6CCP3212 Statistical Mechanics Solutions 3

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1) From
(i) Bookwork.
(ii) The partition function is

$$\begin{aligned} Z_{\rm rot} &= \frac{1}{(2\pi\hbar)^2}\int_0^\pi d\theta \int_0^{2\pi} d\phi \int dp_\phi dp_\theta\ e^{-\beta H_{\rm rot}(p_\phi,p_\theta)} \\ &= \frac{1}{(2\pi\hbar)^2}\int_0^\pi d\theta \int_0^{2\pi} d\phi \int dp_\phi dp_\theta\ e^{-(\beta/2I)(p_\theta^2+p_\phi^2\sin^{-2}\theta)}\ . \end{aligned} \tag{1}$$

We first do the momentum integrals since they are just gaussian integrals,

$$\int d\theta e^{-(\beta/2I)p_\theta^2} = \sqrt{\frac{2I\pi}{\beta}}\ ,\ \int d\phi e^{-(\beta/2I)p_\phi^2\sin^{-2}\theta} = \sqrt{\frac{2I\pi\sin^2\theta}{\beta}} \tag{2}$$

so

$$\begin{aligned} Z_{\rm rot} &= \frac{2\pi}{(2\pi\hbar)^2}\frac{2I}{\beta}\underbrace{\int_0^\pi \sin\theta d\theta}_{1}\underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= \frac{1}{\hbar^2}\frac{2I}{\beta} \\ &= \frac{2Ik_bT}{\hbar^2}\ . \end{aligned} \tag{3}$$

(iii) The Hamiltonian in terms of the canonical variables p_z and z is

$$H_{\rm vib} = \frac{p_z^2}{2m} + \frac{1}{2}m\omega^2 z^2 \tag{4}$$

so the partition function is

$$\begin{aligned} Z_{\rm vib} &= \frac{1}{2\pi\hbar}\int dz dp_z e^{-\beta(p_z^2/2m + m\omega^2 z^2/2)} \\ &= \frac{1}{2\pi\hbar}\sqrt{\frac{2m\pi}{\beta}}\sqrt{\frac{2\pi}{m\omega^2\beta}} \\ &= \frac{k_bT}{\hbar\omega}\ . \end{aligned} \tag{5}$$

(iv) Given Z, the energy is

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} \tag{6}$$

and since it is derivative of a log, the coefficient is simply the *power* of the T term in the partition functions, so the powers of T for the translation, rotation and vibration partition functions are $T^{3/2}$, T and T, the energies are simply

$$E_{\rm trans} = \frac{3}{2}k_bT\ ,\ E_{\rm rot} = k_bT\ ,\ E_{\rm vib} = k_bT\ . \tag{7}$$

2) From

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}} = \beta^{1/2}\sqrt{\frac{2\pi\hbar^2}{m}} \tag{8}$$

then

$$\frac{\partial\lambda}{\partial\beta} = \frac{\lambda}{2\beta} \tag{9}$$

and thus

$$\bar{E} = -\frac{\partial \ln Z}{\partial\beta} = N\frac{\partial}{\partial\beta}\ln\lambda^3 = \frac{3N}{2\beta}\ . \tag{10}$$

Plugging this in

$$\begin{aligned}
S &= k_b(\ln Z + \beta\bar{E}) \\
&= k_b\left(N\ln\frac{V}{\lambda^3} - \ln N! + \frac{3N}{2}\right) \\
&= k_b\left(N\ln\frac{V}{\lambda^3} - N\ln N + N + \frac{3N}{2}\right) \\
&= Nk_b\left[\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right]\ .
\end{aligned} \tag{11}$$

3)

(i) To find the maximum, we take the derivative and set it to zero to solve for v_{max}

$$\frac{\partial}{\partial v}\left[\sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2} v^2 e^{-mv^2/2k_bT}\right] = 0 \tag{12}$$

which gives

$$e^{-mv^2/2k_bT}\left(2v - \frac{m}{k_bT}v^3\right) = 0 \tag{13}$$

and hence $v_{\max} = \sqrt{2k_bT/m}$.

