Oefeningen Statistical Mechanics

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Intro

This text contains solutions to the notes of Statistical Mechanics by E. Carlon (2014). All of these solutions are written by students, so don't take any results in here at face value. I happily receive any corrections or suggestions for the solutions at alexander@wina.be. Any solutions you would like to add to this text, you can send to that same email. Thanks to Quentin Decant for his corrections.

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0 A Brief Review of Thermodynamics

0.1 Internal Energy of Ideal Gas

The first law states $dE(S,V) = T(S,V)dS - P(S,V)dV$. From this we derive

$$dF = d(E - TS) = -SdT - PdV$$

This gives us

$$\begin{aligned}
\left.\frac{\partial F}{\partial T}\right|_V &= -S \\
\left.\frac{\partial F}{\partial V}\right|_T &= -P
\end{aligned}$$

Differentiating the last expression with respect to V gives us

$$\begin{aligned}
\left.\frac{\partial S}{\partial V}\right|_T &= -\left.\frac{\partial}{\partial V}\left(\left.\frac{\partial F}{\partial T}\right|_V\right)\right|_T \\
&= -\left.\frac{\partial}{\partial T}\left(\left.\frac{\partial F}{\partial V}\right|_T\right)\right|_V \\
&= \left.\frac{\partial P}{\partial T}\right|_V
\end{aligned}$$

And so we see

$$\begin{aligned}
\frac{dE}{dV} &= \left.\frac{\partial E}{\partial V}\right|_S + \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T \\
&= -P + T\left.\frac{\partial P}{\partial T}\right|_V \\
&= -P + T\frac{Nk_b}{V} \\
&= 0
\end{aligned}$$

0.2 Adiabatic transformation for an ideal gas

1 Random walks, diffusion and polymers

1.1 One dimensional random walk

Call the probability that you take a step s_n to the right p_R.

a) The probability that the walk of N steps performs n steps to the right is equal to $P(n, N) = \binom{N}{n} p_R^n (1-p_R)^{N-n}$.

b) Consider the function

$$\begin{aligned} f(N, x, y) &= \sum_{n=0}^{N} \binom{N}{n} x^n y^{N-n} \\ &= (x+y)^N \end{aligned}$$

Now notice that

$$\begin{aligned} Nx(x+y)^{N-1} &= x \frac{\partial f(N, x, y)}{\partial x} \\ &= \sum_{n=0}^{N} \binom{N}{n} n x^n y^{N-n} \end{aligned}$$

So we have $Np_R = p_R \left. \frac{\partial f(n,x,y)}{\partial x} \right|_{x=p_R, y=1-p_R} = \langle n \rangle$. In the same way we have $\langle n^2 \rangle = p_R \frac{\partial}{\partial x} \left(x \frac{\partial f(n,x,y)}{\partial x} \right) \Big|_{x=p_R, y=1-p_R} = Np_R + N(N-1)p_R^2$. The variance is then $\mathrm{Var}(n) = Np_R - Np_R^2 = Np_R(1-p_R)$.

c) Now call $x = \sum_{n=0}^{N} s_n$. We see $\langle x \rangle = N\langle s_0 \rangle = 0$. We also find $\langle x^2 \rangle = \sum_{n,m} \langle s_n s_m \rangle = \sum_{n=}^{N} \langle s_n^2 \rangle = N\langle s_0^2 \rangle = N(p_R^2 + (1-p_R)^2)$.

1.2 Diffusion with an absorbing boundary

a) If we mirror the solution by putting the same amount of particles but negative at the beginning at $-x_0$, so $c(x, 0) = N(\delta(x-x_0) - \delta(x+x_0))$ and do not impose that the particles be absorbed. We see that any of the particles arriving from the right, will be cancelled by the "negative" particles coming from the left. The solution is the sum of the two gaussians

$$c(x,t) = \frac{N}{\sqrt{4\pi Dt}}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right) - \exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right]$$

Now if we only take the right part of this solution, and let for every $x < 0$ the solution be zero, we have the solution to our original problem.

b) Using the taylor expansions of the exponentials we see

$$\begin{aligned} c(x,t) &= \frac{N}{\sqrt{4\pi Dt}}\left[-\frac{(x-x_0)^2}{4Dt} + \frac{(x+x_0)^2}{4Dt} + O(x^4)\right] \\ &= \frac{N}{4Dt\sqrt{4\pi Dt}}\left[4xx_0 + O(x^4)\right]. \end{aligned}$$

So $c(x,t)$ vanishes linearly around $x = 0$.

c) The total number of particles at some time t is equal to

$$\begin{aligned} N(t) &= \int_0^{+\infty} c(x,t)dx \\ &= \frac{N}{\sqrt{4\pi Dt}}\int_0^{+\infty}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right) - \exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right]dx \\ &= \frac{N}{\sqrt{4\pi Dt}}\left[\int_{-x_0}^{+\infty}\exp\left(-\frac{x^2}{4Dt}\right)dx - \int_{x_0}^{+\infty}\exp\left(-\frac{x^2}{4Dt}\right)dx\right] \\ &= \frac{N}{\sqrt{4\pi Dt}}\left[\int_{-\infty}^{x_0}\exp\left(-\frac{x^2}{4Dt}\right)dx - \int_{x_0}^{+\infty}\exp\left(-\frac{x^2}{4Dt}\right)dx\right] \end{aligned}$$

1.3 Diffusion with a reflecting boundary

We have a similar situation as in the previous exercise, consider the begin situation that N particles start at x_0 and $-x_0$. Now each time a particle arrives from the right to go to left, a particle will arrive from the left to go to the right, as if the particle from the right bounces back. The solution is

$$c(x,t) = \frac{N}{\sqrt{4\pi Dt}}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right) + \exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right].$$

We have

$$\begin{aligned}\frac{\partial c(0,t)}{\partial x} &= \frac{N}{\sqrt{4\pi Dt}}\left[-2\frac{(x-x_0)}{4Dt}\exp\left(-\frac{(x-x_0)^2}{4Dt}\right)-2\frac{(x+x_0)}{4Dt}\exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right]\Bigg|_{x=0}\\ &= 0.\end{aligned}$$

At some point t', we have $c(0,t')=c(x_0,t')$, so

$$2\exp\left(-\frac{x_0^2}{4Dt'}\right)=1+\exp\left(-\frac{x_0^2}{Dt'}\right)$$

Denote with $x=\exp\left(-\frac{x_0^2}{4Dt'}\right)$, then we solve the following equation

$$1-2x+x^4=0$$

This equation has two real solutions, $x_1=1$ and $x_2\approx 1/2$. If $x=1$, then $t'\to\infty$ but in the other case we have $t'=-\frac{x_0^2}{4D\log x_2}$.

1.4 Fluorescence recovery after photobleaching

The general solution is given by

$$c(x,t)=\int dy c(y)G_y(x,t).$$

So in this case we have

$$c(x,t)=\frac{c_0}{\sqrt{4\pi Dt}}\left[\int_{-\infty}^{-a}\exp\left(-\frac{(x-y)^2}{4Dt}\right)dy+\int_{a}^{+\infty}\exp\left(-\frac{(x-y)^2}{4Dt}\right)dy\right].$$

So at $x=0$ and for $t>0$, we see

$$c(0,t)=c_0\left[1-\frac{1}{\sqrt{4\pi Dt}}\int_{-a}^{a}\exp\left(-\frac{y^2}{4Dt}\right)dy\right].$$

For the half-recovery time τ we have

$$c_0\left[1-\frac{1}{\sqrt{4\pi D\tau}}\int_{-a}^{a}\exp\left(-\frac{y^2}{4D\tau}\right)dy\right]=c(0,\tau)=c_0/2$$

In other words

$$\begin{aligned}\frac{1}{2} &= \frac{1}{\sqrt{4\pi D\tau}}\int_{-a}^{a}\exp\left(-\frac{y^2}{4D\tau}\right)dy \\ &= \frac{1}{\sqrt{\pi}}\int_{-a/\sqrt{4D\tau}}^{a/\sqrt{4D\tau}}\exp(-u^2)du \\ &= \mathrm{Erf}\left(\frac{a}{\sqrt{4D\tau}}\right)\end{aligned}$$

Now if we define $\gamma = (2\,\mathrm{Erf}^{-1}(1/2))^{-2}$, we find that $\gamma = \frac{D\tau}{a^2}$ or $D = \gamma\frac{a^2}{\tau}$.

1.5 Reaction-diffustion equation: a simple example

Notice that

$$\begin{aligned}D\frac{\partial^2 g(x,t)}{\partial x^2} &= De^{-\alpha t}\frac{\partial^2 c(x,t)}{\partial x^2} \\ &= e^{-\alpha t}\frac{\partial c(x,t)}{\partial t}\end{aligned}$$

and

$$\frac{\partial g(x,t)}{\partial t} = -\alpha g(x,t) + e^{-\alpha t}\frac{\partial c(x,t)}{\partial t}$$

holds.
Thus we can conclude

$$\frac{\partial g(x,t)}{\partial t} = D\frac{\partial^2 g(x,t)}{\partial x^2} - \alpha g(x,t),$$

so $g(x,t)$ satisfies equation (1.7.4).

