\alpha \log \frac{1}{\alpha} + (1-\alpha) \log \frac{1}{1-\alpha} \right).$$

Sketch the entropy as a function of α.

(c) Using the definition of temperature, $dS = đQ/T$, show that the system has a temperature of

$$T = \frac{E_0}{k_B} \frac{1}{\log(1-\alpha) - \log \alpha}.$$

Sketch the temperature as a function of α. In particular, what temperature do you need to get $\alpha = 1/2$? How about $\alpha = 1$?

(d) Show that the third law is satisfied.

(e) Now consider just a single one of the N atoms, where the total energy of the system is $\alpha N E_0$ as before. Show that the probability it is excited obeys the Boltzmann distribution.

Solution. (a) To write the expression as a sum, note that

$$\log N! = \log 1 + \cdots + \log N.$$

We can think of this as a lower Riemann sum for an integral,

$$\log N! \approx \int_1^N \log x \, dx = N \log N - N + 1.$$

Dropping the 1, which is small compared to the other terms, gives the desired result. For refinements of this result, e.g. using the trapezoidal rule, see here.

Note that while Stirling's approximation gives a good approximation for $\log N!$, you can't exponentiate both sides and get a good approximation for $N!$. As we mentioned in **P1**, exponentiating turns additive errors into multiplicative errors, and in this case a relatively small additive correction turns into a huge multiplicative correction. In **P2**, we considered a more accurate version of Stirling's approximation which yields a good approximation for $N!$. You can see a derivation of that more accurate result here.

(b) We see that $\Omega = \binom{N}{\alpha N} = \frac{N!}{(\alpha N)!((1-\alpha)N)!}$, so

$$\log \Omega \approx N \log N - \alpha N \log(\alpha N) - (1-\alpha)\log((1-\alpha)N).$$

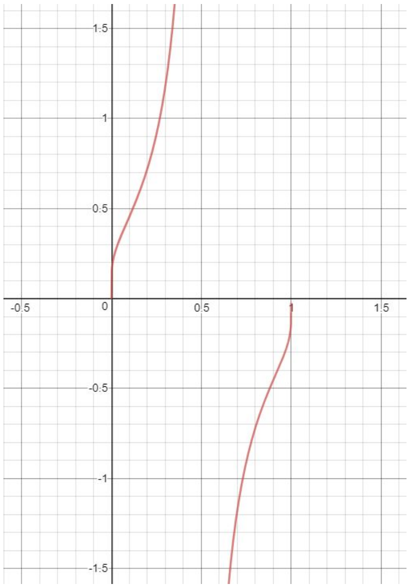
Thus, up to a constant,

$$S = k_B \log \Omega = N k_B \left(\alpha \log \frac{1}{\alpha} + (1-\alpha) \log \frac{1}{1-\alpha} \right).$$

(c) We see that $\text{đ}Q = N E_0 \, d\alpha$, and

$$dS = N k_B \left(\log(1-\alpha) - \log \alpha \right) d\alpha.$$

Thus, $T = \text{đ}Q/dS = \frac{E_0}{k_B} \frac{1}{\log(1-\alpha) - \log \alpha}$. Here is the graph of T as a function of α.



(d) As $\alpha \to 0$, we see $T \to 0$ and $S \to 0$. For the entropy, this requires an application of l'Hospital's rule, which shows that $\lim_{\alpha \to 0} \alpha \log \alpha = 0$.

(e) We know the probability is just α, so

$$\frac{p(\text{excited})}{p(\text{ground})} = \frac{\alpha}{1-\alpha}.$$

By comparison, the Boltzmann distribution states that

$$\frac{p(\text{excited})}{p(\text{ground})} = e^{-E_0/k_B T}.$$

Therefore, the two expressions match if

$$e^{-E_0/k_BT} = \frac{\alpha}{1-\alpha}.$$

This is equivalent to the expression for T we found in part (c), as desired.

[5] **Problem 12.** This long problem illustrates some important features of free energy. A rubber molecule can be modeled in one dimension as a chain consisting of a series of $N = N_+ + N_- \gg 1$ links of length a, where N_+ point in the $+z$ direction and N_- point in the $-z$ direction. The orientations of each of the links are independent, and it costs no energy to rotate a link. Thus all configurations are equally likely at any temperature.

(a) Find the length L of the chain in terms of N_+ and N_-.

(b) Using Stirling's approximation,

$$\log N! \approx N \log N - N$$

and assuming that $L \ll Na$, show that

$$S = Nk_B \left(\log 2 - \frac{L^2}{2N^2a^2} \right)$$

and hence show that the entropy decreases as L increases. This model is very basic; for instance, it tells us nothing about the tension in the chain, but the sign here is correct. (Hint: notice that the changes in entropy are of order L^2/N, and hence are very small. You will have to be careful with your approximations to avoid dropping an important contribution.)

(c) Note that the entropy doesn't depend on temperature, because all configurations have the same energy. In a more realistic model, the total entropy of the molecule would be the sum of the entropy computed above, plus the entropy due to additional thermal motions, such as vibrations of the links. Given this, if a rubber band is quickly stretched, does it feel warm or cold to the touch? (You can check your answer experimentally!)

(d) Now suppose a mass m is hung from the bottom of the chain. Find the average length of the chain at temperature T, using the Boltzmann distribution. Do not assume $L \ll Na$. (The force that raises this mass is another example of an entropic force.)

(e) It turns out that you can also arrive at this answer by maximizing the entropy of the entire universe S_{univ}. Argue in general that S_{univ} is maximized when the Helmholtz free energy

$$F = U - TS$$

is minimized, where U is the total energy of the rubber band and mass, and T is the temperature of the system and its surroundings. (Hint: use the expression for dS_{univ}, along with conservation of energy.)

(f) Show that in the limit $L \ll Na$, F is indeed minimized at the equilibrium length.

Solution. (a) We simply have $L = (N_+ - N_-)a$. For convenience, we'll set $k_B = a = 1$ for now.

(b) We have

$$S = \log \frac{N!}{N_+! N_-!}.$$

Applying Stirling's approximation $\log N! \approx N \log N - N$, the linear terms cancel out, giving

$$\begin{aligned} S &= N \log N - N_+ \log N_+ - N_- \log N_- \\ &= N \log N - \frac{1}{2}(N+L)\log((N+L)/2) - \frac{1}{2}(N-L)\log((N-L)/2) \\ &= N \log 2 + N \log N - \frac{1}{2}(N+L)\log(N+L) - \frac{1}{2}(N-L)\log(N-L). \end{aligned}$$

To simplify further, we write the logarithms as

$$\log(N \pm L) = \log N + \log\left(1 \pm \frac{L}{N}\right).$$

Plugging this in and defining $x = L/N$ gives

$$S = N \log 2 - \frac{N}{2}\left((1+x)\log(1+x) + (1-x)\log(1-x)\right).$$

Expanding the quantity in parentheses is a little tricky, because it vanishes at first order in x. So since the answer is second order, we need to expand the logarithms to second order to make sure we have everything. We have

$$\log(1 \pm x) = \pm x - \frac{x^2}{2}.$$

and plugging this in gives

$$((1+x)\log(1+x) + (1-x)\log(1-x)) = x^2 + \ldots.$$

If we hadn't included the second-order term in the logarithm, we would have gotten $2x^2$ instead, leading to an erroneous result.

Putting everything together and restoring the units, we have

$$S = N \log 2 - \frac{Nx^2}{2} = N k_B \left(\log 2 - \frac{L^2}{2N^2 a^2}\right)$$

as desired.

(c) Since the process is fast, it is adiabatic, so the entropy of the entire rubber band stays the same. But we have shown the entropy of the chain configuration degrees of freedom (i.e. ones which determine the length L) goes down, so the entropy of the other degrees of freedom must go up. Hence these other degrees of freedom receive heat, and the rubber band feels hot.

By the way, this fact provides a new perspective on a classic puzzle. If you take an ordinary metal spring, stretch it with a clamp, and put the whole thing in a bath of acid, then when the acid dissolves the spring, where does the elastic potential energy go? For a metal spring, the answer is that when you stretch it, you're pulling the chemical bonds inside of it longer, so that they're displaced from the minimum of potential energy. The spring's constituent atoms thus start out in a less deep potential well, so when they are dissolved they emerge with higher energy, which ultimately heats up the bath.

Howeer, for a rubber band the answer is different, because the elastic force is entropic. Specifically, though you can describe the force from a rubber band macroscopically with a potential energy, at the microscopic level it *doesn't* correspond to any actual potential energy; we have been assuming throughout this problem that it costs no energy to rotate any of the links! Accordingly, when you stretch a rubber band, the work you put in is not actually stored within it as potential energy. It instead warms up the rubber band, and therefore quickly turns into thermal energy in the room. When the rubber band's temperature returns to its original value, its total energy is the same as before you stretched it. If you put this rubber band in an acid bath, the acid's final temperature will be the same regardless of how the band was stretched, because the energy you put in has already left.

(d) It's easiest to look at each link individually. The energy of the $+z$ configuration now is $2mga$ greater than the $-z$ configuration, so the ratio of their probabilities is $\alpha = e^{-2mga/k_BT}$. Then the probability of $\pm z$ is

$$p_- = \frac{1}{1+\alpha}, \quad p_+ = \frac{\alpha}{1+\alpha}$$

so the expected contribution to the length is

$$\frac{1}{1+\alpha} - \frac{\alpha}{1+\alpha} = \tanh(mga/k_BT).$$

By summing over all links, the expected length is

$$\langle L \rangle = Na \tanh \frac{mga}{k_BT}.$$

Since N is large, thermal fluctuations fall as $1/\sqrt{N}$ by the logic of **P2**, so this is also approximately the observed length at all times.

As mentioned in the problem, this raising of the mass is due to an entropic force. Here's the fascinating thing: we haven't specified anything about the *dynamics* of the molecule in this problem. For example, it could be made of rigid rods connected with pivots, designed to snap to the upward or downward position, and immersed inside an ideal gas of temperature T which occasionally flip them in a collision. Or maybe the rods could be made of iron, and immersed inside a box of permanent magnets flying around with temperature T, which occasionally flip them with the magnetic force. The point is that it doesn't matter! As long as the whole system is at equilibrium at temperature T, and the expressions above correctly describe the rod's entropy, we'll get the same result for the length $\langle L \rangle$. We don't need to talk about where the entropic force comes from, because the result doesn't depend on that.

(e) The entropy of the universe is, up to a constant, $-F/T$, because

$$-\frac{F}{T} = S - \frac{U}{T}.$$

The first term is the rubber band's entropy, while $-U/T$ accounts for the change of entropy of the environment by $\Delta S_{\text{env}} = \Delta U_{\text{env}}/T_{\text{env}} = -\Delta U/T$. For several steps in this argument, it's essential that everything is at temperature T.

(f) In this case the argument of the hyperbolic tangent is small, so

$$L \approx \frac{mgNa^2}{k_BT}.$$

On the other hand, we have

$$F = -mgL - Nk_BT\left(\log 2 - \frac{L^2}{2N^2a^2}\right)$$

and we have

$$\frac{\partial F}{\partial L} = -mg + \frac{k_BTL}{Na^2}$$

which implies that

$$L = \frac{mgNa^2}{k_BT}$$

as expected.

Remark: Heat vs. Work

What is the difference between work and heat? If we have a gas in a cylinder with a piston, moving the piston counts as work. Clearly, if we split the piston into two halves and moved them independently, this would still be work. But we can keep splitting the piston until we are down to individual atoms of the piston. These can transfer energy to gas particles because they can slam into them as the gas particles are bouncing off, like a batter hitting a baseball. But as mentioned in **T1**, this is precisely how a hot wall transfers energy to a gas! So when did we transition from doing work to supplying heat?

The point is that there is no sharp distinction. There's just energy transfer; work is the subset of energy transfers that we keep track of detail, and heat is the subset we don't. Entropy quantifies our ignorance of the precise state a system is in. That's why supplying heat changes the entropy and doing work doesn't.

Remark: Is Entropy Subjective?

Our definition of entropy involved the number of states the system "could" be in, but of course in reality the system is actually in just one state. We really mean the number of states the system could be in given the information you know. For example, for an ideal gas we usually know the temperature, pressure, and volume.

You might find this disturbing because it implies the entropy is subjective, depending on what each person personally knows. But the entropy determines things like F, and hence the amount of work that can be extracted from the system, so how could it differ?

In fact, there is no contradiction between these two things. For example, suppose that besides the usual properties, particles in an ideal gas can be slightly bigger or smaller. If you happen to somehow know that all of the big particles are on the left side of a box and all the small particles are on the right side, then the entropy you assign to the box is lower than somebody who doesn't know about this, and accordingly you can extract more work from the box. For instance, you can put a filter that only allows small particles through in the middle, then collect energy as small particles move from right to left.

On the other hand, if you are hit on the head and forget that the particles are sorted by size, your entropy for the gas goes up. And accordingly, you can now extract less work, because you wouldn't know it made sense to put in such a filter in the first place!

While this example may seem contrived, it's actually exactly the same as our earlier mixing entropy example! If you don't have any equipment that can distinguish between oxygen and nitrogen molecules, then the "unmixed" state already has just as much entropy as the mixed state. In this case, the entropy doesn't change at all when you allow the gases to mix.

What this example shows is that you don't have to know everything about a system to use thermodynamics. Even if you are wrong about how the system behaves microscopically, you can still use the theory to describe what *you* can do with the system, using *your* knowledge. That's the core reason for the longevity of thermodynamics. As a recent paper put it:

> If physical theories were people, thermodynamics would be the village witch. Over the course of three centuries, she smiled quietly as other theories rose and withered, surviving major revolutions in physics, like the advent of general relativity and quantum mechanics. The other theories find her somewhat odd, somehow different in nature from the rest, yet everyone comes to her for advice, and no one dares to contradict her.

For more about this perspective, see the insightful articles by E.T. Jaynes, *The Gibbs Paradox* and *Information Theory and Statistical Mechanics*. (But don't read too much of his later work, since he got pretty cranky with age.)

4 Blackbody Radiation

Idea 8: Planck's Law

As we will show in **X1**, the radiation power per unit area from an object at temperature T at frequency f, per unit frequency, is

$$I(f) = \frac{2\pi h f^3}{c^2} \frac{1}{e^{hf/k_B T} - 1} \, e(f)$$

where $e(f)$ is called the emissivity. For an ideal blackbody, $e(f) = 1$. By integrating over all frequencies, one finds that the total power per unit area from an ideal blackbody is

$$J = \int_0^\infty I(f) \, df = \sigma T^4, \quad \sigma = \frac{2\pi^5 k_B^4}{15 c^2 h^3}.$$

This is the Stefan–Boltzmann law, which can also be derived with dimensional analysis. It's a compact and useful result, which means it comes up quite often in Olympiads.

[2] **Problem 13.** Some basic manipulations with Planck's law.

(a) Show that $J \propto T^4$ by nondimensionalizing the integral, as explained in **P1**.

(b) Prove Wien's displacement law, which states that the maximum of $I(f)$ for an ideal blackbody occurs at a frequency which is proportional to T.

Solution. (a) By definition, we have

$$J = \int_0^\infty \frac{2\pi (k_B T)^3 (hf/k_B T)^3}{c^2 h^2} \frac{1}{e^{hf/k_B T} - 1} \frac{k_B T}{h} d\left(\frac{hf}{k_B T}\right).$$

Let $x \equiv hf/k_B T$. Then we get

$$J = \frac{2\pi (k_B T)^4}{c^2 h^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

The integral will evaluate to a dimensionless constant, so we conclude $J \propto T^4$.

(b) As in part (a), note that we can write $I(f)$ in the form

$$I(f) = (\text{constants independent of } f) \times \frac{x^3}{e^x - 1}, \quad x = \frac{hf}{k_B T}.$$

Therefore, the shape of $I(f)$ depends only on the dimensionless combination x. Therefore, if there exists a maximum in $I(f)$ for some value of x, then this is true for any temperature. Since the maximum happens at the same value of x, we have $hf_{\text{max}}/k_B T$ constant, so $f_{\text{max}} \propto T$ as desired.

Example 6

At high temperatures, the resistivities of many temperatures scale approximately linearly with temperature. Suppose that a light bulb supplies total radiation power P when connected across an AC voltage V. How does P scale with V?

Solution

The total power dissipated in the resistor scales as V^2/R, and $R \propto \rho \propto T$. This power must equal the blackbody radiation power emitted, so by the Stefan–Boltzmann law,

$$P \propto T^4 \propto \frac{V^2}{T}$$

from which we conclude that $T \propto V^{2/5}$, so $P \propto V^{8/5}$.

Example 7

A nonideal blackbody absorbs a fraction $a(f)$ of incident radiation of frequency f. (For an ideal blackbody, $a(f) = 1$.) Show that the second law implies Kirchoff's law, $e(f) = a(f)$.

Solution

First let's consider the case where $a(f)$ and $e(f)$ are constants, which don't depend on f. If we place two blackbodies of temperature T right next to each other, then the rate at which the first heats the second is proportional to $e_1 a_2$, while the rate the second heats the first is proportional to $e_2 a_1$. By the second law, these must be equal, which implies $e_1/a_1 = e_2/a_2$. Hence the ratio is constant. But for a perfect blackbody, $e = a$, so the two are equal.

More generally, suppose we place in between the two blackbodies a filter that only lets light of frequency f through, and blocks everything else. Then the same reasoning gives $e_1(f)/a_1(f) = e_2(f)/a_2(f)$, so $e(f) = a(f)$. Thermodynamics forces good absorbers to also be good emitters. It's possible to derive this microscopically, by considering how individual atoms behave; in that context Kirchoff's law follows from time reversal symmetry.

You might wonder what would happen if we placed a "one-way" filter which only let light through in one direction. Such a filter would act like Maxwell's demons for photons: if you used one to divide a room full of photons, it would start directing photons of certain frequencies to one side or the other, decreasing the entropy. So thermodynamics also forbids the existence of one-way filters; again, microscopically this is a result of time reversal symmetry.

Example 8

A satellite contains a nuclear reactor at its core, fixed at temperature T_H. Suppose the exterior of the satellite is somehow fixed at temperature T_C, and the satellite runs an ideal heat engine, using the core and exterior as hot and cold reservoirs. Treat the exterior as an ideal blackbody, and neglect the temperature of outer space. What value of T_C maximizes the rate of work extracted?

Solution

One might think that T_C should be as low as possible, to increase the efficiency of the cycle. However, a lower T_C means a lower rate of heat emission $\dot{Q}_{\text{out}}$, since we are limited by emission of blackbody radiation, which lowers the rate of work done $\dot{W}$.

