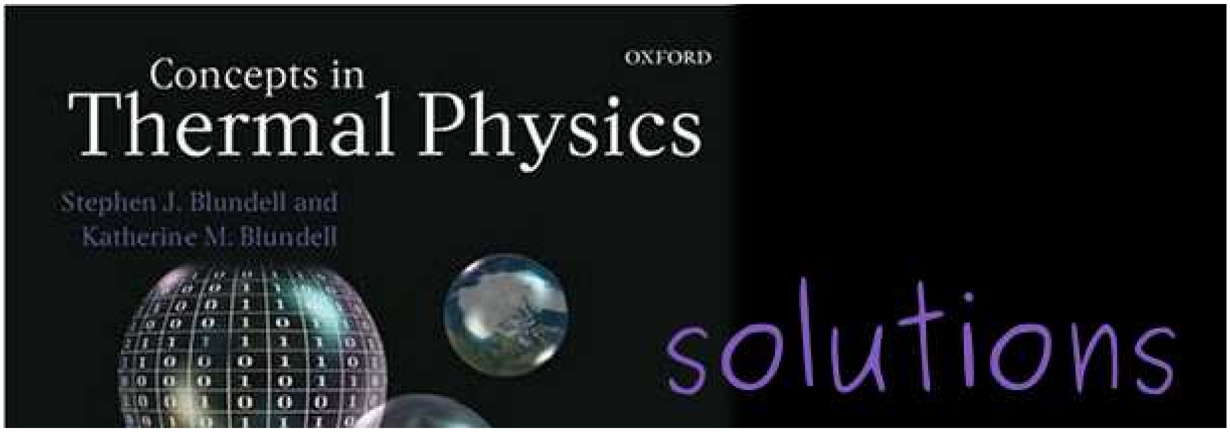


SECOND EDITION

The authors' solutions are included. These should **not** be distributed to students or issued in public, but are for the use of instructors only. Comments or corrections would be gratefully received.

Stephen Blundell and Katherine Blundell, August 11, 2009

`Email: s.blundell@physics.ox.ac.uk`
`Webpage: http://users.ox.ac.uk/~sjb`

`Email: k.blundell@physics.ox.ac.uk`
`Webpage: http://www-astro.physics.ox.ac.uk/~kmb/`

Solutions to Part I–VI

1.1 Mass of 1 mole of CO_2 is $\underset{C}{\underset{\uparrow}{12}} + 2\times\underset{O}{\underset{\uparrow}{16}} = 44\,g$

$\therefore$ 3 moles has mass $= \underline{\underline{132\,g}}$

1.2 $10^{-12}\,g$ is $10^{-15}\,kg$.

1 mole of bacteria $= 6\times10^{23}\times10^{-15} = 6\times10^{8}\,kg$

i.e. $\approx$ $\underline{\underline{1.2\times10^{5}\text{ elephant-masses}}}$

1.3 (a) 1 mole of H_2O is $0.018\,kg$

$\therefore$ 60 kg human composed entirely of H_2O contains $\dfrac{60}{0.018} = 3.3\times10^{3}$ moles $\xrightarrow[\times 6\times10^{23}]{}$ 2×10^{27} molecules

(b) A typical drop of water might have radius 1mm so its mass is $\frac{4}{3}\pi r^3\rho \approx 4\,mg = 4\times10^{-6}\,kg$.

Then the ocean contains $\dfrac{10^{21}}{4\times10^{-6}} = 2.5\times10^{26}$ drops

(c) For this estimate, (a) is bigger, but the numbers might vary.

1.4 See Example 1.3

(a) ${}^{2}C_1 = \underline{\underline{2}}$

(b) ${}^{20}C_{10} = 20!/(10!)^2 = \underline{\underline{1.8\times10^{5}}}$

(c) Use $\ln n! \approx n\ln n - n$

Thus $\ln \dfrac{2\times10^{23}!}{(10^{23}!)^2} = 2\times10^{23}\ln 2\times10^{23} - 2\times(10^{23}\ln 10^{23} - 10^{23})$.

$= 1.38\times10^{23}$.

Divide the answer by $\ln 10$ and you get 6×10^{22}

$\therefore$ ${}^{2\times10^{23}}C_{10^{23}} \approx \underline{\underline{10^{6\times10^{22}}}}$

1.5 $\ln n! \approx n\ln n - n + \frac{1}{2}\ln 2\pi n$ $\therefore$ dominant neglected term is $\frac{1}{2}\ln 2\pi n$.

$\Rightarrow$ fractional error is $\dfrac{\frac{1}{2}\ln 2\pi n}{n\ln n - n}$

(a)	$n=10$	0.159
(b)	$n=100$	0.0089
(c)	$n=1000$	0.00074

1.6 $n! = e^{\ln n!} \approx n^n e^{-n}\sqrt{2\pi n} \approx n^{n+\frac{1}{2}} e^{-n}\sqrt{2\pi}$

$\boxed{2.1}$ For water, $c = 4.2\times10^{3}\ \mathrm{J\,K^{-1}\,kg^{-1}}$

(a) Guess 0.2 kg water, and raise from 20°C to 100°C

$\therefore$ energy $= 0.2\times4.2\times10^{3}\times80 = 6.7\times10^{4}\ \mathrm{J}$ $[\equiv 0.02\ \mathrm{kWh}]$

(b) Guess volume of bath, $\rho = 1000\ \mathrm{kg\,m^{-3}}$ for H_2O,

$\therefore$ 200 kg not unreasonable. This time, may only want to warm it by 15°C

$\therefore$ energy $= 200\times4.2\times10^{3}\times15 = 1.3\times10^{7}\ \mathrm{J}$ $[\equiv 3.6\ \mathrm{kWh}]$

NB these are just estimates!

$\boxed{2.2}$ $4.2\times10^{3}\ \mathrm{J\,K^{-1}\,kg}\times10^{21}\ \mathrm{kg} = 4.2\times10^{24}\ \mathrm{J\,K^{-1}}$

$\boxed{2.3}$ $$\frac{13\times10^{12}\ \overset{\mathrm{J\,s^{-1}}}{\mathrm{W}}}{42\times10^{9}\ \mathrm{J/\,ton\ crude}} \simeq 300 \text{ tons of crude oil } \mathrm{s^{-1}}$$

$\boxed{2.4}$ 1 mole of Au is 197 g.

$$\therefore\ c = \frac{25.4\ \mathrm{J\,mol^{-1}\,K^{-1}}}{0.197\ \mathrm{kg\,mol^{-1}}}\times 19.3\times10^{3}\ \mathrm{kg\,m^{-3}} = 2.5\times10^{6}\ \mathrm{J\,m^{-3}\,K^{-1}}$$

$$C = \frac{25.4\ \mathrm{J\,mol^{-1}\,K^{-1}}}{0.197\ \mathrm{kg\,mol^{-1}}}\times 4\times10^{6}\ \mathrm{kg} = 5.2\times10^{8}\ \mathrm{J\,K^{-1}}$$

$\boxed{2.5}$ Conservation of energy $\therefore$ $C_1T_1 + C_2T_2 = C_1T_f + C_2T_f$

($\because$ equate heat flows $\underbrace{C_1(T_f-T_1)}_{\text{heat gained by 1}} = -\underbrace{C_2(T_f-T_2)}_{\text{heat lost by 2}}$)

$$\therefore\ T_f = \frac{C_1T_1 + C_2T_2}{C_1 + C_2}$$

If $C_1 \gg C_2$, $$T_f = \frac{T_1 + \frac{C_2}{C_1}T_2}{1 + C_2/C_1} = \left(T_1 + \frac{C_2}{C_1}T_2\right)\underbrace{\left(1+\frac{C_2}{C_1}\right)^{-1}}_{\approx\left(1-\frac{C_2}{C_1}\right)}$$

$\therefore$ to leading order in C_2/C_1

$$T_f \simeq T_1 + \frac{C_2}{C_1}(T_2 - T_1).$$

$\boxed{3.1}$ $\langle x\rangle = \sum x_i p_i = (1+2+3+4+5+6)\times\frac{1}{6} = \frac{21}{6} = 3.5$

$\langle x^2\rangle = \sum x_i^2 p_i = (1+4+9+16+25+36)\times\frac{1}{6} = \frac{91}{6}$

Variance = $\langle x^2\rangle - \langle x\rangle^2 = \frac{91}{6} - \frac{49}{4} = \frac{35}{12}$

S.d. = $\sqrt{\text{Variance}} = 1.71$

$\boxed{3.2}$ 3.2 ± 0.5 kg

$\downarrow\times 2.2$ $\downarrow\times 2.2$

7.04 ± 1.1 lb

$\boxed{3.3}$ (a) Uses the identity $e^m = \sum_{x=0}^{\infty} \frac{m^x}{x!}$

(b) straightforward

(c) $\langle x\rangle = \frac{122}{300} = 0.61$. Feed this back into Poisson to get:

# deaths per year per corps	0	1	2	3	4	≥ 5	Total
observed	109	65	22	3	1	0	200
calculated	109	66	20	4	1	0	200

$\boxed{3.4}$ (a) $A = 1/\lambda$ (b) $\langle x\rangle = \lambda$ (c) $\langle x^2\rangle = 2\lambda^2$ so that the variance is $\langle x^2\rangle - \langle x\rangle^2 = \lambda^2$ and the s.d. is λ.

$\boxed{3.5}$ $p(\theta) = \begin{cases} 1/\pi & 0 \leq \theta \leq \pi \\ 0 & \text{otherwise} \end{cases}$

(i) $\pi/2$ (ii) 0 (iii) $\pi^2/3$ (iv) $\pi^n/(n+1)$ (v) 0 (vi) $2/\pi$

(vii) $2/\pi$ (viii) $1/2$ (ix) $1/2$ (x) 1

$\boxed{3.6}$ Rather similar to Example 3.7

$Y = \frac{1}{n}(X_1 + \dots + X_n)$

$\langle Y\rangle = \frac{1}{n}(\langle X_1\rangle + \dots + \langle X_n\rangle) = \frac{1}{n} n \langle X\rangle = \langle X\rangle$

$$\langle Y^2\rangle = \frac{1}{n^2}\langle \underbrace{X_1^2 + \dots + X_n^2}_{n\langle X^2\rangle} + \underbrace{X_1X_2 + X_1X_3 + \dots\dots}_{n(n-1)\langle X\rangle^2} \rangle$$

$$= \frac{1}{n}\langle X^2\rangle + \frac{n-1}{n}\langle X\rangle^2$$

$$\sigma_Y^2 = \langle Y^2\rangle - \langle Y\rangle^2 = \frac{1}{n}\langle X^2\rangle + \left(1-\frac{1}{n}\right)\langle X\rangle^2 - \langle X\rangle^2$$

$$= \frac{1}{n}\left(\langle X^2\rangle - \langle X\rangle^2\right)$$

$$= \sigma_x^2/n$$

$$\therefore \ \sigma_Y = \frac{\sigma_X}{\sqrt{n}} = \frac{\Delta}{\sqrt{n}}$$

$\boxed{3.7}$ (a) $$P(n,k) = \frac{n!}{(n-k)!\,k!} p^k (1-p)^{n-k}$$

$$= \underbrace{\frac{n!}{(n-k)!\,n^k}}_{1 \text{ as } n\to\infty} \frac{m^k}{k!} \underbrace{\left(1-\frac{m}{n}\right)^{n-k}}_{e^{-m} \text{ as } n\to\infty} \qquad m = np$$

$$\longrightarrow \frac{m^k}{k!} e^{-m}, \quad \text{Poisson}$$

(b) $$n = \frac{t}{\tau} \qquad D = \frac{L^2}{2\tau} \Rightarrow L^2 = 2D\tau$$

Random walk: $\langle x\rangle = 0$, $\langle x^2\rangle = nL^2$

$$\exp\left(-\frac{(x-\langle x\rangle)^2}{2\sigma_x^2}\right) = \exp\left(-\frac{x^2}{2nL^2}\right) = \exp\left(-\frac{x^2}{4Dt}\right)$$

(c) $\sigma_x = \sqrt{2Dt}$ $\quad \frac{\sigma_x}{t} \propto t^{-1/2}$ $\quad$ Look for when $\sqrt{2Dt} \approx \ell$ i.e. $t \approx \ell^2/D$

$\ell = 10^{-6}\,\cancel{\mu}\text{m} \Rightarrow t \sim \frac{10^{-12}}{10^{-9}} \approx 1\,\text{ms}$

$\ell = 10^{-2}\,\text{m} \Rightarrow t \sim \frac{10^{-4}}{10^{-9}} = 10^5\,\text{s} \approx 1$ day

$\boxed{3.8}$ $$M(t) = \langle e^{tx}\rangle = \sum_i e^{tx_i} p_i \qquad \langle x^n\rangle = \sum_i x_i^n p_i$$

$$M^{(n)}(t) = \sum_i x_i^n e^{tx_i} p_i \Rightarrow M^{(n)}(0) = \langle x^n\rangle.$$

Clearly $\langle x\rangle = M^{(1)}(0)$, $\quad \langle x^2\rangle - \langle x\rangle^2 = M^{(2)}(0) - \left[M^{(1)}(0)\right]^2$

(a) Bernoulli $M(t) = \sum_i e^{tx_i} p_i = pe^t + 1 - p$

$M^{(1)}(t) = pe^t \quad M^{(1)}(0) = p \quad M^{(2)} = pe^t \quad M^{(2)}(0) = p \quad \Rightarrow \begin{array}{l}\langle x\rangle = p \\ \text{Var}\,X = p(1-p)\end{array}$

(b) Binomial $M(t) = (pe^t + 1 - p)^n$

$M^{(1)}(t) = n(pe^t + 1 - p)\cdot pe^t \quad M^{(1)}(0) = np \quad \langle x\rangle = np$

$M^{(2)}(t) = n(n-1)(pe^t+1-p)^{n-2}(pe^t)^2 + n(pe^t+1-p)^{n-1}pe^t \quad M^{(2)}(0) = n^2p^2 - np^2 + np$

$\text{Var}\,X = np(1-p)$

(c) Poisson $$M(t) = \sum_{k=0}^{\infty} \frac{e^{-m} m^k}{k!} e^{tk} = e^{-m} \sum_{k=0}^{\infty} \frac{(me^t)^k}{k!} = e^{-m} e^{e^t}$$

$$\left.\begin{array}{l} M^{(1)}(t) = me^{m(e^t-1)} \quad M'(0) = m \\ M^{(2)}(t) = me^{m(e^t-1)}e^t + m^2 e^t e^{m(e^t-1)} e^t \;\therefore\; M^{(2)}(0) = m + m^2 \end{array}\right\} \quad \begin{array}{l}\text{Var}\,X = m + m^2 - (m)^2 \\ \quad = m\end{array}$$

(d) Exponential $$M(t) = \int_0^\infty e^{tx} \lambda e^{-\lambda x}\,dx = \left[\frac{\lambda e^{(t-\lambda)x}}{t-\lambda}\right]_0^\infty = \frac{\lambda}{\lambda - t}$$

$$\left.\begin{array}{ll} M^{(1)}(t) = -\frac{\lambda}{(\lambda-t)^2} & M^{(1)}(0) = \frac{1}{\lambda} \\ M^{(2)}(t) = \frac{2\lambda}{(\lambda-t)^3} & M^{(2)}(0) = 2/\lambda^2 \end{array}\right\} \quad \text{Var}\,X = \frac{2}{\lambda^2} - \left(\frac{1}{\lambda}\right)^2 = \frac{1}{\lambda^2}$$

3.8(d) Minor erratum.

In the July 2017 reprinting we changed the generating function $M(t)$ to be $\frac{1}{1-\lambda t}$. This essentially changes our previous λ to be $1/\lambda$ which makes it more consistent with our earlier question in which $P(x) = \frac{1}{\lambda} e^{-x/\lambda}$ [and not $P(x) = \lambda e^{-\lambda x}$].

The new solution goes as follows:

$$M(t) = \langle e^{tx} \rangle = \int_0^\infty e^{tx} \frac{1}{\lambda} e^{-x/\lambda} \, dx$$

$$= \frac{1}{\lambda} \left[\frac{e^{(t-\frac{1}{\lambda})x}}{t-\frac{1}{\lambda}} \right]_0^\infty = \frac{1}{1-\lambda t}$$

$$\left.\begin{aligned} M^{(1)}(t) &= \frac{\lambda}{(1-\lambda t)^2} \qquad M^{(1)}(0) = \lambda \\ M^{(2)}(t) &= \frac{2\lambda^2}{(1-\lambda t)^3} \qquad M^{(2)}(0) = 2\lambda^2 \end{aligned}\right\} \quad \begin{aligned} \langle x \rangle &= M^{(1)}(0) = \lambda \\ \mathrm{Var}\,X &= M^{(2)}(0) - \langle x \rangle^2 \\ &= 2\lambda^2 - \lambda^2 \\ &= \lambda^2 \end{aligned}$$

$\boxed{4.1}$ Trivial.

$\boxed{4.2}$

$$\langle E\rangle = \frac{0\cdot 1+\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{\varepsilon}{e^{\beta\varepsilon}+1}$$

$$\langle E^2\rangle = \frac{0^2\cdot 1+\varepsilon^2 e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{\varepsilon^2}{e^{\beta\varepsilon}+1} = \varepsilon\langle E\rangle$$

$$\langle E^2\rangle - \langle E\rangle^2 = \frac{\varepsilon^2}{e^{\beta\varepsilon}+1}\left(1-\frac{1}{e^{\beta\varepsilon}+1}\right) = \frac{\varepsilon^2 e^{\beta\varepsilon}}{(e^{\beta\varepsilon}+1)^2}$$

$\boxed{4.3}$ $\Omega(r\Delta) = N!/r!(N-r)!$

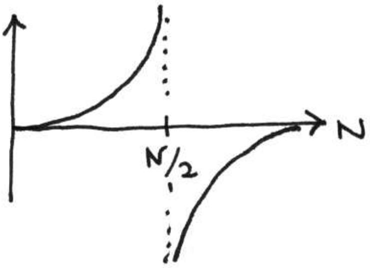
remove $\varepsilon = s\Delta \ll r\Delta$

$$\therefore\ \Omega(E-\varepsilon) = N!\big/(r-s)!(N-r+s)! = \Omega(E)\,\frac{r(r-1)\ldots(r-s+1)}{(N-r+1)\cdots(N-r+s)}$$

$$\approx \Omega(E)\,\frac{r^s}{(N-r)^s} \qquad \because\ s \ll r$$

$$= \Omega(E)\,\exp\Big(-\underset{\overset{\uparrow}{\varepsilon/\Delta}}{s}\,\ln\frac{N-r}{r}\Big) \quad \Rightarrow\ \beta = \frac{1}{k_BT} = \frac{1}{\Delta}\ln\frac{N-r}{r}$$

$$\frac{k_BT}{\Delta} = \left(\ln\frac{N-r}{r}\right)^{-1}$$



$\boxed{4.4}$

$$\varepsilon^2\frac{d^2\ln\Omega}{dE^2} = \frac{\varepsilon^2}{k_B}\frac{d}{dE}\left(\frac{1}{T}\right) = -\frac{\varepsilon^2}{k_BT^2}\frac{dT}{dE} = -\frac{\varepsilon^2}{k_B\underset{\uparrow\ \text{heat capacity}}{C}T^2}$$

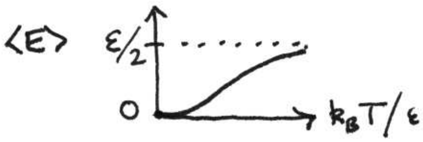
This will be small with respect to ε/k_BT if $\varepsilon \ll CT$, i.e. ε is small compared to the total thermal capacity of reservoir.

$\boxed{4.5}$ $\Delta\ln\Omega \approx \dfrac{\Delta E}{k_BT}$ $\therefore$ Ω changes by a factor $e^{\Delta E/k_BT}$

2eV photon, $e^{\Delta E/k_BT} \approx 6\times 10^{34}$ i.e. huge

100 MHz photon (0.4 μeV) $e^{\Delta E/k_BT} \approx 1.000017$ i.e. very small change

$\boxed{4.6}$



$\boxed{4.7}$ (a)

$$\langle E\rangle = \frac{0\cdot 1+\varepsilon e^{-\beta\varepsilon}+\varepsilon^2 e^{-2\beta\varepsilon}+\cdots+\varepsilon^n e^{-n\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}+\cdots+\varepsilon^n e^{-n\beta\varepsilon}} = -\frac{1}{Z}\frac{dZ}{d\beta}$$

$Z =$ denominator $= (1-e^{-\beta\varepsilon(n+1)})/(1-e^{-\beta\varepsilon})$ $\therefore$ after some algebra...

$$\Rightarrow\ \langle E\rangle = \frac{\varepsilon e^{-\beta\varepsilon}}{(1-e^{-\beta\varepsilon})(1-e^{-\beta\varepsilon(n+1)})}\left[1-(n+1)e^{-n\beta\varepsilon}+n e^{-(n+1)\beta\varepsilon}\right]$$

(b) $n\to\infty$ $\langle E\rangle \to \varepsilon/(e^{\beta\varepsilon}-1)$ [the Bose factor]

$\boxed{4.8}$ $k_BT \simeq 0.025$ eV (a) no. (b) yes.