1.6 Radius of gyration of a polymer

Notice that

$$\mathbf{x}_i = \mathbf{x}_0 + \sum_{k=0}^{i}\mathbf{r}_i.$$

We also see that the following holds

$$(N+1)R_g^2 = \sum_{i=0}^{N} \left\langle \mathbf{x}_i^2 + \mathbf{x}_{\mathrm{CM}}^2 - 2\mathbf{x}_i \cdot \mathbf{x}_{\mathrm{CM}} \right\rangle .$$

We know that $\sum_{i=0}^{N} \langle \mathbf{x}_i \cdot \mathbf{x}_{\mathrm{CM}} \rangle = \left\langle \mathbf{x}_{\mathrm{CM}} \sum_{i=0}^{N} \mathbf{x}_i \right\rangle = \langle \mathbf{x}_{\mathrm{CM}} \cdot (N+1)\mathbf{x}_{\mathrm{CM}} \rangle = (N+1) \left\langle \mathbf{x}_{\mathrm{CM}}^2 \right\rangle$, so we see

$$\begin{aligned}(N+1)R_g^2 &= \left\langle \sum_{i=0}^{N} (\mathbf{x}_i^2 - (N+1)\mathbf{x}_{\mathrm{CM}}^2) \right\rangle \\ &= \left\langle \sum_{i=0}^{N} (\mathbf{x}_i^2) - \frac{1}{N+1} \sum_{i,j} \mathbf{x}_i \cdot \mathbf{x}_j \right\rangle \\ &= \frac{1}{2(N+1)} \left\langle \sum_{i,j} (\mathbf{x}_i^2 + \mathbf{x}_j^2 - 2\mathbf{x}_i \cdot \mathbf{x}_j) \right\rangle \quad = \frac{1}{2(N+1)} \left\langle \sum_{i,j} (\mathbf{x}_i - \mathbf{x}_j)^2 \right\rangle .\end{aligned}$$

Using the previous relation we find

$$(N+1)^2 R_g^2 = \sum_{i<j} \left\langle \left(\sum_{k=0}^{i} \mathbf{r}_k - \sum_{k=0}^{j} \mathbf{r}_k \right)^2 \right\rangle ,$$

where we have dropped the factor 2 because we only sum over $i < j$. Further we calculate

$$\begin{aligned}(N+1)^2 R_g^2 &= \sum_{i<j} \left\langle \left(\sum_{k=i+1}^{j} \mathbf{r}_k \right)^2 \right\rangle \\ &= \sum_{i<j} \sum_{k=i+1}^{j} \sum_{l=i+1}^{j} \langle \mathbf{r}_k \cdot \mathbf{r}_l \rangle ,\end{aligned}$$

When $k \neq l$, the random variables $\mathbf{r}_k$ and $\mathbf{r}_l$ are independent of each other.

So $\langle \mathbf{r}_k \cdot \mathbf{r}_l \rangle = a^2 \delta_{k,l}$. Continuing the calculation we see

$$\begin{aligned}
(N+1)^2 R_g^2 &= \sum_{i<j} \sum_{k=i+1}^{j} \sum_{l=i+1}^{j} a^2 \delta_{k,l} \\
&= \sum_{i<j} \sum_{k=i+1}^{j} a^2 \\
&= a^2 \sum_{j=0}^{N} \sum_{i=0}^{j-1} (j-i) \\
&= a^2 \sum_{j=0}^{N} \left(j^2 - \frac{j(j-1)}{2} \right) \\
&= \frac{a^2}{2} \sum_{j=0}^{N} (j^2 + j) \\
&= \frac{a^2 N(N+1)(N+2)}{6}.
\end{aligned}$$

So we conclude

$$R_g^2 = \frac{a^2 N(N+2)}{6(N+1)}$$

2 Ensembles in Classical Statistical Mechanics

2.1 Surface and Volume of a high dimensional sphere

a)

Notice that

$$\begin{aligned}
I_N &= \int d^N\mathbf{x}e^{-\mathbf{x}^2} \\
&= \int\int\dots\int dx_1dx_2\dots dx_Ne^{-\sum_i x_i^2} \\
&= \int dx_1e^{-x_1^2}\int dx_2e^{-x_2^2}\dots\int dx_Ne^{-x_N^2} \\
&= \left(\int dx_1e^{-x_1^2}\right)^N \\
&= I_1^N.
\end{aligned}$$

The gaussian integral $\int dxe^{-x^2}$ is equal to $\sqrt{\pi}$, so $I_N = \pi^{N/2}$.

b)

Denote with A_N the surface of dimension N with radius 1. We find that if we convert to polar coordinates

$$\begin{aligned}
I_N &= \int_0^\infty\int_{A_N} r^{N-1}e^{-r^2}drd\Omega \\
&= \mu_{N-1}\int_0^\infty r^{N-1}e^{-r^2}dr
\end{aligned}$$

Now substitute with $u = r^2$, so $r^{N-1} = u^{N/2-1/2}$ and $du = 2u^{1/2}dr$. We conclude

$$\begin{aligned}
I_N &= \frac{\mu_{N-1}}{2}\int_0^\infty u^{N/2-1}e^{-u}du \\
&= \frac{\mu_{N-1}\Gamma(N/2)}{2}
\end{aligned}$$

So we conclude $\mu_{N-1} = \frac{2\pi^{N/2}}{\Gamma(N/2)}$.

c)

We find that $\mu_1 = \frac{2\pi}{\Gamma(1)} = \frac{2\pi}{1!} = 2\pi$ and $\mu_2 = \frac{2\pi^{3/2}}{\Gamma(3/2)} = 4\frac{\pi^{3/2}}{\Gamma(1/2)} = 4\pi$.

2.2 Ideal gas in the microcanonical and canonical ensemble

a)

Notice

$$\begin{aligned}\Omega(E,N,V) &= \frac{1}{N!h^{3N}} \int_{\sum p_i^2/2m<E} d\mathbf{p}_1 \dots d\mathbf{p}_N V^N \\ &= \frac{V^N (2m)^{3N/2}}{N!h^{3N}} \int_{S_{3N}(\sqrt{E})} d\mathbf{u}_1 \dots d\mathbf{u}_N.\end{aligned}$$

where we used the substitution $\mathbf{u}_i = \frac{\mathbf{p}_i}{\sqrt{2m}}$ and $S_{3N}(\sqrt{E})$ denotes a sphere in $3N$ dimensions with radius $\sqrt{E}$. The last integral is just the volume of the $3N$ sphere with radius $\sqrt{E}$ so

$$\begin{aligned}\Omega(E,N,V) &= \frac{V^N (2m\pi E)^{3N/2}}{N!h^{3N}\Gamma(3N/2+1)} \\ &\approx \left(\frac{V}{N}\right)^N \left(\frac{4m\pi E}{3N}\right)^{3N/2} e^{5N/2},\end{aligned}$$

where we used $N! \approx N^N e^{-N}$. The microcanonical density of states is just partial derivative of the microcanonical phase space with respect to E. So we see

$$\begin{aligned}\omega(E,N,V) &= \frac{\partial \Omega(E,N,V)}{\partial E} \\ &= \frac{3}{2} V^N N^{1-N} \left(\frac{4m\pi}{3N}\right)^{3N/2} E^{3N/2-1} e^{5N/2}.\end{aligned}$$

b)

The entropy is equal to

$$S(E) = k_B \left(N \log \frac{V}{N} + \frac{3N}{2} \log\left(\frac{4m\pi E}{3N}\right) + \frac{5N}{2}\right).$$

We also see that

$$\begin{aligned}\log\omega(E,V,N) &= (\log\frac{3}{2}N\log V - N\log N + \log N + \frac{3N}{2}\log\left(\frac{4m\pi E}{3N}\right) - \log E + \frac{5N}{2}\\ &\approx \frac{S(E)}{k_B}.\end{aligned}$$

c)

$$\begin{aligned}\frac{S(\alpha E,\alpha V,\alpha N)}{k_B} &= \alpha N\log\frac{V}{N} + \alpha\frac{3N}{2}\log\left(\frac{4m\pi E}{3N}\right) + \alpha\frac{5N}{2}\\ &= \frac{\alpha}{k_B}S(E,V,N).\end{aligned}$$

d)

Notice

$$\begin{aligned}P &= T\left.\frac{\partial S}{\partial V}\right|_{E,N}\\ &= Tk_B\frac{N}{V},\end{aligned}$$

so $PV = Nk_BT$, which is precisely the ideal gas law. We also see that

$$\begin{aligned}\frac{1}{T} &= \left.\frac{\partial S}{\partial E}\right|_{V,N}\\ &= k_B\frac{3N}{2E},\end{aligned}$$

so $E = \frac{3Nk_BT}{2}$.

e)

We calculate the partition function as follows

$$\begin{aligned}Z_N &= \frac{Z_1^N}{N!}\\ &= \frac{V^N\left(\frac{2m\pi}{\beta}\right)^{3N/2}}{N!}.\end{aligned}$$

This gives us

$$\begin{aligned} E &= -\frac{\partial Z_N}{\partial \beta} \\ &= \frac{3N}{2\beta}, \end{aligned}$$

or $E = \frac{3Nk_BT}{2}$.