(ii) Using $a \equiv m/2k_bT$ to save ink, and also keeping the big proportionality constant intact because those are going to cancel at the end, we integrate by parts

$$\begin{aligned}
\langle v\rangle &= \int_0^\infty vf(v)e^{-mv^2/2k_bT} \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_bT}dv \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\left[-\frac{e^{-av^2}}{2a^2}(1+av^2)\right]_0^\infty \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\frac{1}{2a^2}\ .
\end{aligned} \tag{14}$$

Meanwhile,

$$\begin{aligned}
\langle v^{-1}\rangle &= \int_0^\infty v^{-1}f(v)e^{-mv^2/2k_bT} \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\int_0^\infty v e^{-mv^2/2k_bT}dv \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\left[-\frac{e^{-av^2}}{2a}\right]_0^\infty \\
&= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_bT}\right)^{3/2}\frac{1}{2a}\ .
\end{aligned} \tag{15}$$

Thus the ratio

$$\frac{\langle v^{-1}\rangle}{(\langle v\rangle)^{-1}} = \frac{1}{4a^3}\times\frac{2}{\pi}\left(\frac{m}{k_bT}\right)^3 = \frac{4}{\pi}\ . \tag{16}$$

(iii)

(a) $\langle v_x \rangle = 0$ by symmetry (else there is a net movement to the x direction).

(b) $\langle v_y^2 \rangle = k_b T/m$ by equipartition theorem (since $\langle m v_x^2/2 \rangle = (1/2)k_b T$).

(c) $\langle v^2 v_x \rangle = \langle (v_x^2 + v_y^2 + v_z^2) \rangle v_x \rangle = \langle v_x^3 + v_y^2 v_x + v_z^2 v_x \rangle = 0$ using $\langle v_y^2 v_x \rangle = \langle v_y^2 \rangle \langle v_x \rangle = 0$ by symmetry.

(d) $\langle (v_x + b v_y)^2 \rangle = \langle v_x^2 + b^2 v_y^2 + 2b v_x v_y \rangle = (k_b T/m)(1 + b^2)$ where the last term is zero by symmetry again.

(e) $\langle (v_x^3 v_y^2) \rangle = 0$ by symmetry.

(f) $\langle (v_x^2 v_y^2) \rangle = \langle v_x^2 \rangle \langle v_y^2 \rangle = (k_b T/m)^2$.

4)

(i) Taking derivative

$$\frac{d}{dr}\left[4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right] = -4\epsilon\left[\frac{12}{r}\left(\frac{\sigma}{r}\right)^{12} - \frac{6}{r}\left(\frac{\sigma}{r}\right)^{6}\right] = 0 \tag{17}$$

it's easy to see that this occurs when

$$r_{\text{min}} = \left(\frac{1}{2}\right)^{-1/6} \sigma \ . \tag{18}$$

(ii) The calculation is very similar to that of the hardcore-London potential that used in the lecture notes.

$$r_0 \to \sigma \ , \tag{19}$$

and do the I integral for the limit from 0 to σ, which is easily done

$$\int_0^\sigma f(r) d^3 r = 4\pi \int_0^\sigma \left(e^{-\beta U(r)} - 1\right) r^2 dr \ . \tag{20}$$

But now, as $r \ll \sigma$, the term of U that dominates is the $(\sigma/r)^{12}$ term, and as $r \to 0$, $e^{-(\sigma/r)^{12}} \to 0$, thus $f(r) \to -1$ just like the hardcore potential in the lectures. Thus we will get the Van der Waals equation of state, with the new variables σ and ϵ, i.e. the a and b coefficients are now

$$a \equiv \frac{16\pi\sigma^3\epsilon}{3} \ , \ b \equiv \frac{2\pi\sigma^3}{3} \ . \tag{21}$$

[Thanks to Frankie Palmer for pointing out an error in the solution of a previous version.]