$\boxed{5.1}$ Straightforward integrals

$\boxed{5.2}$

$$V_{rms} = \sqrt{\frac{3k_BT}{m}} = \begin{cases} 1.9\ \mathrm{km\,s^{-1}} & H_2 \\ 1.4\ \mathrm{km\,s^{-1}} & \mathrm{He} \\ 0.48\ \mathrm{km\,s^{-1}} & O_2 \end{cases}$$

$$V_{esc} = \sqrt{\frac{2GM}{R}} = \begin{cases} 11.2\ \mathrm{km\,s^{-1}} & \text{Earth} \\ 618\ \mathrm{km\,s^{-1}} & \text{Sun} \end{cases}$$ see Appendix A for data

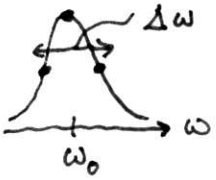
$\boxed{5.3}$ See eqn 5.20 : $\sqrt{\frac{8}{\pi}} = 1.596$

$\sqrt{3} = 1.732$ $\quad\therefore$ fractional error $= 0.08$

$\boxed{5.4}$

$$\left.\begin{aligned} \langle v\rangle &= \frac{\int_0^\infty v^3 e^{-mv^2/2k_BT}\,dv}{\int_0^\infty v^2 e^{-mv^2/2k_BT}\,dv} = \sqrt{\frac{8k_BT}{\pi m}} \\ \left\langle \frac{1}{v}\right\rangle &= \frac{\int_0^\infty v\, e^{-mv^2/2k_BT}\,dv}{\int_0^\infty v^2 e^{-mv^2/2k_BT}\,dv} = \sqrt{\frac{2m}{\pi k_BT}} \end{aligned}\right\} \quad \langle v\rangle\left\langle\frac{1}{v}\right\rangle = \frac{4}{\pi}$$

$\boxed{5.5}$ Half maximum occurs when $\exp\left[-\frac{mc^2\,[\Delta\omega/2]^2}{2k_BT\omega_0^{\,2}}\right] = \frac{1}{2}$



$$\therefore\quad -\frac{mc^2}{2k_BT}\left(\frac{\Delta\omega}{2\omega_0}\right)^2 = -\ln 2$$

$$\therefore\quad \frac{\Delta\omega}{\omega_0} = 2\sqrt{2\ln 2\,\frac{k_BT}{mc^2}}$$

$\omega = \frac{2\pi c}{\lambda} \quad\therefore\quad \frac{\Delta\omega}{\omega} = \left|\frac{\Delta\lambda}{\lambda}\right|$ and $2\sqrt{2\ln 2\,\frac{k_B}{m_pc^2}} = 7.16\times10^{-7}$

result follows.

$\boxed{5.6}$ $\lambda_0 = 0.21\,\mathrm{m}$, $T = 100\,\mathrm{K}$, $m = 1$

using previous result $\frac{\Delta\lambda}{\lambda_0} = 7.16\times10^{-6} = \left|\frac{\Delta\nu}{\nu_0}\right|$ $\quad \nu_0 = \frac{c}{\lambda} \simeq 1.4\,\mathrm{GHz}$

$\therefore\ \Delta\nu \approx 10\,\mathrm{kHz}$

$\boxed{5.7}$

$$V_{rms} = \sqrt{\frac{3k_B\overset{6000\,\mathrm{K}}{T}}{\underset{23m_p}{m}}} = 2.5\,\mathrm{km\,s^{-1}}$$

$$\frac{\Delta\nu}{\nu_0} = \frac{\Delta\lambda}{\lambda_0} = 7.16\times10^{-7}\sqrt{\frac{6000}{23}} = 1.2\times10^{-5} \qquad \nu_0 = \frac{c}{5900\,\text{Å}} = 5.1\times10^{14}\,\mathrm{Hz}$$

$\therefore\ \Delta\nu = 5.8\,\mathrm{GHz}$

$\boxed{6.1}$ eqn 6.20 ∴ $$V = \frac{\overset{1}{n_m} R \overset{\text{assume } 300\,\text{K}}{T}}{\underset{10^{-10}\times 133\,\text{Pa}}{p}} = 1.9\times10^{11}\ \text{m}^3$$

$\boxed{6.2}$ $$u = \frac{3}{2}\underset{10^5\,\text{Pa}}{p} = 1.5\times10^{5}\ \text{J m}^{-3}$$

$\boxed{6.3}$ It stays the same. (p is constant, ∴ u is constant ∴ $U_{tot} = uV$ is constant)

$\boxed{6.4}$ This question should also give a number density! Take $n = 500\ \text{cm}^{-3}$
$\equiv 5\times10^{8}\ \text{m}^{-3}$

$p = nk_BT = 3.5\times10^{-13}\ \text{Pa}$ $\quad \rho = n m_H \Rightarrow V = \dfrac{100\ M_\odot}{n m_H}$
$= 2.4\times10^{50}\ \text{m}^3$

1 light-year $= 9.46\times10^{15}$ m $\Rightarrow V \approx 300$ cubic light-years.

$\boxed{6.5}$ (a) $$\langle\cos\theta\rangle = \frac{\int_0^{\pi/2}\sin\theta\cos^2\theta\,d\theta}{\int_0^{\pi/2}\sin\theta\cos\theta\,d\theta} = \frac{1/3}{1/2} = \frac{2}{3}$$

(b) $$\langle v^2\rangle = \frac{\int_0^\infty v^2\cdot v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dc}{\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dc} = \frac{3k_BT}{m}$$

$$\therefore \langle\tfrac{1}{2}mv^2\rangle = \tfrac{3}{2}k_BT$$

For those hitting the surface, there is an extra factor of c

$$\langle v^2\rangle = \frac{\int_0^\infty v^2\cdot v^3 e^{-\frac{1}{2}mv^2/k_BT}\,dv}{\int_0^\infty v^3 e^{-\frac{1}{2}mv^2/k_BT}\,dv} = \frac{4k_BT}{m}$$

$$\therefore \langle\tfrac{1}{2}mv^2\rangle = 2k_BT$$

$\boxed{6.6}$ Without loss of generality, take $u\parallel z$ so that $u = v\cos\theta$

(a) $\langle u\rangle \propto \int_0^\pi \cos\theta\sin\theta\,d\theta = 0$

(b) $$\langle u^2\rangle = \frac{\int_0^\infty \frac{1}{2}nf(v)v^2\,dv\int_0^\pi\cos^2\theta\sin\theta\,d\theta}{\int_0^\infty\frac{1}{2}nf(v)\,dv\int_0^\pi\sin\theta\,d\theta} = \frac{1}{3}\langle v^2\rangle$$

(c) $$\langle|u|\rangle = \frac{\int_0^\infty\frac{1}{2}nf(v)v\,dv\left\{\int_0^{\pi/2}\cos\theta\sin\theta\,d\theta + \int_{\pi/2}^{\pi}(-\cos\theta\sin\theta)\,d\theta\right\}}{\int_0^\infty\frac{1}{2}nf(v)\int_0^\pi\sin\theta\,d\theta}$$

$$= \frac{1}{2}\frac{\int_0^\infty nf(v)v\,dv}{\int_0^\infty nf(v)\,dv} = \frac{1}{2}\langle v\rangle$$

$\boxed{6.7}$ Take e.g. $v_1 = \cos\theta$, $v_2 = \sin\theta\cos\phi$, $v_3 = \sin\theta\sin\phi$

$v_1v_2 = \cos\theta\sin\theta\cos\phi$ and $\langle v_1v_2\rangle = 0$ ∵ $\int_0^{2\pi}\cos\phi\,d\phi \to 0$.

In fact, since v_1 and v_2 are uncorrelated $\langle v_1v_2\rangle = \langle v_1\rangle\langle v_2\rangle = 0$

∵ $\langle v_1\rangle = \langle v_2\rangle = 0$

$\boxed{6.8}$ $$p_{O_2} = \frac{\frac{23.2}{32}\times 1\ \text{atm}}{\frac{75.5}{28}+\frac{23.2}{32}+\frac{1.3}{40}+\frac{0.05}{44}} = 0.21\ \text{atm}$$ (see example 6.4)

7.1 The flux is $\Phi = 10^{19}\,\mathrm{m}^{-2}/3600\,\mathrm{s}$. Assuming the residual gas is N_2 and $T = 300\,\mathrm{K}$, then

$$p = \phi\sqrt{2\pi m k_\mathrm{B} T} \approx 10^{-7}\,\mathrm{Pa} \approx 10^{-9}\,\mathrm{mbar}$$

7.2 The mean KE in the gas is $\frac{3}{2}k_\mathrm{B}T$, the mean KE in the beam is the same as the mean KE of those hitting the surface, i.e. $2k_\mathrm{B}T$ (see 2.1(b)), so in the box the temperature will settle to the new value T_new given by

$$\frac{3}{2}k_\mathrm{B}T_\mathrm{new} = 2k_\mathrm{B}T,$$

i.e. $T_\mathrm{new} = 4T/3$.

7.3 Assume the vapour pressure is constant, so that there is a constant effusion rate. 0.025 Pa.

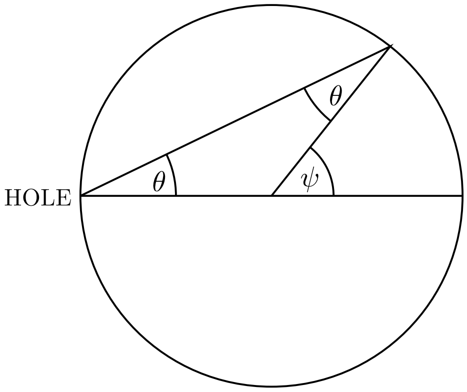
7.4 $f(v) = v^3\,\mathrm{e}^{-mv^2/2k_\mathrm{B}T}$, so that $\langle v\rangle = 3\sqrt{\frac{k_\mathrm{B}T\pi}{8m}} = 1.88\sqrt{\frac{k_\mathrm{B}T}{m}}$ while $v_\mathrm{max} = 1.73\sqrt{\frac{k_\mathrm{B}T}{m}}$.

7.5 θ goes between 0 and $\theta_\mathrm{max} \approx a/d \ll 1$ so that the rate is

$$\frac{n\langle v\rangle A}{4}\int_0^{\theta_\mathrm{max}} \sin 2\theta\,\mathrm{d}\theta$$

and hence the result $\frac{1}{4}nA\langle u\rangle(a^2/d^2)$ follows using the small angle approximation.

7.6 This one is spherical geometry. $\pi - \psi + 2\theta = \pi$ so $\psi = 2\theta$. The solid angle between ψ and $\psi + \mathrm{d}\psi$ is proportional to $\sin\psi\,\mathrm{d}\psi$. The number effusing through the hole between θ and $\theta + \mathrm{d}\theta$ is proportional to $\cos\theta\sin\theta\,\mathrm{d}\theta$. Hence the number deposited per solid angle is independent of θ and the coating is uniform.



7.7 $F = pA \approx 3\times 10^{-7}\,\mathrm{N}$.

7.8 $p = nk_\mathrm{B}T$ and so $\dot{n} = \dot{p}/k_\mathrm{B}T$. By continuity we have

$$\dot{n}V = -\Phi A,$$

because the rate of change of number of molecules in the volume is equal to the effusion rate. Hence, with $\Phi = p/\sqrt{2\pi m k_\mathrm{B}T}$, we have $\mathrm{d}p/p = -\mathrm{d}t/\tau$ with τ as defined in the question.

8.1 For N_2, $\sigma = \pi d^2 = 4.3 \times 10^{-19}\,\mathrm{m}^2$ (see Example 8.1). Then $n = p/k_\mathrm{B}T$ with $p = 10^{-10} \times 10^2\,\mathrm{Pa}$. With $\langle v \rangle = \sqrt{8k_\mathrm{B}T/\pi m} = 475\,\mathrm{m\,s^{-1}}$, we then have

- $\lambda = 1/\sqrt{2}n\sigma \approx 7 \times 10^5\,\mathrm{m}$;
- $\tau = \lambda/\langle v \rangle \approx 25\,\mathrm{minutes}$.

Since the chamber size is 0.5 m, then molecules will collide about 10^6 times more often with the chamber walls than with each other.

If p is raised by a factor of 10^4, then λ and τ will go down by a factor of 10^4.

8.2 $P(x) = \mathrm{e}^{-x/\lambda}$ and so

(a) $\langle x^2 \rangle = 2\lambda^2$ and $x_\mathrm{rms} = \sqrt{2}\lambda$.

(b) $\mathrm{d}P/\mathrm{d}x = 0$ leads to $x = \infty$ (the least probable length) and $x = 0$ (the most probable length).

(c) (i) 36.8%, (ii) 13.5%, (iii) 0.67%.

8.3 The number hitting a plane is proportional to $vg(v)\,\mathrm{d}v\,\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$. Hence

$$\langle x\cos\theta \rangle = \frac{\int_0^\infty x\,\mathrm{e}^{-x/\lambda}\int v\,g(v)\,\mathrm{d}v\int_0^{\pi/2}\cos^2\theta\sin\theta\,\mathrm{d}\theta}{\int_0^\infty \mathrm{e}^{-x/\lambda}\int v\,g(v)\,\mathrm{d}v\int_0^{\pi/2}\cos\theta\sin\theta\,\mathrm{d}\theta} = \frac{2\lambda}{3}.$$

8.4 This question *should* have stated that $n = 500\,\mathrm{cm}^{-3}$ so that $n = 5 \times 10^8\,\mathrm{m}^{-3}$. In this case, and estimating $\sigma = \pi(2a_0)^2 \approx 3 \times 10^{-20}\,\mathrm{m}^2$, we have

- $\langle v \rangle = \sqrt{8k_\mathrm{B}T/\pi m} \approx 10^3\,\mathrm{m\,s^{-1}}$;
- $\lambda = 1/\sqrt{2}n\sigma \approx 5 \times 10^{10}\,\mathrm{m}$;
- $\tau = \lambda/\langle v \rangle \approx$1–2 years.

9.1 Although $\eta_{\text{water}} > \eta_{\text{air}}$, $\nu_{\text{water}} = 10^{-6}\,\text{m}^2\,\text{s}^{-1} < \nu_{\text{air}} = 1.3 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1}$, so it depends what you mean by more viscous!

9.2 $\kappa = \frac{1}{3} C_v \langle c \rangle \lambda = p\lambda\sqrt{\frac{2k_{\text{B}}}{\pi m T}}$.

$\lambda = 2.4 \times 10^{-7}$ m

This leads to $d_{\text{av}} = 1.93 \times 10^{-10}$ m.

The effective atomic radius $r = 1.95 \times 10^{-10}$ m is very similar.

9.3 First part is bookwork. The experiment showed that viscosity was independent of pressure. As you reduce the pressure, fewer molecules collide, but they have travelled further and hence come from a region where the transverse momentum is 'more different'. The experiment would only 'work' until the pressure was so low that λ had reached the dimensions of the apparatus. If this was ~ 0.1 m, then this implies $p \sim 0.1$ Pa.

9.4 Shear stress is $\eta\, \mathrm{d}v/\mathrm{d}r$, so considering a small element

$$\mathrm{d}F = (2\pi r\, \mathrm{d}r) \cdot \eta \cdot \frac{r\omega}{d}$$

and hence

$$G = \int_0^a r\, \mathrm{d}F = \frac{\pi\eta\omega a^4}{2d} = 2.1 \times 10^{-6}\text{Nm}.$$

9.5 Expect $\eta \propto \sqrt{T}$, and $\eta(2000\,\text{K})/\eta(500\,\text{K}) \approx 2.3$ (whereas it 'should' be 2.0), so not bad. The effective diameter $d = (2/3\pi\eta)^{1/2}(mk_{\text{B}}T/\pi)^{1/4}$ comes out as 0.25 nm at 2000 K and 0.27 nm at 500 K, whereas the solid Ar value is 0.34 nm. The effective diameter goes down because the molecules are 'squashy' and penetrate more into each other when they collide at high speed. [Note: if you use the "corrected" formula $d = (5/16\eta)^{1/2}(mk_{\text{B}}T/\pi)^{1/4}$, the answers become 0.31 nm at 2000 K and 0.33 nm at 500 K.]

9.6 Since $C_p = C_V + R$, we have that $C_V = C_P - R = \gamma C_V - R$ and so $(\gamma - 1)C_V = R$ and the result follows.

Writing $C_V'' = C_V - \frac{3}{2}R$, we have that

$$\frac{\kappa}{\eta} = \frac{15R}{4} + C_V - \frac{3}{2}R = \frac{9}{4}(\gamma - 1)C_V - C_V = \frac{1}{4}(9\gamma - 5)C_V$$

Rearranging this we have that

$$\gamma = \frac{1}{9}\left(5 + \frac{4\kappa}{\eta C_V}\right).$$

Species	$\kappa/(\eta C_V)$	γ
He	2.45	1.64
Ne	2.52	1.68
Ar	2.48	1.66
Kr	2.54	1.68
Xe	2.58	1.70

The results are all clustered around $\gamma = 5/3$, not surprising since for a monatomic gas all of the heat capacity is associated with the translational degrees of freedom for these gases.

10.1 A trial solution of $T(x,t) = T(0,0)e^{i(kx-\omega t)}$ in the one-dimensional thermal diffusion equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C}\frac{\partial^2 T}{\partial x^2}$$

(where C is a heat capacity per unit volume) yields $-\mathrm{i}\omega = \frac{\kappa}{C}(-k^2)$. In this problem ω must be real so we write

$$k = \pm(1+\mathrm{i})\sqrt{\frac{\omega C}{2\kappa}} = \pm\frac{1+\mathrm{i}}{\delta}$$

where $\delta = \sqrt{2\kappa/\omega C}$ is the skin depth. We choose the sign of k to get the right boundary condition: here positive so that it doesn't blow up as $x \to \infty$. Hence for $x \geq 0$ we can write in general

$$T(x,t) = \sum_{\omega} A_{\omega} e^{-\mathrm{i}\omega t} e^{(\mathrm{i}-1)x/\delta}.$$

If the boundary condition at the surface is then $T(0,t) = T_0 + T_1 \cos\omega t$ then matching terms we get

$$T(x,t) = T_0 + T_1 \cos(\omega t - \frac{x}{\delta})e^{-x/\delta}.$$

Putting in the numbers, for daily fluctuations $\delta = 0.13$ m and the fluctuations in the cellar are nanoKelvin! Annual fluctuations give $\delta = 2.5$ m and the fluctuations in the cellar come out to about 6°C. The phase lag can be estimated from the $\omega t - \frac{x}{\delta}$ term. The minimum will occur at a time t_0 when $\omega t_0 = \frac{x}{\delta}$, so that putting in the numbers I get t_0 is about 68–70 days, i.e. in March.

10.2 The thermal diffusion equation corrected for heat generation $j^2\rho$ (where j is the current density, $j = I/(\pi a^2)$) per unit volume gives $\nabla^2 T = -I^2\rho/\pi^2 a^4 \kappa$ and hence

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}T}{\mathrm{d}r}\right) = -\frac{I^2\rho}{\pi^2 a^4 \kappa}.$$

This integrates to

$$r\frac{\mathrm{d}T}{\mathrm{d}r} = -\frac{I^2\rho r^2}{2\pi^2 a^4 \kappa} + \text{const},$$

and the constant is clearly zero. Integrating again gives

$$T = -\frac{I^2\rho r^2}{4\pi^2 a^4 \kappa} + \beta$$

where β is a constant.

[A more elegant way of doing this (it saves one integration) is as follows: inside radius $r < a$ the power generated is $j^2\rho\pi r^2$ per unit length; all that power has to move across the surface and so the heat flux J out of the surface is:

$$J(r) = \frac{j^2\rho\pi r^2}{2\pi r} = \frac{1}{2}j^2\rho r = -\kappa\frac{\mathrm{d}T}{\mathrm{d}r}.$$

Hence

$$\frac{\mathrm{d}T(r)}{\mathrm{d}r} = -\frac{I^2\rho r}{2\pi^2 a^4 \kappa},$$

and so

$$T(r) = -\frac{I^2\rho r^2}{4\pi^2 a^4 \kappa} + \beta$$

where β is a constant.]

(a) At $r = a$, $T = T_0$, fixing β and yielding

$$T(r) = T_0 + \frac{\rho I^2}{4\pi^2 a^4 \kappa}(a^2 - r^2).$$

(b) The boundary condition is now

$$-\kappa\left(\frac{\mathrm{d}T}{\mathrm{d}r}\right)_{r=a}=\alpha(T(a)-T_{\mathrm{air}}),$$

so that the final answer becomes

$$T(r)=T_{\mathrm{air}}+\frac{\rho I^2}{4\kappa\pi^2a^4}(a^2-r^2)+\frac{I^2\rho}{2\alpha\pi^2a^3}.$$

10.3 We want to find $[T_1-T(0,t)]/[T_1-T_0]=0.1$, which implies that

$$2\mathrm{e}^{-D(\pi/a)^2t}=0.1$$

and hence $D(\pi/a)^2t=\ln 20$ and the result follows.

10.4 The power coming into a region between x and $x+\mathrm{d}x$ leads to a rate of increase of thermal energy

$$\rho C_p\left(\frac{\partial T}{\partial t}\right)\pi a^2\mathrm{d}x.$$

This is provided by $-\nabla\cdot(-\kappa\nabla T)$ (per unit volume) which is a power

$$\kappa\frac{\partial^2T}{\partial x^2}\pi a^2\,\mathrm{d}x$$

in one-dimension. However, heat can also be lost via the surface of the wire, leading to a term

$$-2\pi a\,\mathrm{d}x\,R(T).$$

The result then follows.

In the steady state, $\partial T/\partial t=0$ and so one has to solve

$$\frac{\partial^2T}{\partial x^2}=\frac{2A(T-T_0)}{a\kappa}.$$

(a) The solution to this is

$$T-T_0=C\mathrm{e}^{\sqrt{\alpha}x}+D\mathrm{e}^{-\sqrt{\alpha}x}$$

where C and D are constants and

$$\alpha=\frac{2A}{a\kappa}.$$

For an infinite rod, we can neglect the $C\mathrm{e}^{\sqrt{\alpha}x}$ term and obtain

$$T=T_0+(T_m-T_0)\mathrm{e}^{-\sqrt{\alpha}x}$$

for the boundary conditions.

(b) Either evaluate the total heat loss:

$$\int_0^\infty A(T-T_0)\,2\pi a\,\mathrm{d}x=2\pi aA(T_m-T_0)\int_0^\infty\mathrm{e}^{-\sqrt{\alpha}x}\,\mathrm{d}x=\pi a^{3/2}(T_m-T_0)\sqrt{2\kappa A},$$

or evaluate the heat transported at $x=0$,

$$-\kappa\left(\frac{\partial T}{\partial x}\right)_{x=0}\pi a^2=\kappa\sqrt{\alpha}(T_m-T_0)\pi a^2=\pi a^{3/2}(T_m-T_0)\sqrt{2\kappa A}.$$

This all fails for finite rods since you cannot then neglect the other term in the solution. It will work well enough if the rods are longer than a few diffusion lengths, where $\delta=1/\sqrt{\alpha}=\sqrt{\frac{a\kappa}{2A}}$ is about 3 cm, so maybe something over 10 cm should be OK for things to be correct at the 5% level.