The rate of heat emitted from the satellite is

$$\dot{Q}_{\text{out}} = \sigma A T_C^4 \propto T_C^4.$$

Therefore, the rate of work done is

$$\dot{W} = \eta \dot{Q}_{\text{in}} = \eta \frac{T_H}{T_C} \dot{Q}_{\text{out}} \propto \left(1 - \frac{T_C}{T_H}\right) \frac{T_H}{T_C} T_C^4 = T_H T_C^3 - T_C^4.$$

This is maximized when $T_C = (3/4) T_H$, at which point the efficiency is $1/4$.

[2] **Problem 14.** Consider two adjacent blackbodies with similar temperatures, exchanging energy by radiation. Show that the rate of change of the temperature difference is approximately proportional to the temperature difference itself. This is an example of Newton's law of cooling, which implies the temperature difference decays exponentially. How does the time scale for cooling depend on the average temperature of the blackbodies?

Solution. We see that the energy transfer rate is proportional to $T_1^4 - T_0^4$ by Stefan–Boltzmann. It's pretty clear that this is linear in $T_1 - T_0$ for small $T_1 - T_0 \ll 1$, by the binomial theorem or really just the tangent line approximation. Therefore, $d\Delta T/dt = -k\Delta T$, so $\Delta T \sim e^{-kt}$, as desired, where $k \propto T^3$.

[3] **Problem 15** (IPhO 1992)**.** A satellite is a sphere of diameter D orbiting about the Earth.

(a) First suppose the satellite is perfectly black. Ignoring the effect of the Earth, find its temperature T in terms of the temperature $T_\odot$ of the Sun, the radius $R_\odot$ of the Sun, and the radius R of Earth's orbit.

(b) How does the answer change if the satellite has a uniform emissivity $e(f) = e_0 < 1$?

(c) If an engineer wishes to make T as small as possible using a special paint, which can have an arbitrary $e(f)$, sketch how the function $e(f)$ should look.

Solution. (a) The power going into the satellite is

$$P = \frac{\sigma(4\pi R_\odot^2)T_\odot^4}{4\pi R^2}\frac{1}{4}\pi D^2.$$

At equilibrium, this should equal to the power that the satellite emits.

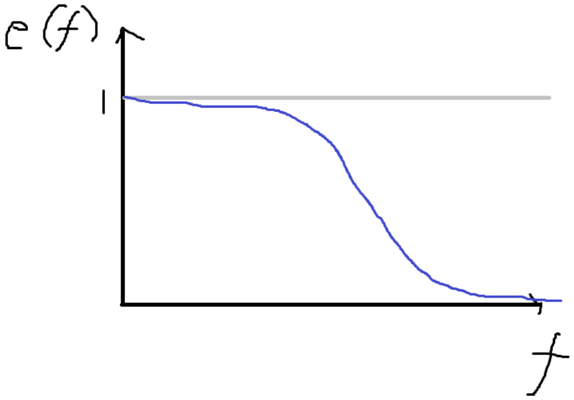
$$P = \sigma\pi D^2 T^4.$$

Equating the two yields

$$T = T_\odot\sqrt{\frac{R_\odot}{2R}}$$

(b) The power that the satellite absorbs will be reduced by a factor of e_0, and the power emitted will also be reduced by a factor of e_0. When equating the powers as in part (a), the e_0 will cancel out, giving the same answer.

(c) As you can check from Planck's law, the Sun has a higher intensity than the satellite at *every* frequency, but *especially* so for high frequencies, where the emission from the satellite falls off. Thus, it is better to have $e(f)$ small at these high frequencies, because energy comes in at these frequencies but doesn't substantially come out. Thus, you could do something like this:



[3] **Problem 16** (IPhO 1996)**.** Two perfectly black surfaces of temperatures T_h and T_ℓ are parallel to each other in vacuum, and the net heat flux from the hotter surface to the colder one is P.

Now suppose that N parallel, thermally insulating, perfectly black plates are placed in between them. This shielding reduces the heat flux to P'. Find P' in terms of P.

Solution. Page 12 of the official solutions here does the problem for the case $N = 2$, getting the answer 1/3. An identical method works for general N, getting the answer $1/(N+1)$.

Example 9

In problem 16 you considered some ideally black surfaces, but things get more complicated when the surfaces have general emissivity. For simplicity, consider two walls facing each other, with emissivities e_1 and e_2. Verify that when both walls have temperature T, there is no net energy flow from one to the other.

Solution

Let $I_0 = \sigma T^4$. The second wall emits radiation of intensity $e_2 I_0$, so in equilibrium it must absorb this amount as well. Verifying this takes a little work.

The first wall emits radiation of intensity $e_1 I_0$, and a fraction e_2 of it gets absorbed by the second wall. The rest bounces back to the first wall, and if it doesn't get absorbed by the first wall, then it comes back to the second wall again for another chance to get absorbed. The total intensity transferred from the first wall to the second is the sum of an infinite series,

$$I_{1\to 2} = (e_1 I_0)\,(e_2 + (1-e_2)(1-e_1)e_2 + \ldots) = \frac{e_1 e_2 I_0}{e_1 + e_2 - e_1 e_2}.$$

This isn't the expected result, because there's another contribution. When the second wall emits radiation, it can reflect off the first wall and then get reabsorbed by the second wall. So the second wall absorbs a total radiation intensity due to its own emission, of

$$I_{2\to 2} = (e_2 I_0)\,((1-e_1)e_2 + (1-e_1)(1-e_2)(1-e_1)e_2 + \ldots) = \frac{(1-e_1)e_2^2 I_0}{e_1 + e_2 - e_1 e_2}.$$

When you sum these contributions, you get $e_2 I_0$ as expected. This is a typical example of the power of thermodynamics: it is often easy to tell what the answer has to be, but the way that answer comes about can be a bit complicated.

Example 10

Suppose a black sphere of radius r is placed inside a large container of arbitrary shape, whose walls are a blackbody with temperature T. In the steady state, what is the rate of power absorbed by the sphere from the walls?

Solution

Radiation is continually emitted from all points on the walls in all directions, so it would seem that we have to do a complicated integral to find how much hits the sphere, which would be hard even if we were given the container's shape. But the problem is actually trivial due to the second law of thermodynamics!

Let's suppose the sphere itself is also at temperature T. Then it sends power $(4\pi r^2)\sigma T^4$ to the walls, since all radiation that exits the sphere hits the walls. But if the sphere and walls are at the same temperature, a temperature difference cannot spontaneously appear. Therefore, the power going from the walls to the sphere must also be $(4\pi r^2)\sigma T^4$. And since this quantity can also be expressed as a geometric integral, it can't depend on the temperature of the sphere, so it must be true for any sphere temperature.

For a tough problem which uses a variant of this idea, see EFPhO 2010, problem 2.

[2] **Problem 17.** USAPhO 2011, problem A3.

[3] **Problem 18.** USAPhO 2006, problem B2. The graphs are hard to read, but do your best!

[3] **Problem 19.** USAPhO 2019, problem A2. An elegant, tricky radiation problem. (This is essentially the same problem as Physics Cup 2022, problem 5.)

[3] **Problem 20.** Planck's law can be used to understand atomic physics, as Einstein showed and as you will now show. Suppose we have a collection of two-state atoms encased inside a cavity, whose walls are blackbodies with temperature T. In equilibrium, there will be N_1 atoms in the ground state and N_2 atoms in the excited state, bathed in a photon gas of temperature T. Three physical processes can occur:

1. Atoms in the excited state can each spontaneously decay with rate A.
2. Atoms in the ground state can absorb a photon. For each atom, the rate of this process is $B\rho(f)$ where $\rho(f)$ is the energy density of radiation at frequency f.
3. Atoms in the excited state can undergo stimulated emission when interacting with a photon, in the process $e + \gamma \to g + \gamma + \gamma$. For each atom, the rate of this process is $B'\rho(f)$.

These three "Einstein coefficients" depend on the frequency, but not on the temperature.

(a) Argue that $\rho(f)$ is proportional to $I(f)$ in Planck's law. In fact,

$$I(f) = \frac{c}{4}\rho(f)$$

though you do not have to show this.

(b) Write down an expression for dN_2/dt.

(c) In the steady state, for any temperature, N_2/N_1 must be given by the Boltzmann distribution. Using this, find A and B' in terms of B.

This is an extraordinary result: one might have expected a difficult calculation to find each of A, B, and B', but if you know one, then by thermodynamics you know them all. In particular, thermodynamics *requires* spontaneous emission to be possible, $A \neq 0$.

Solution. (a) Here $\rho(f)$ refers to the distribution of radiation energy inside the blackbody, while $I(f)$ refers to the intensity of radiation escaping the blackbody if there were a hole. The reason these are proportional is that all electromagnetic radiation travels at the same speed; hence light of all frequencies will escape a blackbody at the same rate. (Note that this would not be true for an ideal gas, where higher-energy particles would escape at a higher rate.)

(b) Adding up the contributions from the three processes,

$$\frac{dN_2}{dt} = -AN_2 + B\rho(f)N_1 - B'\rho(f)N_2.$$

(c) We know that in thermal equilibrium,

$$\frac{N_2}{N_1} = e^{-hf/k_BT}.$$

Plugging this in above and setting $dN_2/dt = 0$, we have

$$\frac{A}{\rho(f)} = Be^{hf/k_BT} - B'.$$

Using the given expression for $\rho(f)$,

$$A\,\frac{c^3}{8\pi hf^3}(e^{hf/k_BT} - 1) = Be^{hf/k_BT} - B'.$$

Now, we see the left-hand side diverges in the limit $T \to \infty$, which is physically reasonable. It is only possible for the right-hand side to do the same thing if

$$B' = B.$$

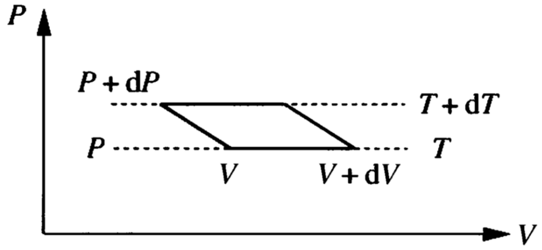
Plugging this back in, we have

$$A = \frac{8\pi hf^3}{c^3}B.$$

[3] **Problem 21.** In **T1**, we derived some properties of photon gases using basic kinetic theory. Here, we'll derive some more properties, starting from Planck's law and then sticking with pure thermodynamics. As in problem 20, we assume there is a photon gas at temperature T, with pressure P within a cavity of volume V, whose walls are perfect blackbodies. (Note that since photons can be absorbed and emitted by the walls, it doesn't make sense to talk about N as for an ideal gas. Instead, N is determined by the other parameters. This actually makes things simpler, since there's one less variable to worry about.)

(a) It turns out that the pressure of the photon gas is $P = AT^4$ where A is a constant. Explain why the pressure depends only on the temperature. (Harder, optional task: explain why $P \propto T^4$ starting from Planck's law.)

(b) Our next goal is to compute $U(T, V)$. Consider an infinitesimal Carnot cycle, shown below.



By equating the efficiency of this cycle to the Carnot efficiency, find $(\partial U/\partial V)|_T$.

(c) By integrating this result, and using $U(T, 0) = 0$, find $U(T, V)$.

(d) We can now use these results to find $S(T, V)$, just as we did for an ideal gas in problem 6, i.e. by considering the change of entropy during some infinitesimal process and then integrating the result. Do this in any way you like. Can the third law be satisfied?

Solution. (a) It's simply because the properties of blackbody radiation don't depend on the volume of its container. The ideal gas pressure depends on volume because increasing the volume dilutes the particles; for radiation, new photons are simply produced to get back up to the same pressure.

Integrating Planck's law gives the Stefan–Boltzmann law, which says the rate of emission of energy per unit area from the surface of a blackbody is σT^4. But energy is directly related to momentum, $p = E/c$, and changes in momentum directly correspond to pressures by the usual kinetic theory argument. So when photons bounce off the inside walls of a blackbody, they impart pressure $P \propto \sigma T^4$.

(b) First, using the chain rule we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial Q}{\partial V}\right)_T - P.$$

That is, we need to compute $(\partial Q/\partial V)|_T$, the rate at which heat is absorbed along an isotherm. And that's exactly what we can find with this Carnot cycle argument.

The work done in the cycle is the area of the parallelogram, $dW = dV\,dP$. The Carnot efficiency is

$$\eta = 1 - \frac{T}{T + dT} = \frac{dT}{T}.$$

Thus, the heat input during the isotherm is

$$đQ_{\text{in}} = \frac{dW}{\eta} = \frac{dV\,dP}{dT}\,T = 4AT^4\,dV.$$

Combining this with the result above gives

$$\left(\frac{\partial U}{\partial V}\right)_T = 4AT^4 - P = 3AT^4.$$

(c) Integrating the above result with respect to volume gives

$$U(T, V) = 3AT^4 V.$$

(d) Let's consider an isothermal process. We just showed above that along an isotherm,

$$đQ = 4AT^4\, dV.$$

Therefore, we have

$$dS = \frac{đQ}{T} = 4AT^3\, dV$$

and integrating gives

$$S = 4AT^3 V + f(T)$$

where the unknown integration constant is any function of temperature. The third law of thermodynamics is satisfied precisely when $f(T) = 0$. (The fact that it can be satisfied is expected, since it is a quantum mechanical law and we are working with photons, the quanta of light.) This gives $S = 4AT^3 V$.

If you prefer, we can reframe the reasoning in the following way. Why isn't the Third Law obvious? It's because in the thermodynamics of gases, we only measure entropy changes $dS = đQ/T$, leaving the integration constant unknown. But when the temperature of a photon gas is lowered to zero, the entire gas just *vanishes*, as the photons get absorbed. And obviously, the entropy of an empty box should be zero! This reasoning doesn't work for an ideal gas because it doesn't just vanish as you cool it; instead, much weirder things happen, as quantum mechanics takes over.

(On the other hand, an indirect method works: consider a plasma of electrons and positrons and no net charge, in equilibrium with a photon gas. This system *does* vanish as the temperature goes to zero, because all the electrons and positrons will annihilate, and the produced photons will be absorbed. So given the absolute entropy of the photon gas, you can use thermodynamic arguments to deduce the absolute entropy of a plasma. It would probably then be possible to extend this argument to find the absolute entropy of an ideal gas, but this approach is a lot more trouble than just invoking the Third Law.)

In part (c), we found that the energy density is proportional to T^4, a result very closely related to the Stefan–Boltzmann law. Stefan was the experimentalist who proposed the law, and Boltzmann was the theorist who derived it. He didn't know about Planck's law, but he was able to use thermodynamic arguments similar to the ones used in this problem, along with the fact that pressure and energy density are proportional for radiation, to derive the result.

[5] **Problem 22.** Physics Cup 2018, problem 9.

Solution. See the official solutions here.

5 Heat Conduction

Idea 9: Fourier's Law

In **T1**, you investigated heat conduction from the standpoint of kinetic theory. Now we revisit the subject from the standpoint of hydrodynamics. The flux of heat (i.e. the power per unit area) due to thermal conduction is proportional to the temperature gradient,

$$J = -\kappa \frac{dT}{dx}.$$

By considering the net heat flowing in and out of a slab of width dx, we have

$$\frac{du}{dt} = -\frac{dJ}{dx} = \kappa \frac{d^2T}{dx^2}.$$

where u is the energy density. Intuitively, this shows how heat conduction works to smooth out temperature gradients. For example, if the temperature had a local minimum, then du/dt would be positive at that point, as heat flows in from all directions.

Example 11

Find the steady state heat flow through a rectangular slab of area A and thickness d, whose left and right ends are held at temperature T and $T + \Delta T$.

Solution

By the argument in the above idea, in the steady state the energy density within the slab is constant, so $d^2T/dx^2 = 0$ and the temperature gradient is uniform. In this steady state, heat simply flows uniformly through the slab, without accumulating anywhere in it, just like current flows uniformly through a resistor. (Since this "internal" steady state is often reached quickly, in many problems it is just assumed to hold, without being explicitly stated.)

Therefore, the temperature gradient is just $\Delta T/d$ everywhere in the slab, so

$$P = JA = \frac{\kappa A \Delta T}{d}.$$

This is single most important equation for heat conduction problems.

Remark: Continuity Equations

We can generalize the results above to three dimensions. In this case, the flux of heat is described by a vector,

$$\mathbf{J} = -\kappa \nabla T.$$

The conservation of energy equation becomes

$$\frac{du}{dt} = -\nabla \cdot \mathbf{J} = \kappa \nabla^2 T.$$

The first equality here is known as a continuity equation, and it is the general way that the density of a conserved quantity is related to a flow. For example, the continuity equation for fluids, which we saw in one-dimensional form in **M7**, is written in three dimensions as

$$\frac{d\rho}{dt} = -\nabla \cdot (\rho \mathbf{v})$$

and expresses conservation of mass. The continuity equation for charge, which we'll see in **E4**, is very similar,

$$\frac{d\rho}{dt} = -\nabla \cdot \mathbf{J}$$

where ρ is a charge density and $\mathbf{J}$ is a current density.

[2] **Problem 23.** Supposing that it takes five minutes to boil an egg. Estimate how long it takes to boil an ostrich egg, which has three times the diameter.

Solution. The thermal gradient dT/dr is of the order $\Delta T/R \propto 1/R$, where R is the radius of the object. The heat flux into the egg is proportional to $A\,dT/dr \propto R^2(1/R) = R$. But the heat capacity of the egg scales as R^3. Thus, the time scales as $R^3/R = R^2$, and hence it takes about 45 minutes to boil an ostrich egg. (This can also be shown by dimensional analysis.)

[2] **Problem 24** (Cahn)**.** Estimate how long it will take for a small pond of depth $D = 0.5\,\mathrm{m}$ to freeze completely in a very cold winter. Take the thermal conductivity of the ice to be $\kappa = 2.2\,\mathrm{W/m\,K}$, the latent heat of fusion $L = 3.4 \times 10^5$ J/kg, and the density $\rho = 0.9 \times 10^3\,\mathrm{kg/m^3}$. Take the outside temperature to be a constant $T_0 \approx -10\,^\circ\mathrm{C}$, and for simplicity, suppose the entire pond starts at a uniform temperature $0\,^\circ\mathrm{C}$.

Solution. Let the ice layer on the top of the lake have thickness x and the temperature differential from bottom (where the lake starts freezing) to the top will be $\Delta T = 10°\mathrm{C}$. Then the rate of heat loss under the ice will be

$$P = \frac{\kappa A \Delta T}{x} = L\rho A \frac{dx}{dt}.$$

Separating and integrating gives

$$\int_0^D x\,dx = \int_0^t \frac{\kappa \Delta T}{L\rho}\,dt.$$

Notice that this implies the growth of the ice slows down over time, $x \propto \sqrt{t}$. This makes sense, since as the ice grows thicker, the temperature gradient gets smaller, slowing the heat transfer. By carrying out the integral, we find

$$t = \frac{D^2 L\rho}{2\kappa\Delta T} = 1.74 \times 10^6 \text{ s} = 20\,\text{days}.$$

Example 12

Model a brick pizza oven as a sphere with inner radius R_1, outer radius R_2, and thermal conductivity κ. The inside of the oven is held at temperature T_1 and the outside of the oven is held at temperature T_2. In equilibrium, find $T(r)$, and the power needed to keep the inside of the oven at temperature T_1.