2.3 Harmonic oscillators in the microcanonical and canonical ensemble

a)

Consider the substitution $u_i = \frac{p_i}{\sqrt{2m}}$ and $v_i = \sqrt{\frac{m}{2}}\omega_i q_i$, so we see

$$\begin{aligned} \Omega(E,V,N) &= \frac{1}{N!h^{3N}} \int_{\sum_i \frac{p_i^2}{2m} + \frac{m\omega_i^2 q_i^2}{2} < E} dp_1 \dots dp_N dq_1 \dots dp_N \\ &= \frac{(2m)^{N/2}\sqrt{2/m}^N}{N!h^{3N}} \prod_i \omega_i^2 (\pi E)^N \frac{1}{N!} \\ &\approx (2\pi E)^N N^{-2N} e^{2N} h^{-3N} \prod_i \omega_i \\ &= (2\pi E)^N \left(\frac{e}{N}\right)^{2N} \omega^N \end{aligned}$$

with $\omega^N = \prod_i \omega_i$. The entropy is then equal to

$$\begin{aligned} S(E,V,N) &= k_B \log \Omega(E,V,N) \\ &= k_B \left[N \log (2\pi E) + 2N - 2N \log N + \sum_i \omega_i \right]. \end{aligned}$$

b)

Now we have

$$\begin{aligned} \frac{1}{T} &= \left.\frac{\partial S}{\partial E}\right|_{V,N} \\ &= k_B \frac{N}{E} \end{aligned}$$

c)

First we calculate the partition function for 1 harmonic oscillator

$$\begin{aligned} Z_i &= \frac{1}{h^3} \int dp dq e^{-\beta(p^2/(2m) + m\omega_i^2 q^2/2)} \\ &= \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{m\omega_i^2 \beta}} h^{-3} \\ &= \frac{2\pi}{\beta} \frac{1}{\omega_i h^3}. \end{aligned}$$

So the total partition function is equal to

$$Z_N = \left(\frac{2\pi}{\beta h^3} \right)^N \omega^{-N}.$$

Finally we have

$$\begin{aligned} E &= -\frac{\partial \log Z_N}{\partial \beta} \\ &= \frac{N}{\beta} \end{aligned}$$

or $E = N k_B T$.

2.4 Maxwell speed distribution

a)

We calculate as follows

$$\begin{aligned}\phi(\mathbf{v}) &= \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta\left(\mathbf{v} - \frac{\mathbf{p}_i}{m}\right)\right\rangle \\ &= \frac{1}{N\cdot N! h^{3N} Z(N,V,T)} \sum_{i=1}^{N} \int d\Gamma \delta\left(\mathbf{v} - \frac{\mathbf{p}_i}{m}\right) \exp\left\{-\beta\mathcal{H}(\Gamma)\right\} \\ &= \frac{1}{N! h^{3N} Z(N,V,T)} \int d\Gamma \delta\left(\mathbf{v} - \frac{\mathbf{p}_1}{m}\right) \exp\left\{-\beta\mathcal{H}(\Gamma)\right\}.\end{aligned}$$

Let's calculate that last integral, we see

$$\begin{aligned}\int d\Gamma \delta\left(\mathbf{v} - \frac{\mathbf{p}_1}{m}\right) \exp\left\{-\beta\mathcal{H}(\Gamma)\right\} &= \int d\Gamma \exp\left\{-\beta\left(\frac{m\mathbf{v}^2}{2} + \sum_{i=2}^{N}\frac{\mathbf{p}_i^2}{2m}\right)\right\} \\ &= e^{-\beta m\mathbf{v}^2/2} \int d\Gamma \exp\left\{-\beta\sum_{i=2}^{N}\frac{\mathbf{p}_i^2}{2m}\right\}.\end{aligned}$$

That last integral is very similar to the integral of the partition function, it is simply the partition function divided by a gaussian integral. So we have

$$\int d\Gamma \delta\left(\mathbf{v} - \frac{\mathbf{p}_1}{m}\right) \exp\left\{-\beta\mathcal{H}(\Gamma)\right\} = \frac{N! h^{3N} Z(N,V,T) m^{3/2}}{(2\pi k_B T)^{3/2}} e^{-\beta m\mathbf{v}^2/2}.$$

So the velocity distribution is equal to

$$\phi(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\beta m v^2/2}.$$

b)

The speed distribution is equal to

$$\begin{aligned}g(v) &= \int d\mathbf{v}\delta(|\mathbf{v}| - v)\phi(\mathbf{v}) \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\beta m v^2/2} \int_{|\mathbf{v}|=v} d\mathbf{v}.\end{aligned}$$

That last integral is simply the surface area of a sphere in 3 dimension with radius v. So we the speed distribution goes as follows

$$g(v) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\beta m v^2/2}.$$

The probability that kinetic energy lies somewhere between 0 and E we can calculate as followed, where $v = \sqrt{\frac{2E}{m}}$ and $v' = \sqrt{\frac{2E'}{m}}$,

$$\begin{aligned}\int_0^E W(E')dE' &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \int_0^v (v')^2 e^{-\beta E'} dv' \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \int_0^E \frac{\sqrt{2E}}{m^{3/2}} e^{-\beta E'} dE'. \\ &= (2\pi k_B T)^{-\frac{3}{2}} 4\sqrt{2}\pi \int_0^E \sqrt{E'} e^{-\beta E'} dE'.\end{aligned}$$

Differentiating this equation with respect to E gives us

$$W(E) = 2\pi(\pi k_B T)^{-\frac{3}{2}} \sqrt{E} e^{-\beta E}.$$

c)

First we calculate $\left\langle v_x^2 + v_y^2 \right\rangle$, because of symmetry obviously $\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle$. So we have $\left\langle v_x^2 + v_y^2 \right\rangle = 2\left\langle v_x^2 \right\rangle$. Finally we see

$$\begin{aligned}\left\langle v_x^2 \right\rangle &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int d^v v_x^2 e^{-\beta m v^2/2} \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int dv_x v_x^2 e^{-\beta m v_x^2/2} \left(\int dv_y e^{-\beta m v_y^2/2}\right)^2 \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \left(-\frac{2}{m}\frac{\partial}{\partial \beta}\sqrt{\frac{2\pi}{m\beta}}\right) \frac{2\pi}{m\beta} \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \left(\frac{2\pi}{m}\right)^{3/2} \frac{1}{m}\beta^{-5/2} \\ &= \frac{1}{\beta m} = \frac{k_B T}{m}.\end{aligned}$$

The probability that $v_x^2 + v_y^2 > \langle v_x^2 + v_y^2 \rangle$ is then

$$\begin{aligned} P &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{v_x^2+v_y^2>2/\beta m} dv_x dv_y dv_z e^{-\beta m v^2/2} \\ &= \frac{m}{2\pi k_B T} \int_{v_x^2+v_y^2>2/\beta m} e^{-\beta m (v_x^2+v_y^2)/2} dv_x dv_y, \end{aligned}$$

because the integral over v_z is simply $\sqrt{\frac{2\pi}{\beta m}}$. For the other integrals we revert to polar coordinates

$$\begin{aligned} P &= \frac{m}{2\pi k_B T} \int_{r>\sqrt{2/\beta m}} \int_0^{2\pi} e^{-\beta m r^2/2} r dr d\theta \\ &= \frac{m}{k_B T} \left[-\frac{1}{\beta m} e^{-\beta m r^2/2}\right]_{\sqrt{\frac{2}{\beta m}}}^{+\infty} \\ &= e^{-1}. \end{aligned}$$

d)

The average kinetic energy we can calculate as follows

$$\begin{aligned} \langle E \rangle &= \left\langle \frac{m v^2}{2} \right\rangle \\ &= \left\langle \frac{m(v_x^2 + v_y^2 + v_z^2)}{2} \right\rangle \\ &= \frac{3m}{2} \langle v_x^2 \rangle \\ &= \frac{3 k_B T}{2}. \end{aligned}$$

The probability that $E > \langle E \rangle$ is then

$$\begin{aligned} P &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \int_{v^2>3/\beta m} v^2 e^{-\beta m v^2/2} dv \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi \int_{u^2>3/2} \left(\frac{2}{\beta m}\right)^{3/2} u^2 e^{-u^2} du, \end{aligned}$$

where we have substituted with $u = \sqrt{\frac{\beta m}{2}} v$. This gives us

$$\begin{aligned} P &= \frac{4}{\sqrt{\pi}} \int_{3/2}^{\infty} u^2 e^{-u^2} du \\ &\approx 0,21 \end{aligned}$$

2.5 Ideal gas in a gravitational field

a)

Denote with V the volume of the container. Let's call r the radius of the cylinder. We calculate the partition function as follows

$$\begin{aligned} Z(N,V,T) &= \frac{1}{N!}(Z_1(V,T))^N \\ &= \frac{1}{N!h^{3N}} \left(\int d\mathbf{p} e^{-\beta \mathbf{p}^2/(2m)} \int d\mathbf{q} e^{-\beta m g q_z} \right)^N \\ &= \frac{1}{N!h^{3N}} \left[\left(\frac{2m\pi}{\beta} \right)^{3/2} \pi r^2 \int_a^b dz e^{-\beta m g z} \right]^N \\ &= \frac{1}{N!h^{3N}} \left[\left(\frac{2m\pi}{\beta} \right)^{3/2} \frac{\pi r^2}{\beta m g} \left(e^{-\beta m g a} - e^{-\beta m g b} \right) \right]^N \\ &= \frac{1}{\lambda_T^{3N}} \frac{A^N}{N!} \left[\frac{1}{\beta m g} \left(e^{-\beta m g a} - e^{-\beta m g b} \right) \right]^N , \end{aligned}$$

where $\lambda_T = \frac{h}{\sqrt{2m\pi k_B T}}$. The free energy is then

$$\begin{aligned} F(N,V,T) &= -k_B T \log Z(N,V,T) \\ &= k_B T \left[N \log N + N \left(-3 \log \lambda_T + \log \frac{A}{\beta m g} + \log \left(e^{-\beta m g a} - e^{-\beta m g b} \right) - 1 \right) \right]. \end{aligned}$$

With $A = \pi r^2$ and $z = b - a$.

b)