10.5 $(\delta_v/\delta)^2 = \eta c_p/\kappa = \sigma_\mathrm{p}$

10.6 Since $i\omega = Dk^2$, $|\mathrm{d}\omega/\mathrm{d}k| = 2Dk$ and this can go to infinity when you consider waves with wavelengths going to zero.

$$\sum_k \hbar\omega_k \tau \dot{n} v_i = -\sum_k \sum_j \hbar\omega_k \tau v_j \frac{\delta n}{\delta x_i} v_i - \sum_k \hbar\omega_k v_i (n - n_0)$$

and so this can be rewritten

$$J_i + \tau \dot{J}_i = -\sum_k \sum_j \hbar\omega_k \tau v_j v_i \frac{\delta n}{\delta T} \frac{\delta T}{\delta x_i}.$$

In an isotropic system one has

$$J_i + \tau \dot{J}_i = -\kappa \frac{\delta T}{\delta x_i}.$$

where

$$\kappa = \frac{1}{3} \sum_k \hbar\omega_k \tau v^2 \frac{\delta n}{\delta T}.$$

For more details, see S. Simons, Am. J. Phys. **54**, 1048 (1986).

10.7 Heat flux is the same throughout and hence

$$\kappa_i \frac{\Delta T_i}{\Delta x_i} = J$$

and $T_i - T_f = \sum \Delta T_i = J \sum_i \Delta x_i/\kappa_i$.

10.8 In cylindrical geometry, we have that

$$\frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r} \right) = 0$$

and hence

$$r \frac{\partial T}{\partial r} = \mathrm{const}$$

and so

$$\frac{\partial T}{\partial r} = \frac{\mathrm{const}}{r}.$$

Hence

$$T_2 - T_1 = \int_{r_1}^{r_2} \frac{\mathrm{const}\,\mathrm{d}r}{r} = \mathrm{const} \ln \frac{r_2}{r_1},$$

which fixes the value of the const. At $r = r_1$, we can write

$$J = -\kappa \frac{\partial T}{\partial r} = -\kappa \frac{\mathrm{const}}{r_1} = \frac{\kappa (T_1 - T_2)}{r_1 \ln(r_2/r_1)}.$$

Hence the heat flow per unit length, which is $2\pi r_1 J$ is given by

$$\frac{2\pi\kappa (T_1 - T_2)}{\ln(r_2/r_1)}.$$

10.9

$$\frac{\partial T}{\partial r} = \frac{\mathrm{const}}{r}$$

and so as before we can write

$$T_r - T = \mathrm{const} \ln \frac{r}{R},$$

where T_r is the temperature at the surface of the lagging. The value of the heat flow at the surface of the pipes is

$$J_R = -\kappa \frac{\mathrm{const}}{R},$$

while by Newton's law of cooling we must have, at the surface of the lagging,

$$J_r = h(T_r - T_a),$$

where T_a is the temperature of the ambient air. The heat flow per unit length, q/L, can therefore be written as

$$\frac{q}{L} = -\kappa \frac{\text{const}}{R} 2\pi R = -2\pi\kappa \text{const},$$

and also as

$$\frac{q}{L} = h(T_r - T_a)2\pi r.$$

Putting these equations together gives

$$\frac{q}{L} = 2\pi hr \left(T + \frac{q \ln(r/R)}{-2\pi\kappa L} - T_a \right),$$

and hence

$$\frac{q}{L} = \frac{2\pi(T - T_a)}{\frac{1}{hr} + \frac{1}{\kappa}\ln(r/R)},$$

as required. The denominator goes through a minimum (which can be found by differentiating by r) at $r = \kappa/h$. When r is smaller, lagging doesn't help. Since we are dealing with thin lagging, r is very close to R (and of course can't be smaller – you can't have negative lagging!); hence the condition is also a condition on R.

11.1 For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and hence U doesn't change.

$$\Delta W = \int_{V_1}^{V_2} (-p\,\mathrm{d}V = \int_{V_1}^{V_2} -\frac{RT_0\,\mathrm{d}V}{V} = -RT_0 \ln(V_2/V_1).$$

The work done by the gas is $RT_0 \ln(V_2/V_1)$.

The heat flow into the gas is $RT_0 \ln(V_2/V_1)$, since $\Delta U = 0$.

11.2 $R = C_V - C_p$ and hence

- dividing by C_V yields $R/C_V = \gamma - 1$;
- dividing by C_p yields $R/C_p = 1 - (1/\gamma)$.

11.3 If $f = x^2y + y^2$, then $\frac{\partial f}{\partial x} = 2xy$ and $\frac{\partial f}{\partial y} = x^2 + 2y$. It is an exact differential. Both methods of integration lead to

$$x_2^2 y_2 - y_1 x_1^2 + y_2^2 - y_1^2.$$

11.4 The problem here is that the question has been (deliberately) misleading about writing down which variables are held constant. One can think of x as a function of r and θ, i.e. $x = x(r,\theta)$, so from the equation

$$x = r\cos\theta,$$

it follows that

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

One can also think of $x = x(y,r)$ from the equation

$$x^2 = r^2 - y^2,$$

in which case

$$2x\left(\frac{\partial x}{\partial r}\right)_y = 2r \qquad \Longrightarrow \qquad \left(\frac{\partial x}{\partial r}\right)_y = \frac{r}{x}.$$

Hence what is actually true is that

$$\left(\frac{\partial x}{\partial r}\right)_\theta = \left(\frac{\partial r}{\partial x}\right)_y.$$

Moral of the story: Think carefully about what is being held constant in a partial derivative.

11.5 No. Work can be converted into heat. Heat can be partially converted into work. They are not the same thing.

12.1 Start with pV^γ is constant and then substitute in $pV \propto T$.

12.2 The first two equations come from straightforward differentiation and then the second two follow from the definitions $C_p = \left(\frac{\partial Q}{\partial T}\right)_p$ and $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$. In an adiabatic change $\mathrm{d}Q = 0$ and so one can write

$$\frac{\mathrm{d}p}{\mathrm{d}V} = -\left(\frac{\partial Q}{\partial V}\right)_p \left(\frac{\partial p}{\partial Q}\right)_V = -\frac{C_p p}{df/dT}\frac{df/dT}{VC_V} = -\frac{C_p p}{V_V V},$$

and hence

$$\frac{\mathrm{d}p}{p} = -\gamma \frac{\mathrm{d}V}{V},$$

and the result follows.

12.3 When T is constant, $\mathrm{d}T = 0$ and hence

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{B}{A}.$$

Now if $\text{đ}Q = 0$, the first two equations immediately yield

$$\begin{aligned} \mathrm{d}p &= -(C_p/A)\mathrm{d}T, \\ \mathrm{d}V &= -(C_V/B)\mathrm{d}T. \end{aligned}$$

Hence

$$\left(\frac{\partial p}{\partial V}\right)_{\text{adiabatic}} = \gamma \left(\frac{\partial p}{\partial V}\right)_T.$$

If p is constant, then we have $C_p - C_V = B\left(\frac{\partial V}{\partial T}\right)_p$ and hence use of $\mathrm{d}V = -(C_V/B)\mathrm{d}T$ yields

$$\left(\frac{\partial V}{\partial T}\right)_{\text{adiabatic}} = -\frac{C_V}{B} = \frac{1}{1-\gamma}\left(\frac{\partial V}{\partial T}\right)_p.$$

If V is constant, then we have $C_p - C_V = -A\left(\frac{\partial p}{\partial T}\right)_V$ and hence use of $\mathrm{d}p = -(C_p/A)\mathrm{d}T$ yields

$$\left(\frac{\partial p}{\partial T}\right)_{\text{adiabatic}} = -\frac{C_p}{A} = \frac{\gamma}{\gamma-1}\left(\frac{\partial p}{\partial T}\right)_V.$$

12.4 The adiabat has a steeper gradient by a factor of γ.

12.5 Do all calculations with one mole of gas without loss of generality.

(a) Cylinders thermally insulated so that $\text{đ}Q = 0$. Hence $C_V\mathrm{d}T = -p\mathrm{d}V = -(RT/V)\mathrm{d}V$ and hence $C_V \ln T = -R\ln V +$const, and hence $T_f = T_i/2^{2/3}$ where T_f is the final temperature.

(b) Initially have $pV = RT_i$ and finally have $p(V+v) = RT_f$ where v is the volume in A after you have pushed it as far as it will go. The work done on the gas is then $p(V-v) = C_V(T_f - T_i)$ where the last equality follows from $\text{đ}Q = 0$. These can be solved to give $T_f = 7T_i/5$.

12.6 The change is adiabatic, so that

$$\frac{\mathrm{d}p}{p} = -\gamma \frac{\mathrm{d}V}{V}. \tag{1}$$

If the ball moves up a distance x, then $\mathrm{d}V = A\mathrm{d}x$ and the extra force on the ball is $A\mathrm{d}p = m\ddot{x}$ and so

$$m\ddot{x} + kx = 0,$$

where

$$k = \frac{A^2 p\gamma}{V}$$

and hence simple harmonic oscillation results with

$$\omega^2 = \frac{A^2 p\gamma}{mV},$$

and the period $\tau = 2\pi/\omega$ results.

In Rinkel's modification, one equates gravitational PE with "spring" energy, so that

$$mgL = \frac{1}{2}k(L/2)^2 = \frac{\gamma p A^2 L^2}{8V}.$$

(Note that in this case the amplitude of the oscillation is L, which is from $-L/2$ to $L/2$, so the stored "spring" energy is $\frac{1}{2}k(L/2)^2$.)

13.1 No: consider the definition of efficiency for a heat pump.

13.2 $\eta = 1 - 273/373 = 0.27$.

13.3 Law I, Law II respectively.

13.4 Label the points A: (p_1, V_1, T_A), B: (p_1, V_2, T_B) and C: (p_2, V_2, T_C). The heat out on the isobar AB is $Q_1 = C_p(T_A - T_B) = \gamma C_V(T_A - T_B)$ as you cool, while the heat in on the isochore BC is $Q_2 = C_V(T_C - T_B)$, and no heat is transferred on the adiabat CA. Hence using $PV \propto T$, the efficiency is $\eta = W/Q_2 = 1 - Q_1/Q_2 = 1 - \gamma(T_A - T_B)/(T_C - T_B) = 1 - \gamma(p_1V_1 - p_1V_2)/(p_2V_2 - p_1V_2)$ which gives the final result.

13.5 $Q_1 = C_V(T_3 - T_2)$ and $Q_2 = C_V(T_4 - T_1)$ and pV^γ is constant on an adiabat (in this case it's better to use $TV^{\gamma-1}$ is constant). $\eta = 1 - Q_2/Q_1$. The result follows after some algebra.

13.6 In steady state $Q = Q_2$.

The 1st law implies $E + Q_2 = Q_1$.

Carnot implies: $Q_1/T_1 = Q_2/T_2$.

Eliminate Q, Q_1 and Q_2 from these equations, for example by putting the third one into the second one and yielding

$$E + Q_2 = Q_2 T_1/T_2$$

which you can use to show that

$$E = A(T_1 - T_2)(T_1/T_2 - 1) = \frac{A}{T_2}(T_1 - T_2)^2$$

This can be expanded to give a quadratic in T_2:

$$T_2^2 - (2T_1 + E/A)T_2 + T_1^2 = 0$$

which has solutions

$$T_2 = T_1 + \frac{E}{2A} \pm \sqrt{\left(\frac{E}{2A}\right)^2 + \frac{ET_1}{A}}.$$

Thus for 30% of $E_{\max}$ you need

$$0.3E_{\max} = \frac{A}{293}10^2$$

and for 100% of $E_{\max}$ you need

$$E_{\max} = \frac{A}{293}(\Delta T)^2$$

so that $T_1 = 20^\circ + \Delta T = 38.3^\circ$C.

13.7 The energy available from body 1 is $C_p(T_1 - T_f)$. The energy available from body 2 is $C_p(T_2 - T_f)$. Hence $W = C_p\,(T_1 + T_2 - 2T_f)$.

The most efficient engine is reversible and so using the Clausius theorem, the integral round a closed loop of $\text{đ}Q/T$ is zero, and hence $\int_{T_1}^{T_f} C_p \mathrm{d}T/T + \int_{T_2}^{T_f} C_p \mathrm{d}T/T = 0$ and the result follows. (This result can equivalently be derived by stating $\Delta S = 0$, using the entropy S defined in the following chapter.)

13.8 In the steady state $\alpha(T - T_0)$ is balanced by the heat power coming from the heat pump, call it $Q_2 = W + Q_1$ where Q_1 is the heat power extracted from the river. The efficiency

$$\eta = \frac{Q_2}{W} = \frac{T}{T - T_0},$$

so rearranging gives

$$\alpha(T - T_0) = \frac{TW}{T - T_0}$$

and hence $TW = \alpha(T - T_0)^2$ which is a quadratic in T. Easiest perhaps to solve for $t = T - T_0$ so that $t^2 - tW/\alpha - T_0W/\alpha = 0$ and the result follows (use the positive root of the quadratic or you have a cooling effect and in this country we tend to think of needing to keep our houses warmed not cooled).

13.9 To save writing lots of zeros, I will measure temperature in units of 100 K. In these units we have temperatures as follows:

initially: 3, 3, 1

finally: T_1, T_1, T_2

Energy conservation implies that $2T_1 + T_2 = 7$.

Connecting them with reversible heat engines implies that $2 \ln T_1 + \ln T_2 = 2 \ln 3 + \ln 1$ and so $T_1^2 T_2 = 9$. Putting this altogether gives a cubic $T_1^3 - \frac{7}{2}T_1^2 + \frac{9}{2} = 0$.

This could be nasty to solve, except that a solution must be $T_1 = 3$ (when you connect up the reversible engines but run them for zero time!) so therefore you know one root. Hence $(T_1 - 3)(T_1^2 + \alpha T_1 + \beta) = 0$ and equating coefficients you can deduce α and β and arrive at $(T_1 - 3)(T_1 - \frac{3}{2})(T_1 + 1) = 0$ so the other positive root is $T_1 = \frac{3}{2}$ (or 150 K in proper units) and hence $T_2 = 4$ (or 400 K in proper units).

13.10

$$\tau_{\text{diffuse}} \propto L^2$$

$$\tau_{\text{mechanical}} \propto L$$

For big engines $\tau_{\text{diffuse}} \gg \tau_{\text{mechanical}}$, and heat engines work as expected. Thermal gradients persist (they do not diffuse away) and mechanical work can be extracted from them.

For small engines $\tau_{\text{diffuse}} \ll \tau_{\text{mechanical}}$, and thermal gradients diffuse away before you can exploit them.

14.1 $\Delta S = -\int_{291}^{363} \frac{C\mathrm{d}T}{T} = -C\ln(363/291) = -185.7$ J K^{-1}. It is negative but the entropy in the surroundings changes by $C(363-291)/291 = +207.8$ J K^{-1} which is positive and larger. Hence the entropy of the Universe goes up.

14.2 Yes: see the box on page 142.

14.3 (a) $\Delta S = 0$ because T is constant.

(b) $I^2Rt = 3\times 10^4$ J flows into the environment. Hence $\Delta S = 3\times 10^4/300 = 100$ J K^{-1}.

14.4 (a) $\Delta S_{\text{bath}} = C\ln 353/293 = 1.9\,\mathrm{kJ\,K^{-1}}$.

(b) $\Delta S_{\text{res}} = C(293-353)/353 = -1.7\,\mathrm{kJ\,K^{-1}}$.

(c) Zero, because reversible.

14.5 (a) $\Delta S_{\text{total}} = -\int_{100}^{200} C_V\mathrm{d}T/T + \int_{100}^{200} C_V\mathrm{d}T/100 = -C_V\ln 2 + C_V = C_V(1-\ln 2) = 0.307$ J K^{-1}.

(b) $\Delta S_{\text{total}} = -\int_{100}^{200} C_V\mathrm{d}T/T + \int_{150}^{200} C_V\mathrm{d}T/150 + \int_{100}^{150} C_V\mathrm{d}T/100 = -C_V\ln 2 + C_V(1/3+1/2) = 0.14$ J K^{-1}.

Last bit:

$\Delta S_{\text{total}} = -\int_{100}^{200} C_V\mathrm{d}T/T + \left(\int_{200-\delta}^{200} C_V\mathrm{d}T/(200-\delta) + \int_{200-2\delta}^{200-\delta} C_V\mathrm{d}T/(200-2\delta) + \cdots\right) = 0.$

14.6 (a) $\Delta S_{\text{Universe}} = \frac{1}{2}CV^2/273 = 18.3$ μJ K^{-1} because QV work is done by the battery and only $\frac{1}{2}QV = \frac{1}{2}CV^2$ is stored in the capacitor, so that $\frac{1}{2}QV = \frac{1}{2}CV^2$ is heat in the battery.

(b) $\Delta S_{\text{Universe}} = \frac{1}{2}CV^2/273 = 18.3$ μJ K^{-1} again because now the stored energy in the capacitor becomes heat in the resistor.

(c) $\mathrm{d}U = 0$ so $\text{đ}W = -RT\ln 2 = -\text{đ}Q$. Hence $\Delta S_{\text{gas}} = R\ln 2$, but $\Delta S_{\text{surroundings}} = -R\ln 2$ so $\Delta S_{\text{universe}} = 0$.

(Or quicker, reversible implies $\Delta S_{\text{universe}} = 0$.)

(d) $\mathrm{d}Q = 0$ so $\Delta S_{\text{gas}} = \Delta S_{\text{surroundings}} = 0$ so $\Delta S_{\text{universe}} = 0$.

(Or quicker, reversible implies $\Delta S_{\text{universe}} = 0$.)

(e) Joule expansion, $\Delta S_{\text{gas}} = R\ln 2$, $\Delta S_{\text{surroundings}} = 0$, so $\Delta S_{\text{universe}} = R\ln 2 = 5.76\,\mathrm{J\,K^{-1}}$.

14.7 (a) $\mathrm{d}U = 0$ because $\mathrm{d}T = 0$ and hence $TdS = pdV$. Hence

$$\Delta S = \int_V^{\alpha V} \frac{p\mathrm{d}V}{T} = nR\int_V^{\alpha V} \frac{\mathrm{d}V}{V} = nR\ln\alpha.$$

(b) S is a function of state, hence it does not depend on which route:

$$\Delta S = nR\ln\alpha.$$

For the van der Waals gas [and on reflection, this part of the question may be a bit too hard for a student at this stage without reading ahead!],

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V.$$

Since $\mathrm{d}T = 0$, we only need to worry about the second term, and in fact we can write this as

$$\mathrm{d}S = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V.$$

Hence

$$\Delta S = \int_V^{\alpha V} \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V = \int_V^{\alpha V} \frac{nR\mathrm{d}V}{V-nb} = nR\ln\left(\frac{\alpha V - nb}{V-nb}\right).$$

In case (b), the temperature changes by

$$\Delta T = -\frac{1}{C_V}\int_V^{\alpha V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] = -\frac{an^2}{C_V V}\left(\frac{\alpha-1}{\alpha}\right).$$

14.8 $S/k_{\mathrm{B}} = -\sum_i P_i \ln P_i = -\sum_i P_i(-\beta E_i - \ln Z) = \ln Z + \beta U$.

14.9 $S/k_{\mathrm{B}} = -\sum_i P_i \ln P_i$. With N molecules and probability $p_2 = x$ that a molecule is type 1 and probability $P_2 = 1 - x$ that it is type 2, we have that

$$S/Nk_{\mathrm{B}} = -x \ln x - (1-x)\ln(1-x).$$

15.1 $C = 5\times10^{-15}$ F and $V = 3$V gives $\frac{1}{2}CV^2 = 1.4\times10^5$ eV which is *much* larger than $k_{\rm B}T\ln 2 \approx 0.02\,$eV.

15.2 (a) $S = -\sum_i P_i \log_2 P_i = -\frac{1}{4}\log_2\frac{1}{4}\frac{1}{4}\log_2\frac{1}{4} - \frac{1}{4}\log_2\frac{1}{4} - \frac{1}{4}\log_2\frac{1}{4} = \log_2 4 = 2$ bits.

(b) $S = -\sum_i P_i \log_2 P_i = -\frac{1}{4}\log_2\frac{1}{4}\frac{1}{4}\log_2\frac{1}{4} - \frac{1}{2}\log_2\frac{1}{2} = \frac{3}{2}$ bits. Information has been lost. The gate is not reversible.

15.3 Set $k = 1$ and use Lagrange multipliers.

$$S = -\sum_i P_i \ln P_i - \alpha\sum_i P_i - \beta\sum_i P_i f(x_i)$$

and differentiate with respect to P_j, yielding

$$-\ln P_j - 1 - \alpha - \beta f(x_j) = 0$$

and hence

$$P_j = \mathrm{e}^{-1-\alpha}\mathrm{e}^{-\beta f(x_j)}.$$

The first exponential can be got rid off by using the constraint that $\sum P_i = 1$ and writing the answer as

$$P_j = \frac{1}{Z(\beta)}\mathrm{e}^{-\beta f(x_j)}$$

with $Z(\beta)$ as defined in the question. The final result follows straightforwardly from

$$\langle f(x_j)\rangle = \sum_j f(x_j)P_j.$$

15.4 Straightforward argument.

15.5 (a)

$$-S(P||Q) = -\sum_i P_i \log\frac{P_i}{Q_i} = \sum_i P_i \log\frac{Q_i}{P_i} \le \sum_i P_i(Q_i/P_i - 1),$$

using the fact that $\log x \le x - 1$. Hence

$$-S(P||Q) \le \sum_i P_i(Q_i/P_i - 1) = \sum_i Q_i - P_i = \sum_i Q_i - \sum_i P_i = 0.$$

(b) Eqn 15.20 implies that

$$S(P||Q) = -S_P - \sum_i P_i \log(1/N) = -S_P - \log(1/N)\sum_i P_i = -S_p + \log N.$$

Since $S(P||Q) \ge 0$, then $S_P \le \log N$.