Solution

Consider a shell of radius r and thickness dr. The outward heat flow through it is

$$P(r) = -\kappa(4\pi r^2)\,\frac{dT}{dr}.$$

In addition, because the shells have constant temperature, there can be no net heat accumulating in any shell. Thus, $P(r)$ must actually be independent of r. Renaming it to P, we can integrate the resulting differential equation to find

$$\int_{T_1}^{T(r)} dT = -\int_{R_1}^{r} \frac{P}{4\pi\kappa r^2}\,dr$$

which gives the solution

$$T(r) = T_1 + (T_2 - T_1)\frac{r - R_1}{r}\frac{R_2}{R_2 - R_1}.$$

Now that we know $T(r)$, we can evaluate dT/dr at any radius to find the total power, using the first equation. Another slicker way, which doesn't even require knowing $T(r)$, is to integrate the first equation all the way from the inside of the oven to the outside,

$$\int_{T_1}^{T_2} dT = -\int_{R_1}^{R_2} \frac{P}{4\pi\kappa r^2}\, dr.$$

This gives an expression for the power in terms of the other parameters, yielding

$$P = 4\pi\kappa(T_1 - T_2)\frac{R_1 R_2}{R_2 - R_1}.$$

[2] **Problem 25.** Consider a sphere of a radioactive rock, which constantly produces heat σ per unit volume. The outside of the sphere is held at temperature T_0, the sphere's radius is R, and its thermal conductivity is κ. Find the temperature at the center of the sphere.

Solution. Just as in the example, we have

$$P(r) = -\kappa(4\pi r^2)\,\frac{dT}{dr}.$$

However, $P(r)$ is not independent of r. It represents the rate at which heat passes through the shell at radius r, so in the steady state it should be equal to the rate at which radioactive heat is produced within that shell,

$$P(r) = \frac{4}{3}\pi r^3 \sigma.$$

Plugging this in gives

$$\frac{dT}{dr} = -\frac{\sigma r}{3k}.$$

Integrating this and using $T(R) = T_0$ gives

$$T(0) = T_0 + \frac{\sigma R^2}{6k}$$

which grows rapidly with R.

There's a neat real-world application of this result. When farmers make hay bales for winter, there's a risk of them spontaneously catching on fire. That's because σ is small but nonzero, due to bacteria feeding on the hay and producing heat, and R can be very large.

[3] **Problem 26.** ⏲ USAPhO 2016, problem A4. A practical conduction question.

[3] **Problem 27.** ⏲ USAPhO 2013, problem A1. An elegant conduction question.

[4] **Problem 28.** ⏲ EuPhO 2023, problem 1. A cute problem on thermal lensing.

Thermodynamics III

For more about surface tension, which can be quite tricky, see section 9.3 of Wang and Ricardo, volume 1, or Kalda's thermodynamics handout, which also covers humidity. Phase transitions are covered clearly in section 4.5 of Wang and Ricardo, volume 2. For more detail, chapter 17 of Blundell and Blundell covers various types of thermodynamic work, chapter 26 covers liquid-gas phase transitions, and chapter 28 covers phase transitions in general. There is a total of **78** points.

1 Surface Tension

Thermodynamics applies to many systems that aren't ideal gases, or even gases at all; in such systems the work is not necessarily $đW = -P dV$. The most important example is surface tension, which we saw in **M2** and **M7**. We begin with the microscopic origin of surface tension.

Idea 1

For a liquid surface in air, there is an associated energy γA where A is the area of the surface. This leads to a contribution to the work

$$đW = \gamma \, dA.$$

The surface tension γ is also the force per length exerted along the surface.

The energy γA comes from the fact that liquid molecules at the surface are "missing" neighbors, and hence cannot lower their energy as much by forming cohesive bonds. (Technically, the same is true for the air molecules too, but air is very sparse compared to liquid, so we just ignore it.)

[3] **Problem 1.** Here, we use the above idea to very roughly estimate the surface tension of water.

(a) Estimate the spacing between water molecules. (Hint: you could use known atomic distance scales, or reverse engineer this from the known density of water.)

(b) Estimate the energy of a hydrogen bond. (Hint: the energy of *any* kind of chemical bond will be close enough.)

(c) Using these results, estimate the surface tension of water, and compare this to actual value $\gamma = 0.073\,\mathrm{N/m}$.

(d) Estimate the typical height of a droplet of water on a flat surface.

Next, we consider problems that combine surface tension with ideas in thermodynamics.

[2] **Problem 2** (PPP 62)**.** Two soap bubbles of radii R_1 and R_2 are joined by a straw. Air goes from one bubble to the other and a single bubble of radius R_3 is formed isothermally. The atmospheric pressure is P.

(a) If $R_1 < R_2$, which bubble loses air and which bubble gains it?

(b) Show that if γ is zero, then $R_3^3 = R_1^3 + R_2^3$.

(c) When γ is nonzero, the relation in part (b) is modified. Solve for γ in terms of R_1, R_2, R_3, and P. Is this a practical way to measure γ for typical soap bubbles?

[2] **Problem 3** (Cahn)**.** A tightly closed jar is completely filled with water. At the bottom of the jar are two small air bubbles. The pressure at the top of the jar is P_0, the radius of each bubble is R_0, and the surface tension is γ. The two bubbles then merge isothermally. Calculate the new pressure at the top of the jar.

[3] **Problem 4.** USAPhO 2007, problem A3.

[3] **Problem 5.** IPhO 2014, problem 1B.

Idea 2

One can also have liquid, solid, and air in the same problem, which leads to some complications. Let A_l and A_s be the surface areas of the liquid and solid exposed to the air, and A_{sl} be the surface area of the liquid-solid interface. Then there are three terms in the work,

$$\text{đ}W = \gamma_l \, dA_l + \gamma_s \, dA_s + \gamma_{sl} \, dA_{sl}.$$

In other words, there are three surface tensions, one associated with each kind of interface.

Both γ_l and γ_s arise from the fact that cohesive liquid-liquid or solid-solid bonds are broken to form a surface. However, γ_{sl} is determined by the adhesive forces between the liquid and solid, which may lead to a positive or negative contribution to the energy.

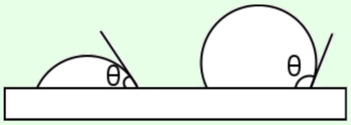
Specifically, let's define the energy of adhesion U_{sl} to be the work needed, per area, to separate a liquid from a solid, thereby turning a liquid-solid interface into a liquid-air and solid-air interface. By the definitions above,

$$U_{sl} = \gamma_s + \gamma_l - \gamma_{sl}.$$

Now, U_{sl} can be computed in terms of microscopic chemical bond energies, like γ_s and γ_l, so this result can also be thought of as an microscopic definition of γ_{sl}. When a liquid is in contact with a solid, the solid exerts a force per length of U_{sl} on the boundary of the liquid, along the solid.

Example 1

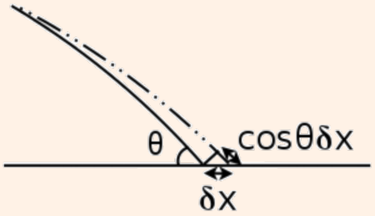
The surface of a drop of water makes a contact angle θ with a solid, as shown.



When θ is acute, the surface is said to be hydrophilic. If θ is obtuse, it is hydrophobic. Find an expression for θ in terms of the relevant surface tensions.

Solution

If the liquid drop expands outward by δx, the areas of various surfaces change, as shown.



The change in energy is

$$dU \propto \gamma_{sl}\,\delta x + \gamma_l \cos\theta\,\delta x - \gamma_s\,\delta x$$

and this must be equal to zero in equilibrium. Thus,

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} = \frac{U_{sl}}{\gamma_l} - 1.$$

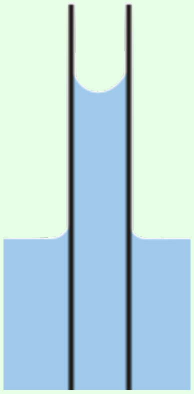
This is Young's equation. The liquid surface tension γ_l must be positive; otherwise the liquid could not exist stably at all, but rather would disperse into gas. Thus, the surface is hydrophilic when $U_{sl} > \gamma_l$ and hydrophobic when $U_{sl} < \gamma_l$.

As extreme cases, note that there is no solution for θ when $U_{sl} > 2\gamma_l$. In this limit, the surface is so hydrophilic that the liquid spreads out and coats the entire solid; this is known as perfect wetting. There is also no solution when $U_{sl} < 0$, in which case the liquid disperses into many tiny nearly spherical drops, each with a tiny area of contact with the solid.

This derivation was in terms of energy, which is typically easier for surface tension. The same result can be derived in terms of forces, but it's more subtle than it looks; the standard derivation in textbooks is wrong. For a clear derivation, see section 9.3 of Wang and Ricardo.

Example 2

A very thin, hollow glass tube of radius r is dipped vertically inside a container of water.



Find the height to which water can climb in the tube.

Solution

We first encountered this problem in **M7**, where we solved it by using Pascal's principle, giving an answer in terms of the contact angle. The derivation above of the contact angle completes this solution. However, we can also solve the problem using energy or force.

In terms of energy, if we move the height of the water up by δh, then

$$dU = \rho \pi r^2 g h \, \delta h + (\gamma_{sl} - \gamma_s) 2\pi r \, \delta h = 0$$

and solving gives

$$h = \frac{2(\gamma_s - \gamma_{sl})}{\rho g r} = \frac{2\gamma_l \cos\theta}{\rho g r}$$

using Young's equation. Alternatively, in terms of force, consider the vertical forces acting on the column of water inside the tube. There is an upward force of adhesion from the solid wall of $2\pi r U_{sl}$, and a downward surface tension force from the liquid below of $2\pi r \gamma_l$. Then

$$F = 2\pi r (U_{sl} - \gamma_l) - \rho \pi r^2 g h = 0$$

which yields precisely the same result.

Example 3

Fill a dish with water, and sprinkle something small over it, such as ground pepper. If you place a drop of detergent in the middle of the dish, then the pepper will "flee" away to the edges. Why does this happen?

Solution

Detergent is a surfactant, meaning that it decreases the surface tension of water. When one places the detergent in the middle of the dish, it diffuses outward, making the surface tension temporarily higher near edges of the dish. This leads to an unbalanced surface tension force on the pepper grains, pulling them to the edges.

This phenomenon is called the Marangoni effect. Of course, the force vanishes once the detergent becomes uniform distributed, and the surface tension is uniform again.

Remark

Here's a neat fact: the number of atoms that fit into a drop of water is comparable to the number of drops of water that fit inside the tallest mountains. We can show this using rough estimates, in the style of **P1**. Let E_b be the energy of a typical chemical bond, let m be the mass of an atom, and let d be the typical distance between atoms.

The size ℓ of a droplet of water, such as one that drips from a leaky ceiling, is the size where surface tension forces balance gravitational ones. By dimensional analysis, we must have

$$\ell \sim \sqrt{\gamma / \rho g}$$

as we showed in **M7**. Now, $\rho \sim m/d^3$, and the logic of problem 1 implies $\gamma \sim E_b/d^2$, so

$$\ell \sim \sqrt{E_b d/mg}.$$

Now consider the height H of the tallest mountains. The height of mountains is limited by the rigidity of rock; if the pressure is too great, then the rock underneath the mountain will deform, causing it to sink into the ground. Let's consider an atom-thick column of this rock. If it sunk down by a distance d, then the gravitational potential energy harvested would be mgH. However, the atom at the bottom would have to break its chemical bonds with its horizontal neighbors, which takes energy E_b. Balancing these gives a maximum height

$$H \sim E_b/mg.$$

We have therefore shown that

$$\ell \sim \sqrt{Hd}$$

which implies the original statement, within a few orders of magnitude.

2 Melting, Freezing, Boiling, Evaporation, and Condensation

Idea 3

A phase transition is a sudden, dramatic change in a system as thermodynamic variables such as the temperature are varied. Most of the ones you'll see have a latent heat

$$Q = mL.$$

For example, if ice is heated up, its temperature will gradually increase until it hits 0 °C. At that point, the temperature will remain constant until all of the ice is melted, i.e. when the full latent heat has been supplied.

Remark

We can roughly estimate the latent heats of melting and evaporation. In general, the latent heat can go into either in breaking molecular bonds, or increasing the entropy.

When a solid melts into a liquid, the molecules stay right next to each other, so changing bond energy isn't the dominant effect. Instead, it's the increase in entropy as the liquid molecules become free to rotate. Let's suppose that the molecules each gain a few extra possible quantum states. This corresponds to an entropy increase per molecule $\Delta S \sim k_B$, which means a latent heat per mass of

$$L = \frac{T\Delta S}{m_{\text{mol}}} \sim \frac{k_B T}{m_{\text{mol}}} = \frac{RT}{\mu}$$

where μ is the molar mass, or equivalently a latent heat per mole $\mathcal{L} \sim RT$. For water, we get $L \sim 2 \times 10^5$ J/kg, which is of the same order of magnitude as the true value 3.3×10^5 J/kg.

When a liquid becomes a gas, the dominant effect is typically the huge increase in entropy $k_B \log(V_{\text{gas}}/V_{\text{liq}})$ per molecule because they get much more space to move. The ratio inside the logarithm is huge, which means that while the volumes per molecule V_{gas} and V_{liq} vary by order-one amounts between phase transitions, the logarithm of their ratio is always around the same value, which turns out to be about 10. This gives a latent heat per mass of

$$L \sim \frac{10 k_B T}{m_{\text{mol}}} = \frac{10RT}{\mu}.$$

This result is called Trouton's rule, and it is surprisingly accurate for most liquids. However, the latent heat of vaporization for water is noticeably higher, $L = 2.26 \times 10^6$ J/kg. This is because of the extra energy needed to break hydrogen bonds.

[3] **Problem 6.** The temperature T at which a phase transition happens depends on the pressure P, yielding a "coexistence curve" $P(T)$ where the two phases can be in equilibrium with each other. The exact relationship is given by the Clausius–Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

where L is the total latent heat for some amount of material, and V_2 and V_1 are the corresponding volumes of that material when it is in each of the phases. (Depending on convention, L could be the latent heat per mole, in which case the V_i are volumes per mole, or both quantities could be per unit mass, in which case the V_i become densities.) In this problem, you will derive this equation.

(a) Consider an infinitesimal Carnot cycle operating between temperatures T and $T + dT$, and pressures P and $P + dP$, chosen so that the isothermal heating and cooling steps involve supplying latent heat. Compute the work done by the cycle.

(b) Argue that we may ignore all heat transfer except for the latent heat.

(c) Derive the Clausius–Clapeyron equation by setting the efficiency equal to the Carnot efficiency.

This classic setup is also considered in the second half of USAPhO 2023, problem A3.

[3] **Problem 7.** [A] In this exercise you'll find a quicker, more advanced derivation of the Clausius–Clapeyron equation.

(a) The Gibbs free energy is defined as $G = U + PV - TS$. Show that for reversible processes,

$$dG = V\,dP - S\,dT.$$

Two phases can only be in thermodynamic equilibrium if they have the same Gibbs free energy per molecule. Otherwise, turning one phase to the other would reduce the Gibbs free energy, which turns out to be equivalent to increasing the entropy of the universe. (For more details, see section 16.5 of Blundell and Blundell.)

(b) Suppose that the Gibbs free energies per molecule G/N for two phases are equal at temperature T_0 and pressure P_0. Derive the Clausius–Clapeyron equation by demanding this is also true at temperature $T_0 + dT$ and $P_0 + dP$.

Remark: Thermodynamic Potentials

You might sometimes see the Clausius–Clapeyron equation written in terms of a difference in enthalpy ΔH rather than a latent heat. The enthalpy is the state function $H = U + PV$, so

$$dH = V\,dP + đQ.$$

This is useful because many lab experiments happen at constant pressure, $dP = 0$, leaving $dH = đQ$. That is, only heat changes the enthalpy, so the latent heat of a phase transition must be the difference in enthalpies of the two phases, $L = \Delta H$. That in turn is useful because enthalpy is a state function, so given a new phase transition you can calculate L by just looking up the enthalpy values for each of the phases in a table.

We've now covered all the classic "thermodynamic potentials". As we just saw, the enthalpy H is useful for bookkeeping heat. As we saw in **T2**, the Helmholtz free energy F is minimized in thermodynamic equilibrium, given constant temperature and volume. (This is the relative of the statement that the system's internal energy U is minimized in equilibrium, given constant entropy and volume, which is just the usual statement of mechanical equilibrium.) And as we saw in the problem above, the Gibbs free energy G is minimized in thermodynamic equilibrium, given constant temperature and pressure.

More generally, what's going on is that the number of possibly useful potentials doubles every time we add another pair of "thermodynamic conjugate variables". Before learning about thermodynamics, we just had U. When we learned about temperature and entropy, we additionally cared about F. And now upon accounting for pressure and volume, we have H and G. If we had another pair, such as magnetization and external magnetic field, we could define 4 more potentials, which would each be useful in different situations.

[2] **Problem 8.** Ice skaters can move with little friction because they actually glide on a thin layer of water. Estimate how heavy an ice skater has to be to melt ice by just standing on their skates, assuming the ice is at temperature $-5\,^\circ\mathrm{C}$.

Now we focus on the specifics of liquid-gas phase transitions.

[3] **Problem 9.** Suppose that at pressure P_0, a liquid-gas phase transition takes place at temperature T_0. Assume the gas obeys the ideal gas law, and neglect the volume of the liquid.

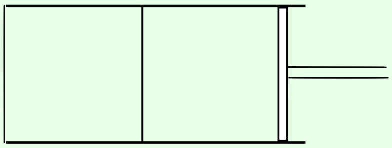
(a) Assuming the latent heat is temperature-independent, compute the coexistence curve $P(T)$.

(b) In reality, the latent heat has a mild dependence on temperature, changing the results. As a crude model, suppose that the latent heat per molecule for a monatomic liquid-gas phase transition has two components: a fixed energy E_0 required to break the bonds with other molecules in the liquid, and the $P\,dV$ work that must be done to "push" the rest of the gas away, since the new gas molecule takes up space. Under these assumptions, what is the latent heat per molecule, and qualitatively how does the dependence $P(T)$ change?

(c) A closed container of constant volume contains both liquid and gas in equilibrium, at temperature T. Let the latent heat of vaporization per mole be $\mathcal{L}$, and neglect the volume of the liquid. If the temperature is increased by a very small amount ΔT, by what factor does the number of moles in gas form change?