The work being done is equal to

$$dW = -F_a da + F_b db$$

where F_a is the force on the lower piston and F_b is the force on the upper piston. So we have

$$\begin{aligned}
\frac{\partial F}{\partial a} &= -F_a \\
\frac{\partial F}{\partial b} &= F_b
\end{aligned}$$

So calculating this

$$\begin{aligned}
F_a &= N k_b T \frac{\beta m g e^{-\beta m g a}}{e^{-\beta m g a} - e^{-\beta m g b}} = \frac{N m g e^{-\beta m g a}}{e^{-\beta m g a} - e^{-\beta m g b}} \\
F_b &= \frac{N m g e^{-\beta m g b}}{e^{-\beta m g a} - e^{-\beta m g b}}
\end{aligned}$$

c)

The hamiltonian remains unchanged when we interchange particles so $\langle \mathbf{r} - \mathbf{r}_i \rangle = \langle \mathbf{r} - \mathbf{r}_1 \rangle$. Now we can calculate

$$\begin{aligned}
\rho(\mathbf{r}) &= N \langle \mathbf{r} - \mathbf{r}_1 \rangle \\
&= \frac{1}{Z(N-1)! h^{3N}} \int d\mathbf{p}_! e^{-\beta \mathbf{p}_1^2/(2m)} \int \delta(\mathbf{r} - \mathbf{q}_1) d\mathbf{q}_1 e^{-\beta m g q_z} \prod_{i=2}^{N} \int d\mathbf{p}_i e^{-\beta \mathbf{p}_i^2/(2m)} \int d\mathbf{q}_i e^{-\beta m g q_{i,z}} \\
&= \frac{1}{Z(N-1)!} \frac{A^N}{\lambda_T^{3N}} e^{-\beta m g z} \left[\frac{1}{\beta m g} \left(e^{-\beta m g a} - e^{-\beta m g b} \right) \right]^{N-1} \\
&= \frac{N \beta m g e^{-\beta m g z}}{e^{-\beta m g a} - e^{-\beta m g b}}
\end{aligned}$$

where $\hat{z} \cdot \mathbf{r} = z$. So

$$\begin{aligned}
p(z) &= \frac{N m g e^{-\beta m g z}}{A \left(e^{-\beta m g a} - e^{-\beta m g b} \right)} \\
&= k_B T \frac{N \beta m g e^{-\beta m g z}}{A \left(e^{-\beta m g a} - e^{-\beta m g b} \right)} \\
&= k_B T \frac{\rho(\mathbf{r})}{A} \\
&= k_B T \rho'(z)
\end{aligned}$$

2.6 Energy fluctuations in an ideal gas

$$\begin{aligned}\left\langle E^2\right\rangle &= \frac{1}{N!h^{3N}Z}\int \mathcal{H}(\Gamma)^2 e^{-\beta\mathcal{H}(\Gamma)}d\Gamma \\ &= \frac{1}{N!h^{3N}Z}\frac{\partial^2}{\partial\beta^2}\int e^{-\beta\mathcal{H}(\Gamma)}d\Gamma \\ &= Z^{-1}\frac{\partial^2 Z}{\partial\beta^2}.\end{aligned}$$

We already know the identity $\langle E\rangle = -\frac{\partial \log Z}{\partial\beta}$, so we can conclude

$$\begin{aligned}\frac{\partial^2 \log Z}{\partial\beta^2} &= \frac{\partial}{\partial\beta}\left(Z^{-1}\frac{\partial Z}{\partial\beta}\right) \\ &= Z^{-1}\frac{\partial^2 Z}{\partial\beta^2} - \left(Z^{-1}\frac{\partial Z}{\partial\beta}\right)^2 \\ &= \left\langle E^2\right\rangle - \langle E\rangle^2.\end{aligned}$$

In the ideal gas we have $E = -\frac{\partial \log Z}{\partial\beta} = \frac{3N}{2\beta}$. So we see

$$\begin{aligned}\mathrm{Var}(E) &= \frac{\partial^2 \log Z}{\partial\beta^2} \\ &= -\frac{\partial}{\partial\beta}\left(\frac{3N}{2\beta}\right) \\ &= \frac{3N}{2\beta^2}.\end{aligned}$$

Ultimately we have $\frac{\mathrm{Var}(E)}{\langle E\rangle^2} = \frac{3N}{2\beta^2}\frac{4\beta^2}{9N^2} = \frac{2}{3N}$, which goes to zero as $N \to +\infty$.

2.7 Generalized equipartition theorem

Notice that for any i we have

$$\begin{aligned}
\frac{\partial H}{\partial p_{i,x}} &= \operatorname{sgn}(p_{i,x})\alpha_i s |p_{i,x}|^{s-1}, \\
\frac{\partial H}{\partial q_{i,x}} &= \operatorname{sgn}(q_{i,x})\gamma_i r |q_{i,x}|^{r-1},
\end{aligned}$$

These relations give us

$$\begin{aligned}
E &= \langle H \rangle \\
&= \sum_{i=1}^{N}\sum_{x=1}^{d} \langle \alpha_i \,|\, p_{i,x} \,|\,^{s} + \gamma_i \,|\, q_{i,x} \,|\,^{r} \rangle \\
&= \sum_{i=1}^{N}\sum_{x=1}^{d} \left\langle \frac{1}{s}\left(p_{i,x}\frac{\partial H}{\partial p_{i,x}}\right) + \frac{1}{r}\left(q_{i,x}\frac{\partial H}{\partial q_{i,x}}\right)\right\rangle,
\end{aligned}$$

where the summation over x goes over each coordinate. The equipartition theorem then gives us

$$\begin{aligned}
E &= \sum_{i=1}^{N}\sum_{x=1}^{d}\left(\frac{1}{s}+\frac{1}{r}\right)k_B T \\
&= N\left(\frac{s+r}{sr}\right) d k_B T,
\end{aligned}$$

The specific heat is then easily calculated as follows

$$c_V = N\left(\frac{s+r}{sr}\right) d k_B.$$

Now the transformation $\gamma_i \to \frac{3\gamma_i}{2}$ leaves the specific heat unchanged. For the case of the three-dimensional harmonic oscillator we find $E = \frac{9}{4} N k_B T$ and $c_V = \frac{9}{4} N k_B$.

2.8 Harmonic Oscillator in polar coordinates

a)

We calculate the one particle partition function as follows, with the polar coordinates $p^2 = px_2^2 + p_y^2$, $\theta = \text{bgtan}\left(\frac{p_y}{p_x}\right)$, $r^2 = x^2 + y^2$ and $\varphi = \text{bgtan}\left(\frac{y}{x}\right)$,

$$\begin{aligned}
Z_1 &= \frac{4\pi^2}{h^2} \int_0^\infty p e^{-\frac{\beta}{2m}p^2} dp \int_0^\infty r e^{-\frac{m\beta\omega^2}{2}r^2} dr \\
&= \frac{4\pi^2}{h^2} \left[\frac{-m}{\beta} e^{-\frac{\beta}{2m}p^2}\right]_0^\infty \left[-\frac{1}{m\beta\omega^2} e^{-\frac{m\beta\omega^2}{2}r^2}\right]_0^\infty \\
&= \frac{4\pi^2}{\omega^2\beta^2h^2}
\end{aligned}$$

b)

The kinetic energy is then

$$\begin{aligned}
E &= \frac{m}{2}(\dot{x}^2 + \dot{y}^2) \\
&= \frac{m}{2}((\dot{r}\cos\phi - r\sin\phi\cdot\dot{\phi})^2 + (\dot{r}\sin\phi + r\cos\phi\cdot\dot{\phi})^2) \\
&= \frac{m}{2}(\dot{r}^2 + r^2\dot{\phi}^2).
\end{aligned}$$

So the conjugated momenta are

$$\begin{aligned}
p_r &= m\dot{r}, \\
p_\phi &= mr^2\dot{\phi}.
\end{aligned}$$

The hamiltonian then becomes

$$\begin{aligned}
H &= \frac{1}{2m}(m^2\dot{r}^2 + m^2r^2\dot{\phi}^2) + \frac{m\omega^2r^2}{2} \\
&= \frac{1}{2m}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) + \frac{m\omega^2r^2}{2}.
\end{aligned}$$

c)

The one particle partition function is now given by

$$\begin{aligned}
Z_1 &= \frac{1}{h^2}\int e^{-\frac{\beta}{2m}p_r^2}dp_r \int e^{-\beta m\omega^2 r^2/2}dr \int e^{-\beta\frac{p_\phi^2}{2mr^2}}dp_\phi \int d\theta \\
&= \frac{2\pi}{h^2}\sqrt{\frac{2m\pi}{\beta}}\int re^{-\beta m\omega^2 r^2/2}\sqrt{\frac{2m\pi}{\beta}}dr \\
&= \frac{4m\pi^2}{h^2\beta}\left[-\frac{e^{-\beta m\omega^2 r^2/2}}{\beta m\omega^2}\right]_0^\infty \\
&= \frac{4\pi^2}{\omega^2\beta^2h^2}.
\end{aligned}$$

d)

e)

The partition function of N particles is now given by

$$\begin{aligned}
Z(N,V,T) &= \frac{Z_1^N}{N!} \\
&= \frac{1}{N!}\left(\frac{2\pi}{\omega\beta h}\right)^{2N}.
\end{aligned}$$

We also find

$$\log Z \approx N - N\log N + 2N\log\left(\frac{2\pi}{\omega\beta h}\right)$$

So the internal energy is equal to

$$\begin{aligned}
\langle E\rangle &= -\frac{\partial \log Z}{\partial\beta} \\
&= \frac{2N}{\beta} \\
&= 2Nk_BT.
\end{aligned}$$