15.6 This is the “Monty Hall problem” and is a deceptively hard question. Many people think that it doesn’t make any difference, but *it does.* She should swap.

The easiest way of seeing this is to say, for the sake of argument, that the contestant chooses door number one. Then there are three possibilities:

- The car is behind door number one: the host will open door number two or three to reveal a goat. In this case, swapping is the wrong thing to do and will lead to LOSING the car.
- The car is behind door number two: the host will open door number three to reveal a goat. In this case, swapping is the right thing to do and will lead to WINNING the car.
- The car is behind door number three: the host will open door number two to reveal a goat. In this case, swapping is the right thing to do and will lead to WINNING the car.

The probability that she picked the right door first time was 1/3. With the additional information given, the probability that the car is behind the other, unopened door, is now 2/3.

[If a student doesn’t get this, try the following variant of the problem: you have 100 doors, 99 of which conceal a goat and only one the car. The contestant makes a choice, and the game show host opens 98 of the other doors to reveal a goat behind which. Now the car can either be behind the door the contestant chose or the other non-opened door. It’s now pretty obvious that the contestant should switch.]

16.1 Bookwork: $H = U + PV$, $F = U - TS$, $G = H - TS$ and so

$$\begin{aligned}
\mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V \\
\mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}p \\
\mathrm{d}F &= -S\mathrm{d}T - p\mathrm{d}V \\
\mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p
\end{aligned}$$

and

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\
\left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\
\left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p
\end{aligned}$$

16.2 (a) (i) $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T = -(1/C_V)[T\left(\frac{\partial S}{\partial V}\right)_T - p]$ and use $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.

(ii) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T$ and use $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.

(iii) $\left(\frac{\partial T}{\partial V}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T = (1/C_p)[T\left(\frac{\partial S}{\partial p}\right)_T + V]$ and use $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$.

(i) Joule expansion; (ii) adiabatic expansion; (iii) Joule-Kelvin expansion.

(b) use $pV = nRT$ and substitute in. The adiabatic expansion leads to $\left(\frac{\partial T}{\partial V}\right)_S = -p/C_V$ so that $\mathrm{d}T = -nRT\mathrm{d}V/(VC_V)$ and the result follows from integrating. (Remember $C_V/n = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$.)

16.3 $\mathrm{d}U = \text{đ}W + \text{đ}Q = -p\mathrm{d}V + \text{đ}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$. and so rearranging gives

$$\text{đ}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\mathrm{d}V$$

We therefore can write

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

and use

$$\beta_p = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p \quad \text{and} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

and the result follows.

16.4 (a) $U = U(S, V)$ and so $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ and hence

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_S.$$

(b) If $U = U(T, V)$, then

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p,$$

and so

$$\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial (P/T)}{\partial T}\right)_V,$$

and integrating yields

$$\frac{p}{T} = \int \left(\frac{\partial U}{\partial V}\right)_T \frac{\mathrm{d}T}{T^2} + f(V),$$

where $f(V)$ is an unknown function of V.

16.5 This follows from the previous question. If $U = U(T, V)$, then we can write

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p,$$

and the result follows.

16.6 Eqn 16.82 gives us $S = C_V \ln T + R\ln V + \text{constant}$. Using $pV = RT$ for one mole and $C_p = C_V + R$ yields the result.

16.7 Eqn 16.82 gives us $S = C_V \ln T + R\ln V + \text{constant}$. Using $pV = RT$ for one mole gives

$$S = C_V \ln(pV) + R\ln V + \text{constant}$$

and hence

$$S = C_V \ln(pV^{1+R/C_V}) + \text{constant}$$

which implies

$$S = C_V \ln(pV^{\gamma}) + \text{constant}.$$

Now $\rho = M/V$ where M is the total mass, so $\ln\rho = -\ln V + \text{constant}$ and hence the result follows. Note the constants in these equations are not all the same.

17.1

$$\left(\frac{\partial C_L}{\partial L}\right)_T = \frac{\partial}{\partial L}\left[T\left(\frac{\partial S}{\partial T}\right)_L\right]_T = T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial L}\right)_T = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_L,$$

where the last step has ysed a Maxwell relation.

17.2

$$\left(\frac{\partial T}{\partial L}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_L\left(\frac{\partial S}{\partial L}\right)_T = -\frac{TAE_T\alpha_f}{C_L}$$

where we have used $C_L = T\left(\frac{\partial S}{\partial T}\right)_L$ and $\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L$ and eqn 17.5.

17.3 The first two bits are essentially obvious. You can use them to write down $N_\pm = \frac{N}{2}(1 \pm \frac{L}{Na})$. Then use Stirling's approximation to get

$$\ln N! = N\ln N - N$$

and

$$\ln N_\pm! = \frac{N}{2}(1 \pm \frac{L}{Na})[\ln\frac{N}{2} + \ln(1 \pm \frac{N}{La})] - \frac{N}{2}(1 \pm \frac{L}{Na}).$$

Using $\ln(1 \pm x) \approx \pm x - \frac{x^2}{2} + \cdots$, you have

$$\ln\Omega = \ln N! - \ln N_+! - \ln N_-! = N\ln 2 - \frac{NL^2}{2N^2a^2} + \cdots$$

[You miss the factor of two in the last term if you don't expand $\ln(1+x)$ up to x^2.]

17.4 If $S = S(A, T)$, then

$$\mathrm{d}S = \left(\frac{\partial S}{\partial A}\right)_T \mathrm{d}A + \left(\frac{\partial S}{\partial T}\right)_A \mathrm{d}T = -\left(\frac{\partial \gamma}{\partial T}\right)_A \mathrm{d}A + \frac{C_A}{T}\,\mathrm{d}T,$$

using 17.22. Eqn 17.20 implies that $\mathrm{d}U = T\,\mathrm{d}S + \gamma\mathrm{d}A$ and the result follows.

17.5 The number of molecules per unit volume is $N_A\rho/M$, so at a surface you expect the number per unit area to go as the 2/3 power of this. Putting in the numbers yields 0.043 eV per molecule, which is less than 0.45 eV per molecule which is what the latent heat works out as.

17.6 First some thermodynamic potentials:

$\mathrm{d}U = T\mathrm{d}S + f\mathrm{d}L$ and $\left(\frac{\partial f}{\partial T}\right)_L = \xi(L)$ where $\xi(L)$ is a function only of L. Also $f = \xi(L)T$ (because of the proportionality).

$\mathrm{d}F = -S\mathrm{d}T + f\mathrm{d}L$ and therefore $\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L = -\xi(L)$.

$\mathrm{d}G = -S\mathrm{d}T - L\mathrm{d}f$ and therefore $\left(\frac{\partial L}{\partial T}\right)_f = \left(\frac{\partial S}{\partial f}\right)_T$.

Hence

(i) $\left(\frac{\partial U}{\partial L}\right)_T = f + T\left(\frac{\partial S}{\partial L}\right)_T = 0$.

(ii) adiabatic, so $\mathrm{đ}Q = 0$ and $\mathrm{d}U = C_L\mathrm{d}T = f\mathrm{d}L$.

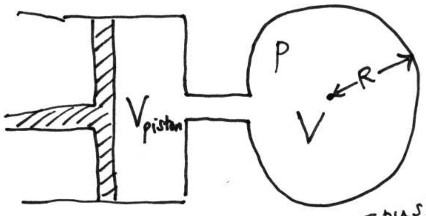
Since f, $\mathrm{d}L$, and C_L are all positive, $\mathrm{d}T > 0$.

(iii) $\left(\frac{\partial L}{\partial T}\right)_f = \left(\frac{\partial S}{\partial f}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_f\left(\frac{\partial T}{\partial f}\right)_S$.

Now $\left(\frac{\partial S}{\partial T}\right)_f = C_f/T > 0$; also $\left(\frac{\partial T}{\partial f}\right)_S > 0$ (from (ii)). Hence $\left(\frac{\partial L}{\partial T}\right)_f < 0$ and you get contraction with warming.

Maybe a better route is to say: $\left(\frac{\partial L}{\partial T}\right)_f = -\left(\frac{\partial L}{\partial f}\right)_T\left(\frac{\partial f}{\partial T}\right)_L < 0$ since $\left(\frac{\partial L}{\partial f}\right)_T > 0$ because of elasticity and $\left(\frac{\partial f}{\partial T}\right)_L = \xi(L) > 0$.

17.7



Same amount of gas

$$\Rightarrow p(V_{\text{piston}} + V) = p_2 V_2$$

push piston fully home

$$\Delta W = \underbrace{\int_{V_1 + V_{\text{piston}}}^{V_2} p \, dV_{\text{total}}}_{p_2 V_2 \ln \frac{p_2}{p_1}} + \underbrace{\int_S \gamma \, dA}_{\underset{\text{2 surfaces}}{8\pi\gamma (R_2^2 - R_1^2)}}$$

plus, add the work done against the atmosphere

$$p_0 \left[V_2 - V_1 - V_{\text{piston}} \right]$$

18.1 This is just a reading comprehension from the chapter.

18.2 Eqn 16.26 implies that

$$G - H = T \left(\frac{\partial G}{\partial T} \right)_p , \tag{1}$$

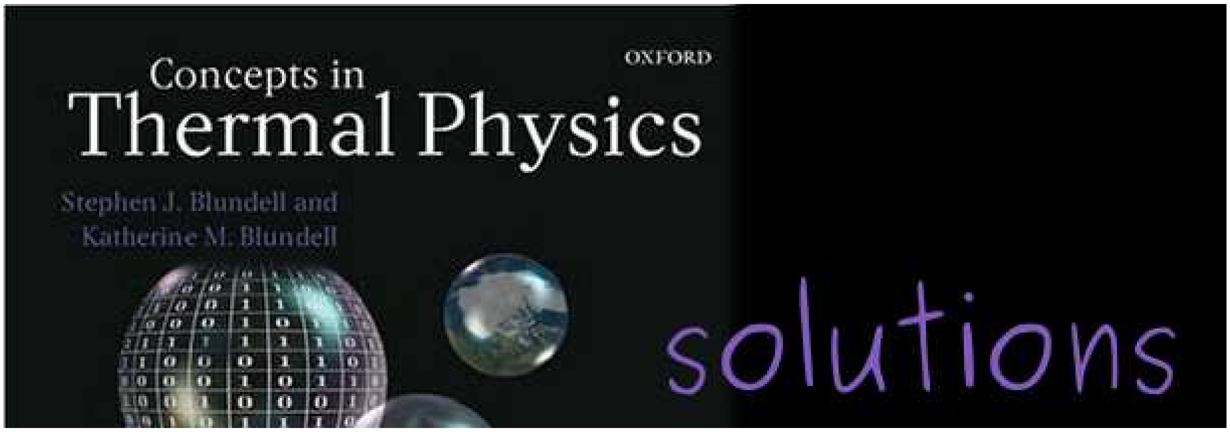
and so

$$\Delta G - \Delta H = T \left(\frac{\partial \Delta G}{\partial T} \right)_p , \tag{2}$$

and using $\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T$, we can write this as

$$\Delta G - \Delta H = -T \Delta S. \tag{3}$$

As $T \to 0$, $\Delta S \to 0$ and so the right-hand side definitely goes to zero, so the left-hand side must as well.



SECOND EDITION

The authors' solutions are included. These should **not** be distributed to students or issued in public, but are for the use of instructors only. Comments or corrections would be gratefully received.

Stephen Blundell and Katherine Blundell, August 11, 2009

`Email: s.blundell@physics.ox.ac.uk`
`Webpage: http://users.ox.ac.uk/~sjb`

`Email: k.blundell@physics.ox.ac.uk`
`Webpage: http://www-astro.physics.ox.ac.uk/~kmb/`

Solutions to Part VII–IX

19.1 A trick question. The mean kinetic energy is the same for each case, $\frac{3}{2}k_{\mathrm{B}}T = 38\,\mathrm{meV}$.

19.2 $C_p = C_V + R$ and $C_p = \frac{5}{2}R = 20.785$ (for a gas with only translational modes excited or a monatomic gas; i.e. Ar, He, Ne, Xe), $C_p = \frac{7}{2}R = 29.099$ (for a gas with translational and rotational modes excited; $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$), and $C_p = 3R = 24.94$ (for solids, such as Al, Au, Cu, Fe, Pb, Ag and Zn).

19.3 Taking the well as a one-dimensional problem, $dV/dr = 0$ gives a minimum at $r_0^{n-1} = nA/B$ and one can Taylor expand around the bottom of this well to show that $V = V_0 + \alpha(r - r_0)^2$ where α is a constant. The particle can execute simple harmonic motion around the bottom of this well, giving two degrees of freedom (one kinetic, one potential), and so the mean thermal energy is $2 \times \frac{1}{2}k_{\mathrm{B}}T = k_{\mathrm{B}}T$.

19.4

$$\langle x_i^2 \rangle = \frac{\int_{-\infty}^{\infty} x_i^2 \mathrm{e}^{-\beta\alpha_i x_i^2}\,\mathrm{d}x_i}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta\alpha_i x_i^2}\,\mathrm{d}x_i = \frac{1}{2\alpha_i\beta}} = \frac{k_{\mathrm{B}}T}{2\alpha_i}.$$

19.5 Writing $E = \alpha|x|$, we have $\mathrm{d}E = \alpha\,\mathrm{d}x$ and $\mathrm{d}x = \alpha^{-1}\,\mathrm{d}E$. Hence

$$\langle E \rangle = \frac{\int_0^{\infty} E\mathrm{e}^{-\beta E}\,\mathrm{d}x}{\int_0^{\infty} \mathrm{e}^{-\beta E}\,\mathrm{d}x} = \frac{\int_0^{\infty} E\,\mathrm{e}^{-\beta E}\,\mathrm{d}E}{\int_0^{\infty} \mathrm{e}^{-\beta E}\,\mathrm{d}E} = k_{\mathrm{B}}T.$$

19.6 Writing $E = \alpha|x|^n$, we have $\mathrm{d}E = n\alpha|x|^{n-1}\,\mathrm{d}x = \frac{nE}{|x|}\,\mathrm{d}x$ and $\mathrm{d}x = \kappa E^{\frac{1}{n}-1}\,\mathrm{d}E$ where κ is a constant. Hence

$$\langle E \rangle = \frac{\int_0^{\infty} E\mathrm{e}^{-\beta E}\,\mathrm{d}x}{\int_0^{\infty} \mathrm{e}^{-\beta E}\,\mathrm{d}x} = \frac{\int_0^{\infty} E^{\frac{1}{n}}\mathrm{e}^{-\beta E}\,\mathrm{d}E}{\int_0^{\infty} E^{\frac{1}{n}-1}\mathrm{e}^{-\beta E}\,\mathrm{d}E} = k_{\mathrm{B}}T\frac{\Gamma(1+\frac{1}{n})}{\Gamma(\frac{1}{n})} = \frac{k_{\mathrm{B}}T}{n}.$$

Note, if $n = 1$ then the answer is

$$k_{\mathrm{B}}T,$$

in agreement with the previous question. If $n = 2$ then the answer is

$$\frac{k_{\mathrm{B}}T}{2},$$

in agreement with the equipartition theorem.

19.7 $\ddot{\theta} + (g/\ell)\sin\theta = 0$ and so if $\theta \ll 1$, then we have

$$\ddot{\theta} + \omega^2\theta = 0,$$

where $\omega^2 = g/\ell$ so that the period is $T = 2\pi/\omega = 2\pi\sqrt{\ell/g}$. If the angle θ deviates from zero, the potential energy increases by

$$\ell(1 - \cos\theta) \approx \ell\theta^2/2,$$

when $\theta \ll 1$. Hence the mean P.E. (using equipartition) is

$$\langle mg\ell\theta^2/2 \rangle = \frac{1}{2}k_{\mathrm{B}}T$$

and hence

$$\langle \theta^2 \rangle = \frac{k_{\mathrm{B}}T}{mg\ell}.$$

$\boxed{20.1}$ SHO $Z = \dfrac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$ $\quad \beta \to 0 \Rightarrow e^{-\beta\hbar\omega} \to 1 - \beta\hbar\omega$

$\Rightarrow Z \to 1/\beta\hbar\omega$

$$U = -\frac{d\ln Z}{d\beta} = -\beta\hbar\omega\left(\frac{-1}{\beta^2\hbar\omega}\right) = \frac{1}{\beta} \quad \Rightarrow \quad C = k_B$$

$$F = -k_B T \ln Z = k_B T \ln(\hbar\omega/k_B T)$$

$$S = -(\partial F/\partial T)_V = -k_B \ln(\hbar\omega/k_B T) - k_B T \cdot \frac{k_B T}{\hbar\omega} \cdot \frac{\hbar\omega}{k_B}\left(-\frac{1}{T^2}\right)$$

$$= k_B\left[\ln(k_B T/\hbar\omega) + 1\right]$$

Rotational levels analogous with $\hbar\omega \to \hbar^2/2I$

$\boxed{20.2}$ eqn 20.11 $\Rightarrow \ln P_j = -\beta E_j - \ln Z$

eqn 20.14 $\Rightarrow F = -k_B T \ln Z \Rightarrow -\ln Z = \beta F \Rightarrow$ result.

$\boxed{20.3}$ eqn 20.29 is $U = \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right] = \frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega}+1}{e^{\beta\hbar\omega}-1}\right]$

$$= \frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}\right] = \text{result.}$$

$$\frac{\beta\hbar\omega}{2}\coth\frac{\beta\hbar\omega}{2} = \frac{\hbar\omega}{2} + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$-\ln(1-e^{-\beta\hbar\omega}) = -\ln\left[\frac{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}}\right] = \frac{\beta\hbar\omega}{2} - \ln\left[2\sinh\frac{\beta\hbar\omega}{2}\right]$$

$\Rightarrow$ result.

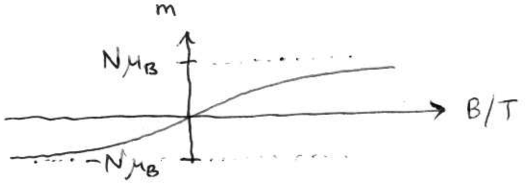
$\boxed{20.4}$ Apparent from eqns 20.29 – 20.32, and exactly as you would expect

$\boxed{20.5}$ (a) $Z = e^{\beta\mu_B B} + e^{-\beta\mu_B B} = 2\,\underline{\underline{\cosh}}\,(\beta\mu_B B)$

(b) $F = -k_B T \ln Z_N = -N k_B T \ln\left[2\cosh(\beta\mu_B B)\right]$

(c) $m = -(\partial F/\partial B)_T = N k_B T \dfrac{\sinh(\beta\mu_B B)}{\cosh(\beta\mu_B B)} \cdot \beta\mu_B B$

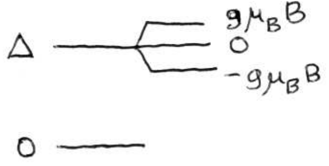
$$= N\mu_B \tanh(\beta\mu_B B)$$



(d) $\tanh x \approx x$ for $x \ll 1 \Rightarrow m \approx N\mu_B^2 B/k_B T$

(e) $\chi \approx \dfrac{\mu_0 M}{B} = \mu_0 \dfrac{N}{V}\dfrac{\mu_B^2}{k_B T} \propto \dfrac{1}{T}$ (Curie's law)

$\boxed{20.6}$



4 energy levels.

$$Z = 1 + e^{-\beta\Delta}\left(1 + 2\cosh(g\mu_B B\beta)\right)$$

$$F = -N k_B T \ln Z$$

$$m = -\left(\frac{\partial F}{\partial B}\right)_T = N \cancel{k_B T}\ \frac{2e^{-\beta\Delta}\sinh(g\mu_B B\beta)\cdot \cancel{\beta} g\mu_B}{1 + e^{-\beta\Delta}(1 + 2\cosh g\mu_B B\beta)}$$

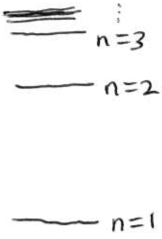
and in the limit as $B \to 0$,

$$m \to \frac{2N(g\mu_B)^2 B\beta\, e^{-\beta\Delta}}{1 + 3e^{-\beta\Delta}} = \frac{2N(g\mu_B)^2 B}{k_B T\,(3 + e^{\beta\Delta})}$$

So $M = \frac{m}{V}$, $\chi = \frac{\mu_0 M}{B}$ yields $\chi = \frac{2n\mu_0 (g\mu_B)^2}{k_B T\,(3 + e^{\beta\Delta})}$.

$\boxed{20.7}$ Simple harmonic oscillators independent $\Rightarrow$ Z multiply $\Rightarrow$ $\ln Z$ adds $\Rightarrow$ eqn 20.51 $=$ 3 × (eqn 20.31) and $C = 3k_B$ at high T.

$\boxed{20.8}$ (a)



the usual Rydberg series.

$$E = -\frac{R}{n^2}, \quad \text{degeneracy } 2n^2$$

$$\Rightarrow Z = \sum_{n=1}^{\infty} 2n^2 e^{\beta R/n^2}.$$

(b) Keeping only the lowest two terms, $Z = 2e^{\beta R} + 8e^{\beta R/4}$

$$\left.\begin{array}{l} R = 13.6\,\text{eV} \\ k_B T = 0.0259\,\text{eV} \end{array}\right\} \Rightarrow \beta R = 525.6 \gg 1$$

$\therefore$ only ground state occupied.

In fact, $$U = -\frac{d\ln Z}{d\beta} = -R\left(\frac{e^{\beta R} + e^{\beta R/4}}{e^{\beta R} + 4e^{\beta R/4}}\right)$$

$$\approx -R\,(1 - \underbrace{3e^{-3\beta R/4}}_{\approx 2\times 10^{-171}})$$

$\Rightarrow$ mean energy $\approx -R$.