Example 4: APhO 2004.3

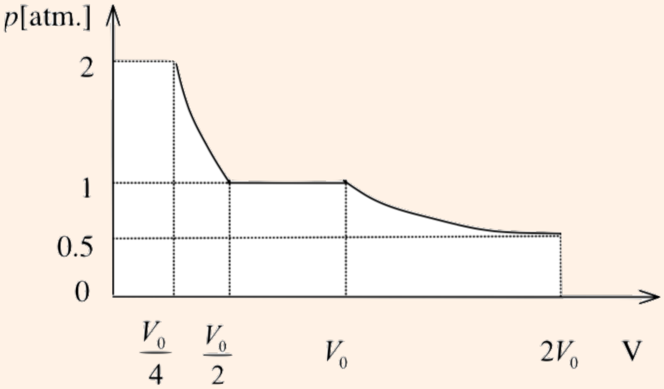
A cylinder is divided into two parts by a mobile partition, which is free to move and conducts heat well. One compartment contains one mole of water vapor, and the other contains one mole of nitrogen gas. Initially, both compartments have volume V_0, pressure 0.5 atm, and temperature 373 K. A piston is then slowly inserted, compressing the system isothermally.



Sketch the $P(V)$ curve.

Solution

The answer is shown below.



Initially, we just have an ordinary isothermal compression. Both the water vapor and nitrogen gas compartments are compressed at the same rate, since they must have equal pressures and temperatures. When the total volume is halved, the pressure in both reaches one atmosphere. Now, water condenses at temperature 373 K at pressure $p = 1$ atm. Thus, as the volume continues to decrease, the pressure stays constant, the nitrogen compartment's volume stays the same, and the water compartment shrinks, as the vapor gradually condenses to liquid. This process completes once all the vapor is condensed, which is roughly when the total volume has halved again. After this point, we again have ordinary isothermal compression, of the nitrogen gas alone.

[3] **Problem 10.** NBPhO 2016, day 2, problem 2. A problem on phase transitions with data analysis.

[3] **Problem 11.** USAPhO 2015, problem A4. A heat engine with phase transitions.

In practice, water on Earth is more subtle because there are three substances at play: liquid water, water vapor, and the rest of the atmosphere.

Idea 4: Humidity

Consider a box at constant temperature T containing only water, and let $P(T)$ be the liquid water-water vapor coexistence curve. In equilibrium, if we apply any pressure below $P(T)$, all of the water will be in vapor form, and if we apply any pressure above $P(T)$, all of the water will be in liquid form. Physically, applying a higher pressure forces the water vapor to condense into liquid, as it packs the molecules closer together, and applying a lower pressure forces the liquid to evaporate into vapor, as it cannot hold itself together against the thermal motion of the molecules. Coexistence is impossible, except at *exactly* the pressure $P(T)$.

However, in everyday life, the two easily coexist over a wide range of pressures. The subtlety is that the total air pressure has two contributions,

$$P_{\text{tot}} = P_{\text{atm}} + P_{\text{vap}}$$

where the first is the pressure due to atmospheric gases, such as nitrogen and oxygen, and the second is the pressure due to water vapor in the air. In everyday conditions, P_{atm} is about 100 times larger than P_{vap}, and the liquid water feels the pressure P_{tot}. But water vapor evaporates and condenses independently of the air, so P_{atm} has no effect on it at all. As a result, in equilibrium liquid water and water vapor can coexist, with the vapor having a pressure $P_{\text{vap}} = P(T)$. The coexistence curve $P(T)$ is thus also called the (equilibrium) vapor pressure.

The relative humidity ϕ is defined as

$$\phi = P_{\text{vap}}/P(T)$$

and quantifies how saturated the air is with water vapor. In equilibrium, $\phi = 1$, while for $\phi < 1$ people can cool down by sweating. It is also possible to have $\phi > 1$, which occurs in humid air high in the atmosphere just before it condenses into a cloud.

The dew point T_d satisfies

$$P(T_d) = P_{\text{vap}}$$

and represents the temperature at which water would begin condensing out of a given parcel of air, cooled at constant pressure.

The boiling temperature T_b satisfies

$$P(T_b) = P_{\text{atm}}.$$

This is the temperature at which a bubble of pure water vapor, which forms inside the liquid, has a high enough pressure to push the liquid away and continue to expand. Beyond this temperature, liquid water can't exist; it all turns to vapor. This is why pressure cookers are useful: they increase P_{atm}, thereby increasing T_b and allowing food to cook faster. (Technically, we should have P_{tot} rather than P_{atm} on the right-hand side, but in practice whenever we boil things, we let the resulting water vapor fly away. So the actual vapor pressure P_{vap} never gets that high.)

At the interface between two liquids, boiling can start at a significantly lower temperature than the boiling temperature of either liquid, because both of the liquids contribute to the vapor pressure. This is called border boiling, and is treated in IZhO 2020, problem 2.

Example 5

How does alcohol distillation work?

Solution

Let alcohol and water have coexistence curves/equilibrium vapor pressures of $P_a(T)$ and $P_w(T)$. The vapor pressure of alcohol is higher, with pure alcohol boiling at about 80° C.

Consider heating a mixture of alcohol and water, with mole fractions X_a and X_w, with $X_a + X_w = 1$. If a small bubble of gas forms inside, then Raoult's law states that both alcohol and water vapor will be present, and contribute independently in proportion to their mole fractions. Then the boiling point satisfies

$$X_a P_a(T_b) + X_w P_w(T_b) = P_{\text{atm}}.$$

This is in between the boiling points of alcohol and water individually. By the ideal gas law, the ratio of mole fractions of alcohol and water in the vapor is the ratio of vapor pressures, so

$$\frac{X_a'}{X_w'} = \frac{X_a}{X_w} \frac{P_a(T_b)}{P_w(T_b)}.$$

Since the fraction is greater than one, the alcohol in the distilled vapor is more concentrated than in the liquid.

By the above logic, we could get completely pure alcohol by just repeating the distillation procedure several times. Actually, it's more complicated than that because the alcohol and water molecules will interact, causing Raoult's law to break down; our calculation above only applies for an "ideal mixture". For more about distillation, see these notes.

[3] **Problem 12.** Kalda Thermodynamics, problem 22. A problem on practically measuring humidity.

[3] **Problem 13.** EFPhO 2006, problem 1. (Note that the comma in the density of air in part 4 denotes a decimal point.)

3 General Phase Transitions

In this section we'll illustrate some of the ideas needed to analyze phase transitions in general.

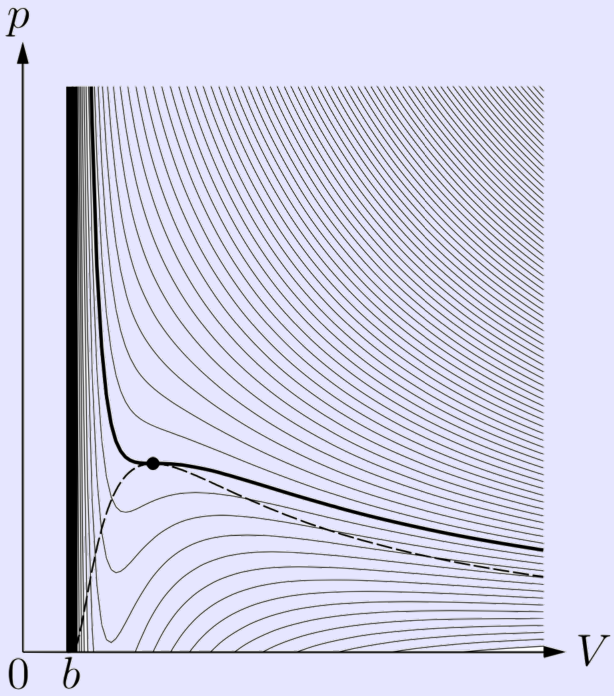
Idea 5

A nonideal gas can be described by the van der Waals equation of state,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT.$$

You derived the pressure correction in **T1** assuming weak attractive intermolecular forces; the modification of the volume accounts for the fact that the molecules can't overlap each other. Remarkably, this equation of state also contains a liquid-gas phase transition!

To see this, consider a plot of the isotherms on a PV diagram.



At low temperatures, the isotherms can have negative compressibility, meaning that the pressure decreases as the volume decreases. This is unphysical, and means that the fluid is unstable at these points: if you push on it, it'll just keep shrinking, until it condenses into a dense liquid. Therefore, parts of these isotherms should be replaced with horizontal lines; along these horizontal parts liquid and gas coexist, in varying proportions.

Specifically, everything underneath the dotted line should be replaced with horizontal lines. As described in more detail in section 26.1 of Blundell, this can be shown by demanding that the liquid and gas have equal Gibbs free energy. As a result, the total area on the PV diagram of the isotherm that goes underneath the horizontal line equals the area that goes above it; this is called Maxwell's equal area rule.

There is a critical isotherm marked in bold above. Above this temperature, there is no liquid-gas phase transition at all; instead we just have one phase, called a supercritical fluid. Specifically, this is the temperature of the first isotherm that no longer has a local minimum in pressure, which means

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

at the critical temperature $T = T_c$. As you will see in problem 14, this occurs at

$$V_c = 3nb, \quad T_c = \frac{8a}{27Rb}, \quad P_c = \frac{a}{27b^2}.$$

This point, marked above, is called the critical point.

Remark

The van der Waals equation of state is accurate for a sparse gas with weak attractive interactions; you shouldn't expect it to be accurate for dense gases or the liquid state. However, it still is extremely important because it is one of the simplest equations of state that gives a liquid-gas phase transition. What's more, if you zoom in near the critical point and write the pressure, volume, and temperature as multiples of the critical pressures, volumes, and temperatures, it turns out that *all* equations of state give the same results! This deep phenomenon is known as universality, but unfortunately I can't explain the reason why without using statistical field theory.

[3] **Problem 14.** INPhO 2018, problem 6. A series of exercises on the van der Waals gas. Feel free to look up definitions for part (a).

[4] **Problem 15.** [A] Here we'll introduce a simple model for a ferromagnetic phase transition. Consider N electrons, which may have spins $s_i = \pm 1$. The energy of a configuration is

$$E = -B \sum_i s_i - \frac{J}{2N} \sum_{i \neq j} s_i s_j.$$

The first term represents the effect of an external magnetic field B, while the second term represents an interaction, with strength described by the constant J, which tries to make the spins parallel. (In this simple model, we suppose all distinct pairs of spins interact equally. We could also make spins only interact with their neighbors, but this would complicate the analysis.)

(a) Define the average magnetization as $m = \sum_i s_i / N$. Find $E(m)$, the energy in terms of m and the other constants in the problem.

(b) For a fixed value of m, write down the number of states $\Omega(m)$ with that magnetization.

(c) The probability of having a given value of m is proportional to $e^{-\beta E(m)} \Omega(m)$. Argue that this probability is maximized for the value of m that minimizes the free energy

$$F = E - TS.$$

Hence the equilibrium configuration minimizes the free energy. This is the statistical mechanical way to argue that F is minimized; the thermodynamic way was covered in **T2**.

(d) Assuming that $N \gg 1$ and applying Stirling's approximation (introduced in **T2**), show that the free energy $F(m)$ is minimized when

$$m = \tanh(\beta B + \beta J m), \quad \beta = \frac{1}{k_B T}.$$

(e) For a fixed $B > 0$, plot $m(T)$. This should match with Curie's law, which you proved in **T1**.

(f) Now let $B = 0$. Show that there exists a critical temperature T_c, above which $m(T)$ is exactly zero and below which it is nonzero; also find an approximate expression for the magnetization just below T_c.

This is a phase transition where the material spontaneously becomes magnetized, and the simplest example of a phase transition which can be understood analytically.

[5] **Problem 16.** ⏱ APhO 2011, problem 3. A nice problem on a real-world *mechanical* phase transition. Some of the intuition you gained studying the var der Waals gas will be useful.

4 Thermodynamic Systems

Now that we know all about the different methods of heat transfer, as well as phase transitions, we consider some questions involving a mix of these concepts as well as mechanics.

Example 6: IPhO 1967.3

Consider two identical homogeneous balls with the same initial temperatures. One of them is at rest on a horizontal plane, while the other hangs on a thread.

The same quantity of heat is supplied to both balls. Which has the higher final temperature?

Solution

This infamous problem, which appeared on the first IPhO, was the original "troll" Olympiad question. The balls are different because the one on the plane thermally expands upward, while the one on a thread thermally expands downward. This tiny change in gravitational potential energy means that the ball on the thread ends up hotter.

This is an incredible solution – in the sense that it is *not* credible. About fifty years after it was written, physicists at Oxford showed that it is wrong! Suppose the logic above were actually right. Then a heat engine can be constructed with these four steps:

1. Heat the ball on the plane, therefore raising its center of mass.
2. Attach the ball to a thread and remove the plane.
3. Cool the ball on the thread, therefore raising its center of mass.
4. Put a plane just under the ball's new position and remove the thread.

This is a heat engine, where the work goes into raising the ball. If the ball is only heated and cooled a tiny amount dT, then the heat supplied is proportional to dT, but the distance through which the ball rises is also proportional to dT. Therefore, the efficiency of the cycle becomes a constant as dT goes to zero, which exceeds the Carnot efficiency (which instead goes to zero) and hence violates the second law of thermodynamics.

A real ball doesn't violate the second law, because it also stretches while hanging on the thread, and squashes while on the plane. The slick solution neglects these effects and considers only thermal expansion, but the above argument shows that this assumption is inconsistent: you can't have the latter without the former. This is an example of how thermodynamic considerations alone can, perhaps surprisingly, yield information about mechanical properties. The paper linked above performs a careful analysis and shows that, for most materials, the ball on the thread instead ends up *colder*.

Example 7

Why does a breeze cool you down, and why do clothes make you warmer?

Solution

Like most gases, air has a very small thermal conductivity, and enough viscosity so that you carry around a thin layer of warm air with you wherever you go. (The main reason you cool down is because this warm air rises away from you, by convection.) When a breeze is blowing, it strips off this cushion of warm air, which is why you feel colder.

When you're sweaty, the same logic applies. The layer of air you carry around is also moist, saturated with water vapor from your sweat. Again, a breeze removes this layer, allowing more evaporation to happen, cooling you down.

Clothing material itself actually has a higher thermal conductivity than air. Its real purpose is to trap the layer of warm, moist air around you, preventing it from being blown away by breezes or rising from convection. (That's also how greenhouses keep plants warm: the sun warms air near the ground, and the glass room prevents that air from rising away. Confusingly, this has nothing to do with the atmospheric "greenhouse effect.")

Example 8

Can you boil water in a pot by putting it into a bigger pot of boiling water?

Solution

No, because boiling is a phase transition that requires latent heat. The water in the small pot can get heated up to boiling temperature, but it can't start boiling, because at that point it'll be at the same temperature as the bigger pot, and no more heat can flow.

[1] **Problem 17** (IPhO 1996)**.** A thermally insulated piece of metal is heated under atmospheric pressure by an electric current so that it receive a constant power P. The temperature is

$$T(t) = T_0(1 + a(t - t_0))^{1/4}$$

where T_0, t_0, and a are constants. Find the heat capacity $C(T)$.

[3] **Problem 18.** EFPhO 2011, problem 8. A tricky data analysis problem.

[3] **Problem 19.** EFPhO 2014, problem 9. A nice problem reviewing radiation and kinetic theory.

[4] **Problem 20.** EuPhO 2019, problem 1.

5 Thermodynamic Fluids

In this section, we focus on problems combining thermodynamics with fluids, as covered in **M7**. We begin with some questions which only require fluid statics.

[5] **Problem 21.** IPhO 1998, problem 2. A very nice real-world fluids/thermo question.

[5] **Problem 22.** APhO 2009, problem 3. Another nice, simple model of a real-world phenomenon.

Idea 6

In **M7** we considered Bernoulli's principle for incompressible liquids with no temperature. However, in general fluids are compressible and carry internal energy. To derive Bernoulli's principle in this more general context, we apply conservation of energy to a tube of streamlines, as one mole of ideal gas flows through it. We neglect gravity, since it typically is unimportant for such rapid flows. The energy of a mole of gas at the entry of the tube is

$$\frac{1}{2}\mu v_1^2 + c_V T_1$$

where μ is the molar mass, and c_V is the heat capacity per mole. Similarly, the energy of a mole of gas at the other end is

$$\frac{1}{2}\mu v_2^2 + c_V T_2.$$

Assuming there's no heat transfer, the difference must be the work done on the tube of fluid as a mole of gas flows through,

$$p_1 \delta V_1 - p_2 \delta V_2 = R(T_1 - T_2)$$

where the δV_i are the volumes of a mole of gas at the entry and exit, and we used the ideal gas law. Combining and using $c_p = c_V + R$ gives

$$\frac{1}{2}\mu v^2 + c_p T = \text{const}$$

along a streamline in steady flow.

Remark

You might also see Bernoulli's principle in the form

$$\frac{1}{2}v^2 + gh + c_p T = \text{const}$$

where we've added on the contribution of gravitational potential energy. In this case, c_p is the heat capacity at constant pressure per unit mass, not per mole. Unfortunately, people use the letter c or C to denote many different kinds of (specific) heat capacities. Whenever doing a problem where a heat capacity is given, check the dimensions!

Example 9: Wang and Ricardo

A rocket propels itself by burning fuel to release diatomic gas of temperature T_1 in its combustion chamber, which has cross-sectional area A_1. The gas then flows adiabatically and is expelled out of the nozzle, which has a cross-sectional area A_2, at a speed v_2 relative to the rocket, pressure p_2, and temperature $T_2 < T_1$. In the limit of steady flow, determine the thrust experienced by the rocket.

Solution

Since the flow is adiabatic and the gas is diatomic,

$$p_1 = p_2 \left(\frac{T_1}{T_2}\right)^{7/2}.$$

As discussed in **M7**, mass conservation in steady flow means $\rho A v$ must be the same on both sides of the nozzle. The ideal gas law tells us that $\rho \propto p/T$, so

$$\frac{p_1 A_1 v_1}{T_1} = \frac{p_2 A_2 v_2}{T_2}.$$

Combining these two gives a relation between the velocities,

$$v_1 = v_2 \frac{A_2}{A_1}\left(\frac{T_2}{T_1}\right)^{5/2}.$$

Bernoulli's principle gives

$$\frac{1}{2}\mu v_1^2 + \frac{7}{2}RT_1 = \frac{1}{2}\mu v_2^2 + \frac{7}{2}RT_2$$

where we neglected the gravitational energy. Combining with our previous relation gives

$$v_2^2 = \frac{7R(T_1 - T_2)}{\mu\,(1 - (A_2/A_1)^2 (T_2/T_1)^5)}.$$

Finally, the thrust is

$$F = \frac{dp}{dt} = \rho_2 A_2 v_2^2 = \frac{\mu p_2 A_2 v_2^2}{RT_2} = \frac{7p_2A_2(T_1 - T_2)}{T_2(1 - (A_2/A_1)^2(T_2/T_1)^5)}.$$

Example 10

How does the Bernoulli's principle above reduce to the incompressible one used in **M7**?