The specific heat is then

$$\begin{aligned}
c_V &= \frac{\partial E}{\partial T} \\
&= 2Nk_B
\end{aligned}$$

2.9 Diatomic molecules (1)

a)

Calculating the partition function for one diatomic molecule gives us

$$\begin{aligned} Z_1 &= \frac{1}{\lambda_T^6}\int d\mathbf{r}_1 d\mathbf{r}_2 e^{-\beta\frac{K}{2}|\mathbf{r}_1-\mathbf{r}_2|^2} \\ &= \frac{V}{\lambda_T^6}\int d\mathbf{r} e^{-\beta\frac{K}{2}\mathbf{r}^2}. \end{aligned}$$

Where we used the substitution $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. We can approximate this integral by simply integrating over entire $\mathbb{R}^3$ instead of just the volume V. Since for large volumes V, the factor $e^{-\beta\frac{K}{2}|\mathbf{r}_1-\mathbf{r}_2|^2}$ dies off exponentially fast, this is a good approximation. We see

$$Z_1 \approx \frac{V}{\lambda_T^6}\left(\frac{2\pi}{\beta K}\right)^{3/2}.$$

The total partition function is then given by

$$Z(N,V,T) = \frac{V^N}{N!\lambda_T^{6N}}\left(\frac{2\pi}{\beta K}\right)^{3N/2}$$

The free energy is given by

$$F = \frac{1}{\beta}\left(-N + N\log N + 6N\log\lambda_T - N\log V - \frac{3N}{2}\log\frac{2\pi}{\beta K}\right).$$

b)

The specific heat is given by

$$\begin{aligned} c_v &= \frac{\partial E}{\partial T} \\ &= -\frac{\partial^2 \log Z}{\partial \beta^2}\frac{\partial \beta}{\partial T} \\ &= \frac{\partial \frac{9N}{2\beta}}{\partial \beta}\left(-\frac{1}{k_B T^2}\right) \\ &= \frac{9Nk_B}{2} \end{aligned}$$

c)

Notice that

$$\begin{aligned}
\langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \rangle &= \frac{1}{Z_1} \int |\mathbf{r}_1 - \mathbf{r}_2|^2 \frac{\exp\left(-\beta\left[\frac{\mathbf{p}_1^2+\mathbf{p}_2^2}{2m} + \frac{K}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2\right]\right)}{h^{3N}} d\Gamma \\
&= \frac{1}{Z_1}\left(-\frac{2}{\beta}\right)\frac{\partial}{\partial K}\int \frac{\exp\left(-\beta\left[\frac{\mathbf{p}_1^2+\mathbf{p}_2^2}{2m} + \frac{K}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2\right]\right)}{h^{3N}} d\Gamma \\
&= -\frac{2}{\beta}\frac{\partial \log Z_1}{\partial K} \\
&= \frac{3}{\beta K}
\end{aligned}$$

2.10 Diatomic molecules (2)

a)

We calculate the partition function as follows

$$Z(N,V,T) = \frac{1}{N! I \lambda_T^{6N}} \left(\int d\mathbf{r}_1 \int d\mathbf{r}_2 e^{-\beta\epsilon|r_{12}-r_0|} \right)^N .$$

When we take $\mathbf{r}_2$ to be constant to calculate the second integral, and denote with $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. The integral then becomes if we turn to spherical coordinates

$$\begin{aligned}
I &= \int d\mathbf{r}_2 e^{-\beta\epsilon|r_{12}-r_0|} \\
&= \int d\mathbf{r} e^{-\beta\epsilon|r-r_0|} \\
&= \int dr d\theta d\varphi \cos\theta r^2 e^{-\beta\epsilon|r-r_0|}
\end{aligned}$$

The term $e^{-\beta\epsilon|r'-r_0|}$ will become small for large r, so we can approximate the integral over the volume V with the integral over the entire volume.

$$I = 4\pi \int_0^{r_0} r^2 e^{\beta\epsilon(r-r_0)} + 4\pi \int_{r_0}^{\infty} r^2 e^{\beta\epsilon(r_0-r)}$$

The primitive of the functions we are integrating can be calculated using integration by parts. The primitives of the first and second functions are respectively

$$\begin{aligned}&e^{\beta\epsilon(r-r_0)}\left(\frac{r^2}{\beta\epsilon}-\frac{2r}{\beta^2\epsilon^2}+\frac{2}{\beta^3\epsilon^3}\right),\\ &-e^{\beta\epsilon(r_0-r)}\left(\frac{r^2}{\beta\epsilon}+\frac{2r}{\beta^2\epsilon^2}+\frac{2}{\beta^3\epsilon^3}\right).\end{aligned}$$

So the integral simply becomes

$$\begin{aligned}I&=4\pi\left(\frac{r_0^2}{\beta\epsilon}-\frac{2r_0}{\beta^2\epsilon^2}+\frac{2}{\beta^3\epsilon^3}-\frac{2e^{-\beta\epsilon r_0}}{\beta^3\epsilon^3}\right)-4\pi\left(-\frac{r_0^2}{\beta\epsilon}-\frac{2r_0}{\beta^2\epsilon^2}-\frac{2}{\beta^3\epsilon^3}\right)\\&=4\pi\left(\frac{2r_0^2}{\beta\epsilon}+\frac{4-e^{-\beta\epsilon r_0}}{\beta^3\epsilon^3}\right)\end{aligned}$$

Finally we have for the partition function

$$Z(N,V,T)=\frac{(8\pi V)^N}{N!(\beta\epsilon)^{3N}(\lambda_T)^{6N}}\left(\beta^2\epsilon^2r_0^2+2-e^{-\beta\epsilon r_0}\right)^N$$

The free energy is given by

$$\begin{aligned}F&=-\frac{\log Z}{\beta}\\&\approx\frac{1}{\beta}\left(N-N\log N+3N\log(\beta\epsilon)+6N\log(\lambda_T)\right.\\&\left.+N\log(8\pi V)+N\log\left(\beta^2\epsilon^2r_0^2+2-e^{-\beta\epsilon r_0}\right)\right).\end{aligned}$$

b)

The internal energy we can calculate by

$$\begin{aligned}E&=-\frac{\partial\log Z}{\partial\beta}\\&=\frac{6N}{\beta}+\frac{N\left(\beta\epsilon^2r_0^2+\epsilon r_0e^{-\beta\epsilon r_0}\right)}{\beta^2\epsilon^2r_0^2+2-e^{-\beta\epsilon r_0}}.\end{aligned}$$

The specific heat we then find as follows

$$\begin{aligned}c_V &= \frac{\partial E}{\partial T}\\ &= k_B\frac{\partial E}{\partial(1/\beta)}\\ &= 6Nk_B + Nk_B\frac{\partial\beta}{\partial(1/\beta)}\frac{\partial}{\partial\beta}\left(\frac{\beta\epsilon^2r_0^2+\epsilon r_0e^{-\beta\epsilon r_0}}{\beta^2\epsilon^2r_0^2+2-e^{-\beta\epsilon r_0}}\right)\end{aligned}$$

2.11 Langevin's theory of paramagnetism

Consider the Hamiltonian

$$H(\Gamma) = \sum_{i=1}^N\frac{\mathbf{p}_i^2}{2m} - \mu B\sum_{i=1}^N\cos\alpha_i$$

of a system enclosed in a sphere of radius R. We use polar coordinates so $\mathbf{r}_i = r_i(\sin\alpha_i\cos\varphi_i, \sin\alpha_i\sin\varphi_i, \cos\alpha_i)$. Now calculating the partition function we have

$$\begin{aligned}Z &= \frac{1}{N!\lambda_T^{3N}}\prod_i\int_0^R r_i^2dr_i\int_0^{2\pi}d\varphi_i\int_0^\pi\sin\alpha_ie^{\mu\beta B\cos\alpha_i}d\alpha_i\\ &= \frac{1}{N!\lambda_T^{3N}}\frac{(2\pi R^3)^N}{3^N}\left(\int_0^\pi\sin\alpha e^{\mu\beta B\cos\alpha}d\alpha\right)^N.\end{aligned}$$

Using the substitution $u = \cos\alpha$ we find

$$\begin{aligned}\int_0^\pi\sin\alpha e^{\mu\beta B\cos\alpha}d\alpha &= -\int_1^{-1}e^{\mu\beta Bu}du\\ &= \frac{2\sinh(\mu\beta B)}{\mu\beta B}.\end{aligned}$$

The partition function then becomes

$$\begin{aligned}Z &= \frac{1}{N!\lambda_T^{3N}}\left(\frac{4\pi R^3\sinh(\mu\beta B)}{3\mu\beta B}\right)^N\\ &= \frac{1}{N!\lambda_T^{3N}}\left(\frac{V\sinh(\mu\beta B)}{\mu\beta B}\right)^N.\end{aligned}$$

The induced magnetic moment we can calculate as follows

$$
\begin{aligned}
M &= \left\langle \sum_{i=1}^{N} \mu \cos\alpha_i \right\rangle \\
&= \frac{1}{ZN!\lambda_T^{3N}} \int \sum_{i=1}^{N} \mu \cos\alpha_i e^{\mu\beta B \sum_{i=1}^{N} \cos\alpha_i} \prod_i d\mathbf{r}_i \\
&= \frac{1}{ZN!\lambda_T^{3N}} \frac{1}{\beta} \frac{\partial}{\partial B} \int^{\mu\beta B \sum_{i=1}^{N} \cos\alpha_i} \prod_i d\mathbf{r}_i \\
&= \frac{1}{\beta} \frac{\partial \log Z}{\partial B}.
\end{aligned}
$$