$\boxed{20.9}$

$$TS = -m.B + F$$

fix T

$$T\delta S = -m.\delta B - B.\delta m + \left(\frac{\partial F}{\partial B}\right)_T \delta B$$

now $dF = -S\,dT - m.\delta B \Rightarrow m = -\left(\frac{\partial F}{\partial B}\right)_T$

$$\Rightarrow \underline{T\delta S = -B.\delta m}$$

$$U = -m.B$$

$$\Rightarrow \delta U = -m.\delta B - B.\delta m = T\delta S - m.\delta B$$

21.1

$$g(k)\,dk = \frac{2\pi k\,dk}{(2\pi/L)^2} \times \underset{\text{spinless}}{1} = \frac{A\,k\,dk}{2\pi}$$

$$Z_1 = \int_0^\infty e^{-\beta\hbar^2k^2/2m} \cdot \frac{A\,k\,dk}{2\pi}$$

$$y = \beta\hbar^2k^2/2m$$
$$dy = \frac{\beta\hbar^2}{m}\,k\,dk$$

$$= \frac{A}{2\pi}\cdot\frac{m}{\beta\hbar^2}\underbrace{\int_0^\infty e^{-y}\,dy}_{0!=1}$$

$$= A\cdot\frac{2\pi m k_B T}{h^2} = \frac{A}{\lambda_{th}^2}$$

21.2

Sackur Tetrode $\quad S = Nk_B \ln\left[e^{5/2}/n\lambda_{th}^3\right] = Nk_B\left[\frac{5}{2} - \ln(n\lambda_{th}^3)\right]$

extensive $\because$ halve system size $N \to \frac{N}{2}$, $V \to \frac{V}{2}$, $n \to n$

$\Rightarrow S \to \frac{S}{2}$.

For distinguishable particles, $Z = Z_1^N$ not $Z = Z_1^N/N!$,

$\Rightarrow \ln Z$ is larger by $\ln N! = N\ln N - N$

$\Rightarrow F = -k_BT\ln Z$ has an extra term $-k_BT(N\ln N - N)$

and $S = -(\partial F/\partial T)_V$ has an extra $Nk_B[\ln N - 1]$

$\Rightarrow S = S_{\text{Sackur-Tetrode}} + Nk_B[\ln N - 1] = Nk_B\left[\frac{3}{2} - \ln(\lambda_{th}^3/V)\right]$

now if $N \to \frac{N}{2}$, $V \to \frac{V}{2}$, $S \to \frac{Nk_B}{2}\left[\frac{3}{2} - \ln(2\lambda_{th}^3/V)\right]$

$\to \frac{Nk_B}{2}\left[S_{\text{initial}} - \ln 2\right]$

$\Rightarrow$ not extensive.

21.3

$\#$ states below $E_{max} = \frac{\hbar^2 k_{max}^2}{2m}$ is $\int_0^{k_{max}} g(k)\,dk$

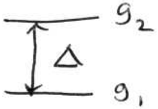
$$= \int_0^{\sqrt{\frac{2m}{\hbar^2}E_{max}}} \frac{Vk^2\,dk}{2\pi^2} = \frac{V}{2\pi^2}\left[\frac{k_{max}^3}{3}\right] = \frac{V}{6\pi^2}\left(\frac{2m}{\hbar^2}E_{max}\right)^{3/2}$$

If $E_{max} = \frac{3}{2}k_BT$, $\quad \#$ states $= \frac{V}{6\pi^2}3^{3/2} \quad \frac{(k_BT)^{3/2}m^{3/2}(2\pi)^{3/2}}{h^3}\cdot(2\pi)^{3/2}$

$$= \frac{\cancel{3}\sqrt{3}}{\cancel{6}\pi^{\cancel{2}}}\cdot\cancel{2\pi}\cdot\sqrt{\pi}\sqrt{2}\;Vn_Q$$

$$= \sqrt{\frac{6}{\pi}}\,Vn_Q\,.$$

$\boxed{21.4}$ $$Z = \sum e^{-\beta E} = g_1 + g_2 e^{-\beta\Delta}$$



$$U = -\frac{d\ln Z}{d\beta} = -\frac{-\Delta g_2 e^{-\beta\Delta}}{g_1+g_2 e^{-\beta\Delta}} = \frac{\Delta g_2 e^{-\beta\Delta}}{g_1+g_2 e^{-\beta\Delta}}$$

$$C = \frac{dU}{dT} = \Delta g_2 \frac{(g_1+g_2 e^{-\beta\Delta})\left[-\frac{d\beta}{dT}\Delta e^{-\beta\Delta}\right] - e^{-\beta\Delta}\cdot g_2\left[-\frac{d\beta}{dT}\Delta e^{-\beta\Delta}\right]}{(g_1+g_2 e^{-\beta\Delta})^2}$$

$$\frac{d\beta}{dT} = -\frac{1}{k_B T^2}$$

$$\Rightarrow \quad C = \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 (g_1+g_2 e^{-\beta\Delta})^2}$$

Z's multiply ⇒ C's add ⇒ $$C = N\left[\underbrace{\tfrac{3}{2}k_B}_{\text{eqn}(21.31)} + \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2(g_1+g_2 e^{-\beta\Delta})^2}\right]$$

$\boxed{21.5}$ $C_p = C_v + R \Rightarrow C_v = \frac{3}{2}R$ at low T, only translational modes excited.

$C_v = \frac{5}{2}R$ above ≈ 300K as rotational modes excited.

$\boxed{21.6}$ $Z_1 = \dfrac{V}{\lambda_{th}^3}$ and if ignore excited states, the zero of energy is at $E = -R$ $\Rightarrow$ $Z_1 \to \dfrac{V}{\lambda_{th}^3} e^{\beta R}$.

22.1

$$\frac{\partial}{\partial P_j}\left[\sum_i -P_i \ln P_i - \alpha P_i - \beta P_i E_i - \gamma P_i N_i\right] = 0$$

$$\Rightarrow -\ln P_j - 1 - \alpha - \beta E_j - \gamma N_j = 0 \quad \Rightarrow \quad P_j = \frac{e^{-\beta E_j} e^{-\gamma N_j}}{e^{1+\alpha}}$$

Set $\mathcal{Z} = e^{1+\alpha}$, $\gamma = -\beta\mu$ $\Rightarrow$ $P_j = \frac{1}{\mathcal{Z}}\left[e^{-\beta(E_j - \mu N_j)}\right]$ i.e. G.C.E.

22.2

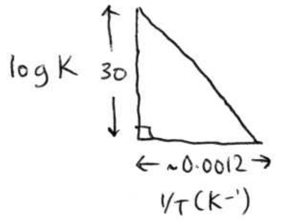
eqn 22.15 $\Rightarrow$ $\mu = k_B T \ln(n\lambda_{th}^3)$ $\Rightarrow$ $z = e^{\beta\mu} = e^{\ln(n\lambda_{th}^3)} = n\lambda_{th}^3 \equiv \frac{n}{n_Q}$

$z \ll 1$ $\Rightarrow$ low-density ($n \ll n_Q$) and can ignore multiple occupancy of states

$z \gg 1$ $\Rightarrow$ high-density ($n \gg n_Q$) and multiple occupancy of states inevitable $\Rightarrow$ quantum effects.

22.3

gradient of line $\approx -\frac{30}{0.0012} = -\frac{\Delta H}{R}$



$\Rightarrow$ $\Delta H \approx 200$ kJ mol⁻¹ [a bit more accurately 193 kJ mol⁻¹]

↑ Positive ∴ endothermic – you have to break a bond!

22.4

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta = \frac{1}{\mathcal{Z}}\sum_i \beta N_i e^{\beta(\mu N_i - E_i)} = \frac{1}{k_B T}\sum_i N_i P_i$$

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu = \frac{1}{\mathcal{Z}}\sum_i (\mu N_i - E_i) e^{\beta(\mu N_i - E_i)} = \mu \sum_i N_i P_i - \sum E_i P_i = \mu N - U$$

22.5

$$F = -N k_B T \ln Z_1 + k_B T(N \ln N - N)$$

$$\mu = -\frac{\partial F}{\partial N} = k_B T \ln Z_1 - k_B T[1 + \ln N - 1] = k_B T \ln(Z_1/N).$$

22.6

(a) $H^+ \rightleftharpoons p^+ + e^-$. (22.94) justified by argument leading to (22.78)

$Z_1 = \frac{V}{\lambda_{th}^3} e^{\beta R}$ (21.50) insert in (22.92) $\Rightarrow$ $Z^H = -k_B T \ln \frac{Z_1^H}{N_H} e^{\beta R}$

and hence (22.95) follows.

$\Rightarrow$ $e^{-\beta R} = \frac{Z_1^H}{N_H} \cdot \frac{N_e N_p}{Z_1^p Z_1^e}$ For an ideal gas $Z_1 = \frac{V}{h^3}(2\pi m k_B T)^{3/2}$ and take $m_H \approx m_p$.

$\Rightarrow$ $e^{-\beta R} = \frac{n_e n_p}{n_H} \frac{(2\pi m_H k_B T)^{3/2}}{h^3} \cdot \frac{h^6}{(2\pi m_e k_B T)^{3/2}(2\pi m_p k_B T)^{3/2}}$ $\Rightarrow$ Saha equation. (22.96)

(b) $n_p = yn$, $\Rightarrow$ $n_H = n - n_p = (1-y)n$

$n_e = n_p = yn$ $\Rightarrow$ $\frac{n_e n_p}{n_H} = \frac{y^2}{1-y} = \frac{e^{\beta R}}{n \lambda_{th}^{e\,3}}$

At 1000 K, $\lambda_{th}^e = \frac{h}{\sqrt{2\pi m_e k_B T}} = 2.4 \times 10^{-9}$ m $\Rightarrow$ $\frac{e^{\beta R}}{n\lambda_{th}^{e\,3}} \approx 2 \times 10^{-63}$

$y \ll 1$ $\frac{y^2}{1-y} \approx y^2$ $\Rightarrow$ $y \approx 5 \times 10^{-32}$.

(c) The reaction occurs because the particles are bathed in a radiation field. Ionization rate per volume is proportional to number density, but the recombination rate per volume is proportional to the product of the number densities of the recombining particles ⇒ if density ↓, the recombination is hit more dramatically ⇒ degree of ionization ↑.

(see also G.H. Nickel, Am. J. Phys. 46, 448 (1980).)

$\boxed{23.1}$ Earth absorbs $\pi R_{Earth}^2 S(1-A)$ ①

and emits $4\pi R_{Earth}^2 \sigma T_{Earth}^4$ ②

where $S = \dfrac{L_{sun}}{4\pi D^2}$ and $L_{sun} = 4\pi R_{sun}^2 \sigma T_{sun}^4$

① = ② $\Rightarrow$ $T_{Earth} = T_{sun}(1-A)^{1/4}\left(\dfrac{R_{sun}}{2D}\right)^{1/2}$.

cf eq. (37.5)

$\boxed{23.2}$ 23.43, 23.44 $\Rightarrow$ $\dfrac{x^\alpha}{e^x-1}$ where $x = \beta h\nu = \dfrac{\beta hc}{\lambda}$

$$\frac{d}{dx}\left[\frac{x^\alpha}{e^x-1}\right] = 0 \Rightarrow (e^x-1)\cdot\alpha x^{\alpha-1} - x^\alpha\cdot e^x = 0$$

$$\Rightarrow x = \alpha(1-e^{-x})$$

α	iterated value of x	
1.5	0.87422	
2	1.59362	
3	2.82144	
4	3.92069	relevant ones for us
5	4.96511	
6	5.98490	

$\boxed{23.3}$ (a) $u = \dfrac{4\sigma}{c}T^4 = \dfrac{4\times5.67\times10^{-8}}{3\times10^{8}}\times(2.73)^4 = 4\times10^{-14}\,\mathrm{J\,m^{-3}}$

(c) Power per unit area $= \sigma T^4 = 3.1\,\mu\mathrm{W\,m^{-2}}$, area of hand $\approx 0.01\,\mathrm{m^2}$
$\Rightarrow$ $\approx 30\,\mathrm{nJ}$ arrives every second

(b) (23.75) $\Rightarrow$ average energy / photon is $2.7\,k_BT \approx 10^{-22}\,\mathrm{J}$
[though if guess k_BT you're not far out]
$\therefore$ 30 nJ equates to 3×10^{14} photons / second

(d) Radiation pressure $= \dfrac{u}{3} \approx 10^{-14}\,\mathrm{Pa}$. i.e. very small!

$\boxed{23.4}$ Power from Sun at Earth is $\dfrac{L_{Sun}}{4\pi D^2} \approx 1.4\,\mathrm{kW\,m^{-2}}$ where $L_{sun} = 4\pi R_{Sun}^2\sigma T_{Sun}^4$

$$\text{Ratio is}\quad \frac{\dfrac{\overset{4\pi R_{Sun}^2\sigma T_{Sun}^4}{L_{Sun}}}{4\pi D^2}\times\dfrac{1}{2.7k_BT_{Sun}}}{\sigma T_{CMB}^4\times\dfrac{1}{2.7k_BT_{CMB}}} \simeq \left(\frac{T_{Sun}}{T_{CMB}}\right)^3\left(\frac{R_{Sun}}{D}\right)^2 \approx 2\times10^5.$$

23.5 $U = uV$, $p = u/3$ and can write $u = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$

(a) so $4u/3T = s$ and result follows

(b) $G = U + PV - TS = uV + \frac{u}{3}V - \frac{4u}{3}V = 0$

(c) use $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ and $S = 4uV/3T$.

It is maybe quicker to use $C_V = \left(\frac{\partial U}{\partial T}\right)_V = V\left(\frac{\partial u}{\partial T}\right)_V = 3V\left(\frac{\partial p}{\partial T}\right)_V = 3V\left(\frac{\partial S}{\partial V}\right)_T = 3Vs$.

(d) $G = 0$ so $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p = 0$. Hence $s = S/V = \mathrm{d}p/\mathrm{d}T$ and therefore at constant p, since s is non-zero we have that $\mathrm{d}T = 0$ so that C_p is infinite. There are other ways of achieving the same result. (e.g. one can write $H = U + PV = 4uV/3$ and $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ where constant p means constant u. You end up evaluating $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V / \left(\frac{\partial p}{\partial V}\right)_T$, where the denominator $\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{3}\left(\frac{\partial u}{\partial V}\right)_T = 0$.)

What's going on? The pressure in a photon gas depends only on the energy density which depends only on the temperature. If the constraint is constant pressure, then we must be at constant temperature. (In fact if were to add heat to a photon gas at constant pressure, we would have to let it expand to take up the extra energy but the temperature would be the same. Adding heat but producing no change in temperature is an infinite heat capacity!)

23.6 $Z = \prod Z_\omega$ where Z_ω is the partition function for one mode. Hence

$$\ln Z = \sum \ln Z_\omega = \int_0^\infty g(\omega)\,\mathrm{d}\omega \ln\left[\frac{1}{1 - e^{-\beta\hbar\omega}}\right],$$

and hence the result follows. This can then be integrated by parts, using

$$\int_0 \omega^2 \ln(1 - e^{-\beta\hbar\omega})\,d\omega = \left[\frac{\omega^3}{3}\ln(1 - e^{-\beta\hbar\omega})\right]_0^\infty - \int_0^\infty \frac{\omega^3}{3}\frac{\beta\hbar e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})} = -\frac{(k_\mathrm{B}T)^3}{3\hbar^3}\int_0^\infty \frac{x^3\,dx}{e^x - 1},$$

and the answer then follows. This can then be written as

$$\ln Z = \frac{4\sigma V}{3k_\mathrm{B}c}T^3,$$

and use of $F = -k_\mathrm{B}T\ln Z$, $S = -pdFT_V$, $U = F + TS$ and $p = -pdFV_T$ produces the rest. The results clearly satisfy $U = -3F$, $pV = U/3$ and $S = 4U/3T$.

23.7

$$N = \int_0^\infty \frac{g(\omega)\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} = \frac{V(k_\mathrm{B}T)^3}{\pi^2 c^3\hbar^3}\int_0^\infty \frac{x^2\,\mathrm{d}\omega}{e^x - 1},$$

and the integral is $\zeta(3)\Gamma(3) = 2\zeta(3)$ and hence the result follows. Now $U = 4V\sigma T^4/c = \pi^2 k_\mathrm{B}^4 VT^4/15c^2\hbar^3 c$ and hence

$$\frac{U}{N} = \frac{\pi^4}{30\zeta(3)}k_\mathrm{B}T = 2.701k_\mathrm{B}T,$$

and $S = 4U/3T$ then yields

$$\frac{S}{N} = \frac{2\pi^4}{45\zeta(3)}k_\mathrm{B} = 3.602k_\mathrm{B}.$$

The ideal gas is in a limit where there are far far more possible states than particles, permitting quite a low average energy ($1.5k_\mathrm{B}T$ per particle) but quite high entropy ($S = k_\mathrm{B}(2.5 - \ln(n\lambda_\mathrm{th})^3)$ per particle, high if $n\lambda_\mathrm{th}^3 \ll 1$).

$\boxed{24.1}$ $\quad n = \frac{1}{a^3} \qquad \Theta_D = \frac{\hbar\omega_D}{k_B}$

$$\omega_D^3 = 6 n \pi^2 v_s^3$$

$$v_s = \frac{\cancel{\omega_D}\, k_B\Theta_D/\hbar}{(6\pi^2 n)^{1/3}} = \frac{k_B \Theta_D\, a}{\hbar(6\pi^2)^{1/3}}$$

$$=$$

For monatomic chain,

$$\omega^2 = \frac{4K}{m}\sin^2\frac{qa}{2}, \quad \text{but} \quad v_s = a\left(\frac{K}{m}\right)^{1/2}$$

$$\Rightarrow \omega = 2\left(\frac{K}{m}\right)^{1/2}\sin\frac{qa}{2} = \frac{2v_s}{a}\sin\frac{qa}{2}$$

$$\Rightarrow \omega_{max} = \frac{2v_s}{a} \quad \Rightarrow \quad \nu_{max} = \frac{v_s}{\pi a}$$

$$=$$

$\boxed{24.2}$ $\quad U = \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3\,d\omega}{e^{\hbar\omega\beta}-1}$

$$x = \hbar\beta\omega \Rightarrow dx = \hbar\beta\, d\omega$$

∴ per mole for $N = N_A$

$$U = \frac{9}{8}N_A\hbar\omega_D + \frac{9N_A\cancel{\hbar}(k_BT)^{\cancel{4}}}{x_D^3\,\cancel{(k_BT)^3}}\,\frac{\cancel{\hbar^3}}{\cancel{\hbar^4}}\int_0^{x_D}\frac{x^3\,dx}{e^x-1}$$

$(R = N_A k_B)$

$$= \frac{9}{8}N_A\hbar\omega_D + \frac{9RT}{x_D^3}\int_0^{x_D}\frac{x^3\,dx}{e^x-1}$$

as req$^{\underline{d}}$

$\boxed{24.3}$ In D dimensions $g(q) \propto q^{D-1} \Rightarrow g(\omega) \propto \omega^{D-1}$

$$\Rightarrow U = \text{const} + \text{const} \times \int_0^{\omega_D}\frac{\omega^D\,d\omega}{e^{\beta\hbar\omega}-1}$$

$$= \text{const} + \text{const} \times (k_BT)^{D+1}$$

$$C = \frac{\partial U}{\partial T} \propto T^D.$$

$\boxed{24.4}$ $$\omega = \left(\frac{4K}{m}\right)^{1/2} \left|\sin\frac{qa}{2}\right|$$

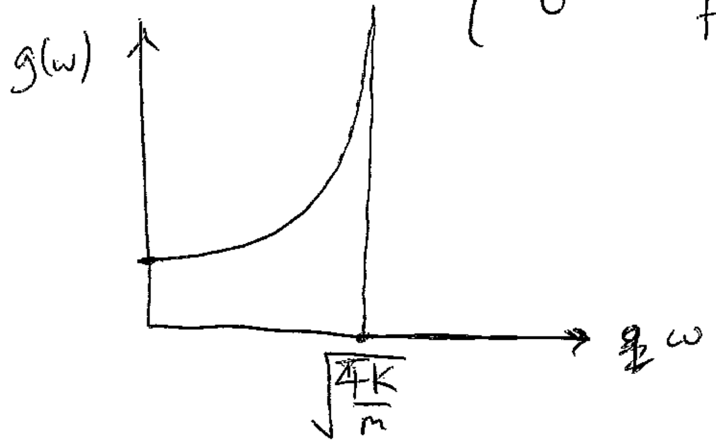
In 1D $$g(q) = \frac{2\,dq}{2\pi/L} = \frac{L\,dq}{\pi}$$

$$\frac{d\omega}{dq} = \left(\frac{4K}{m}\right)^{1/2} \cdot \frac{a}{2} \cos\frac{qa}{2}$$

$$= \frac{a}{2}\left[\frac{4K}{m} - \omega^2\right]^{1/2}$$

$$g(\omega) = \frac{g(q)}{d\omega/dq} = \begin{cases} \dfrac{2L}{\pi a}\left(\dfrac{4K}{m} - \omega^2\right)^{-1/2} & \omega \le \sqrt{\dfrac{4K}{m}} \\ 0 \quad \text{for } \omega > \sqrt{\dfrac{4K}{m}} \end{cases}$$

note error in eqn as printed in first edition



Singularity due to $v_g \to 0$ as $q \to \frac{\pi}{a}$.

$\boxed{24.5}$ $$-m\omega^2 = K\left(e^{iq_xa} - 2 + e^{-iq_xa} + e^{iq_ya} - 2 + e^{-iq_ya}\right)$$

$$m\omega^2 = 2K\left(2 - \cos q_xa - \cos q_ya\right)$$

$$\Rightarrow \quad \omega = \left(\frac{2K}{m}\right)^{1/2}\left[2 - \cos q_xa - \cos q_ya\right]^{\boxed{1/2}}$$

Error as printed in first edition

For small q_x, q_y

$$\omega \approx \left(\frac{2K}{m}\right)^{1/2}\left[\frac{(q_x^2+q_y^2)a^2}{2}\right]^{1/2}$$

$$\Rightarrow \quad v_s = a\left(\frac{K}{m}\right)^{1/2}$$ as before in (24.34).