Solution

This is trickier than it seems. For simplicity, let's neglect the gravitational contribution. Then by the ideal gas law, the compressible Bernoulli's principle derived above is

$$\frac{1}{2}v^2 + \frac{\gamma}{\gamma - 1}\frac{P}{\rho} = \text{const.}$$

When the flow is incompressible, ρ is constant, but if we just multiply by ρ we get

$$\frac{1}{2}\rho v^2 + \frac{\gamma}{\gamma - 1}P = \text{const}$$

which is not the expected result!

In fact, there's something more troubling under the surface. The Bernoulli's principle derived in **M7** applies to water flow, since water is incompressible. And the compressible version derived above applies to ideal gas flow, since gas is compressible. But in **M7**, we applied the incompressible Bernoulli's principle to gas flow! How does that even make sense?

The resolution to the two questions is the same: the key assumption needed to get to the original form of Bernoulli's principle is *not* that an ideal gas is incompressible, because that's simply not true. Instead, the key assumption is that the gas flow is much slower than the speed of sound, $v^2 \ll c_s^2 \sim P/\rho$. In this limit, the kinetic energy term in the generalized Bernoulli's principle is much smaller than the internal energy term. Thus, in the course of subsonic flow, the temperature, pressure, and density of the gas can only change by a small relative amount. For example, the pressure is $P(x) = P_0 + \Delta P(x)$ where $\Delta P \ll P_0$. (To avoid some confusion, remember that Bernoulli's principle always assumes steady flow. The air in my bike tires has $\Delta P \approx 6P_0$, but that's because the process of pumping a tire is not a steady flow.)

But if that's true, then what went wrong with just multiplying our result above by ρ? The point is that for very subsonic flows, the v^2 term is much smaller than the P/ρ term, so we need to evaluate the P/ρ term to a very good relative precision to get correct results. (If my bank was careless and randomly misplaced 0.1% of its money, then that might mean losing 100% of my savings, since my account's value is small compared to its total.)

Now we're ready to do the derivation properly. We start from the first equation above, but we don't multiply by ρ. Instead, we note that P/ρ^γ is constant because the gas is compressed adiabatically, since we neglected heat transfer, so we multiply by $\rho(P_0/P)^{1/\gamma}$, giving

$$\left(\frac{P_0}{P}\right)^{1/\gamma}\frac{1}{2}\rho v^2 + \frac{\gamma}{\gamma - 1}\left(\frac{P}{P_0}\right)^{(\gamma-1)/\gamma}P_0 = \text{const.}$$

Since the first term is the small one, we can approximate $P_0 \approx P$ there without much error. As for the second term, we expand $(P/P_0)^{(\gamma-1)/\gamma}$ with the binomial theorem to get

$$\frac{1}{2}\rho v^2 + \frac{\gamma}{\gamma - 1}P_0 + \Delta P = \text{const}$$

and subtracting the constant $P_0/(\gamma - 1)$ recovers the "incompressible" Bernoulli's principle.

In conclusion, the Bernoulli's principle derived in this problem set works for arbitrarily fast gas flows, while the incompressible form in **M7** only works for very subsonic flows. But that doesn't mean you should never use the latter. When the flow is subsonic, the incompressible form is easy to use, while the more general form requires great care to get the correct result. You should only use the general form when it's actually necessary, i.e. for the very fast gas flows considered in the following problems.

[3] **Problem 23** (Feynman)**.** Air with density ρ, pressure P, and adiabatic index γ is flowing at uniform speed v through a smooth pipe of constant cross-sectional area A. It is heated as it passes a wire grid, which offers negligible resistance to the flow, with a power $\dot{Q}$. This is a simple model for a jet engine. For simplicity, suppose the output pressure is also P, though this would not be true in a high efficiency engine.

(a) Find the speed v' with which the air exits the tube, in terms of the given parameters.

(b) Find the thrust produced, in terms of v' and the other parameters.

[3] **Problem 24** (Wang 2.17)**.** Consider an ideal gas with pressure p, density ρ, and adiabatic index γ. A density pulse is set up in the gas, traveling along the $-x$ direction with speed c. Inside the pulse, the gas has local velocity $v \ll c$ in the lab frame, and a local density $\rho + \Delta\rho$, where $\Delta\rho \ll \rho$.

(a) Transform to the reference frame where the pulse is at rest, and find three constraints, using mass conservation, energy conservation, and the fact that the gas is compressed and expanded adiabatically when it enters and leaves the pulse (i.e. heat conduction is negligible).

(b) Combine these relations to find c. Work to lowest order in the small quantities v/c and $\Delta\rho/\rho$.

The quantity c is the adiabatic speed of sound in a gas, which we'll derive in a different way in **W3**. For more about sound waves, see chapter 31 of Blundell, or section 14.1 of Lautrup.

Example 11

Show that the kinetic and potential energy of a sinusoidal, adiabatic sound wave are equal.

Solution

First, we explicitly define our notation. The sound wave profile is

$$P = P_0 + \Delta P \cos(kx - \omega t), \quad \rho = \rho_0 + \Delta\rho \cos(kx - \omega t)$$

and

$$\frac{v}{c} = \frac{v_0}{c}\cos(kx - \omega t), \quad T = T_0 + \Delta T \cos(kx - \omega t).$$

In problem 24, you derived relations between the parameters $(\Delta P)/P_0$, $(\Delta\rho)/\rho_0$, v_0/c, and $(\Delta T)/T_0$, which are all assumed small, and of the same order of magnitude. The total energy density of the fluid, up to second order, is

$$u = \frac{1}{2}\rho_0 v^2 + c_v \rho T$$

where here c_v is the heat capacity per unit mass. The first term is the bulk kinetic energy density, while the change in the second term is the potential energy density, where we're using the usual meaning of potential energy as any energy which isn't kinetic.

This all looks pretty straightforward, but there's a reason that most introductory textbooks never write down this expression. You can see the issue by applying the ideal gas law to the second term. Since $P \propto \rho T$, this term is proportional to P, but the average of P is just P_0. This suggests that sound waves have no potential energy density at all, which is wrong. For instance, if you instantly take out all the macroscopic kinetic energy, setting v to zero, then there is still energy remaining that can be harvested because the pressure is nonuniform.

Here's the problem: energy is inherently a second order quantity. If ρ and T were both small quantities, then it would be good enough to multiply them to get the answer to second order. But instead, ρ and T are the quantities ρ_0 and T_0 shifted by small quantities $\Delta\rho$ and ΔT. That means that to get the quantity ρT correct to second order, we need to get both ρ and T individually correct to second order, which is beyond the first order approximations we started with! This is a conceptual issue that occurs whenever you have a perturbation that shifts existing properties of a medium. (It doesn't happen for waves on a string, which we cover in **W1**, because those waves are parametrized by y, and $y = 0$ when there is no wave.)

It's possible to fix this issue, but we need to be careful. First, let's use the ideal gas law to change variables to pressure, so we only have one quantity to deal with,

$$c_v \rho T = \frac{R}{\mu} \frac{1}{\gamma - 1} \rho T = \frac{P}{\gamma - 1}.$$

The key insight is that we can keep our expression for ρ the same. The reason is that for the wave equation to continue to be satisfied at second order, we can only add second order terms that are constant, or also sinusoids. Adding a constant to the density is not allowed because we know the total number of particles is conserved, so the mass $\int \rho \, dV$ is, and adding a sinusoid can be absorbed by simply redefining $\Delta\rho$.

Now, we know that $P \propto \rho^\gamma$, and letting $\delta\rho = \Delta\rho \cos(kx - \omega t)$ for convenience, we have

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0}\right)^\gamma = 1 + \frac{\gamma \, \delta\rho}{\rho_0} + \frac{\gamma(\gamma - 1)}{2} \left(\frac{\delta\rho}{\rho_0}\right)^2.$$

When we integrate the first term, we get the internal energy of the fluid at rest. The second term averages to zero, and so can be disregarded. The third term gives the desired result,

$$u = \frac{1}{2} \rho_0 v^2 + \frac{\gamma P_0}{2} \left(\frac{\delta\rho}{\rho_0}\right)^2.$$

Now that the energy is in terms of small quantities squared, we can relax and use first order results. Using the results derived in problem 24, this can be simplified to

$$u = \frac{1}{2} \rho_0 v^2 + \frac{1}{2} \rho_0 c^2 \left(\frac{\delta\rho}{\rho_0}\right)^2$$

and the two contributions are equal, because $v/c = -\delta\rho/\rho_0$.

As a check on this result, it is often true that the energy density is equal to the momentum density times the wave speed, $u = pc$. (For example, this corresponds to $E = pc$ for photons.) The momentum density is $p = \rho v = (\rho_0 + \delta\rho)v$. The first order term represents the overall momentum of all of the gas, not the momentum due to the sound wave itself, so it can be ignored. The second order term is

$$p = \delta\rho\, v = \frac{\rho_0 v^2}{c}$$

which is exactly the expected result.

Ironically, while we began this discussion by noting that the energy of a transverse wave on a string is more straightforward, the longitudinal momentum of a transverse wave on a string is far more confusing – how can there be any if the string moves only transversely? Does the above identity $u = pc$ break down for these waves, or do we just need to evaluate p more carefully? (For one perspective in this ongoing debate, see this paper.) All of this is too subtle to be relevant to Olympiads; even string theorists get confused about it. It's just a reminder that there are always subtleties lurking in even basic physics.

[3] **Problem 25.** 🕒 IPhO 2012, problem 1B. A tricky real-world problem on fluids and condensation.

Thermodynamics III

For more about surface tension, which can be quite tricky, see section 9.3 of Wang and Ricardo, volume 1, or Kalda's thermodynamics handout, which also covers humidity. Phase transitions are covered clearly in section 4.5 of Wang and Ricardo, volume 2. For more detail, chapter 17 of Blundell and Blundell covers various types of thermodynamic work, chapter 26 covers liquid-gas phase transitions, and chapter 28 covers phase transitions in general. There is a total of **78** points.

1 Surface Tension

Thermodynamics applies to many systems that aren't ideal gases, or even gases at all; in such systems the work is not necessarily $đW = -P dV$. The most important example is surface tension, which we saw in **M2** and **M7**. We begin with the microscopic origin of surface tension.

Idea 1

For a liquid surface in air, there is an associated energy γA where A is the area of the surface. This leads to a contribution to the work

$$đW = \gamma \, dA.$$

The surface tension γ is also the force per length exerted along the surface.

The energy γA comes from the fact that liquid molecules at the surface are "missing" neighbors, and hence cannot lower their energy as much by forming cohesive bonds. (Technically, the same is true for the air molecules too, but air is very sparse compared to liquid, so we just ignore it.)

[3] **Problem 1.** Here, we use the above idea to very roughly estimate the surface tension of water.

(a) Estimate the spacing between water molecules. (Hint: you could use known atomic distance scales, or reverse engineer this from the known density of water.)

(b) Estimate the energy of a hydrogen bond. (Hint: the energy of *any* kind of chemical bond will be close enough.)

(c) Using these results, estimate the surface tension of water, and compare this to actual value $\gamma = 0.073\,\text{N/m}$.

(d) Estimate the typical height of a droplet of water on a flat surface.

Solution. (a) The size of one hydrogen atom is about $10^{-10}\,\text{m}$, also known as an angstrom. Since water is H_2O and oxygen atoms are a bit bigger, we can estimate the distance between water molecules to be $10^{-9}\,\text{m}$.

(b) The typical energy of a chemical bond is about $1\,\text{eV}$. There are a few ways to do this. You can remember that the binding energy of an electron in a hydrogen atom is $13.6\,\text{eV}$, and the chemical bond energies are a bit smaller. Or, you can recall that the electrons in batteries are pushed by chemical reactions, and a typical battery voltage is $1\,\text{V}$.

(c) The number of water molecules in an area of $1\,\mathrm{m}^2$ is about 10^{18}, and the energy of each missing bond is $1\,\mathrm{eV} = 1.6 \times 10^{-19}\,\mathrm{J}$, giving an estimate of about $0.1\,\mathrm{J/m}^2$. This is fairly close to the true value of $0.07\,\mathrm{J/m}^2$.

(d) By dimensional analysis, this must be $h \sim \sqrt{\sigma/g\rho}$ where ρ is the density of water. (This can also be obtained by heuristically minimizing the sum of gravitational potential energy and surface tension, where the first favors a small height and the second favors a large height.) Plugging in numbers, we get $h \sim 3\,\mathrm{mm}$, which is quite reasonable.

Another way of saying this is that there's only one dimensionless quantity you can build out of the given variables, $g\rho h^2/\sigma$. This is known as the Eotvos number, and quantifies the ratio of the importance of gravitational and surface tension forces (just like the Reynolds number you found in **M7** quantities the ratio of inertial and viscous forces). Since a droplet requires these forces to balance, the Eotvos number should be of order 1, recovering the answer.

Next, we consider problems that combine surface tension with ideas in thermodynamics.

[2] **Problem 2** (PPP 62)**.** Two soap bubbles of radii R_1 and R_2 are joined by a straw. Air goes from one bubble to the other and a single bubble of radius R_3 is formed isothermally. The atmospheric pressure is P.

(a) If $R_1 < R_2$, which bubble loses air and which bubble gains it?

(b) Show that if γ is zero, then $R_3^3 = R_1^3 + R_2^3$.

(c) When γ is nonzero, the relation in part (b) is modified. Solve for γ in terms of R_1, R_2, R_3, and P. Is this a practical way to measure γ for typical soap bubbles?

Solution. We use the fact, derived in **M2**, that a bubble with radius R has excess pressure $4\gamma/R$.

(a) The bubble with a smaller radius has a larger excess pressure. Thus when the bubbles are connected, bubble 1 will lose air, and bubble 2 will gain it.

(b) All the bubbles have the same temperature, and the number of moles adds, so the ideal gas law gives

$$P_1V_1 + P_2V_2 = P_3V_3.$$

If there is no surface tension, then all the P_i are equal to P, so $V_3 = V_1 + V_2$.

(c) Accounting for the excess pressure, we have

$$\left(P + \frac{4\gamma}{R_1}\right) R_1^3 + \left(P + \frac{4\gamma}{R_2}\right) R_2^3 = \left(P + \frac{4\gamma}{R_3}\right) R_3^3$$

and solving for γ gives

$$\gamma = \frac{P}{4}\frac{R_3^3 - R_1^3 - R_2^3}{R_1^2 + R_2^2 - R_3^2}.$$

Since γ is small, the numerator will be quite small relative to the radii of the bubbles, so the answer will have a large relative error even if each length is determined precisely. So this method isn't very practical.

[2] **Problem 3** (Cahn)**.** A tightly closed jar is completely filled with water. At the bottom of the jar are two small air bubbles. The pressure at the top of the jar is P_0, the radius of each bubble is R_0, and the surface tension is γ. The two bubbles then merge isothermally. Calculate the new pressure at the top of the jar.

Solution. Since the air-water surface has only one "side", the excess pressure is $\Delta P = 2\gamma/R_0$. The process is isothermal and the number of moles of gas stays the same, so by the ideal gas law,

$$\left(P_1 + \frac{2\gamma}{R_1}\right) R_1^3 = 2\left(P_0 + \frac{2\gamma}{R_0}\right) R_0^3.$$

Since water is incompressible, the volume of gas should also stay the same, $R_1^3 = 2R_0^3$, which gives

$$P_1 = P_0 + \frac{\gamma}{R_0}(2 - 2^{2/3}).$$

[3] **Problem 4.** USAPhO 2007, problem A3.

[3] **Problem 5.** IPhO 2014, problem 1B.

Idea 2

One can also have liquid, solid, and air in the same problem, which leads to some complications. Let A_l and A_s be the surface areas of the liquid and solid exposed to the air, and A_{sl} be the surface area of the liquid-solid interface. Then there are three terms in the work,

$$\text{đ}W = \gamma_l \, dA_l + \gamma_s \, dA_s + \gamma_{sl} \, dA_{sl}.$$

In other words, there are three surface tensions, one associated with each kind of interface.

Both γ_l and γ_s arise from the fact that cohesive liquid-liquid or solid-solid bonds are broken to form a surface. However, γ_{sl} is determined by the adhesive forces between the liquid and solid, which may lead to a positive or negative contribution to the energy.

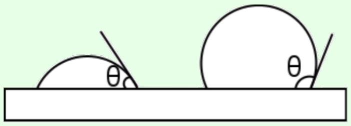
Specifically, let's define the energy of adhesion U_{sl} to be the work needed, per area, to separate a liquid from a solid, thereby turning a liquid-solid interface into a liquid-air and solid-air interface. By the definitions above,

$$U_{sl} = \gamma_s + \gamma_l - \gamma_{sl}.$$

Now, U_{sl} can be computed in terms of microscopic chemical bond energies, like γ_s and γ_l, so this result can also be thought of as an microscopic definition of γ_{sl}. When a liquid is in contact with a solid, the solid exerts a force per length of U_{sl} on the boundary of the liquid, along the solid.

Example 1

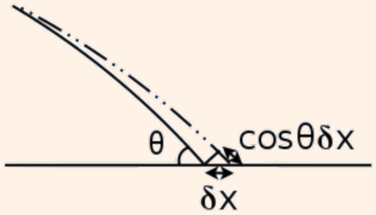
The surface of a drop of water makes a contact angle θ with a solid, as shown.



When θ is acute, the surface is said to be hydrophilic. If θ is obtuse, it is hydrophobic. Find an expression for θ in terms of the relevant surface tensions.

Solution

If the liquid drop expands outward by δx, the areas of various surfaces change, as shown.



The change in energy is

$$dU \propto \gamma_{sl}\,\delta x + \gamma_l \cos\theta\,\delta x - \gamma_s\,\delta x$$

and this must be equal to zero in equilibrium. Thus,

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} = \frac{U_{sl}}{\gamma_l} - 1.$$

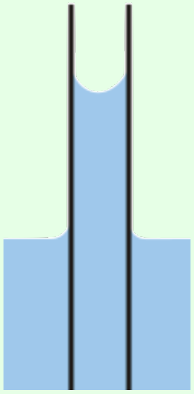
This is Young's equation. The liquid surface tension γ_l must be positive; otherwise the liquid could not exist stably at all, but rather would disperse into gas. Thus, the surface is hydrophilic when $U_{sl} > \gamma_l$ and hydrophobic when $U_{sl} < \gamma_l$.

As extreme cases, note that there is no solution for θ when $U_{sl} > 2\gamma_l$. In this limit, the surface is so hydrophilic that the liquid spreads out and coats the entire solid; this is known as perfect wetting. There is also no solution when $U_{sl} < 0$, in which case the liquid disperses into many tiny nearly spherical drops, each with a tiny area of contact with the solid.