5)

(i) The partition function for a single particle is

$$\begin{aligned} Z_1 &= \frac{1}{(2\pi\hbar)^2} \underbrace{\int d^2 x}_{A} \, d^2 p e^{-\beta \mathbf{p}^2/2m} \\ &= \frac{A}{(2\pi\hbar)^2}\left(\frac{2m\pi}{\beta}\right) \\ &= \frac{A}{\lambda^2} \end{aligned} \tag{22}$$

where we have used the gaussian integral $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$ twice in the 2nd line. The total partition function is then

$$Z = \frac{1}{N!} \prod_N Z_1 = \frac{1}{N!}\left(\frac{A}{\lambda^2}\right)^N \ . \tag{23}$$

(ii) The Helmholtz free energy is $F = -k_b T \ln Z = -k_b T N(\ln A - \ln(N!\lambda^2))$, and the pressure is given by (note that the "Volume" is now simply the area A)

$$P = -\left(\frac{\partial P}{\partial A}\right)_T = \frac{N k_b T}{A} \tag{24}$$

6)

(i) This is trivial.

(ii) The partition function for a single particle is

$$\begin{aligned} Z_1 &= \frac{1}{(2\pi\hbar)^3}\int d^3p d^3x \; e^{-\beta pc} \\ &= \frac{V}{(2\pi\hbar)^3}\int d^3p \; e^{-\beta pc} \\ &= \frac{V}{(2\pi\hbar)^3}\int_0^\infty (4\pi)p^2 dp \; e^{-\beta pc} \\ &= \frac{4\pi V}{(2\pi\hbar)^3}\left[\frac{-1}{\beta^3c^3}e^{-\beta pc}(2+2\beta pc+\beta^2p^2c^2)\right]_0^\infty \\ &= \frac{V}{\pi^2}\left(\frac{k_bT}{\hbar c}\right)^3 , \end{aligned} \tag{25}$$

where in the 4th line we integrate by parts twice. Thus the partition function for N such non-interacting particles is

$$Z = \prod_N Z_1 = \frac{1}{N!}\left[\frac{V}{\pi^2}\left(\frac{k_bT}{\hbar c}\right)^3\right]^N . \tag{26}$$

(iii) The Helmholtz free energy is $F = -k_bT\ln Z$, and the equation of state is then

$$\begin{aligned} P &= -\left(\frac{\partial F}{\partial V}\right)_T \\ &= k_bT\left(\frac{\partial \ln Z}{\partial V}\right)_T \\ &= k_bT\left(\frac{\partial N\ln V}{\partial V}\right)_T \\ &= \frac{Nk_bT}{V} . \end{aligned} \tag{27}$$

7)

(i) This calculation is identical to the lecture notes for the derivation of the Van der Waals force. The Helmholtz free energy is

$$F = F_{\rm id} - k_bT\times I \tag{28}$$

with

$$I = \frac{N^2}{2V}\int d^3 f(r) \tag{29}$$

and

$$f(r) = e^{-\beta U(r)} - 1 . \tag{30}$$

Note that since the potential only has a hard core, $f(r)=0$ for $r>r_0$, so the only part of the integral I that has support is

$$\int_\infty^{r_0} f(r)d^3r = \int_0^{r_0} 4\pi r^2(-1)dr = -\frac{4\pi r_0^3}{3} . \tag{31}$$

Comparing this to the Van der Waals case, we see that this imply that the Van der Waals coefficients are

$$a=0 \; , \; b = \frac{2\pi r_0^3}{3} . \tag{32}$$

So the equation of state is hence

$$k_bT = \frac{PV}{N}\left(1+\frac{N}{V}b\right)^{-1} . \tag{33}$$

Expressing it as a virial expansion

$$\frac{P}{k_b T} = \frac{N}{V}\left(1 + \frac{N}{V}b\right) \tag{34}$$

which is 2nd order in N/V with the Virial coefficient b.