24.6

Diatomic chain.

$$M\ddot{u}_n = K(v_n - 2u_n + v_{n-1})$$

$$m\ddot{v}_n = K(u_{n+1} - 2v_n + u_n)$$

$$u_n = u\, e^{i(qna-\omega t)}$$

$$v_n = v\, e^{i(qna-\omega t)}$$

$$-M\omega^2 u = Kv(1+e^{-iqa}) - 2Ku$$

$$-m\omega^2 v = Ku(e^{iqa}+1) - 2Kv$$

$$\begin{vmatrix} 2K - M\omega^2 & -K(1+e^{-iqa}) \\ -K(1+e^{iqa}) & 2K - m\omega^2 \end{vmatrix} = 0$$

$$(2K-M\omega^2)(2K-m\omega^2) - K^2(2+2\cos qa) = 0$$

$$Mm\omega^4 - 2K(M+m)\omega^2 + 2K^2(1-\cos qa) = 0$$

$$\omega^2 = \frac{2K(M+m) \pm \sqrt{4K^2(M+m)^2 - 8MmK^2(1-\cos qa)}}{2Mm}$$

$$\frac{-b \pm \sqrt{b^2-2ac}}{2a} \qquad \frac{\omega^2}{K} = \frac{M+m}{Mm} \pm \sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2\frac{qa}{2}}$$

= result.

NB $\boxed{\text{FACTOR OF 2}}$ misprint in 1st edition — now corrected.

$\boxed{24.7}$

$$m\ddot{u}_n = \sum_{j=1}^{\infty} K_j \left[u_{n+j} - 2u_j + u_{n-j} \right]$$

with $u_n = u\, e^{i(qna-\omega t)}$

$$\Rightarrow \; -m\omega^2 = \sum_{j=1}^{\infty} 2K_j \, [\underbrace{\cos jqa - 1}_{-2\sin^2\frac{jqa}{2}}]$$

$$\Rightarrow \; \omega^2 = \frac{4}{m} \sum_{j=1}^{\infty} K_j \sin^2 \frac{jqa}{2}$$

no K misprint in 1st edition

$$\text{or} \quad \omega^2 = \frac{2}{m} \sum_{j=1}^{\infty} K_j \left(1 - \cos jqa\right)$$

$$\int_{-\pi/a}^{\pi/a} \omega^2(q) \cos jqa = -\frac{2}{m} \sum_{\substack{\cancel{j}=1 \\ i}}^{\infty} K_{\substack{\cancel{j} \\ i}} \underbrace{\int_{-\pi/a}^{\pi/a} \cos jqa \cos iqa \, dq}_{\frac{2\pi}{a} \cdot \frac{1}{2} \cdot \delta_{ij}}$$

$$= -\underline{\frac{2\pi}{ma} K_j} \qquad \Rightarrow \text{result}$$

$\boxed{25.1}$ $E^2 = p^2c^2 + m_0^2c^4 \Rightarrow 2E\,dE = 2pc^2\,dp \Rightarrow \frac{dE}{dp} = \frac{pc^2}{E}$

Phase velocity $V_\phi = \frac{E}{p}$ $\quad V_g = \frac{dE}{dp} = \frac{pc^2}{E} = \frac{c^2}{V_\phi}$

$$V_\phi = c\left(1 + \frac{m_0c^2}{p^2}\right)^{1/2} \Rightarrow V_g = c\left(1 + \frac{m_0^2c^2}{p^2}\right)^{-1/2}$$

$$p \gg m_0c \Rightarrow \frac{V_\phi}{c} = 1 + \frac{1}{2}\left(\frac{m_0c}{p}\right)^2 \qquad \frac{V_g}{c} = 1 - \frac{1}{2}\left(\frac{m_0c}{p}\right)^2$$

$$p \ll m_0c \Rightarrow V_\phi = \frac{m_0c^2}{p}\underbrace{\left(1 + \frac{p^2}{m_0^2c^2}\right)^{1/2}}_{\approx 1 + \frac{1}{2}\frac{p^2}{m_0^2c^2}} \simeq \frac{m_0c^2}{p} + \frac{1}{2}\frac{p^2}{m_0} \approx \frac{m_0c^2}{p}$$

$$V_g = \frac{c^2}{V_\phi} \approx \frac{p}{m_0}$$

elemental "area" in D dimensions

No factor of 2 : misprint in question in 1st edition

$\boxed{25.2}$ $$g(k)\,dk = \frac{g \times dV_D}{(2\pi/L)^D} \qquad V_D = \pi^{D/2}k^D / \Gamma\left(\frac{D}{2}+1\right)$$

$$\Rightarrow dV_D = \frac{\pi^{D/2}.\,D\,k^{D-1}\,dk}{\Gamma\left(\frac{D}{2}+1\right)}$$

$$\Rightarrow g(k)\,dk = \frac{g\,\overset{L^D}{V}.\,D\,\pi^{D/2}k^{D-1}\,dk}{\Gamma\left(\frac{D}{2}+1\right)(2\pi)^D}$$

$\boxed{25.3}$ $E = \alpha p^s = \alpha\hbar^s k^s \Rightarrow dE = s\alpha\hbar^s k^{s-1}\,dk$

$$k^{s-1}\,dk = \frac{dE}{s\alpha\hbar^s} \qquad k^{D-s} = \left(\frac{E}{\alpha\hbar^s}\right)^{\frac{D-s}{s}} = \frac{E^{\frac{D}{s}-1}}{\alpha^{\frac{D}{s}-1}\hbar^{D-s}}$$

$$\Rightarrow g(E)\,dE = \underset{\frac{gVD\pi^{D/2}}{\Gamma(\frac{D}{2}+1)(2\pi)^D}}{A}\,\frac{dE}{s\alpha\hbar^s}\,\frac{E^{\frac{D}{s}-1}}{\alpha^{\frac{D}{s}-1}\hbar^{D-s}} = \frac{A\,E^{\frac{D}{s}-1}\,dE}{s\,\alpha^{D/s}\hbar^D}$$

$$Z_1 = \int_0^\infty e^{-\beta E}\,g(E)\,dE$$

$$= \frac{A}{\hbar^D s\alpha^{D/s}}\int_0^\infty e^{-\beta E}E^{\frac{D}{s}-1}\,dE \qquad x = \beta E$$

$$= \frac{A}{\hbar^D s\alpha^{D/s}}(k_BT)^{D/s} \underbrace{\int_0^\infty e^{-x}x^{\frac{D}{s}-1}\,dx}_{\Gamma(\frac{D}{s})}$$

Putting $Z_1 = \frac{V}{\lambda^D}$

$$\Rightarrow \lambda = \frac{h}{\pi^{1/2}}\underbrace{\left(\frac{s}{D}\right)^{1/D}\left[\frac{\Gamma(\frac{D}{2}+1)}{\Gamma(\frac{D}{s})}\right]^{1/D}}_{\left[\frac{\Gamma(\frac{D}{2}+1)}{\Gamma(\frac{D}{s}+1)}\right]^{1/D}}\left(\frac{\alpha}{k_BT}\right)^{1/s}$$

(i) $s = 2 \Rightarrow \lambda = \frac{h}{\sqrt{\pi k_BT/\alpha}}$ $\quad \left(\alpha = \frac{1}{2m}\right)$

(ii) $s = 1 \Rightarrow \lambda = \frac{hc}{2\pi^{1/3}k_BT} = \frac{\hbar c\pi^{2/3}}{k_BT}$.

$\boxed{26.1}$

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \Rightarrow \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad (26.13)$$

$$\Rightarrow \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \left[\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}\right]^{-1}$$

At the critical volume, $V = 3b$

$$\kappa_T = \left[\frac{RT.3b}{4b^2} - \frac{2a}{9b^2}\right]^{-1} = \frac{4b/3R}{T-T_c} \quad \text{where } T_c = \frac{8a}{27Rb^2}.$$

Question should state "at the critical volume".

$\boxed{26.2}$

Estimate: an atom might fit in a box 0.2 nm in side $\Rightarrow$ volume $\approx 10^{-29}\,m^3$ $\Rightarrow$ for one 1 mole, excluded volume $\approx 10^{-5}\,m^3$.

[reasonable, Ar has a $b = 3.2\times10^{-5}\,m^3\,mol^{-1}$]

$$p = \frac{RT}{V-b} = -\left(\frac{\partial F}{\partial V}\right)_T \Rightarrow F = -RT\ln(V-b) + f(T)$$

$$dF = -SdT - pdV$$

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V = R\ln(V-b) - \frac{df}{dT}$$

$$U = F + TS = f(T) - T\frac{df}{dT} = \text{a function of } T \text{ only.}$$

$\boxed{26.3}$

$$\underset{\overset{\uparrow}{\frac{a}{4e^2b^2}}}{p_c}\tilde{p}\,(\underset{\overset{\uparrow}{2b}}{V_c}\tilde{V} - b) = R\underset{\overset{\nwarrow}{\frac{a}{4Rb}}}{T_c}\tilde{T}\, e^{-a/R\tilde{T}T_c\tilde{V}V_c}$$

$$T_c \leftarrow \frac{a}{4Rb}, \quad V_c \leftarrow 2b$$

simple algebra $\longrightarrow$ answer.

$\boxed{26.4}$

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\,; \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\therefore \beta_p = \frac{-\frac{1}{V}\frac{R}{(V-b)}}{\frac{-RT}{(V-b)^2} + \frac{2a}{V^3}} = \frac{1}{\frac{V(V-b)}{R}\left[-\frac{2a}{V^3} + \frac{RT}{(V-b)^2}\right]} = \frac{1}{T\left[\underbrace{\frac{V}{V-b}}_{1+\frac{b}{V-b}} - \underbrace{\frac{2a}{V^2}\frac{(V-b)}{RT}}_{\frac{2a}{pV+a^2}}\right]}$$

$$\text{vdW} \Rightarrow pV^2 + a = \frac{RTV^2}{V-b}$$

At critical point $\frac{V}{V-b} \to \frac{3b}{3b-b} = \frac{3}{2}$ $\quad \frac{2a}{V^2}\frac{(V-b)}{RT} \to \frac{2a}{9b^2}\cdot\frac{2b}{R\cdot\frac{8a}{27Rb}} = \frac{3}{2}$

$$\Rightarrow \beta_p \to \infty.$$

$\boxed{26.5}$

Eqn (26.9) $\Rightarrow$ $$Z_N = \frac{1}{N!}\left(\frac{V - n_{\text{moles}}\, b}{\lambda_{th}^{3}}\right)^{N} e^{\beta a n_{\text{moles}}/V}$$

with $n_{\text{moles}} = 1$

$$U = -\frac{d\ln Z_N}{d\beta} = -\frac{a}{V} - \frac{3N}{2T}\overbrace{\left(\frac{dT}{d\beta}\right)}^{-k_B T^2} = -\frac{a}{V} + \frac{3}{2}RT$$

($\because$ $\ln Z_N = \frac{\beta a}{V} + \frac{3N}{2}\ln T$ + terms not involving T)

$\boxed{26.6}$ $$U = \frac{f}{2}RT - \frac{a}{V}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2}R$$

Eqn (11.26) $\Rightarrow$ $$C_p - C_V = \underbrace{\left(\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{a/V^2} + p\right)}_{\frac{RT}{V-b}} \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{V\beta_p} = \frac{V/T}{\frac{V}{V-b} - \frac{2a(V-b)}{V^2RT}}$$

from Q $\boxed{26.4}$

$$\Rightarrow \quad C_p - C_V = \frac{R}{1 - \frac{2a}{VTR}\frac{(V-b)^2}{V^2}}$$

So if $V \gg b$ (usual case) and for weak intermolecular forces $a \ll VTR$

$$\Rightarrow \quad C_p - C_V \approx R\left(1 + \frac{2a}{VTR}\right) = R + \frac{2a}{VT}.$$

27.1 (See also 16.2). (a) $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -(1/C_V)[T\left(\frac{\partial S}{\partial V}\right)_T - p]$ and use $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.

(b) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$ and use $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.

(c) $\left(\frac{\partial T}{\partial V}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T = (1/C_p)[T\left(\frac{\partial S}{\partial p}\right)_T + V]$ and use $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$.

(a) Joule expansion; (b) adiabatic expansion; (c) Joule-Kelvin expansion.

Last bits, use $pV = nRT$ and substitute in. The adiabatic expansion leads to $\left(\frac{\partial T}{\partial V}\right)_S = -p/C_V$ so that $\mathrm{d}T = -nRT\mathrm{d}V/(VC_V)$ and the result follows from integrating. (Remember $C_V/n = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$.)

27.2 The first part is a standard result.

The inversion curve is given by

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0.$$

Now p is easily made the subject of the equation of state, and the hint says to use $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V / \left(\frac{\partial p}{\partial V}\right)_T$ which is easily proved from the standard identities for partial differentials which are in their handout. Since

$$p = \frac{RT}{V} + \frac{bRT}{V^2} - \frac{a}{V^2}$$

then

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} + \frac{bR}{V^2}$$

and

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2bRT}{V^3} + \frac{2a}{V^3}$$

and after some algebra one finds

$$T = \frac{2a}{bR} = 2T_{\mathrm{B}} = 38\,\mathrm{K}.$$

Is it so surprising that the inversion temperature and the Boyle temperature are related? Answer: not really - because at the Boyle temperature the system behaves like a perfect gas and you get no J-K cooling for a perfect gas. The Boyle temperature is a characteristic temperature of this interacting gas and so the fact that the inversion temperature turns out to be a simple multiple of this is not such a shock.

27.3 Again, use $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V / \left(\frac{\partial p}{\partial V}\right)_T$ and the result then follows after some rather yawn-inducing algebra.

It's quite instructive to see what the solution does in high T and low T limits. It then becomes clear that the highest inversion temperature must be when $p = 0$ and hence $T = 2a/bR$.

27.4 Using

$$p = \frac{RT}{V-b}\mathrm{e}^{-a/RTV},$$

one can evaluate $\left(\frac{\partial p}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$ to find the critical points:

$$p_c = a/4e^2b^2; \qquad T_c = a/4Rb; \qquad V_c = 2b.$$

Hence substituting in

$$p = \tilde{p}a/4e^2b^2; \qquad T = \tilde{T}a/4Rb; \qquad V = \tilde{V}2b$$

to the equation of state, we have

$$\tilde{P}(2\tilde{V} - 1) = \tilde{T}\exp\left[2\left(1 - \frac{1}{\tilde{T}\tilde{V}}\right)\right].$$

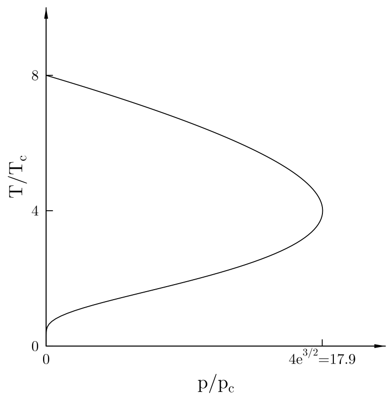
Then use

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{T}}\right)_{\tilde{p}} = -\left(\frac{\partial \tilde{p}}{\partial \tilde{T}}\right)_{\tilde{V}} / \left(\frac{\partial \tilde{p}}{\partial \tilde{V}}\right)_{\tilde{T}}$$

and algebra leads to

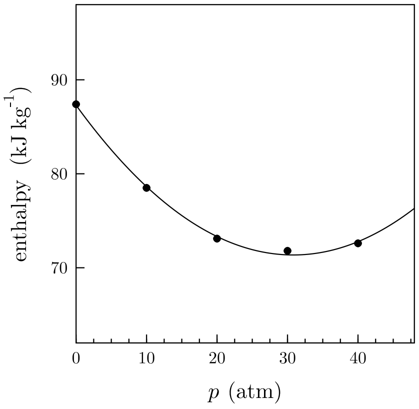
$$\tilde{P} = (8 - \tilde{T}) \exp\left[\frac{5}{2} - \frac{4}{\tilde{T}}\right]$$

The turning point can be found using $\mathrm{d}\tilde{p}/\mathrm{d}\tilde{T} = 0$ which leads to $\tilde{T}$ is -8 (unphysical) or 4.



27.5 Look for

$$\left(\frac{\partial h}{\partial p}\right)_T = 0.$$



Since $h_L = 10.1$, $h_f = 86$ (1 atm), and I estimate from the graph that $h_i = 71$ is the minimum enthalpy, then

$$\alpha = \frac{h_f - h_i}{h_f - h_L} \sim 0.2.$$

28.1 $\mathrm{d}p/\mathrm{d}T = L/(T\Delta V)$ (by Clausius-Clapeyron) and $\Delta V = \rho_{\text{liq}}^{-1} - \rho_{\text{sol}}^{-1}$ per kg.

I get $\mathrm{d}p/\mathrm{d}T = 1.25 \times 10^7$ Pa K^{-1} and if you increase the pressure by 99 atmospheres (i.e. from 1 to 100 atmospheres) you get $\Delta T = 0.75°$C so answer is 327.8°C.

28.2 Clausius-Clapeyron:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T\Delta V} \approx \frac{L}{TV_v}$$

where $\Delta V = V_v - V_L \approx V_v$ and V_v and V_L are the volumes of vapour and liquid respectively. Treating the vapour as an ideal gas ($pV_v = nRT$) leads to

$$p = p_0 \mathrm{e}^{-L/nRT}$$

so that after putting in the numbers, we get the boiling point to be 87.4°C. The tea up there is dreadful. (We have verified this fact experimentally.)

28.3 Clausius-Clapeyron yields $dp/dT = L/(T\Delta V) = 1.4 \times 10^7\,\mathrm{Pa\,K^{-1}}$.

The heat flow is $\kappa dT/dz = 115\,\mathrm{W\,m^{-2}}$ (using $dT/dz = 0.5/0.01 = 50\mathrm{K\,m^{-1}}$). Divide by the latent heat of fusion and multiply by the specific volume, yields the rate of ice growth: $3.5\times10^{-7}\,\mathrm{m\,s^{-1}}$ or about 3 cm per day.

The word "eventually" signifies steady state, so the heat flux must be the same throughout. Thus if $1-x$ metres is water and x metres is ice, so that the temperature gradient across the ice is $0.5/x$ and across the water it is $2/(1-x)$, we have that

$$\kappa_{\text{ice}}\frac{0.5}{x} = \kappa_{\text{water}}\frac{2}{1-x},$$

and this yields $x = 0.5\,\mathrm{m}$.

28.4 Use $L = T(S_v - S_L)$ and also

$$\frac{\mathrm{d}}{\mathrm{d}T} = \left.\frac{\partial}{\partial T}\right)_P + \frac{\mathrm{d}p}{\mathrm{d}T}\left.\frac{\partial}{\partial p}\right)_T.$$

Hence

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right) = \frac{C_{pv} - C_{pL}}{T} + \frac{\mathrm{d}p}{\mathrm{d}T}\left[\left(\frac{\partial S_v}{\partial p}\right)_T - \left(\frac{\partial S_L}{\partial p}\right)_T\right]$$

and using $\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p$ and ignoring V_L the result follows.