This derivation was in terms of energy, which is typically easier for surface tension. The same result can be derived in terms of forces, but it's more subtle than it looks; the standard derivation in textbooks is wrong. For a clear derivation, see section 9.3 of Wang and Ricardo.

Example 2

A very thin, hollow glass tube of radius r is dipped vertically inside a container of water.



Find the height to which water can climb in the tube.

Solution

We first encountered this problem in **M7**, where we solved it by using Pascal's principle, giving an answer in terms of the contact angle. The derivation above of the contact angle completes this solution. However, we can also solve the problem using energy or force.

In terms of energy, if we move the height of the water up by δh, then

$$dU = \rho \pi r^2 g h \, \delta h + (\gamma_{sl} - \gamma_s) 2\pi r \, \delta h = 0$$

and solving gives

$$h = \frac{2(\gamma_s - \gamma_{sl})}{\rho g r} = \frac{2\gamma_l \cos\theta}{\rho g r}$$

using Young's equation. Alternatively, in terms of force, consider the vertical forces acting on the column of water inside the tube. There is an upward force of adhesion from the solid wall of $2\pi r U_{sl}$, and a downward surface tension force from the liquid below of $2\pi r \gamma_l$. Then

$$F = 2\pi r (U_{sl} - \gamma_l) - \rho \pi r^2 g h = 0$$

which yields precisely the same result.

Example 3

Fill a dish with water, and sprinkle something small over it, such as ground pepper. If you place a drop of detergent in the middle of the dish, then the pepper will "flee" away to the edges. Why does this happen?

Solution

Detergent is a surfactant, meaning that it decreases the surface tension of water. When one places the detergent in the middle of the dish, it diffuses outward, making the surface tension temporarily higher near edges of the dish. This leads to an unbalanced surface tension force on the pepper grains, pulling them to the edges.

This phenomenon is called the Marangoni effect. Of course, the force vanishes once the detergent becomes uniform distributed, and the surface tension is uniform again.

Remark

Here's a neat fact: the number of atoms that fit into a drop of water is comparable to the number of drops of water that fit inside the tallest mountains. We can show this using rough estimates, in the style of **P1**. Let E_b be the energy of a typical chemical bond, let m be the mass of an atom, and let d be the typical distance between atoms.

The size ℓ of a droplet of water, such as one that drips from a leaky ceiling, is the size where surface tension forces balance gravitational ones. By dimensional analysis, we must have

$$\ell \sim \sqrt{\gamma/\rho g}$$

as we showed in **M7**. Now, $\rho \sim m/d^3$, and the logic of problem 1 implies $\gamma \sim E_b/d^2$, so

$$\ell \sim \sqrt{E_b d/mg}.$$

Now consider the height H of the tallest mountains. The height of mountains is limited by the rigidity of rock; if the pressure is too great, then the rock underneath the mountain will deform, causing it to sink into the ground. Let's consider an atom-thick column of this rock. If it sunk down by a distance d, then the gravitational potential energy harvested would be mgH. However, the atom at the bottom would have to break its chemical bonds with its horizontal neighbors, which takes energy E_b. Balancing these gives a maximum height

$$H \sim E_b/mg.$$

We have therefore shown that

$$\ell \sim \sqrt{Hd}$$

which implies the original statement, within a few orders of magnitude.

2 Melting, Freezing, Boiling, Evaporation, and Condensation

Idea 3

A phase transition is a sudden, dramatic change in a system as thermodynamic variables such as the temperature are varied. Most of the ones you'll see have a latent heat

$$Q = mL.$$

For example, if ice is heated up, its temperature will gradually increase until it hits 0 °C. At that point, the temperature will remain constant until all of the ice is melted, i.e. when the full latent heat has been supplied.

Remark

We can roughly estimate the latent heats of melting and evaporation. In general, the latent heat can go into either in breaking molecular bonds, or increasing the entropy.

When a solid melts into a liquid, the molecules stay right next to each other, so changing bond energy isn't the dominant effect. Instead, it's the increase in entropy as the liquid molecules become free to rotate. Let's suppose that the molecules each gain a few extra possible quantum states. This corresponds to an entropy increase per molecule $\Delta S \sim k_B$, which means a latent heat per mass of

$$L = \frac{T\Delta S}{m_{\text{mol}}} \sim \frac{k_B T}{m_{\text{mol}}} = \frac{RT}{\mu}$$

where μ is the molar mass, or equivalently a latent heat per mole $\mathcal{L} \sim RT$. For water, we get $L \sim 2 \times 10^5$ J/kg, which is of the same order of magnitude as the true value 3.3×10^5 J/kg.

When a liquid becomes a gas, the dominant effect is typically the huge increase in entropy $k_B \log(V_{\text{gas}}/V_{\text{liq}})$ per molecule because they get much more space to move. The ratio inside the logarithm is huge, which means that while the volumes per molecule V_{gas} and V_{liq} vary by order-one amounts between phase transitions, the logarithm of their ratio is always around the same value, which turns out to be about 10. This gives a latent heat per mass of

$$L \sim \frac{10 k_B T}{m_{\text{mol}}} = \frac{10RT}{\mu}.$$

This result is called Trouton's rule, and it is surprisingly accurate for most liquids. However, the latent heat of vaporization for water is noticeably higher, $L = 2.26 \times 10^6$ J/kg. This is because of the extra energy needed to break hydrogen bonds.

[3] **Problem 6.** The temperature T at which a phase transition happens depends on the pressure P, yielding a "coexistence curve" $P(T)$ where the two phases can be in equilibrium with each other. The exact relationship is given by the Clausius–Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

where L is the total latent heat for some amount of material, and V_2 and V_1 are the corresponding volumes of that material when it is in each of the phases. (Depending on convention, L could be the latent heat per mole, in which case the V_i are volumes per mole, or both quantities could be per unit mass, in which case the V_i become densities.) In this problem, you will derive this equation.

(a) Consider an infinitesimal Carnot cycle operating between temperatures T and $T + dT$, and pressures P and $P + dP$, chosen so that the isothermal heating and cooling steps involve supplying latent heat. Compute the work done by the cycle.

(b) Argue that we may ignore all heat transfer except for the latent heat.

(c) Derive the Clausius–Clapeyron equation by setting the efficiency equal to the Carnot efficiency.

This classic setup is also considered in the second half of USAPhO 2023, problem A3.

Solution. (a) Almost all the work is done in the isothermal processes, due to the changes in volume in the phase transitions. (The adiabatic steps are negligible, because not only is the temperature change infinitesimal, but the volume change is also infinitesimal!) The positive work is thus $(P+dP)(V_2-V_1)$ and the negative work is $P(V_2-V_1)$, giving

$$W=(V_2-V_1)\,dP.$$

(b) The non-latent heat transfer is infinitesimal compared to the latent heat, since it is proportional to dT, so we only need to count the latent heat $Q_{\text{in}}=L$. (This is also very nearly the same as Q_{out}, with the difference being the infinitesimal amount of work done.)

(c) The efficiency $\epsilon=W/Q_{\text{in}}$ is equal to dT/T by expanding the Carnot efficiency, so

$$\frac{dT}{T}=\frac{(V_2-V_1)\,dP}{L}$$

which is just what we want after a little rearranging.

[3] **Problem 7.** [A] In this exercise you'll find a quicker, more advanced derivation of the Clausius–Clapeyron equation.

(a) The Gibbs free energy is defined as $G=U+PV-TS$. Show that for reversible processes,

$$dG=V\,dP-S\,dT.$$

Two phases can only be in thermodynamic equilibrium if they have the same Gibbs free energy per molecule. Otherwise, turning one phase to the other would reduce the Gibbs free energy, which turns out to be equivalent to increasing the entropy of the universe. (For more details, see section 16.5 of Blundell and Blundell.)

(b) Suppose that the Gibbs free energies per molecule G/N for two phases are equal at temperature T_0 and pressure P_0. Derive the Clausius–Clapeyron equation by demanding this is also true at temperature T_0+dT and P_0+dP.

Solution. (a) By the first law, we have $\text{đ}Q=dU+\text{đ}W$, where $\text{đ}W=PdV$ and, by reversibility, $\text{đ}Q=TdS$. Differentiating the definition of Gibbs free energy, we have

$$dG=dU+PdV+VdP-TdS-SdT=TdS-PdV+PdV+VdP-TdS-SdT$$

which simplifies to the desired answer.

(b) Consider a sample of the first phase with a given total particle number N. The change in Gibbs free energy along the coexistence curve is

$$dG_1=V_1\,dP-S_1\,dT.$$

Similarly, for the second phase,

$$dG_2=V_2\,dP-S_2\,dT.$$

By the definition of the coexistence curve, these two must be equal, so

$$(V_1-V_2)\,dP=(S_1-S_2)\,dT.$$

We also know that S_1-S_2 is precisely L/T, so rearranging gives the desired result.

Remark: Thermodynamic Potentials

You might sometimes see the Clausius–Clapeyron equation written in terms of a difference in enthalpy ΔH rather than a latent heat. The enthalpy is the state function $H = U + PV$, so

$$dH = V\,dP + đQ.$$

This is useful because many lab experiments happen at constant pressure, $dP = 0$, leaving $dH = đQ$. That is, only heat changes the enthalpy, so the latent heat of a phase transition must be the difference in enthalpies of the two phases, $L = \Delta H$. That in turn is useful because enthalpy is a state function, so given a new phase transition you can calculate L by just looking up the enthalpy values for each of the phases in a table.

We've now covered all the classic "thermodynamic potentials". As we just saw, the enthalpy H is useful for bookkeeping heat. As we saw in **T2**, the Helmholtz free energy F is minimized in thermodynamic equilibrium, given constant temperature and volume. (This is the relative of the statement that the system's internal energy U is minimized in equilibrium, given constant entropy and volume, which is just the usual statement of mechanical equilibrium.) And as we saw in the problem above, the Gibbs free energy G is minimized in thermodynamic equilibrium, given constant temperature and pressure.

More generally, what's going on is that the number of possibly useful potentials doubles every time we add another pair of "thermodynamic conjugate variables". Before learning about thermodynamics, we just had U. When we learned about temperature and entropy, we additionally cared about F. And now upon accounting for pressure and volume, we have H and G. If we had another pair, such as magnetization and external magnetic field, we could define 4 more potentials, which would each be useful in different situations.

[2] **Problem 8.** Ice skaters can move with little friction because they actually glide on a thin layer of water. Estimate how heavy an ice skater has to be to melt ice by just standing on their skates, assuming the ice is at temperature $-5\,°\mathrm{C}$.

Solution. To melt the ice, we need to apply enough pressure to reach the water-ice equilibrium point, which we can find with the Clausius–Clapeyron equation. We need to reach 0°C, so

$$\Delta T = 5°\mathrm{C} = 5\,\mathrm{K}, \quad T = 273\,\mathrm{K}.$$

The Clausius–Clapeyron equation gives

$$P = \frac{\Delta T}{T} L \left(\frac{1}{\rho_i} - \frac{1}{\rho_w} \right)^{-1} \approx 6.76 \times 10^7 \text{ Pa}$$

where we used

$$\rho_i = 917\,\mathrm{kg/m^3}, \quad \rho_w = 1000\,\mathrm{kg/m^3}, \quad L = 334000\,\mathrm{J/kg}.$$

Ice skate blades have a thickness of around 1 mm and a length of around 25 cm, so the total area with two feet will be around $5 \times 10^{-4}\ \mathrm{m}^2$. The weight PA needed will then be around $30,000\,\mathrm{N}$, corresponding to a weight of about $3,000\,\mathrm{kg}$. Thus, unless you are incredibly massive, or the ice is very close to melting already, pressure alone is not enough to melt the ice. Scientists are still arguing over the true explanation; you can see a recent review here.

Now we focus on the specifics of liquid-gas phase transitions.

[3] **Problem 9.** Suppose that at pressure P_0, a liquid-gas phase transition takes place at temperature T_0. Assume the gas obeys the ideal gas law, and neglect the volume of the liquid.

(a) Assuming the latent heat is temperature-independent, compute the coexistence curve $P(T)$.

(b) In reality, the latent heat has a mild dependence on temperature, changing the results. As a crude model, suppose that the latent heat per molecule for a monatomic liquid-gas phase transition has two components: a fixed energy E_0 required to break the bonds with other molecules in the liquid, and the $P\,dV$ work that must be done to "push" the rest of the gas away, since the new gas molecule takes up space. Under these assumptions, what is the latent heat per molecule, and qualitatively how does the dependence $P(T)$ change?

(c) A closed container of constant volume contains both liquid and gas in equilibrium, at temperature T. Let the latent heat of vaporization per mole be $\mathcal{L}$, and neglect the volume of the liquid. If the temperature is increased by a very small amount ΔT, by what factor does the number of moles in gas form change?

Solution. (a) We have $V_2 = nRT/P$ and V_1 can be ignored, so

$$\frac{dP}{dT} = \frac{L}{Nk_B}\frac{P}{T^2}.$$

Separating and integrating,

$$\int_{P_0}^{P} \frac{dP}{P} = \int_{T_0}^{T} \frac{L}{nRT^2}dT$$

which gives

$$P(T) = P_0 e^{-\frac{L}{nR}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \propto e^{-L/nRT}.$$

(b) The latent heat per molecule is now

$$\mathcal{L} = E_0 + P\,\Delta V$$

where ΔV is the change in volume due to that molecule. But $\Delta V = V/N$, so

$$\mathcal{L} = E_0 + \frac{PV}{N} = E_0 + k_B T.$$

The total latent heat is $L = N\mathcal{L}$. The Clausius–Clapeyron equation now looks like

$$\frac{dP}{dT} = \frac{E_0}{k_B}\frac{P}{T^2} + \frac{P}{T}.$$

Separating and integrating gives

$$\int \frac{dP}{P} = \frac{E_0}{k_B}\int \frac{dT}{T^2} + \int \frac{dT}{T}$$

which gives

$$P(T) = P_0\left(\frac{T}{T_0}\right)e^{-\frac{E_0}{k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right)}.$$

In other words, compared to part (a) where we neglected the $P\,\Delta V$ contribution, there is now an additional linear temperature dependence.

(c) We apply the Clausius–Clapeyron equation to a small temperature change,

$$\frac{\Delta P}{\Delta T} \approx \frac{\mathcal{L}}{T\mathcal{V}}$$

where $\mathcal{L}$ and $\mathcal{V}$ are the latent heat per mole and volume per mole. By the ideal gas, $\mathcal{V} = RT/P$. Then

$$\frac{\Delta P}{\Delta T} = \frac{\mathcal{L}}{RT^2/P}$$

which solves to give

$$\frac{\Delta P}{P} = \frac{\mathcal{L}}{RT}\frac{\Delta T}{T}.$$

The ideal gas law tells us that $P \propto nT$, which means for small changes,

$$\frac{\Delta P}{P} \approx \frac{\Delta n}{n} + \frac{\Delta T}{T}.$$

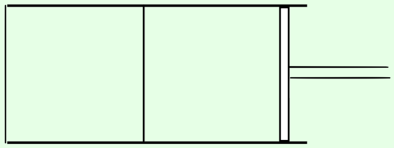
Combining these results,

$$\frac{n + \Delta n}{n} = 1 + \frac{\Delta P}{P} - \frac{\Delta T}{T} = 1 + \frac{\Delta T}{T}\left(\frac{\mathcal{L}}{RT} - 1\right).$$

In other words, while the pressure and temperature of the vapor both certainly go up, whether the number of moles goes up or down depends on the specific substance! However, most liquids obey Trouton's rule, $\mathcal{L} \approx 10RT$, as explained in a remark above, so that $\mathcal{L}/RT - 1$ is positive and the number of moles of gas goes up.

Example 4: APhO 2004.3

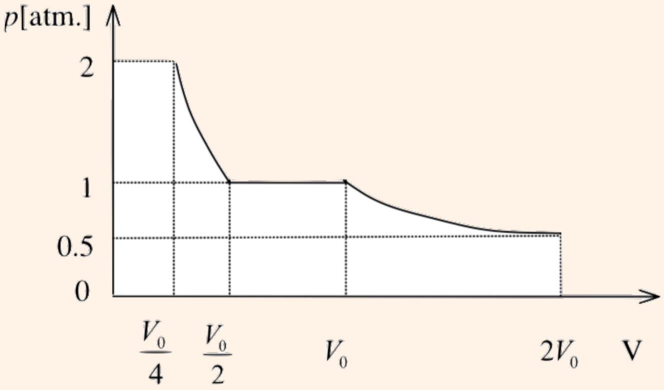
A cylinder is divided into two parts by a mobile partition, which is free to move and conducts heat well. One compartment contains one mole of water vapor, and the other contains one mole of nitrogen gas. Initially, both compartments have volume V_0, pressure 0.5 atm, and temperature 373 K. A piston is then slowly inserted, compressing the system isothermally.



Sketch the $P(V)$ curve.

Solution

The answer is shown below.



Initially, we just have an ordinary isothermal compression. Both the water vapor and nitrogen gas compartments are compressed at the same rate, since they must have equal pressures and temperatures. When the total volume is halved, the pressure in both reaches one atmosphere. Now, water condenses at temperature 373 K at pressure $p = 1\,\text{atm}$. Thus, as the volume continues to decrease, the pressure stays constant, the nitrogen compartment's volume stays the same, and the water compartment shrinks, as the vapor gradually condenses to liquid. This process completes once all the vapor is condensed, which is roughly when the total volume has halved again. After this point, we again have ordinary isothermal compression, of the nitrogen gas alone.

[3] **Problem 10.** NBPhO 2016, day 2, problem 2. A problem on phase transitions with data analysis.

Solution. See the official solutions here.

[3] **Problem 11.** USAPhO 2015, problem A4. A heat engine with phase transitions.

In practice, water on Earth is more subtle because there are three substances at play: liquid water, water vapor, and the rest of the atmosphere.

Idea 4: Humidity

Consider a box at constant temperature T containing only water, and let $P(T)$ be the liquid water-water vapor coexistence curve. In equilibrium, if we apply any pressure below $P(T)$, all of the water will be in vapor form, and if we apply any pressure above $P(T)$, all of the water will be in liquid form. Physically, applying a higher pressure forces the water vapor to condense into liquid, as it packs the molecules closer together, and applying a lower pressure forces the liquid to evaporate into vapor, as it cannot hold itself together against the thermal motion of the molecules. Coexistence is impossible, except at *exactly* the pressure $P(T)$.

However, in everyday life, the two easily coexist over a wide range of pressures. The subtlety is that the total air pressure has two contributions,

$$P_{\text{tot}} = P_{\text{atm}} + P_{\text{vap}}$$

where the first is the pressure due to atmospheric gases, such as nitrogen and oxygen, and the second is the pressure due to water vapor in the air. In everyday conditions, P_{atm} is about 100 times larger than P_{vap}, and the liquid water feels the pressure P_{tot}. But water vapor evaporates and condenses independently of the air, so P_{atm} has no effect on it at all. As a result, in equilibrium liquid water and water vapor can coexist, with the vapor having a pressure $P_{\text{vap}} = P(T)$. The coexistence curve $P(T)$ is thus also called the (equilibrium) vapor pressure.