This we can calculate so

$$
\begin{aligned}
M &= \frac{1}{\beta} \frac{\partial[N\log(\sinh(\mu\beta B)) - N\log(\mu\beta B)]}{\partial B} \\
&= \frac{N}{\beta}\left(\beta\mu \frac{\cosh(\mu\beta B)}{\sin(\mu\beta B)} - \frac{1}{\mu\beta B}\right) \\
&= N\mu\left(\coth(\mu\beta B) - \frac{1}{\mu\beta B}\right).
\end{aligned}
$$

b)

The magnetic susceptibility per atom is given by

$$
\begin{aligned}
\chi &= \frac{1}{N}\frac{\partial M}{\partial B} \\
&= \mu^2\beta \frac{\partial}{\partial(\mu\beta B)} \left(\frac{\cosh(\mu\beta B)}{\sinh(\mu\beta B)} - \frac{1}{\mu\beta B}\right) \\
&= \mu^2\beta \left(\frac{\sinh^2(\mu\beta B) - \cosh^2(\mu\beta B)}{\sinh^2(\mu\beta B)} + \frac{1}{(\mu\beta B)^2}\right) \\
&= \mu^2\beta \left(\frac{1}{(\mu\beta B)^2} - \frac{1}{\sinh^2(\mu\beta B)}\right)
\end{aligned}
$$

2.12 Van Leeuwen's theorem

2.13 Stretching DNA

a)

Notice

$$\begin{aligned}
Z_L &= \int \prod_{i=1}^{L} \left(\frac{d\mathbf{b}_i}{4\pi b^2} \delta(|\mathbf{b}_i| - b) \right) e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)} \\
&= \int \prod_{i=2}^{L} \left(\frac{d\mathbf{b}_i}{4\pi b^2} \delta(|\mathbf{b}_i| - b) \right) e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_1)} \int \frac{d\mathbf{b}_1}{4\pi b^2} e^{\beta \mathbf{F}\cdot(\mathbf{r}_1 - \mathbf{r}_0)} \\
&= Z_{L-1} Z_1.
\end{aligned}$$

So we have $Z_L = Z_1^L$. We can calculate Z_1 as follows

$$Z_1 = \int \frac{d\mathbf{b}_0}{4\pi b^2} \delta(|\mathbf{b}_0| - b) e^{\beta \mathbf{F}\cdot\mathbf{b}_0}$$

We revert to polar coordinates, where we choose the z-axis along $\mathbf{F}$ such that $\mathbf{F}\cdot\mathbf{b}_0 = F b_0 \cos\theta$. So we see

$$\begin{aligned}
Z_1 &= \int db_0 b_0^2 \frac{\delta(|\mathbf{b}_0| - b)}{4\pi b^2} \int_0^{\pi} d\theta \sin\theta e^{\beta b_0 F \cos\theta} \int_0^{2\pi} d\varphi \\
&= \frac{1}{2} \int_0^{\pi} d\theta \sin\theta e^{\beta b F \cos\theta} \\
&= -\frac{1}{2b\beta F} \int_{\beta b F}^{-\beta b F} e^u \\
&= \frac{1}{\beta b F} \sinh(\beta b F) \\
&= \frac{1}{f} \sinh f
\end{aligned}$$

where we used the substitution $u = \beta b F \cos\theta$ and have denoted with f the product $\beta b F$.

b)

Notice that

$$\begin{aligned}\frac{\partial e^{\beta \mathbf{F}\cdot\mathbf{r}}}{\partial F} &= \frac{\partial e^{\beta F r_x}}{\partial F} \\ &= \beta r_x e^{\beta \mathbf{F}\cdot\mathbf{r}}\end{aligned}$$

Now for the average extension of the chain along the x-direction, we see

$$\begin{aligned}X &= \langle x_L - x_0\rangle \\ &= \frac{1}{Z_L}\int \prod_{i=1}^{L}\left(\frac{d\mathbf{b}_i}{4\pi b^2}\delta(|\mathbf{b}_i| - b)\right)(x_L - x_0)e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)} \\ &= \frac{1}{\beta Z_L}\int \prod_{i=1}^{L}\left(\frac{d\mathbf{b}_i}{4\pi b^2}\delta(|\mathbf{b}_i| - b)\right)\frac{\partial}{\partial F}e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)} \\ &= \frac{1}{\beta}\frac{\partial \log Z_L}{\partial F} \\ &= b\frac{\partial \log Z_L}{\partial f}.\end{aligned}$$

The previous part of the exercise gives us

$$\log Z_L = L\log(\sinh f) - L\log f.$$

So finally we have

$$\begin{aligned}X &= b\left(\frac{L\cosh f}{\sinh f} - \frac{L}{f}\right) \\ &= Lb\left(\coth(\beta bF) - \frac{1}{\beta bF}\right)\end{aligned}$$

c)

Expanding X in terms of f we find

$$\begin{aligned} X &= Lb\left(\frac{1+\frac{f^2}{2}+\dots}{f(1+\frac{f^2}{6}+\dots)} - \frac{1}{f}\right) \\ &\approx \frac{Lb}{f}\left(\frac{1+f^2/2}{1+f^2/6} - 1\right) \\ &\approx \frac{Lb}{f}\left(\frac{f^2}{3(1+\frac{f^2}{6})}\right) \\ &\approx Lb\left(\frac{f}{3(1+\frac{f^2}{6})}\right) \\ &\approx \frac{Lb}{3}f \\ &\approx \frac{Lb^2\beta F}{3}, \end{aligned}$$

where we made the approximations $\cosh(f) \approx 1 + f^2/2$, $\sinh f = 1 + f^2/6$ and $1 + f^2/6 \approx 1$. Ultimately we have $F \approx \frac{3k_BTX}{Lb^2}$.

d)

We know

$$\begin{aligned} X &= Lb\left(\frac{e^f + e^{-f}}{e^f - e^{-f}} - \frac{1}{f}\right) \\ &= Lb\left(1 - \frac{1}{f} - \frac{2}{1-e^{2f}}\right) \end{aligned}$$

At high forces, f too wil be large so we can approximate $\frac{1}{1-e^{2f}} \approx 0$ and so

$$X \approx Lb\left(-1 - \frac{1}{f}\right)$$

This gives us $F = \frac{k_BT}{b}\frac{1}{Lb-X}$ which is not in agreement with experiment. [1]

---

[1] I'm not entirely sure about the last section of this exercise, anyone willing to confirm?

2.14 Stretching a polymer: the low force limit

We recalculate the partition function

$$Z_L = \int \prod_{i=1}^{L} d\mathbf{b}_i e^{-\beta H(\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_L)} e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)}.$$

Denote with Z'_L the partition function of the system in absence of the force

$$Z'_L = \int \prod_{i=1}^{L} d\mathbf{b}_i e^{-\beta H(\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_L)},$$

and denote with X' end to end distance in absence of the force, so

$$X' = \frac{1}{Z'_L} \int \prod_{i=1}^{L} d\mathbf{b}_i (x_L - x_0) e^{-\beta H(\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_L)}$$

Approximating the second exponential by $e^{\beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)} \approx 1 + \beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)$. We find that

$$\begin{aligned} Z_L &\approx \int \prod_{i=1}^{L} d\mathbf{b}_i e^{-\beta H(\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_L)} \left(1 + \beta \mathbf{F}\cdot(\mathbf{r}_L - \mathbf{r}_0)\right) \\ &\approx Z'_L \left(1 + \frac{\beta F}{Z'_L} \int \prod_{i=1}^{L} d\mathbf{b}_i e^{-\beta H(\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_L)} (x_L - x_0)\right) \\ &\approx Z'_L \left(1 + \beta F X'\right) \end{aligned}$$

In the previous exercise we proved that $X = \frac{1}{\beta}\frac{\partial \log Z_L}{\partial F}$ so we find[2]

$$\begin{aligned} X &\approx \frac{1}{\beta}\frac{\partial}{\partial F}\left(\log Z'_L + \log(1 + \beta F X')\right) \\ &\approx \frac{1}{\beta}\frac{\beta X'}{1 + \beta F X'}. \end{aligned}$$

2.15 Worm like chain

[3]

---

[2] Obviously this is false, I would be very grateful to anyone who can show me a more correct method.