(ii) In 2-dimensions, instead of a hard core, we have a hard disc. The partition function of ideal 2D gas is given by Q5, so we can calculate the corresponding $F_{\text{id}} = -k_b T \ln Z$. Using the results from the lecture notes, we can split the F into ideal and non-ideal case as usual

$$F = F_{\text{id}} - k_b T \times I \tag{35}$$

with

$$I = \frac{N^2}{2A}\int_0^\infty d^2 r f(r) \ , \tag{36}$$

where A is the area of the container. We now need to do this integral. Again like (i) above, the only part where the integral has support is $f(0 < r < r_0) = -1$ (i.e. $f(r > r_0) = 0$ as you should be able to see easily)

$$\begin{aligned} I &= \frac{N^2}{2A}\int_0^\infty d^2 r f(r) \\ &= \frac{N^2}{2A}\int_0^{r_0} (2\pi) r(-1) \\ &= -\frac{N^2}{2A}\pi r_0^2. \end{aligned} \tag{37}$$

So

$$F = F_{\text{id}} + k_b T \frac{N^2}{2A}(\pi r_0^2) \tag{38}$$

and using

$$\begin{aligned} P &= -\left(\frac{\partial F}{\partial A}\right)_T \\ &= \frac{N k_b T}{A} + k_b T(\pi r_0^2)\frac{N^2}{2A^2} \\ &= \frac{N k_b T}{A}\left(1 + \frac{N}{2A}(\pi r_0^2)\right) \end{aligned} \tag{39}$$

which is a virial expansion to 2nd order in N/A with coefficient πr_0^2.

8)

(i) Plugging in the ansatz $y(x,t)$ into the wave equation, we get

$$k_n^2 y(x,t) = \frac{\rho}{\tau}\omega_n^2 y(x,t) \tag{40}$$

so it will be a solution as long as $k_n = \sqrt{\rho/\tau}\omega_n$. Since the string is fixed $x = 0$ and $x = L$, this means that

$$y(0,t) = y(L,t) \tag{41}$$

or

$$\sin(k_n L) = 0 \tag{42}$$

and this equation has solutions when $k_n = n\pi/L$ for $n = 0, 1, 2, 3, \ldots$. The $n = 0$ mode is the "zero mode" (i.e. the string is not vibrating), so we can ignore it. Using the above result, the spectrum of frequencies is then

$$\omega_n = n\frac{\pi}{L}\sqrt{\frac{\tau}{\rho}} \ , \ n = 1, 2, 3, \ldots \tag{43}$$

(ii) To obtain the *total* energy, we have to integrate the over the length of the string, so

$$\begin{aligned} E_{Kin} &= \int_0^L K(x,t)dx \\ &= \int_0^L \frac{1}{2}\rho\zeta^2\omega_n^2 \sin^2(k_n x)\sin^2(\omega_n t) \\ &= \frac{1}{4}\rho\zeta^2\omega_n^2 \sin^2(\omega_n t)\ , \end{aligned} \tag{44}$$

where we have used $\sin^2 kx = 1/2(1+\cos(2kx))$. Similarly the potential energy

$$\begin{aligned} E_{pot} &= \int_0^L V(x,t)dx \\ &= \int_0^L \frac{1}{2}\tau\zeta^2\omega_n^2 \cos^2(k_n x)\cos^2(\omega_n t) \\ &= \frac{1}{4}\tau\zeta^2\omega_n^2 \cos^2(\omega_n t)\ , \end{aligned} \tag{45}$$

where we have used $\cos^2 kx = 1/2(1-\cos(2kx))$. The total energy per mode n is then

$$E_n = E_{kin} + E_{pot} = \frac{1}{4}\zeta^2(\rho k_n^2 \sin^2(\omega t) + \tau\omega_n^2 \sin^2(\omega t)) = \frac{1}{4}\frac{\tau}{L}n^2\pi^2\zeta^2 \tag{46}$$

using the relation between k_n and ω_n in (i).
(iii) The probability of a mode n being occupied is given by

$$P_n = \frac{1}{Z}e^{-\beta E_n}\ . \tag{47}$$

Now since $E_n \propto n^2$, so the energies of higher harmonics are larger, $\beta E_n = E_n/k_b T$ is larger for higher harmonics, and hence $e^{-E_n/k_b T}$ is smaller, so P_n is smaller for higher harmonics. But since as T increases, $E_n/k_b T$ decreases for fixed n, and thence P_n is larger for higher T.
(iv) The work done is split into two components. The first component is simply the work required to extend the string of tension τ (sometimes this is called the zero mode), so $(đW)_0 = \tau dL$. The second component is more tricky – as we stretch the string, the *energies* of each mode E_n also changes. Recall from the lecture notes that work done on the system changes the energy of the spectrum E_n

$$\begin{aligned} đW &= \langle \delta E_n \rangle \\ &= -\frac{1}{\beta}\frac{\partial \ln Z}{\partial L}dL \\ &= -\frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial L}dL \\ &= -\frac{1}{\beta}\frac{1}{Z}\sum_n \left(-\beta\frac{\partial E_n}{\partial L}e^{-\beta E_n}\right)dL \end{aligned} \tag{48}$$