For the next bit, it is helpful to write this in the form

$$\frac{\mathrm{d}p}{\mathrm{d}T}\left(\frac{\partial V_v}{\partial T}\right)_p = \frac{C_{pv} - C_{pL}}{T} - \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right).$$

(b) Adiabatic implies for the vapour that

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p = 0$$

i.e.

$$\mathrm{d}S = \frac{C_{pv}}{T}\mathrm{d}T - \left(\frac{\partial V_v}{\partial T}\right)_p \mathrm{d}p = 0$$

so that

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{C_{pv}}{T\left(\frac{\partial V_v}{\partial T}\right)_p}.$$

Liquid will condense out if this gradient is smaller than the gradient of the phase boundary in the p–T plane as evaluated by the Clausius Clapeyron equation (remember, we are doing an expansion, so that p goes down). The gradient evaluated by the Clausius Clapeyron equation is

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{C_{pv} - C_{pL} - T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right)}{T\left(\frac{\partial V_v}{\partial T}\right)_p}$$

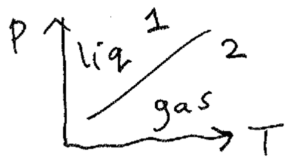
based on the arguments in (a). Hence we require that

$$\frac{C_{pv}}{T\left(\frac{\partial V_v}{\partial T}\right)_p} < \frac{C_{pv} - C_{pL} - T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right)}{T\left(\frac{\partial V_v}{\partial T}\right)_p},$$

$$0 < -C_{pL} - T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right),$$

$$C_{pL} + T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right) < 0.$$

28.5



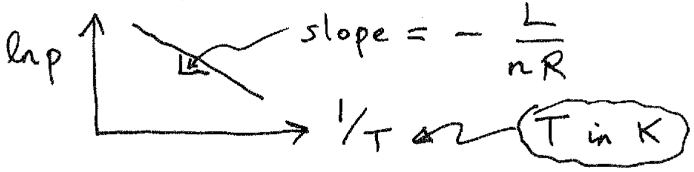
$\Delta V \simeq V_2 \qquad V_2 \gg V_1$

$pV_2 = nRT$

↑ # moles

$$\frac{dp}{dT} = \frac{L}{T\Delta V} = \frac{Lp}{nRT^2}$$

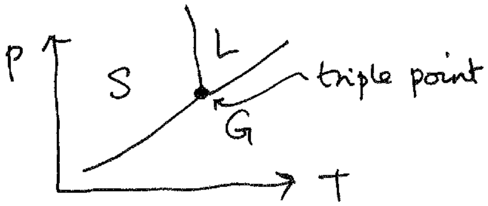
$$\frac{dp}{p} = \frac{L}{nR}\frac{dT}{T^2} \quad \therefore \ p = p_0 \exp\left(-\frac{L}{nRT}\right)$$

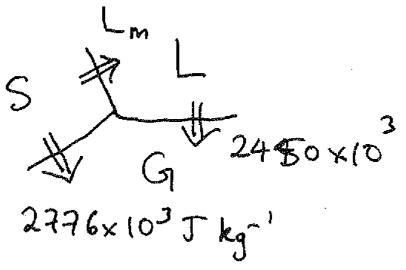


L per kg

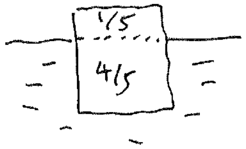
$1\ \mathrm{kg} = \frac{1000}{18}$ moles

$\Rightarrow \quad L_v = 2.45 \times 10^6\ \mathrm{J\ kg^{-1}}$





$$L_m = (2776 - 2449) \times 10^3$$
$$= 327\ \mathrm{kJ\ kg^{-1}}$$



volume of ice

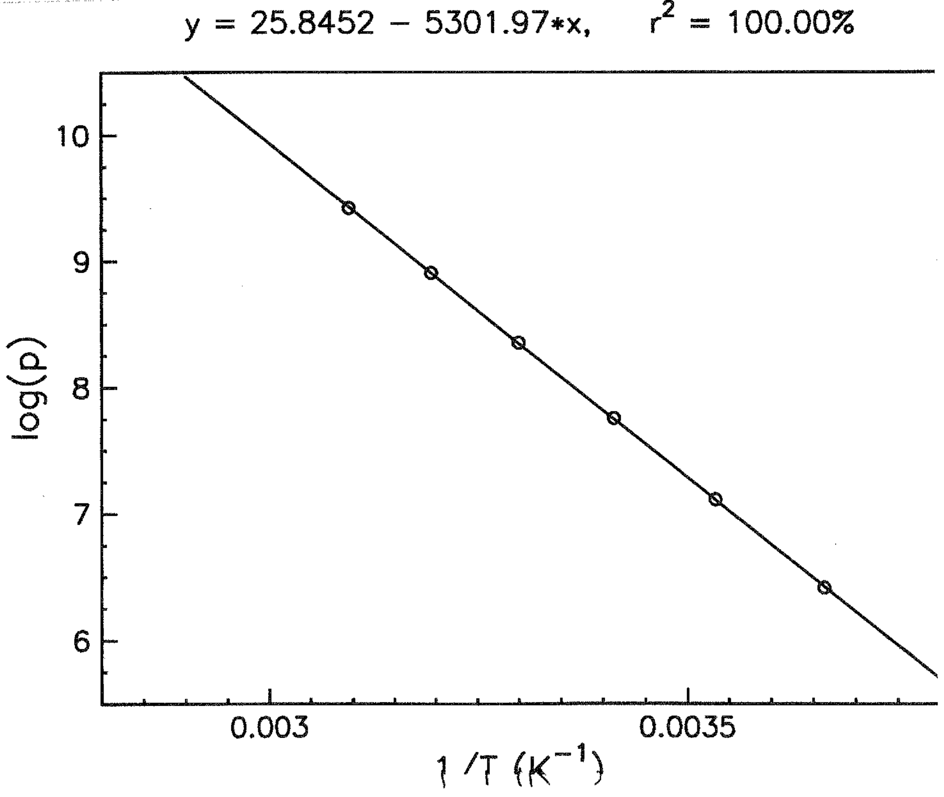
$= \frac{5}{4}$ volume of water

$$\Delta V = -\frac{10^{-3}}{4}\ m^3\ (kg^{-1})$$

$$\frac{dp}{dT} = -\frac{327 \times 10^3\ J\,kg^{-1}}{273\,K \times \frac{10^{-3}}{4}\ m^3\,kg^{-1}} = -4.8 \times 10^6\ Pa\,K^{-1}$$

drop to −2°C $\quad p \rightarrow 9.6 \times 10^6\ Pa$

$\simeq \underline{100\ atm}$



28.6

Even if we go for a very heavy skater (100 kg), only making contact on the ice over an area 10 cm by 1 mm ($10^{-4}\,m^2$), the pressure is only 10^7 *Pa*, and the melting line has a gradient 1.4×10^7 Pa (see previous questions). This is not enough to melt the ice. The two articles quoted in the question are excellent sources of further information.

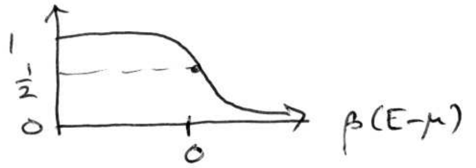
29.1 Recap of section 29.1 and examples in Example 29.1

29.2 (a) $\frac{1}{4}$ (b) $\frac{1}{4}$ (c) $\frac{1}{3}$ (d) 0.

29.3 $\tanh \beta\frac{(E-\mu)}{2}$ is symmetric about $E=\mu$ $\Rightarrow$ so is $f(E)$

(i) $E \ll \mu$ $\quad f(E) \to 1$

(ii) $E \gg \mu$ $\quad f(E) \to 0$



(iii) E near μ, $\tanh \frac{1}{2}\beta(E-\mu) \approx \frac{1}{2}\beta(E-\mu)$

$$\therefore f(E) \approx \tfrac{1}{2}\left(1 - \tfrac{1}{2}\beta(E-\mu)\right)$$

29.4 No, you can label them by, for example, localising them at different spatial locations so that they are distinguished by their site.

29.5

$$\overset{\leftarrow d \rightarrow}{\circ\!\!-\!\!-\!\!-\!\!\circ}$$

$$I = \sum_i m_i r_i = 2m_p\left(\frac{d}{2}\right)^2 = \frac{1}{2}m_p d^2 = 4.6\times10^{-48}\ \mathrm{kg\,m^2}$$

$$k_B \Theta = \frac{2(2+1)\hbar^2}{2I} \Rightarrow \Theta = 524\ \mathrm{K}.$$

Triplet state has degeneracy $2\times1+1 = 3$ $\quad J = 1, 3, 5, \ldots$

Singlet " " " $2\times0+1 = 1$ $\quad J = 0, 2, 4, \ldots$

$$E_J = \boxed{\frac{\hbar^2}{2I}}\, J(J+1)$$

call this ξ

$\Rightarrow$ Ratio of partition functions

$$f = \frac{3\sum_{J=1,3,5,\ldots}(2J+1)\,e^{-\beta\xi J(J+1)}}{1\sum_{J=0,2,4,\ldots}(2J+1)\,e^{-\beta\xi J(J+1)}}$$

$$\approx 3\left[\frac{3e^{-2\beta\xi} + 7e^{-12\beta\xi}}{1+5e^{-6\beta\xi}}\right] = 0.27$$

$\beta\xi = 1.75$

(taking first few terms only)

29.6 n_j particles in g_j states

- Fermions: state either has 0 or 1 occupancy
  $\therefore$ # ways of arranging n_j 1's and $(g_j - n_j)$ 0's is
  $$\Omega_j = \frac{g_j!}{n_j!(g_j-n_j)!}$$
- Bosons: no restriction. Write a state as $|\circ\circ\circ|\circ\circ|\circ||\circ\circ\circ|\cdots$ etc and see that we want # ways of arranging n_j ~~states~~ particles and g_j-1 "boundaries" between states $\Rightarrow$ $\Omega_j = \dfrac{(g_j-1+n_j)!}{n_j!\,(g_j-1+n_j)!}$

(a) $$S = k_B \sum_j \left[g_j \ln g_j - \cancel{g_j} - n_j \ln n_j + \cancel{n_j} - (g_j - n_j)\ln(g_j - n_j) + \cancel{g_j} - \cancel{n_j} \right]$$

$$n_j = \bar{n}_j \, g_j$$

$$\Rightarrow S = k_B \sum_j g_j \left[\cancel{\ln g_j} - \bar{n}_j \ln \bar{n}_j - \cancel{\bar{n}_j \ln g_j} - \cancel{(1-\bar{n}_j)\ln g_j} - (1-\bar{n}_j)\ln(1-\bar{n}_j) \right]$$

$$= -k_B \sum_j g_j \left[\bar{n}_j \ln \bar{n}_j + (1-\bar{n}_j)\ln(1-\bar{n}_j) \right]$$

Write $S/k_B + \alpha(N - \sum g_j \bar{n}_j) + \beta(E - \sum g_j \bar{n}_j E_j)$

and $\partial / \partial \bar{n}_i$ this, equating to zero.

$$\Rightarrow \quad -\left[\left(-\cancel{\frac{1-\bar{n}_i}{1-\bar{n}_i}} - \ln(1-\bar{n}_i) + \cancel{\frac{\bar{n}_i}{\bar{n}_i}} + \ln \bar{n}_i \right) \right] - \alpha - \beta E_i = 0$$

$$\Rightarrow \quad \ln \frac{1-\bar{n}_i}{\bar{n}_i} = \alpha + \beta E_i \quad \Rightarrow \quad \frac{g_i}{n_i} - 1 = e^{\alpha + \beta E_i}$$

$$\Rightarrow \bar{n}_i = \frac{n_i}{g_i} = \underline{\frac{1}{e^{\alpha + \beta E_i} + 1}}$$

(b) If $g_j \gg 1$, write $\Omega_j \approx \dfrac{(g_j + n_j)!}{n_j! \, g_j!}$ [i.e. replace $g_j - 1$ by g_j]

$$\Rightarrow S = k_B \sum_j (g_j + n_j)\ln(g_j + n_j) - \cancel{g_j} - \cancel{n_j} - n_j \ln n_j + \cancel{n_j} - g_j \ln g_j + \cancel{g_j} \,]$$

$$= k_B \sum_j g_j \left[(1+\bar{n}_j)\left[\ln(1+\bar{n}_j) + \ln g_j\right] - \bar{n}_j(\ln \bar{n}_j + \ln g_j) - \ln g_j \right]$$

$$= k_B \sum_j g_j \left[(1+\bar{n}_j)\ln(1+\bar{n}_j) - \bar{n}_j \ln \bar{n}_j \right]$$

Minimising as above

$$\Rightarrow \quad \cancel{\frac{1+\bar{n}_i}{1+\bar{n}_i}} + \ln(1+\bar{n}_i) - \cancel{\frac{\bar{n}_i}{\bar{n}_i}} - \ln \bar{n}_i - \alpha - \beta E_i = 0$$

$$\Rightarrow \quad \ln \frac{1+\bar{n}_i}{\bar{n}_i} = \alpha + \beta E_i \quad \Rightarrow \quad \frac{g_i}{n_i} + 1 = e^{\alpha + \beta E_i}$$

$$\Rightarrow \bar{n}_i = \frac{n_i}{g_i} = \underline{\frac{1}{e^{\alpha + \beta E_i} - 1}}$$

$\boxed{30.1}$ Classical limit

$$N = \frac{(2S+1)V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} e^{\beta\mu}\int_0^\infty e^{-\beta\varepsilon}\,\varepsilon^{1/2}\,d\varepsilon$$

$$= \frac{(2S+1)V\,e^{\beta\mu}}{\lambda_{th}^3}$$

$$\Rightarrow \frac{\lambda_{th}^3}{(2S+1)\frac{V}{N}} = e^{\beta\mu} = \frac{\text{thermal volume}}{\text{volume per particle}}$$

$\boxed{30.2}$

$$U = n\langle E\rangle = n\,\frac{\int_0^{E_F} E\cdot E^{1/2}\,dE}{\int_0^{E_F} E^{1/2}\,dE} = \frac{3}{5}nE_F$$

$$(30.30) \Rightarrow p = \frac{2U}{3V} \Rightarrow p = \frac{2}{5}nE_F$$

$\boxed{30.3}$

$$n = \int_0^\infty g(E)f(E)\,dE \doteq \int_0^\mu g(E)\,dE + \frac{\pi^2}{6}(k_BT)^2\left(\frac{dg}{dE}\right)_{E=\mu} + \dots$$

To 1st order, $\int_0^\mu g(E)\,dE = \int_0^{E_F} g(E)\,dE + (\mu - E_F)\,g(E_F)$

At $T=0$, $\mu = E_F$ and so $n = \int_0^{E_F} g(E)\,dE$. At higher T, n is still the same!

$$\Rightarrow (\mu - E_F)\,g(E_F) + \frac{\pi^2}{6}(k_BT)^2\,g'(E_F) = 0$$

$$\Rightarrow \mu = E_F - \frac{\pi^2}{6}(k_BT)^2\,\frac{g'(E_F)}{g(E_F)}.$$

$\boxed{30.4}$

$$(30.44) \Rightarrow U = \frac{3}{2}\underset{\uparrow \atop \frac{(2S+1)V}{\lambda_{th}^3}\mathrm{Li}_{3/2}(z)}{N}k_BT\,\frac{\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)} = \frac{3}{2}k_BT\,\frac{(2S+1)V}{\lambda_{th}^3}\,\mathrm{Li}_{5/2}(z)$$

For $T<T_c$, $z=1$, $U = \frac{3}{2}Nk_BT_c\,\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\left(\frac{T}{T_c}\right)^{5/2}$ see (30.61)

$$\Rightarrow C = \frac{\partial U}{\partial T} = \frac{15}{4}\,\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\,Nk_B\left(\frac{T}{T_c}\right)^{3/2}$$

For $T>T_c$, harder $\because$ $z<1$ and z is a function of T

$$n = \frac{(2S+1)V}{\lambda_{th}^3}\mathrm{Li}_{3/2}(z) \Rightarrow \mathrm{Li}_{3/2}(z) \propto \lambda_{th}^3 \propto T^{-3/2}$$ $\Rightarrow$ write $\mathrm{Li}_{3/2}(z) = aT^{-3/2}$

$$\therefore \frac{d}{dz}\mathrm{Li}_{3/2}(z)\cdot\frac{dz}{dT} = -\frac{3}{2}aT^{-5/2}$$

$$\Rightarrow \frac{1}{z}\mathrm{Li}_{1/2}(z)\,\frac{dz}{dT} = -\frac{3}{2T}\mathrm{Li}_{3/2}(z)$$

$$\Rightarrow \frac{dz}{dT} = -\frac{3z}{2T}\,\frac{\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)} \quad ①$$

$$\left[\mathrm{Li}_n(z) = \sum_{k=1}^\infty \frac{z^k}{k^n} \quad \therefore \quad \frac{d\,\mathrm{Li}_n(z)}{dz} = \sum_{k=1}^\infty \frac{z^{k-1}}{k^{n-1}} = \frac{\mathrm{Li}_{n-1}(z)}{z}\right]$$

$$\Rightarrow C = \frac{\partial U}{\partial T} = \frac{3}{2}k_B(2S+1)V\left[\mathrm{Li}_{5/2}(z)\underbrace{\frac{\partial}{\partial T}\left[\frac{T}{\lambda_{th}^3}\right]}_{\substack{\wr \\ \propto T^{5/2}}} + \frac{T}{\lambda_{th}^3}\underbrace{\frac{d\mathrm{Li}_{5/2}(z)}{dT}}_{\frac{\mathrm{Li}_{3/2}(z)}{z}\cdot\frac{dz}{dT}}\right]$$

$$\left[\text{using } \frac{d\mathrm{Li}_n(z)}{dz} = \frac{1}{z}\mathrm{Li}_{n-1}(z)\right]$$

$$\Rightarrow C = \frac{3}{2}k_B(2S+1)V\left[\mathrm{Li}_{5/2}(z)\cdot\frac{5}{2}\frac{1}{\lambda_{th}^3} + \frac{T}{\lambda_{th}^3}\left(-\frac{3}{2T}\right)\frac{\mathrm{Li}_{3/2}^2(z)}{\mathrm{Li}_{1/2}(z)}\right]$$

$$= \frac{3}{2}k_B\underbrace{\frac{(2S+1)V\,\mathrm{Li}_{3/2}(z)}{\lambda_{th}^3}}_{N}\left[\frac{5}{2}\frac{\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)} - \frac{3}{2}\frac{\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)}\right].$$

$\boxed{30.5}$ In 2D, $g(k) = \frac{2\pi k\,dk\,(2S+1)}{(2\pi/L)^2} = \frac{(2S+1)A\,k\,dk}{2\pi^2}$

$$E = \frac{\hbar^2k^2}{2m},\quad dE = \frac{\hbar^2 k\,dk}{m} \Rightarrow g(E)\,dE = \frac{(2S+1)A\,dE\cdot m}{2\pi^2\hbar^2}$$

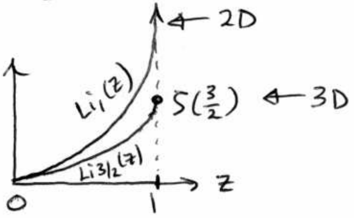
$$\Rightarrow N = \int_0^\infty \frac{g(E)\,dE}{e^{\beta(E-\mu)}-1} = \frac{(2S+1)A}{2\pi^2}\cdot\frac{m}{\hbar^2}\underbrace{\int_0^\infty\frac{dE}{z^{-1}e^{\beta E}-1}}_{k_BT\,\underbrace{\Gamma(1)}_{1}\cdot\mathrm{Li}_1(z)}$$

$$\lambda_{th}^2 = \frac{h^2}{2\pi m k_B T} = \frac{2\pi\hbar^2}{mk_BT}$$

$$\Rightarrow N = \frac{(2S+1)A}{\pi\lambda_{th}^2}\mathrm{Li}_1(z)$$

Now $\mathrm{Li}_1(z) = -\ln(1-x) \to \infty$ as $x \to 1$

∴ BEC argument fails in 2D



$\boxed{30.6}$ Boson in a box $E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2+n_z^2)$

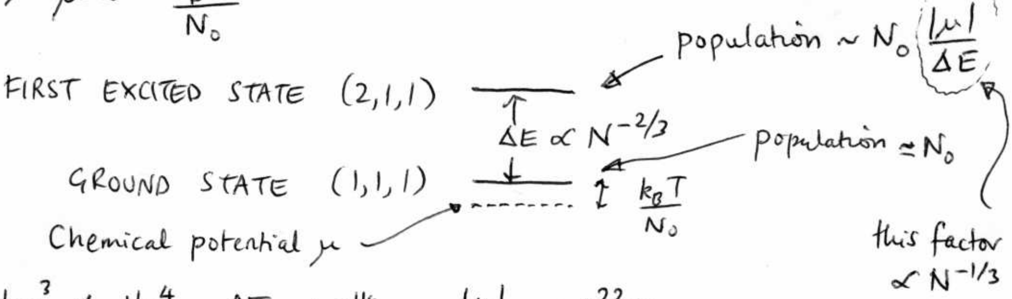
$\Delta E = E(2,1,1) - E(1,1,1) = \frac{3\hbar^2\pi^2}{2mL^2} \approx \frac{\hbar^2}{mL^2}$, so if in a box of volume V, so that $N \sim \left(\frac{L}{a}\right)^3$,

$\Delta E \propto N^{-2/3}$

$$N_0(T) \approx \frac{1}{e^{-\mu\beta}-1} \approx -\frac{k_BT}{\mu}$$

$$\Rightarrow \mu \simeq -\frac{k_BT}{N_0}$$

i.e.



e.g. for $1\,\mathrm{cm}^3$ of He^4, $\frac{\Delta E}{k_B} \sim 10^{-14}\,K$, $\frac{|\mu|}{k_B} \sim 10^{-22}\,K$

⇒ ground state <u>is</u> macroscopically occupied but the 1st excited state isn't.

31.1 $V_s = \sqrt{\dfrac{\gamma k_B T}{m}}$

Assuming γ doesn't change, expect $V_s \propto \sqrt{T}$

$$\Rightarrow V_s(-60°C) = 331.5\sqrt{\frac{213}{273}} = 292.8 \text{ ms}^{-1}$$

31.2 N_2 has mass $28 m_p$. Take $\gamma = 7/5$.

$\Rightarrow V_s = 442 \text{ ms}^{-1}$

[If take $\gamma = 9/7 \Rightarrow V_s = 424 \text{ ms}^{-1}$]

31.4 Speeds should be in the ratio $\dfrac{1}{\sqrt{28}} : \dfrac{1}{\sqrt{2}} : \dfrac{1}{\sqrt{44}}$

assume air = N_2

i.e. 1 : 3.74 : 0.80

actually 1 : 3.83 : 0.78 So not bad.

31.3 Take $V_s = 330 \text{ ms}^{-1}$ so $v = f\lambda$

$\Rightarrow$

f	1 Hz	20 kHz
λ	330 m	0.0165 m

$d = 2.5$ Å ?

$\sigma = \pi d^2$

$\dfrac{k_B T}{\sqrt{2} p \sigma}$

1.4×10^{-7} m

$$\delta = \sqrt{\frac{2D}{\omega}} \qquad \frac{K}{C} = \frac{1}{3}\lambda_{mfp}\langle v \rangle$$

$\omega = 2\pi f$

$$= \sqrt{\frac{D}{\pi f}}$$

$\sqrt{\dfrac{8 k_B T}{\pi m}}$

450 ms^{-1}

f	1 Hz	20 kHz
δ	2.5 mm	~~1.8×10~~ 18 μm

$\sim 2 \times 10^{-5} \text{ m}^2\text{s}^{-1}$

$\lambda = \delta$ when $\dfrac{V_s}{f} = \sqrt{\dfrac{D}{\pi f}}$

i.e. $\dfrac{\pi V_s^2}{D} = f \sim 1.7 \times 10^{10}$ Hz

for which $\lambda = \delta = 2 \times 10^{-8}$ m

$< \lambda_{mfp}$

31.5 The vocal cords generate sounds and vibrate at a frequency determined by the tension in the muscles that control them and by the mass of tissue vibrating. (Men have lower voices than women and children ∵ more mass in the vocal cords.) Helium does nothing to this.

However, the sound from the chords goes through the vocal tract which is the mouth + throat and changing the shape of the mouth acts like a variable filter (sing a note and go aaaaah - ooooh - eeeeh!), selecting certain harmonics. This works because of the resonant properties of the cavity formed by your mouth and throat.

Inhaling helium changes the resonant frequencies of the cavity. Because $m\downarrow$ and $\langle v \rangle \uparrow$, you select higher frequencies. If you sing on helium, you are still in tune (you're singing the same notes as fundamentals) but sound "squeaky" because higher harmonics are selected.

Note the warning: inhaling helium is dangerous. People die trying it.