[3] Working on this

a)

Consider the unit vectors $\hat{t}_i$ and $\hat{t}_{i+l}$ in polar coordinates

$$\begin{aligned}\hat{t}_i &= \cos\theta\hat{z} + \sin\theta\sin\varphi\hat{y} + \sin\theta\cos\varphi\hat{x}\\ \hat{t}_{i+l} &= \cos\theta'\hat{z} + \sin\theta'\sin\varphi'\hat{y} + \sin\theta'\cos\varphi'\hat{x}\end{aligned}$$

2.16 Stretching a gaussian polymer

If we write $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_{i-1}$, we see

$$Z_L = \int \prod_i d\mathbf{r}_i e^{-\beta K \sum_{i=1}^L \mathbf{r}_i^2 + \beta \mathbf{F}\cdot\sum_{i=1}^L \mathbf{r}_i}.$$

This we can factorize as follows

$$\begin{aligned}Z_L &= \prod_i \left(\int d\mathbf{r}_i e^{-\beta K \mathbf{r}_i^2 + \beta\mathbf{F}\cdot\mathbf{r}_i}\right)\\ &= \prod_i Z_1\\ &= (Z_1)^L\end{aligned}$$

Now notice that $\mathbf{R}_{m+n} - \mathbf{R}_n = \sum_{i=1}^m \mathbf{r}_{n+i}$. Since the partition function factorizes, we have $\langle \mathbf{r}_i \mathbf{r}_j\rangle = \langle \mathbf{r}_i\rangle\langle \mathbf{r}_j\rangle$ when $i \neq j$. All of this gives us

$$\begin{aligned}\left\langle (\mathbf{R}_{m+n} - \mathbf{R}_n)^2\right\rangle &= \left\langle \left(\sum_{i=1}^m \mathbf{r}_{n+i}\right)^2\right\rangle\\ &= \left\langle \left(\sum_{i=1}^m \mathbf{r}_{n+i}\right)\cdot\left(\sum_{j=1}^m \mathbf{r}_{n+j}\right)\right\rangle\\ &= \sum_{i=1}^m\sum_{j=1}^m \langle \mathbf{r}_{n+i}\cdot\mathbf{r}_{n+j}\rangle\\ &= \sum_{i=j}^m \left\langle \mathbf{r}_{n+i}^2\right\rangle + \sum_{i\neq j}^m \langle \mathbf{r}_{n+i}\rangle\cdot\langle \mathbf{r}_{n+j}\rangle.\end{aligned}$$

We find that because we can interchange all of the vectors $\mathbf{r}_i$ in the hamiltonian that $\langle \mathbf{r}_i\rangle = \langle \mathbf{r}_L\rangle$ and $\left\langle \mathbf{r}_i^2\right\rangle = \left\langle \mathbf{r}_L^2\right\rangle$. So we have

$$\left\langle (\mathbf{R}_{m+n} - \mathbf{R}_n)^2 \right\rangle = m \left\langle \mathbf{r}_L^2 \right\rangle + m(m-1) \left\langle \mathbf{r}_L \right\rangle^2$$

because if i and j vary from 1 to m there are m ways for i to be equal to j and $m(m-1)$ ways to be different from each other.

$$\begin{aligned}
\langle \mathbf{r}_L \rangle &= \frac{1}{Z_L} \int \prod_i d\mathbf{r}_i \mathbf{r}_L e^{-\beta K \sum_{i=1}^{L} \mathbf{r}_i^2 + \beta \mathbf{F} \cdot \sum_{i=1}^{L} \mathbf{r}_i}. \\
&= \frac{1}{Z_L} \int d\mathbf{r}_L e^{-\beta K \mathbf{r}_L^2 + \beta \mathbf{F} \cdot \mathbf{r}_L} \mathbf{r}_L \int \prod_{i=1}^{L-1} d\mathbf{r}_i e^{-\beta K \sum_{i=1}^{L} \mathbf{r}_i^2 + \beta \mathbf{F} \cdot \sum_{i=1}^{L} \mathbf{r}_i}. \\
&= \frac{Z_{L-1}}{Z_L} \int d\mathbf{r}_L e^{-\beta K \mathbf{r}_L^2 + \beta \mathbf{F} \cdot \mathbf{r}_L} \mathbf{r}_L.
\end{aligned}$$

We have proven before that $\frac{Z_{L-1}}{Z_L} = \frac{Z_1^{L-1}}{Z_1^L} = \frac{1}{Z_1}$. Now if we write $\mathbf{F} = (F_x, F_y, F_z)$ and $\mathbf{r}_i = (x_i, y_i, z_i)$ we see

$$\begin{aligned}
\langle x_i \rangle &= \frac{1}{Z_1} \int d\mathbf{r}_L x_L e^{-\beta K \mathbf{r}_L^2 + \beta \mathbf{F} \cdot \mathbf{r}_L} \\
&= \frac{1}{Z_1 \beta} \int d\mathbf{r}_L \frac{\partial}{\partial F_x} e^{-\beta K \mathbf{r}_L^2 + \beta \mathbf{F} \cdot \mathbf{r}_L} \\
&= \frac{1}{Z_1 \beta} \frac{\partial Z_1}{\partial F_x} \\
&= \frac{1}{\beta} \frac{\partial \log Z_1}{\partial F_x}.
\end{aligned}$$

In an analogous way we can prove that $\langle \mathbf{r}_L^2 \rangle = -\frac{1}{\beta} \frac{\partial \log Z_1}{\partial K}$. Now all that is left is to calculate Z_1; if we identify x with 1, y with 2 and z with 3 we see

$$\begin{aligned}
Z_1 &= \int d\mathbf{r} e^{-\beta K \mathbf{r}^2 + \beta \mathbf{F} \cdot \mathbf{r}} \\
&= \prod_{\alpha=1}^{3} \int d\alpha e^{-\beta K \alpha^2 + \beta F_\alpha \alpha}
\end{aligned}$$

The gaussian integral is equal to $\int dx e^{-ax^2 + bx} = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}$ for any $a > 0$ and

$b \in \mathbb{R}$. So we have

$$\begin{aligned} Z_1 &= \prod_{\alpha=1}^{3} \sqrt{\frac{\pi}{\beta K}} e^{\frac{\beta^2 F_\alpha^2}{4\beta K}} \\ &= \left(\frac{\pi}{\beta K}\right)^{3/2} e^{\frac{\beta}{4K}\mathbf{F}^2}. \end{aligned}$$

Finally we see

$$\begin{aligned} \langle \mathbf{r}_L \rangle^2 &= \sum_{\alpha=1}^{3} \langle \alpha \rangle^2 \\ &= \frac{1}{\beta^2} \sum_{\alpha=1}^{3} \left(\frac{\partial \log Z_1}{\partial F_\alpha}\right)^2 \\ &= \frac{1}{\beta^2} \sum_{\alpha=1}^{3} \left(\frac{\partial \left(-\frac{3}{2}\log(\beta K) + \frac{\beta \mathbf{F}^2}{4K}\right)}{\partial F_\alpha}\right)^2 \\ &= \frac{1}{\beta^2} \sum_{\alpha=1}^{3} \frac{\beta^2 F_\alpha^2}{4K^2} \\ &= \frac{\mathbf{F}^2}{4K^2} \end{aligned}$$

and

$$\begin{aligned} \langle \mathbf{r}_L^2 \rangle &= -\frac{1}{\beta}\frac{\partial \log Z_1}{\partial K} \\ &= -\frac{1}{\beta}\frac{\partial \left(-\frac{3}{2}\log(\beta K) + \frac{\beta \mathbf{F}^2}{4K}\right)}{\partial K} \\ &= \frac{3}{2\beta K} + \frac{\mathbf{F}^2}{4K^2} \\ &= \frac{3}{2\beta K} + \langle \mathbf{r}_L \rangle^2 \equiv a^2. \end{aligned}$$

Ultimately we find that [4]

---

[4] Obviously this answer differs from that in the text, anyone spotting my mistake?

$$
\begin{aligned}
\left\langle (\mathbf{R}_{m+n} - \mathbf{R}_n)^2 \right\rangle &= m \left\langle \mathbf{r}_L^2 \right\rangle + m(m-1) \left\langle \mathbf{r}_L \right\rangle^2 \\
&= ma^2 + m(m-1) \frac{\mathbf{F}^2}{4K^2} \\
&= ma^2 + m(m-1)a^2 \left(\frac{Fa}{3k_B T} \right)^2
\end{aligned}
$$

2.17 Rigid monomeric chain

The hamiltonian is given by

$$
\mathcal{H} = \sum_{i=1}^{N} (\epsilon_i - F l_i).
$$

Now because there are $\binom{N}{i}$ to choose i particles (with energy ϵ_α and length a) out of N particles we find for the partition function

$$
\begin{aligned}
Z &= \sum_s e^{-\beta \sum_{i=1}^{N} (\epsilon_i - F l_i)} \\
&= \sum_{i=0}^{N} \binom{N}{i} \exp\left(-\beta [i\epsilon_\alpha + (N-i)\epsilon_\beta] + \beta F [ia + (N-i)b] \right) \\
&= e^{-\beta N(\epsilon_\beta - Fb)} \sum_{i=0}^{N} \binom{N}{i} \left[\exp\left(-\beta(\epsilon_\alpha - \epsilon_\beta) + \beta F(a-b) \right) \right]^i \\
&= e^{-\beta N(\epsilon_\beta - Fb)} \left(1 + e^{-\beta(\epsilon_\alpha - \epsilon_\beta) + \beta F(a-b)} \right)^N \\
&= \left(e^{-\beta\epsilon_\beta + \beta F b} + e^{-\beta\epsilon_\alpha + \beta F a} \right)^N .
\end{aligned}
$$

The mean length of the chain molecule is then

$$\begin{aligned}
L &= \left\langle \sum_{i=1}^{N} l_i \right\rangle \\
&= \frac{1}{Z} \sum_s \sum_{i=1}^{N} l_i e^{-\beta \sum_{i=1}^{N} (\epsilon_i - F l_i)} \\
&= \frac{1}{Z} \frac{1}{\beta} \frac{\partial}{\partial F} \sum_s e^{-\beta \sum_{i=1}^{N} (\epsilon_i - F l_i)} \\
&= \frac{1}{\beta} \frac{\partial \log Z}{\partial F} \\
&= \frac{N}{\beta} \frac{\beta b e^{-\beta\epsilon_\beta + \beta F b} + \beta a e^{-\beta\epsilon_\alpha + \beta F a}}{e^{-\beta\epsilon_\beta + \beta F b} + e^{-\beta\epsilon_\alpha + \beta F a}} \\
&= N \frac{b e^{-\beta\epsilon_\beta + \beta F b} + a e^{-\beta\epsilon_\alpha + \beta F a}}{e^{-\beta\epsilon_\beta + \beta F b} + e^{-\beta\epsilon_\alpha + \beta F a}}.
\end{aligned}$$