The relative humidity ϕ is defined as

$$\phi = P_{\text{vap}}/P(T)$$

and quantifies how saturated the air is with water vapor. In equilibrium, $\phi = 1$, while for $\phi < 1$ people can cool down by sweating. It is also possible to have $\phi > 1$, which occurs in humid air high in the atmosphere just before it condenses into a cloud.

The dew point T_d satisfies

$$P(T_d) = P_{\text{vap}}$$

and represents the temperature at which water would begin condensing out of a given parcel of air, cooled at constant pressure.

The boiling temperature T_b satisfies

$$P(T_b) = P_{\text{atm}}.$$

This is the temperature at which a bubble of pure water vapor, which forms inside the liquid, has a high enough pressure to push the liquid away and continue to expand. Beyond this temperature, liquid water can't exist; it all turns to vapor. This is why pressure cookers are useful: they increase P_{atm}, thereby increasing T_b and allowing food to cook faster. (Technically, we should have P_{tot} rather than P_{atm} on the right-hand side, but in practice whenever we boil things, we let the resulting water vapor fly away. So the actual vapor pressure P_{vap} never gets that high.)

At the interface between two liquids, boiling can start at a significantly lower temperature than the boiling temperature of either liquid, because both of the liquids contribute to the vapor pressure. This is called border boiling, and is treated in IZhO 2020, problem 2.

Example 5

How does alcohol distillation work?

Solution

Let alcohol and water have coexistence curves/equilibrium vapor pressures of $P_a(T)$ and $P_w(T)$. The vapor pressure of alcohol is higher, with pure alcohol boiling at about 80° C.

Consider heating a mixture of alcohol and water, with mole fractions X_a and X_w, with $X_a + X_w = 1$. If a small bubble of gas forms inside, then Raoult's law states that both alcohol and water vapor will be present, and contribute independently in proportion to their mole fractions. Then the boiling point satisfies

$$X_a P_a(T_b) + X_w P_w(T_b) = P_{\text{atm}}.$$

This is in between the boiling points of alcohol and water individually. By the ideal gas law, the ratio of mole fractions of alcohol and water in the vapor is the ratio of vapor pressures, so

$$\frac{X'_a}{X'_w} = \frac{X_a}{X_w} \frac{P_a(T_b)}{P_w(T_b)}.$$

Since the fraction is greater than one, the alcohol in the distilled vapor is more concentrated than in the liquid.

By the above logic, we could get completely pure alcohol by just repeating the distillation procedure several times. Actually, it's more complicated than that because the alcohol and water molecules will interact, causing Raoult's law to break down; our calculation above only applies for an "ideal mixture". For more about distillation, see these notes.

[3] **Problem 12.** Kalda Thermodynamics, problem 22. A problem on practically measuring humidity.

Solution. (a) The dry bulb thermometer is just at room temperature, $T_0 = 20\,^\circ\text{C}$. Meanwhile, the wet bulb thermometer is cooled down by evaporation. In this part, we are neglecting heat conduction, so equilibrium is only reached when evaporation from the wet bulb stops. This occurs when the relative humidity at the wet bulb thermometer itself reaches is 100%.

Let $p_s(T)$ be the saturation pressure as shown in the graph. The vapor pressure of water vapor in the room is

$$p_a = r p_s(T_0) = (0.9)(2.3\,\text{kPa}) = 2.07\,\text{kPa}$$

by reading off the graph. The wet bulb temperature T satisfies

$$p_a = p_s(T)$$

and from the graph we read off $T = 18.5\,^\circ\text{C}$. Thus, the difference is $1.5\,^\circ\text{C}$.

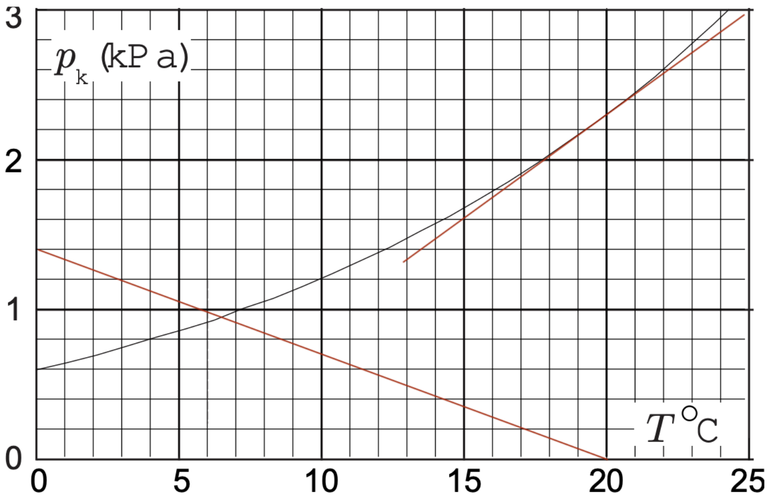
(b) We balance the heat flowing in and out of the wet bulb thermometer,

$$a(T_0 - T) = b(p_s(T) - p_a).$$

In this part, p_a is zero, so we have

$$-65\,\text{Pa/K} = \frac{p_s(T)}{T - T_0}.$$

Therefore, to find T, we draw a line on the graph passing through $p = 0$ and $T = 20\,^\circ\text{C}$ and slope $-65\,\text{Pa/K}$. The solution is where this line intersects the curve $p_s(T)$, giving $6.5\,^\circ\text{C}$.



(c) The temperature we're looking for satisfies

$$-65\,\mathrm{Pa/K} = \frac{p_s(T) - r p_s(T_0)}{T - T_0}.$$

The solution will be near T_0 itself, which means it suffices to approximate $p_s(T)$ near $T_0 = 20\,^\circ\mathrm{C}$. By reading off the graph again, we have the linear approximation

$$p_s(T) \approx 2.3\,\mathrm{kPa} + (T - T_0)(0.14\,\mathrm{kPa}/^\circ\mathrm{C}).$$

Plugging in and simplifying, we find the temperature difference obeys

$$\Delta T \approx (11\,^\circ\mathrm{C})(1 - r).$$

Any answer within $\sim 15\%$ of this is good enough.

(d) The way evaporation works is that every water vapor molecule on the laundry has some probability per time of jumping off, while every water vapor molecule in the surrounding air has some probability per time for sticking to the laundry. The two processes balance when the humidity is 100%. Thus, the net rate of evaporation is proportional to $1 - r$, which means the laundry in 80% humidity dries 4 times faster.

[3] **Problem 13.** EFPhO 2006, problem 1. (Note that the comma in the density of air in part 4 denotes a decimal point.)

Solution. See the official solutions here.

3 General Phase Transitions

In this section we'll illustrate some of the ideas needed to analyze phase transitions in general.

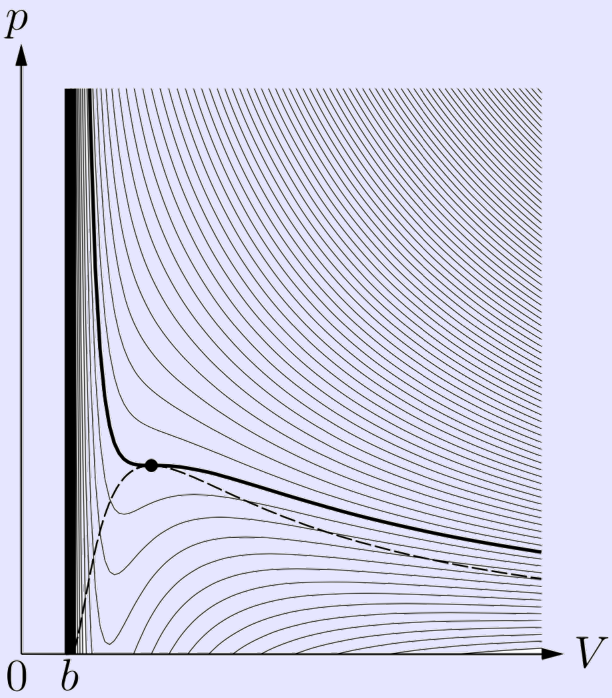
Idea 5

A nonideal gas can be described by the van der Waals equation of state,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT.$$

You derived the pressure correction in **T1** assuming weak attractive intermolecular forces; the modification of the volume accounts for the fact that the molecules can't overlap each other. Remarkably, this equation of state also contains a liquid-gas phase transition!

To see this, consider a plot of the isotherms on a PV diagram.



At low temperatures, the isotherms can have negative compressibility, meaning that the pressure decreases as the volume decreases. This is unphysical, and means that the fluid is unstable at these points: if you push on it, it'll just keep shrinking, until it condenses into a dense liquid. Therefore, parts of these isotherms should be replaced with horizontal lines; along these horizontal parts liquid and gas coexist, in varying proportions.

Specifically, everything underneath the dotted line should be replaced with horizontal lines. As described in more detail in section 26.1 of Blundell, this can be shown by demanding that the liquid and gas have equal Gibbs free energy. As a result, the total area on the PV diagram of the isotherm that goes underneath the horizontal line equals the area that goes above it; this is called Maxwell's equal area rule.

There is a critical isotherm marked in bold above. Above this temperature, there is no liquid-gas phase transition at all; instead we just have one phase, called a supercritical fluid. Specifically, this is the temperature of the first isotherm that no longer has a local minimum in pressure, which means

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

at the critical temperature $T = T_c$. As you will see in problem 14, this occurs at

$$V_c = 3nb, \quad T_c = \frac{8a}{27Rb}, \quad P_c = \frac{a}{27b^2}.$$

This point, marked above, is called the critical point.

Remark

The van der Waals equation of state is accurate for a sparse gas with weak attractive interactions; you shouldn't expect it to be accurate for dense gases or the liquid state. However, it still is extremely important because it is one of the simplest equations of state that gives a liquid-gas phase transition. What's more, if you zoom in near the critical point and write the pressure, volume, and temperature as multiples of the critical pressures, volumes, and temperatures, it turns out that *all* equations of state give the same results! This deep phenomenon is known as universality, but unfortunately I can't explain the reason why without using statistical field theory.

[3] **Problem 14.** INPhO 2018, problem 6. A series of exercises on the van der Waals gas. Feel free to look up definitions for part (a).

Solution. See the official solutions here.

[4] **Problem 15.** [A] Here we'll introduce a simple model for a ferromagnetic phase transition. Consider N electrons, which may have spins $s_i = \pm 1$. The energy of a configuration is

$$E = -B\sum_i s_i - \frac{J}{2N}\sum_{i\neq j} s_i s_j.$$

The first term represents the effect of an external magnetic field B, while the second term represents an interaction, with strength described by the constant J, which tries to make the spins parallel. (In this simple model, we suppose all distinct pairs of spins interact equally. We could also make spins only interact with their neighbors, but this would complicate the analysis.)

(a) Define the average magnetization as $m = \sum_i s_i/N$. Find $E(m)$, the energy in terms of m and the other constants in the problem.

(b) For a fixed value of m, write down the number of states $\Omega(m)$ with that magnetization.

(c) The probability of having a given value of m is proportional to $e^{-\beta E(m)}\Omega(m)$. Argue that this probability is maximized for the value of m that minimizes the free energy

$$F = E - TS.$$

Hence the equilibrium configuration minimizes the free energy. This is the statistical mechanical way to argue that F is minimized; the thermodynamic way was covered in **T2**.

(d) Assuming that $N \gg 1$ and applying Stirling's approximation (introduced in **T2**), show that the free energy $F(m)$ is minimized when

$$m = \tanh(\beta B + \beta J m), \quad \beta = \frac{1}{k_B T}.$$

(e) For a fixed $B > 0$, plot $m(T)$. This should match with Curie's law, which you proved in **T1**.

(f) Now let $B = 0$. Show that there exists a critical temperature T_c, above which $m(T)$ is exactly zero and below which it is nonzero; also find an approximate expression for the magnetization just below T_c.

This is a phase transition where the material spontaneously becomes magnetized, and the simplest example of a phase transition which can be understood analytically.

Solution. (a) The first term is easy,

$$-B \sum_i s_i = -NmB.$$

To do the second term, we note that

$$\sum_{i \neq j} s_i s_j = \sum_i \sum_j s_i s_j - \sum_i s_i s_i = \left(\sum_i s_i \right)^2 - \sum_i s_i^2 = N^2 m^2 - N.$$

We hence have

$$E = -NmB - \frac{1}{2} J N m^2 + \frac{1}{2} J.$$

(b) Of all N electrons, N_+ have $s_i = +1$ and N_- have $s_i = -1$, where $N_+ + N_- = N$ and $mN = N_+ - N_-$. Thus $N_+ = N/2 + mN/2$ and $N_- = N/2 - mN/2$. The number of states is N choose N_+.

$$\Omega(m) = \frac{N!}{\left(\frac{N}{2}(1+m)\right)! \left(\frac{N}{2}(1-m)\right)!}.$$

(c) The probability $P(m) = e^{-\beta E(m)} \Omega(m)$ is found with Boltzmann's theorem, where each state has a probability of $e^{-E/k_B T}$, so $\beta = 1/k_B T$. Maximizing $P(m)$ is the same as maximizing $\log(P(m))$, which gives

$$\log(P(m)) = -\frac{E}{k_B T} + \log(\Omega(m)).$$

Since we're optimizing with respect to m, we can multiply both sides by $-k_B T$ and maximize $P(m)$ by minimizing $-k_B T \log(P(m))$.

$$-k_B T \log(P(m)) = E - T k_B \log(\Omega(m)) = E - TS.$$

This is just the expression for free energy, thus minimizing free energy for a given value of m will maximize the probability.

(d) Stirling's approximation gives

$$\log\left(\frac{N!}{\left(\frac{N}{2}(1+m)\right)!\left(\frac{N}{2}(1-m)\right)!}\right) \approx N\log N - \frac{N}{2}(1+m)\log\frac{N(1+m)}{2} - \frac{N}{2}(1-m)\log\frac{N(1-m)}{2}.$$

To simplify this, we can expand the logarithms to get

$$N\biggl(\log N - \frac{1+m}{2}\left(\log N + \log\frac{1+m}{2}\right) - \frac{1-m}{2}\left(\log N + \log\frac{1-m}{2}\right)\biggr)$$

and various factors cancel to give

$$-N\left(\frac{1+m}{2}\log\frac{1+m}{2} + \frac{1-m}{2}\log\frac{1-m}{2}\right).$$

Setting dF/dm to zero gives

$$0 = -NB - NJm - T\frac{\partial S}{\partial m}$$

which is equivalent to

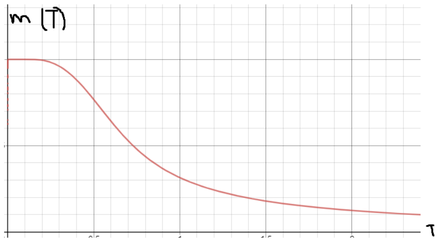
$$N(B+Jm) = -k_B T\frac{\partial \log\Omega}{\partial m} = Nk_B T\left(\frac{1}{2}\log\frac{1+m}{2} - \frac{1}{2}\log\frac{1-m}{2}\right).$$

Then we have

$$\beta B + \beta J m = \frac{1}{2}\log\frac{1+m}{1-m} = \tanh^{-1} m$$

which gives the desired result.

(e) The graph should look something like this:



(f) With $B = 0$, for the magnetization to be nonzero, we need a non-zero solution to

$$m = \tanh\left(\frac{Jm}{k_B T}\right).$$

Since the second derivative of $\tanh(ax)$, $-2a^2\operatorname{sech}^2(ax)\tanh(ax)$ is always negative for $x > 0$, that means that the slope of $\tanh(ax)$ will always be decreasing for $x > 0$. In order for the graphs of x and $\tanh(ax)$ to intersect again after $x = 0$, the slope of $\tanh(ax)$ must be greater than the slope of x, which is 1. Thus the critical value is where $a = 1$, so

$$T_c = \frac{J}{k_B}.$$

To find what happens just below T_c, we Taylor expand the hyperbolic tangent about zero, which is useful because m will be small,

$$\tanh(x) = x - \frac{x^3}{3} + O(x^5).$$

Letting $T = (1-\epsilon)T_c$, we have $Jm/k_BT = m/(1-\epsilon)$, giving

$$m \approx \frac{m}{1-\epsilon} - \frac{1}{3}\frac{m^3}{(1-\epsilon)^3}$$

which means that at lowest order at epsilon,

$$m \approx \sqrt{3\epsilon} = \left(\frac{3(T_c - T)}{T_c}\right)^{1/2}.$$

[5] **Problem 16.** APhO 2011, problem 3. A nice problem on a real-world *mechanical* phase transition. Some of the intuition you gained studying the var der Waals gas will be useful.

4 Thermodynamic Systems

Now that we know all about the different methods of heat transfer, as well as phase transitions, we consider some questions involving a mix of these concepts as well as mechanics.

Example 6: IPhO 1967.3

Consider two identical homogeneous balls with the same initial temperatures. One of them is at rest on a horizontal plane, while the other hangs on a thread.

The same quantity of heat is supplied to both balls. Which has the higher final temperature?

Solution

This infamous problem, which appeared on the first IPhO, was the original “troll” Olympiad question. The balls are different because the one on the plane thermally expands upward, while the one on a thread thermally expands downward. This tiny change in gravitational potential energy means that the ball on the thread ends up hotter.

This is an incredible solution – in the sense that it is *not* credible. About fifty years after it was written, physicists at Oxford showed that it is wrong! Suppose the logic above were actually right. Then a heat engine can be constructed with these four steps:

1. Heat the ball on the plane, therefore raising its center of mass.

2. Attach the ball to a thread and remove the plane.
3. Cool the ball on the thread, therefore raising its center of mass.
4. Put a plane just under the ball's new position and remove the thread.

This is a heat engine, where the work goes into raising the ball. If the ball is only heated and cooled a tiny amount dT, then the heat supplied is proportional to dT, but the distance through which the ball rises is also proportional to dT. Therefore, the efficiency of the cycle becomes a constant as dT goes to zero, which exceeds the Carnot efficiency (which instead goes to zero) and hence violates the second law of thermodynamics.

A real ball doesn't violate the second law, because it also stretches while hanging on the thread, and squashes while on the plane. The slick solution neglects these effects and considers only thermal expansion, but the above argument shows that this assumption is inconsistent: you can't have the latter without the former. This is an example of how thermodynamic considerations alone can, perhaps surprisingly, yield information about mechanical properties. The paper linked above performs a careful analysis and shows that, for most materials, the ball on the thread instead ends up *colder*.

Example 7

Why does a breeze cool you down, and why do clothes make you warmer?