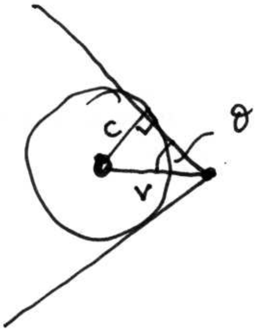
31.6

$$V_s = \sqrt{\frac{\overset{5/3}{\gamma}\, k_B T}{m_p/2}} = 4.1\times10^{5}\ \mathrm{m\,s^{-1}}$$

$$R_\odot \sim 7\times10^{8}\ \mathrm{m} \Rightarrow t \sim 1\ \mathrm{hr.}$$

Shock waves

32.1 follows from geometry:



$$\sin\theta = \frac{c}{v} = \frac{1}{M}$$

$$\Rightarrow \quad \theta = \sin^{-1}\frac{1}{M}$$

32.5 $M_1 \gg 1 \Rightarrow \quad 2\gamma M_1^2 - (\gamma-1) \rightarrow 2\gamma M_1^2$

and $2 + (\gamma-1)M_1^2 \rightarrow (\gamma-1)M_1^2$

$\Rightarrow$ (32.28) $\rightarrow$ (32.33)

32.2

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}\,\frac{\rho_2^{-1}}{\rho_1^{-1}} =$$

$$= \left(\frac{2\gamma M_1^2 - (\gamma-1)}{(\gamma+1)}\right)\left(\frac{2+(\gamma-1)M_1^2}{(\gamma+1)M_1^2}\right)$$ using 32.19 & 32.20

= (32.29).

$$M_1 \gg 1 \qquad \frac{T_2}{T_1} \rightarrow \frac{2\gamma(\gamma-1)M_1^2}{(\gamma+1)^2}$$

32.3 Monatomic $\gamma = \frac{5}{3}$, $\gamma - 1 = 2/3$, $\gamma + 1 = 8/3$

$\Rightarrow$ (32.31)

32.4 Diatomic $\gamma = \frac{7}{5}$

$\Rightarrow$ (32.32)

$\boxed{33.1}$

$$p(x) \propto e^{S(x,E)/k_B}$$

$$(33.47) \Rightarrow dS_{tot} = -\frac{dA}{T_0}$$

$$\Rightarrow p(x) \propto e^{-\beta A(x)}$$

with constant p, T, N $\quad A(x) = G(x)$

$$\Rightarrow p(x) \propto e^{-\beta G(x)} .$$

$\boxed{33.2}$

$$f(t) = f_0 e^{i\omega t}$$

$$x(t) = \chi f(t) = f_0 [\tilde{\chi}'(\omega) + i\tilde{\chi}''(\omega)] e^{i\omega t}$$

$$\dot{x}(t) = i\omega f_0 [\tilde{\chi}' + i\tilde{\chi}''] e^{i\omega t}$$

$$\langle f \dot{x} \rangle = \frac{1}{2} \omega f_0^2 \tilde{\chi}''$$

$\uparrow$ ∵ average of $\cos^2$ gives $\frac{1}{2}$

$\boxed{33.3}$

$$y(-t) = y(t) \quad \Rightarrow \quad \tilde{y}(\omega) \text{ purely real.}$$

$$\tilde{\chi}(\omega) = \tilde{\chi}'(\omega) + i\tilde{\chi}''(\omega) \qquad (33.70)$$

$$\tilde{\chi}(\omega) = \frac{1}{2}\tilde{y}(\omega) - \frac{i}{2\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\tilde{y}(\omega')\,d\omega'}{\omega' - \omega} \qquad (33.69)$$

equating the real parts of these equations $\Rightarrow \chi'(\omega) = \frac{1}{2}\tilde{y}(\omega) \Rightarrow \tilde{y}(\omega) = 2\tilde{\chi}'(\omega)$

∴ equating the imaginary parts $\Rightarrow$

$$\chi''(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega'\,\chi'(\omega')}{\omega' - \omega} .$$

$\boxed{34.1} \equiv 33.1$ (oops!)

$\boxed{34.2}$

$$\mathcal{L}_{\varepsilon\varepsilon} = \underline{\sigma}$$

$$-\frac{\mathcal{L}_{\varepsilon T}}{\mathcal{L}_{\varepsilon\varepsilon}} = \underset{(34.45)}{\varepsilon} \quad \Rightarrow \quad \mathcal{L}_{\varepsilon T} = -\underline{\sigma\varepsilon}$$

$$\frac{\mathcal{L}_{T\varepsilon}}{\mathcal{L}_{\varepsilon\varepsilon}} = \Pi \quad \Rightarrow \quad \mathcal{L}_{T\varepsilon} = \underset{\substack{\uparrow \\ T\varepsilon \quad (34.56)}}{\Pi}\,\sigma = \underline{T\sigma\varepsilon}$$

$$\kappa = -\left[\frac{\mathcal{L}_{\varepsilon\varepsilon}\mathcal{L}_{TT} - \mathcal{L}_{T\varepsilon}\mathcal{L}_{\varepsilon T}}{\mathcal{L}_{\varepsilon\varepsilon}}\right]$$

$$\therefore \quad \kappa\sigma = -\sigma\mathcal{L}_{TT} - T\sigma^2\varepsilon^2$$

$$\mathcal{L}_{TT} = \underline{-\kappa - \sigma\varepsilon^2 T}$$

then (34.54)

$$L_{\varepsilon\varepsilon} = \sigma T$$

$$L_{T\varepsilon} = \sigma\varepsilon T^2$$

$$L_{\varepsilon T} = -\sigma\varepsilon T^2$$

$$L_{TT} = +\kappa T^2 + \sigma\varepsilon^2 T^3$$

$\boxed{34.3}$

$$\varepsilon = \frac{\Pi \leftarrow 5.08\,\text{mV}}{T \leftarrow 273\,\text{K}} = 18.6\,\mu\text{V}\,\text{K}^{-1}$$

$\boxed{34.4}$

(a) $$\left.\begin{array}{ll}\underline{J}_e = n\overset{\text{charge per particle}}{q}\,\underline{v} & \text{electrical current}\\ \underline{J}_Q = n\underset{\text{heat capacity per particle}}{c}T\underline{v} & \text{heat current}\end{array}\right\} \quad J_Q = \overset{\text{Peltier coefficient}}{\Pi}\, J_e$$

$$\Rightarrow \quad \Pi = \frac{cT}{q}$$

Thermopower $$\epsilon = \frac{\Pi}{T} = \frac{c}{q}$$

Now cT = "heat per carrier" $\Rightarrow$ c = entropy per carrier

$$\therefore \quad \epsilon = \frac{\text{entropy per carrier}}{q}$$

[NB it is therefore ZERO for superconductors]

(b) classical gas, $c \sim \frac{3k_B}{2}$ $\Rightarrow$ $\epsilon \approx \frac{3k_B}{2e} \approx \frac{k_B}{e}$

(c) For metals, $c = c_{el} \approx \left(\frac{k_BT}{E_F}\right)k_B$ $\Rightarrow$ $\epsilon \approx \frac{k_B}{e}\left(\frac{k_BT}{E_F}\right)$
$\ll \frac{k_B}{e}$

(d) The heat carried is the difference in a carrier's energy from μ and is therefore $\approx \frac{E_g}{2}$ (half the gap) $\Rightarrow$ $\epsilon \approx \frac{E_g/2}{eT} = \frac{k_B}{e}\left(\frac{E_g}{2k_BT}\right)$
$\gg \frac{k_B}{e}$

(e) As $T \to 0$, there are no carriers and so it doesn't matter if their entropy diverges. Although S diverges as $T \to 0$, the conductivity ($\propto$ number density) decreases faster.

[Thus our revised 3rd law is $\lim_{T\to 0} \sigma S = 0$.]

35.1

$$\text{number} \approx \frac{M_\odot \leftarrow 2\times10^{30}\,\text{kg}}{m_p \leftarrow 1.67\times10^{-27}\,\text{kg}} \approx 10^{57}$$

(assuming all protons)

35.2

$$\rho_J = \frac{3}{4\pi \underset{\uparrow \atop 1000\,M_\odot}{M^2}}\left(\frac{3k_B \overset{20\,\text{K}}{T}}{2G\underset{\wr \atop 2m_p}{m_{H_2}}}\right)^3$$

$$= 3.8\times10^{-22}\ \text{kg m}^{-3} \xrightarrow[\div 2m_p]{} \approx 10^{5}\ \text{particles m}^{-3}$$

(a) ~~M~~ $1000\,M_\odot \to M_\odot$ $\approx 10^{11}$ particles m^{-3}

(b) $20\,\text{K} \to 100\,\text{K}$ $\approx 10^{7}$ particles m^{-3}

35.3

$$M_{\text{universe}} \sim \underset{\uparrow \atop 3\times10^{-27}\,\text{kg m}^{-3}}{\rho}\,(c\overset{13\times10^{9}\text{ years}}{\tau})^3 \sim \underbrace{6\times10^{51}\,\text{kg}}$$

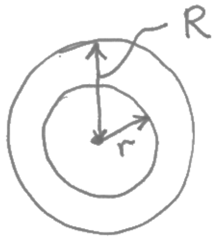
$$\downarrow \div 10^{11}\,M_\odot$$

$$3\times10^{10}\ \text{galaxies}$$

$$\#\,\text{protons} \sim \frac{M_{\text{universe}}}{m_p} \sim 4\times10^{78}$$

(assuming that all matter is due to protons)

35.4



$$\int_0^R -\underbrace{\rho\cdot 4\pi r\,dr}_{dm}\cdot\frac{GM}{r}\frac{r^3}{R^3}$$

$$\rho = \frac{M}{\frac{4}{3}\pi R^3}$$

$$= -\frac{3GM^2}{R^6}\underbrace{\int_0^R r^4\,dr}_{\frac{R^5}{5}} = -\frac{3GM^2}{5R}$$

35.5

DERIVATION OF C_V

specific (per unit mass) U, V

$$U = \frac{3}{2} n V k_B T + \chi n_+ V \qquad V = \frac{1}{m_p \underbrace{(n_0+n_+)}_{\text{number of } H^0, H^+ \, m^{-3}}} \Rightarrow n_+ + n_0 = \frac{1}{m_p V} \quad (m_p \gg m_e)$$

$$n = \underbrace{n_0 + 2n_+}_{\text{number of } H, H^+, e^- \, m^{-3}}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} n V k_B + \frac{3}{2} k_B T V \left(\frac{\partial n}{\partial T}\right)_V + \chi V \left(\frac{\partial n_+}{\partial T}\right)_V$$

$$\left(\frac{\partial n}{\partial T}\right)_V = \left(\frac{\partial n^+}{\partial T}\right)_V = -\left(\frac{\partial n_0}{\partial T}\right)_V \quad Ⓑ$$

$$\Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} n V k_B \left[1 + \frac{2T}{3n}\left(\frac{3}{2} + \beta\chi\right)\left(\frac{\partial n^+}{\partial T}\right)_V\right] \quad Ⓐ$$

Saha equation $\Rightarrow$ $$\frac{n_+^2}{n_0} = \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{-\beta\chi} = g(T)$$

$$\frac{\left(\frac{1}{m_p V} - n_0\right)^2}{n_0}$$

$\xrightarrow{d/dT}$

$$\frac{dg}{dT} = \left(\frac{3}{2} + \beta\chi\right)\frac{g}{T} \quad ①$$

$$\left(\frac{\partial n_0}{\partial T}\right)_V \frac{n_0 \cdot 2\left(\frac{1}{m_p V} - n_0\right)(-1) - \left(\frac{1}{m_p V} - n_0\right)^2 \cdot 1}{n_0^2} \equiv \left[1 - \frac{(1/m_p V)^2}{n_0^2}\right]\left(\frac{\partial n_0}{\partial T}\right)_V \quad ②$$

$$① = ② \Rightarrow \left(\frac{\partial n_0}{\partial T}\right)_V = \left(\frac{3}{2} + \beta\chi\right)\frac{\overset{n_+^2/n_0}{g}}{T} \times \frac{n_0^2}{n_0^2 - (n_+ + n_0)^2}$$

$$= \frac{-n_+ n_0}{n_+ + 2n_0}\left(\frac{3}{2} + \beta\chi\right) \cdot \frac{1}{T}$$

and using Ⓐ, Ⓑ get

$$C_V = \frac{3}{2} n V k_B \left[1 + \frac{2}{3}\left[\frac{3}{2} + \beta\chi\right]^2 \frac{n_+ n_0}{(n_0 + 2n_+)(n_+ + 2n_0)}\right]$$

Degree of ionization $x = \dfrac{n_+}{n_0 + n_+}$ $\Rightarrow$

$n \equiv n_0 + 2n_+ = (1+x)[n_0 + n_+]$

$n_+ \equiv x[n_0 + n_+]$

$n_0 = (1-x)[n_0 + n_+]$

$n_+ + 2n_0 = (2-x)[n_0 + n_+]$

$$\therefore C_V = \frac{k_B}{2}(1+x)[n_0 + n_+]\left(3 + \frac{2x(1-x)}{(2-x)(1+x)}\left[\frac{3}{2} + \beta x\right]^2\right)$$

35.6

$$L \propto \frac{M^{5.5}}{R^{0.5}} \quad \text{(from 35.63)} \Rightarrow R \propto M^{11} L^{-2}$$

$$L = 4\pi \underset{\propto M^{22} L^{-4}}{R^2} \sigma T_{eff}^4 \Rightarrow L^5 \propto M^{22} T_{eff}^4$$

$$\Rightarrow L \propto M^{22/5} T_{eff}^{4/5}$$

not 11/5.

$\boxed{36.1}$

(36.12) $R \propto M^{-1/3} \Rightarrow V \propto R^3 \propto M^{-1} \Rightarrow MV = \text{const}.$

$\boxed{36.2}$

assuming constant density

$$(36.10) \quad \rho = \frac{3M}{4\pi R^3} = \frac{4G^3M^2m_e^3}{27\pi^3\hbar^6}\left(\frac{Am_p}{Z}\right)^5$$

$$\Rightarrow R^3 = \frac{3\cancel{M}}{4\cancel{\pi}} \cdot \frac{27\pi^{\cancel{3}\,2}\hbar^6}{4G^3M^{\cancel{2}}m_e^3}\left(\frac{Z}{Am_p}\right)^5$$

$$= \frac{81\pi^2\hbar^6}{16G^3m_e^3M}\left(\frac{Z}{Am_p}\right)^5$$

$$\Rightarrow R = \sqrt[3]{\frac{81\pi^2}{16M}} \cdot \frac{\hbar^2}{Gm_e}\left(\frac{Z}{Am_p}\right)^{5/3} \qquad ①$$

Take $\frac{Z}{A} = 0.5$ for a carbon-oxygen white dwarf.

and for $M = M_\odot$

$\Rightarrow R \approx 7 \times 10^6\ \text{m}$

$\boxed{36.3}$ Now supported by neutron degeneracy pressure,

$m_e \to m_n$ and $\frac{Z}{Am_p} \to \frac{1}{m_n}$ in ①

$$\Rightarrow R = \sqrt[3]{\frac{81\pi^2}{\underset{\underset{2M_\odot}{\uparrow}}{16M}}} \cdot \frac{\hbar^2}{Gm_n^{8/3}} \approx 10\ \text{km}$$

$$\tau = 2\pi\sqrt{\frac{R^3}{GM}} = 0.5\ \text{ms}$$

Note that $R^3 \propto M^{-1}$ so that $\tau \propto M^{-1}$, $\omega = \frac{2\pi}{\tau} \propto M$

and more massive neutron stars spin faster.

$\boxed{36.4}$ $(36.24) \Rightarrow R_s = 2GM/c^2$

(i) $10\,M_\odot$ $R_s = 30\text{ km}$

(ii) $10^8\,M_\odot$ $R_s = 3\times10^{11}\text{ m}$

(iii) $10^{-8}\,M_\odot$ $R_s = 3\times10^{-5}\text{ m}$

$\boxed{36.5}$ $M = 100\,M_\odot \Rightarrow R_s = 300\text{ km}$

$$T_H = \frac{\hbar c^3}{8\pi k_B G M} = 6\times10^{-10}\text{ K}$$

$$S = k_B \cdot \frac{\overset{4\pi R_s^2}{A}}{4\ell_p^2} = \frac{\pi R_s^2 k_B}{\ell_p^2}$$

$$\ell_p = \left(\frac{G\hbar}{c^3}\right)^{1/2} = 1.6\times10^{-35}\text{ m}$$

$$\simeq 10^{81}\,k_B$$

$$= 10^{58}\text{ J k}^{-1}$$

$\boxed{37.1}$ (a)

1.36 kW m^{-2}

$$\text{illumination} = \begin{cases} S\cos\phi & -90 < \phi < 90 \quad \text{(day time)} \\ 0 & 90 < \phi < 270 \quad \text{(night time)} \end{cases}$$

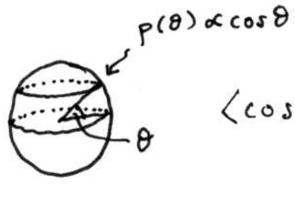
$$\Rightarrow \text{averages at} \quad S \cdot \frac{1}{2\pi}\int_{-\pi/2}^{\pi/2} \cos\phi \, d\phi = \frac{S}{\pi}$$

$\Rightarrow$ in 1 year, average energy received is $\frac{S}{\pi} \times (\text{year})$

$$= 1.37 \times 10^{10}\,\text{J}$$

(b) Previous answer × $\underset{\uparrow 35^\circ}{\cos\theta} = 1.11 \times 10^{10}\,\text{J}$

(c)



$$\langle \cos\theta \rangle = \frac{\int_0^{\pi/2} \cos\theta \cdot \cos\theta \, d\theta}{\int_0^{\pi/2} \cos\theta \, d\theta} = \frac{\pi}{4}$$

$$\Rightarrow \text{answer} = \frac{S}{\pi} \times (1\,\text{year}) \times \frac{\pi}{4} = 1.07 \times 10^{10}\,\text{J}$$

OR $\quad \underset{1\text{ year}}{t} \cdot \frac{S(\pi r^2)\leftarrow\text{projected area}}{(4\pi r^2)\leftarrow\text{surface area}} = \frac{tS}{4} = 1.07 \times 10^{10}\,\text{J}$

$\boxed{37.2}$ $M_{atmos} = 5.3 \times 10^{18}\,\text{kg} \Rightarrow C_{atmos} = M_{atmos} \times 1005\,\text{J kg}^{-1}\text{K}^{-1}$
$= 5.30 \times 10^{21}\,\text{J K}^{-1}$ ($\approx 0.1\%$ C_{ocean})

$\boxed{37.3}$ $M_{ocean} = 1.38 \times 10^{21}\,\text{kg} \Rightarrow C_{ocean} = M_{ocean} \times 4217\,\text{J kg}^{-1}\text{K}^{-1}$
$= 5.82 \times 10^{24}\,\text{J K}^{-1}$

$\boxed{37.4}$ Energy to boil oceans (from 10° to 100°?) is, using answer above
$\approx 5 \times 10^{26}\,\text{J}$

$S \cdot \pi R_\oplus^2 \sim 1.8 \times 10^{17}\,\text{W}$ and if all that is available to heat the oceans, then you can bring them to the boil in ~100 years.

$\boxed{37.5}$ (a) need 13 TW = P, $\eta = 0.15$

$\Rightarrow \text{area} = \frac{P}{S\eta} = 6.4 \times 10^{10}\,\text{m}^2$ ① if Sun is overhead, permanently (unrealistic!)

or $\frac{\pi P}{S\eta} = 2 \times 10^{11}\,\text{m}^2$ if at various points on equator. ②

i.e. an area 450 km × 450 km ③

(b) divide all answers by cos(35)

① $7.8 \times 10^{10}\,\text{m}^2$
② $2.4 \times 10^{11}\,\text{m}^2$
③ area 500 km × 500 km

$\boxed{37.6}$

$$\underbrace{\sigma T_{moon}^{4}}_{\text{energy emitted}} = \underbrace{S\cos\theta\,(1-A)}_{\text{energy absorbed}}$$

ignoring heat capacity of Moon, etc, etc.

$$T_{moon}(\theta) = \left[\frac{S(1-A)}{\sigma}\cos\theta\right]^{1/4}$$

$\boxed{37.7}$ radiance ⊥ to surface $I(\theta,\phi)\cos\theta$

$$\therefore \quad \Phi = \int I(\theta,\phi)\cos\theta\, d\Omega$$

$$= \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \int_0^{\pi/2} \underbrace{I(\theta,\phi)}_{\frac{n\langle v\rangle}{4\pi}} \cos\theta \cdot \sin\theta\, d\theta$$

$$= \frac{n\langle v\rangle}{4\pi}\cdot 2\pi \cdot \underbrace{\left[\frac{1}{2}\sin^2\theta\right]_0^{\pi/2}}_{1/2} = \frac{1}{4}n\langle v\rangle .$$

$\boxed{37.8}$

$$-\frac{dF^{\uparrow}}{d\chi^*} + F^{\uparrow} = \pi B$$

$$\frac{dF^{\downarrow}}{d\chi^*} + F^{\downarrow} = \pi B$$

$$F^{\uparrow} - F^{\downarrow} = \phi = \text{const}$$

$$F^{\uparrow} + F^{\downarrow} = \psi$$

$$\frac{d\psi}{d\chi^*} = \frac{dF^{\uparrow}}{d\chi^*} + \frac{dF^{\downarrow}}{d\chi^*} = F^{\uparrow} - F^{\downarrow} = \phi$$

$$\frac{d\phi}{d\chi^*} = \frac{dF^{\uparrow}}{d\chi^*} - \frac{dF^{\downarrow}}{d\chi^*} = F^{\uparrow} + F^{\downarrow} - 2\pi B = \psi - 2\pi B$$

ϕ constant $\Rightarrow \frac{d\phi}{d\chi^*} = 0 \Rightarrow \psi = 2\pi B$

and $\frac{d\psi}{d\chi^*} = \phi \Rightarrow \frac{dB}{d\chi^*} = \frac{\phi}{2\pi} \Rightarrow B = \frac{\phi\chi^*}{2\pi} + \text{constant}$

Top of atmosphere $\chi^* = 0$, $F^{\downarrow} = 0$, $\Rightarrow \psi = \phi \Rightarrow B = \frac{\phi}{2\pi}(\chi^* + 1)$