But now using the results of (ii) for E_n,

$$\frac{\partial E_n}{\partial L} = -\frac{E_n}{L} \tag{49}$$

so we finally have

$$\begin{aligned} đW &= \sum_n \frac{-E_n}{L}\frac{e^{-\beta E_n}}{Z}dL \\ &= -\frac{\langle E_n \rangle}{L}dL\ . \end{aligned} \tag{50}$$

Notice that the energy per mode goes *down* as L increases – the energy of the mode is proportional to ω_n and as L increases, the frequency decreases. Thus, the vibration energy actually helps us stretch the length of the string! The total work is then the sum of both components

$$đW = \left(\tau - \frac{\langle E\rangle}{L}\right) dL \ . \tag{51}$$

9)
(i) The partition function for a single particle is

$$\begin{aligned} Z &= \frac{1}{(2\pi\hbar)^3}\int d^3p \int dxdy \int_0^\infty dz\ e^{-\beta E} \\ &= \underbrace{\frac{1}{(2\pi\hbar)^3}\int d^3p e^{-\beta \mathbf{p}^2/2m}}_{\lambda^{-3} \text{ as usual}} \underbrace{\int dxdy}_{A} \int_0^\infty dz e^{-\beta mgz} \\ &= \frac{1}{\lambda^3}\times A \times \int_0^\infty dz e^{-\beta mgz} \\ &= \frac{Ak_bT}{mg\lambda^3} \ . \end{aligned} \tag{52}$$

(ii) The probability of finding a particle depends on its momentum $\mathbf{p}$ and position $\mathbf{x}$,

$$P(\mathbf{p}, x, y, z) = \frac{1}{Z}e^{-\beta E} \ . \tag{53}$$

If we want to find the probability of finding *any* particle at position z, we need to integrate over $\mathbf{p}$, x and y, i.e.

$$P(z) = \int d^3p \int dxdy P(\mathbf{p}, x, y, z) = \int d^3p \int dxdy e^{-\mathbf{p}^2/2m} \times e^{-\beta mgz} \tag{54}$$

the integrals are identical to those of (i), but since there is no z integral, we get the probability *as a distribution in* z, i.e.

$$P(z) = Ce^{-\beta mgz} \ . \tag{55}$$

Recall that $P(z)$ is the probability of finding a *single* particle in the entire atmosphere as a function of z. Hence it follows that if we have N particles, $NP(z)$ is the probability of finding the the fraction of the particles in z, it is the distribution of particles as a function of z, or its density. (Think of the Maxwell-Boltzmann distribution of particles as a function of velocity v – here the variable is z.)
(iii) $\rho(100\text{km}) = 1.34 \times 10^{-8}$ g/cm^3.

10) Using the Equipartition theorem

$$\langle x\frac{\partial H}{\partial x}\rangle = k_bT \tag{56}$$

for $x = p, q$, we can calculate the mean energy per particle

$$\begin{aligned} \langle E\rangle &= \langle \frac{p^2}{2m} + \lambda q^4\rangle \\ &= \frac{1}{2}\langle p\frac{\partial H}{\partial p}\rangle + \frac{1}{4}\langle q\frac{\partial H}{\partial q}\rangle \\ &= \frac{3}{4}k_bT \end{aligned} \tag{57}$$

and hence the total energy for n particles is $\langle E_N\rangle(3/4)Nk_bT$. The heat capacity is then

$$\left(\frac{\partial C_V}{\partial T}\right)_V = \frac{3}{4}Nk_b \ . \tag{58}$$