Solution

Like most gases, air has a very small thermal conductivity, and enough viscosity so that you carry around a thin layer of warm air with you wherever you go. (The main reason you cool down is because this warm air rises away from you, by convection.) When a breeze is blowing, it strips off this cushion of warm air, which is why you feel colder.

When you're sweaty, the same logic applies. The layer of air you carry around is also moist, saturated with water vapor from your sweat. Again, a breeze removes this layer, allowing more evaporation to happen, cooling you down.

Clothing material itself actually has a higher thermal conductivity than air. Its real purpose is to trap the layer of warm, moist air around you, preventing it from being blown away by breezes or rising from convection. (That's also how greenhouses keep plants warm: the sun warms air near the ground, and the glass room prevents that air from rising away. Confusingly, this has nothing to do with the atmospheric "greenhouse effect.")

Example 8

Can you boil water in a pot by putting it into a bigger pot of boiling water?

Solution

No, because boiling is a phase transition that requires latent heat. The water in the small pot can get heated up to boiling temperature, but it can't start boiling, because at that point it'll be at the same temperature as the bigger pot, and no more heat can flow.

[1] **Problem 17** (IPhO 1996)**.** A thermally insulated piece of metal is heated under atmospheric pressure by an electric current so that it receive a constant power P. The temperature is

$$T(t) = T_0(1 + a(t - t_0))^{1/4}$$

where T_0, t_0, and a are constants. Find the heat capacity $C(T)$.

Solution. By definition, $C(T) = dQ/dT$. With constant power P, $dQ = P\,dt$, and

$$\frac{dT}{dt} = \frac{P}{C(T)} = \frac{1}{4} T_0 \left(1 + a(t - t_0)\right)^{-3/4} a = \frac{aT_0^4}{4T^3}.$$

This gives the answer,

$$C(T) = \frac{4T^3 P}{aT_0^4}.$$

[3] **Problem 18.** EFPhO 2011, problem 8. A tricky data analysis problem.

Solution. See the official solutions here.

[3] **Problem 19.** EFPhO 2014, problem 9. A nice problem reviewing radiation and kinetic theory.

Solution. See the official solutions here.

[4] **Problem 20.** EuPhO 2019, problem 1.

Solution. See the official solutions here.

5 Thermodynamic Fluids

In this section, we focus on problems combining thermodynamics with fluids, as covered in **M7**. We begin with some questions which only require fluid statics.

[5] **Problem 21.** IPhO 1998, problem 2. A very nice real-world fluids/thermo question.

[5] **Problem 22.** APhO 2009, problem 3. Another nice, simple model of a real-world phenomenon.

Idea 6

In **M7** we considered Bernoulli's principle for incompressible liquids with no temperature. However, in general fluids are compressible and carry internal energy. To derive Bernoulli's principle in this more general context, we apply conservation of energy to a tube of streamlines, as one mole of ideal gas flows through it. We neglect gravity, since it typically is unimportant for such rapid flows. The energy of a mole of gas at the entry of the tube is

$$\frac{1}{2}\mu v_1^2 + c_V T_1$$

where μ is the molar mass, and c_V is the heat capacity per mole. Similarly, the energy of a mole of gas at the other end is

$$\frac{1}{2}\mu v_2^2 + c_V T_2.$$

Assuming there's no heat transfer, the difference must be the work done on the tube of fluid as a mole of gas flows through,

$$p_1 \delta V_1 - p_2 \delta V_2 = R(T_1 - T_2)$$

where the δV_i are the volumes of a mole of gas at the entry and exit, and we used the ideal gas law. Combining and using $c_p = c_V + R$ gives

$$\frac{1}{2}\mu v^2 + c_p T = \text{const}$$

along a streamline in steady flow.

Remark

You might also see Bernoulli's principle in the form

$$\frac{1}{2}v^2 + gh + c_p T = \text{const}$$

where we've added on the contribution of gravitational potential energy. In this case, c_p is the heat capacity at constant pressure per unit mass, not per mole. Unfortunately, people use the letter c or C to denote many different kinds of (specific) heat capacities. Whenever doing a problem where a heat capacity is given, check the dimensions!

Example 9: Wang and Ricardo

A rocket propels itself by burning fuel to release diatomic gas of temperature T_1 in its combustion chamber, which has cross-sectional area A_1. The gas then flows adiabatically and is expelled out of the nozzle, which has a cross-sectional area A_2, at a speed v_2 relative to the rocket, pressure p_2, and temperature $T_2 < T_1$. In the limit of steady flow, determine the thrust experienced by the rocket.

Solution

Since the flow is adiabatic and the gas is diatomic,

$$p_1 = p_2 \left(\frac{T_1}{T_2}\right)^{7/2}.$$

As discussed in **M7**, mass conservation in steady flow means $\rho A v$ must be the same on both sides of the nozzle. The ideal gas law tells us that $\rho \propto p/T$, so

$$\frac{p_1 A_1 v_1}{T_1} = \frac{p_2 A_2 v_2}{T_2}.$$

Combining these two gives a relation between the velocities,

$$v_1 = v_2 \, \frac{A_2}{A_1} \left(\frac{T_2}{T_1} \right)^{5/2}.$$

Bernoulli's principle gives

$$\frac{1}{2} \mu v_1^2 + \frac{7}{2} R T_1 = \frac{1}{2} \mu v_2^2 + \frac{7}{2} R T_2$$

where we neglected the gravitational energy. Combining with our previous relation gives

$$v_2^2 = \frac{7R(T_1 - T_2)}{\mu \left(1 - (A_2/A_1)^2 (T_2/T_1)^5\right)}.$$

Finally, the thrust is

$$F = \frac{dp}{dt} = \rho_2 A_2 v_2^2 = \frac{\mu p_2 A_2 v_2^2}{R T_2} = \frac{7 p_2 A_2 (T_1 - T_2)}{T_2 (1 - (A_2/A_1)^2 (T_2/T_1)^5)}.$$

Example 10

How does the Bernoulli's principle above reduce to the incompressible one used in **M7**?

Solution

This is trickier than it seems. For simplicity, let's neglect the gravitational contribution. Then by the ideal gas law, the compressible Bernoulli's principle derived above is

$$\frac{1}{2} v^2 + \frac{\gamma}{\gamma - 1} \frac{P}{\rho} = \text{const.}$$

When the flow is incompressible, ρ is constant, but if we just multiply by ρ we get

$$\frac{1}{2} \rho v^2 + \frac{\gamma}{\gamma - 1} P = \text{const}$$

which is not the expected result!

In fact, there's something more troubling under the surface. The Bernoulli's principle derived in **M7** applies to water flow, since water is incompressible. And the compressible version derived above applies to ideal gas flow, since gas is compressible. But in **M7**, we applied the incompressible Bernoulli's principle to gas flow! How does that even make sense?

The resolution to the two questions is the same: the key assumption needed to get to the original form of Bernoulli's principle is *not* that an ideal gas is incompressible, because that's simply not true. Instead, the key assumption is that the gas flow is much slower than the speed of sound, $v^2 \ll c_s^2 \sim P/\rho$. In this limit, the kinetic energy term in the generalized Bernoulli's principle is much smaller than the internal energy term. Thus, in the course of subsonic flow, the temperature, pressure, and density of the gas can only change by a small relative amount. For example, the pressure is $P(x) = P_0 + \Delta P(x)$ where $\Delta P \ll P_0$. (To avoid some confusion, remember that Bernoulli's principle always assumes steady flow. The air in my bike tires has $\Delta P \approx 6P_0$, but that's because the process of pumping a tire is not a steady flow.)

But if that's true, then what went wrong with just multiplying our result above by ρ? The point is that for very subsonic flows, the v^2 term is much smaller than the P/ρ term, so we need to evaluate the P/ρ term to a very good relative precision to get correct results. (If my bank was careless and randomly misplaced 0.1% of its money, then that might mean losing 100% of my savings, since my account's value is small compared to its total.)

Now we're ready to do the derivation properly. We start from the first equation above, but we don't multiply by ρ. Instead, we note that P/ρ^γ is constant because the gas is compressed adiabatically, since we neglected heat transfer, so we multiply by $\rho(P_0/P)^{1/\gamma}$, giving

$$\left(\frac{P_0}{P}\right)^{1/\gamma} \frac{1}{2}\rho v^2 + \frac{\gamma}{\gamma - 1}\left(\frac{P}{P_0}\right)^{(\gamma-1)/\gamma} P_0 = \text{const.}$$

Since the first term is the small one, we can approximate $P_0 \approx P$ there without much error. As for the second term, we expand $(P/P_0)^{(\gamma-1)/\gamma}$ with the binomial theorem to get

$$\frac{1}{2}\rho v^2 + \frac{\gamma}{\gamma - 1} P_0 + \Delta P = \text{const}$$

and subtracting the constant $P_0/(\gamma - 1)$ recovers the "incompressible" Bernoulli's principle.

In conclusion, the Bernoulli's principle derived in this problem set works for arbitrarily fast gas flows, while the incompressible form in **M7** only works for very subsonic flows. But that doesn't mean you should never use the latter. When the flow is subsonic, the incompressible form is easy to use, while the more general form requires great care to get the correct result. You should only use the general form when it's actually necessary, i.e. for the very fast gas flows considered in the following problems.

[3] **Problem 23** (Feynman). Air with density ρ, pressure P, and adiabatic index γ is flowing at uniform speed v through a smooth pipe of constant cross-sectional area A. It is heated as it passes a wire grid, which offers negligible resistance to the flow, with a power $\dot{Q}$. This is a simple model for a jet engine. For simplicity, suppose the output pressure is also P, though this would not be true in a high efficiency engine.

(a) Find the speed v' with which the air exits the tube, in terms of the given parameters.

(b) Find the thrust produced, in terms of v' and the other parameters.

Solution. (a) We will conserve mass and energy. Denote quantities that leave with a prime, and let μ be the molar mass. The rate of mass flow in must match the rate out,

$$J = \rho A v = \rho' A v'.$$

To apply energy conservation, we use a modified form of Bernoulli's principle, which accounts for the inflow of heat,

$$\frac{\dot{Q}}{J} = \frac{1}{2}(v'^2 - v^2) + \frac{c_P}{\mu}(T' - T).$$

The ideal gas law states

$$\rho = \frac{\mu P}{RT}$$

which we can use to eliminate μ. Additionally using $c_p = \gamma R/(\gamma - 1)$ gives

$$\frac{\dot{Q}}{J} = \frac{1}{2}(v'^2 - v^2) + \frac{P}{\rho T}\frac{\gamma}{\gamma - 1}(T' - T).$$

Since $P = P'$, combining the ideal gas law with mass conservation gives

$$\frac{v}{T} = \frac{v'}{T'}.$$

Using this to eliminate T' will give a quadratic equation for v' in terms of known parameters,

$$\frac{1}{2}v'^2 + \frac{c_0^2}{v}v' - \left(\frac{1}{2}v^2 + c_0^2 + \frac{\dot{Q}}{J}\right) = 0, \quad c_0^2 = \frac{\gamma}{\gamma - 1}\frac{P}{\rho}.$$

Using the quadratic equation and taking the physical root,

$$v' = \sqrt{(v + c_0^2/v)^2 + 2\dot{Q}/J} - c_0^2/v.$$

As a check, note that $v' = v$ when $\dot{Q} = 0$.

(b) By conservation of momentum, the thrust must be

$$F = J\Delta v = \rho A v(v' - v)$$

Incidentally, the power $P = Fv$ can be approximated when $\dot{Q}$ is small by taking the result of part (a) and applying the binomial theorem a few times. The result is

$$P \approx \frac{\dot{Q}}{2(1 + c_0^2/v^2)}$$

which is small for low v, and approaches an efficiency of $1/2$ as $v \to \infty$.

[3] **Problem 24** (Wang 2.17). Consider an ideal gas with pressure p, density ρ, and adiabatic index γ. A density pulse is set up in the gas, traveling along the $-x$ direction with speed c. Inside the pulse, the gas has local velocity $v \ll c$ in the lab frame, and a local density $\rho + \Delta\rho$, where $\Delta\rho \ll \rho$.

(a) Transform to the reference frame where the pulse is at rest, and find three constraints, using mass conservation, energy conservation, and the fact that the gas is compressed and expanded adiabatically when it enters and leaves the pulse (i.e. heat conduction is negligible).

(b) Combine these relations to find c. Work to lowest order in the small quantities v/c and $\Delta\rho/\rho$.

The quantity c is the adiabatic speed of sound in a gas, which we'll derive in a different way in **W3**. For more about sound waves, see chapter 31 of Blundell, or section 14.1 of Lautrup.

Solution. (a) We work in the reference frame moving to the left with speed c. In this frame, the gas has velocity c everywhere, except at the pulse, where it has velocity $c+v$. The density away from the pulse is ρ and the density at the pulse is $\rho+\Delta\rho$.

Mass conservation gives

$$(c+v)(\rho+\Delta\rho)=c\rho.$$

Using $c_p=(\gamma/(\gamma-1))R$, Bernoulli's principle gives

$$\frac{1}{2}\mu c^2+\frac{\gamma}{\gamma-1}RT=\frac{1}{2}\mu(c+v)^2+\frac{\gamma}{\gamma-1}R(T+\Delta T).$$

Finally, since the gas is compressed adiabatically we have

$$T\propto\rho^{\gamma-1}.$$

(b) Mass conservation gives the relation

$$\frac{\Delta\rho}{\rho}\approx-\frac{v}{c}$$

to lowest order. Bernoulli's principle gives

$$\mu cv=-\frac{\gamma}{\gamma-1}R\Delta T$$

to lowest order. Finally, the adiabatic condition to lowest order is

$$\frac{\Delta T}{T}\approx(\gamma-1)\frac{\Delta\rho}{\rho}.$$

Combining this with Bernoulli's principle to eliminate ΔT gives

$$\mu cv\approx-\gamma RT\,\frac{\Delta\rho}{\rho}\approx\gamma RT\,\frac{v}{c}.$$

Thus, solving for c, we conclude

$$c^2=\frac{\gamma RT}{\mu}=\frac{\gamma pV}{\mu n}=\frac{\gamma p}{\rho}$$

which is the adiabatic speed of sound.

Example 11

Show that the kinetic and potential energy of a sinusoidal, adiabatic sound wave are equal.

Solution

First, we explicitly define our notation. The sound wave profile is

$$P=P_0+\Delta P\,\cos(kx-\omega t),\quad \rho=\rho_0+\Delta\rho\,\cos(kx-\omega t)$$

and

$$\frac{v}{c}=\frac{v_0}{c}\,\cos(kx-\omega t),\quad T=T_0+\Delta T\,\cos(kx-\omega t).$$

In problem 24, you derived relations between the parameters $(\Delta P)/P_0$, $(\Delta\rho)/\rho_0$, v_0/c, and $(\Delta T)/T_0$, which are all assumed small, and of the same order of magnitude. The total energy density of the fluid, up to second order, is

$$u = \frac{1}{2}\rho_0 v^2 + c_v \rho T$$

where here c_v is the heat capacity per unit mass. The first term is the bulk kinetic energy density, while the change in the second term is the potential energy density, where we're using the usual meaning of potential energy as any energy which isn't kinetic.

This all looks pretty straightforward, but there's a reason that most introductory textbooks never write down this expression. You can see the issue by applying the ideal gas law to the second term. Since $P \propto \rho T$, this term is proportional to P, but the average of P is just P_0. This suggests that sound waves have no potential energy density at all, which is wrong. For instance, if you instantly take out all the macroscopic kinetic energy, setting v to zero, then there is still energy remaining that can be harvested because the pressure is nonuniform.

Here's the problem: energy is inherently a second order quantity. If ρ and T were both small quantities, then it would be good enough to multiply them to get the answer to second order. But instead, ρ and T are the quantities ρ_0 and T_0 shifted by small quantities $\Delta\rho$ and ΔT. That means that to get the quantity ρT correct to second order, we need to get both ρ and T individually correct to second order, which is beyond the first order approximations we started with! This is a conceptual issue that occurs whenever you have a perturbation that shifts existing properties of a medium. (It doesn't happen for waves on a string, which we cover in **W1**, because those waves are parametrized by y, and $y = 0$ when there is no wave.)

It's possible to fix this issue, but we need to be careful. First, let's use the ideal gas law to change variables to pressure, so we only have one quantity to deal with,

$$c_v \rho T = \frac{R}{\mu}\frac{1}{\gamma - 1}\rho T = \frac{P}{\gamma - 1}.$$

The key insight is that we can keep our expression for ρ the same. The reason is that for the wave equation to continue to be satisfied at second order, we can only add second order terms that are constant, or also sinusoids. Adding a constant to the density is not allowed because we know the total number of particles is conserved, so the mass $\int \rho\, dV$ is, and adding a sinusoid can be absorbed by simply redefining $\Delta\rho$.

Now, we know that $P \propto \rho^\gamma$, and letting $\delta\rho = \Delta\rho \cos(kx - \omega t)$ for convenience, we have

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0}\right)^\gamma = 1 + \frac{\gamma\,\delta\rho}{\rho_0} + \frac{\gamma(\gamma - 1)}{2}\left(\frac{\delta\rho}{\rho_0}\right)^2.$$

When we integrate the first term, we get the internal energy of the fluid at rest. The second term averages to zero, and so can be disregarded. The third term gives the desired result,

$$u = \frac{1}{2}\rho_0 v^2 + \frac{\gamma P_0}{2}\left(\frac{\delta\rho}{\rho_0}\right)^2.$$

Now that the energy is in terms of small quantities squared, we can relax and use first order results. Using the results derived in problem 24, this can be simplified to

$$u = \frac{1}{2}\rho_0 v^2 + \frac{1}{2}\rho_0 c^2 \left(\frac{\delta\rho}{\rho_0}\right)^2$$

and the two contributions are equal, because $v/c = -\delta\rho/\rho_0$.

As a check on this result, it is often true that the energy density is equal to the momentum density times the wave speed, $u = pc$. (For example, this corresponds to $E = pc$ for photons.) The momentum density is $p = \rho v = (\rho_0 + \delta\rho)v$. The first order term represents the overall momentum of all of the gas, not the momentum due to the sound wave itself, so it can be ignored. The second order term is

$$p = \delta\rho\, v = \frac{\rho_0 v^2}{c}$$

which is exactly the expected result.

Ironically, while we began this discussion by noting that the energy of a transverse wave on a string is more straightforward, the longitudinal momentum of a transverse wave on a string is far more confusing – how can there be any if the string moves only transversely? Does the above identity $u = pc$ break down for these waves, or do we just need to evaluate p more carefully? (For one perspective in this ongoing debate, see this paper.) All of this is too subtle to be relevant to Olympiads; even string theorists get confused about it. It's just a reminder that there are always subtleties lurking in even basic physics.

[3] **Problem 25.** 🕑 IPhO 2012, problem 1B. A tricky real-world problem on fluids and condensation.