2.18 Solid-Gas equilibrium

a)

The hamiltonian of the particles in solid phase is that of N_s independent harmonic oscillators

$$\mathcal{H}_s(\Gamma) = \sum_{i=1}^{N_s} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N_s} \frac{m\omega^2 \mathbf{r}_i^2}{2}.$$

Now the partition function of this system is

$$\begin{aligned}
Z_s(T, V, N_s) &= \frac{1}{N_s! h^{3N_s}} \left(\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d\mathbf{p} \int e^{-\beta \frac{m\omega^2 \mathbf{r}^2}{2}} d\mathbf{r} \right)^{N_s} \\
&= \frac{1}{N_s! h^{3N_s}} \left(\frac{4\pi^2}{\beta^2 \omega^2} \right)^{3N_s/2} \\
&= \frac{1}{N_s!} \left(\frac{2\pi}{\beta \omega h} \right)^{3N_s}.
\end{aligned}$$

The hamiltonian of the particles in gas phase are

$$\mathcal{H}_g(\Gamma) = \sum_{i=1}^{N_g} \frac{\mathbf{p}_i^2}{2m} + N_g \Phi.$$

Now the partition function of this system is

$$
\begin{aligned}
Z_g(T,V,N_g) &= \frac{1}{N_g! h^{3N_g}} \left(\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d\mathbf{p} \int d\mathbf{r} e^{-\beta\Phi} \right)^{N_g} \\
&= \frac{V^{N_g} e^{-N_g\beta\Phi}}{N_g! h^{3N_g}} \left(\frac{2m\pi}{\beta} \right)^{3N_g/2}
\end{aligned}
$$

b)

The total free energy is then given by

$$
\begin{aligned}
F(T,V,N,N_g) &= -\frac{1}{\beta}(\log Z_s(T,V,N-N_g) + \log Z_g(T,V,N_g)) \\
&= -\frac{1}{\beta}\left(-(N-N_g)\log(N-N_g) + (N-N_g) + 3(N-N_g)\log\frac{2\pi}{\beta\omega h} \right. \\
&\left. -N_g\beta\Phi + N_g\log V - N_g\log N_g + N_g + \frac{3N_g}{2}\log\frac{2m\pi}{\beta h^2} \right) \\
&= \frac{(N-N_g)\log(N-N_g) + N_g\log N_g + N + 3(N-N_g)}{\beta}\log\frac{\beta\omega h}{2\pi} \\
&+ N_g\Phi - \frac{N_g}{\beta}\log V + \frac{3N_g}{2\beta}\log\frac{\beta h^2}{2m\pi}.
\end{aligned}
$$

There is only equilibrium when $\frac{\partial F}{\partial N_g} = 0$ so there is equilibrium when

$$
\begin{aligned}
0 &= \frac{\partial F}{\partial N_g} \\
&= -\log(N-N_g) + \log N_g - 3\log\frac{\beta\omega h}{2\pi} + \beta\Phi - \log V + \frac{3}{2}\log\frac{\beta h^2}{2m\pi}
\end{aligned}
$$

holds. This is equivalent to

$$
\begin{aligned}
\left(\frac{N}{N_g} - 1\right) &= \left(\frac{2\pi}{\beta\omega h}\right)^3 \left(\frac{\beta h^2}{2m\pi}\right)^{3/2} \\
&= \frac{1}{V} e^{\beta\Phi} \left(\frac{2\pi}{m\beta\omega^2}\right)^{3/2}.
\end{aligned}
$$

That gives us

$$\begin{aligned}\frac{Z_g(T,V,1)}{Z_s(T,V,1)} &= \frac{Ve^{-\beta\Phi}}{h^3}\left(\frac{2m\pi}{\beta}\right)^{3/2}\left(\frac{2\pi}{\beta\omega h}\right)^{-3} \\ &= Ve^{-\beta\Phi}\left(\frac{\beta\omega^2}{2\pi}\right)^{3/2} \\ &= \frac{N_g}{N-N_g}\end{aligned}$$

c)

$$\begin{aligned}P &= -\frac{\partial F}{\partial V} \\ &= \frac{N_g k_B T}{V}\end{aligned}$$

2.19 Ideal gas in grand canonical ensemble

a)

Remember that the partition function of the ideal gas is

$$Z(N,V,T) = \frac{V^N}{N!\lambda_T^{3N}}.$$

So we know that

$$\begin{aligned}\Xi(\mu,V,T) &= \sum_N e^{\beta\mu N} Z(N,V,T) \\ &= \sum_N e^{\beta\mu N}\frac{V^N}{N!\lambda_T^{3N}} \\ &= \sum_N \frac{1}{N!}\left(\frac{Ve^{\beta\mu}}{\lambda_T^3}\right)^N \\ &= \exp\left(\frac{Ve^{\beta\mu}}{\lambda_T^3}\right)\end{aligned}$$

b)

The distribution of the total number of particles is

$$\begin{aligned} P(N) &= \frac{e^{\beta\mu N} Z(N,V,T)}{\Xi(\mu,V,T)} \\ &= \exp\left(-\frac{Ve^{\beta\mu}}{\lambda_T^3}\right) e^{\beta\mu N} \frac{V^N}{N!\lambda_T^{3N}} \\ &= \exp\left(-\langle N\rangle\right) \frac{\langle N\rangle^N}{N!} \end{aligned}$$

with $\langle N\rangle = \frac{Ve^{\beta\mu}}{\lambda_T^3}$.

c)

Now we see

$$\begin{aligned} \left\langle N^2\right\rangle &= \sum_N N^2 P(N) \\ &= \sum_N N^2 \exp\left(-\langle N\rangle\right) \frac{\langle N\rangle^N}{N!} \\ &= e^{-\langle N\rangle} \langle N\rangle \sum_N N \frac{\partial \mu^N}{\partial \langle N\rangle} \frac{1}{N!} \\ &= e^{-\langle N\rangle} \langle N\rangle \frac{\partial}{\partial \langle N\rangle} \left(e^{\langle N\rangle} \sum_N N e^{-\langle N\rangle} \frac{\langle N\rangle^N}{N!} \right). \end{aligned}$$

Now the expression $\sum_N Ne^{-\langle N\rangle} \frac{\langle N\rangle^N}{N!} = \sum_N NP(N)$ is the mean number of particles $\langle N\rangle$ so we have

$$\begin{aligned} \left\langle N^2\right\rangle &= e^{-\langle N\rangle} \langle N\rangle \frac{\partial}{\partial \langle N\rangle} \left[e^{\langle N\rangle} \langle N\rangle \right] \\ &= \langle N\rangle^2 + \langle N\rangle . \end{aligned}$$

Ultimately this gives us

$$\left\langle N^2\right\rangle - \langle N\rangle^2 = \langle N\rangle .$$

2.20 Coexisting phases

a)

There are $\binom{N}{i}$ ways to choose i particles (in the solution) out of N particles. So the partition function is

$$\begin{aligned} Z &= \frac{1}{\lambda_T^{3N} N!} \sum_{i=0}^{N} \binom{N}{i} V_1^i V_2^{N-i} e^{i\beta\alpha} \\ &= \frac{1}{\lambda_T^{3N} N!} \left(V_1 e^{\beta\alpha} + V_2 \right)^N , \end{aligned}$$

where $\lambda_T = \frac{h}{\sqrt{2m\pi k_B T}}$.

b)

The average number of particles in solution is given by

$$\begin{aligned} \langle N_1 \rangle &= \frac{1}{Z \lambda_T^{3N} N!} \sum_{i=0}^{N} \binom{N}{i} i V_1^i V_2^{N-i} e^{i\beta\alpha} \\ &= \frac{V_1}{Z \lambda_T^{3N} N!} \frac{\partial}{\partial V_1} \sum_{i=0}^{N} \binom{N}{i} V_1^i V_2^{N-i} e^{i\beta\alpha} \\ &= V_1 \frac{\partial \log Z}{\partial V_1} \\ &= N V_1 \frac{\partial \log(V_1 e^{\beta\alpha} + V_2)}{\partial V_1} \\ &= N \frac{V_1 e^{\beta\alpha}}{V_1 e^{\beta\alpha} + V_2} . \end{aligned}$$

The average number of particles in gas phase is then

$$\begin{aligned} \langle N_2 \rangle &= N - \langle N_1 \rangle \\ &= N \frac{V_2}{V_1 e^{\beta\alpha} + V_2} . \end{aligned}$$

c)

The grand canonical partition functions are given by

$$\begin{aligned}\Xi_1(V_1,T,\mu_1) &= \sum_N \frac{V_1^N e^{N\beta\alpha} e^{\beta\mu_1 N}}{\lambda_T^{3N} N!}\\ &= \sum_N \frac{1}{N!}\left(V_1 \frac{e^{\beta(\alpha+\mu_1)}}{\lambda_T^3}\right)^N\\ &= \exp\left(\frac{V_1 e^{\beta(\alpha+\mu_1)}}{\lambda_T^3}\right)\end{aligned}$$

and

$$\Xi_2(V_2,T,\mu_2) = \exp\left(\frac{V_2 e^{\beta\mu_2}}{\lambda_T^3}\right).$$

Now the average number of particles in solution are given by

$$\begin{aligned}\langle N_1\rangle &= \frac{1}{\Xi_1(V_1,T,\mu_1)} \sum_N N \frac{V_1^N e^{N\beta\alpha} e^{\beta\mu_1 N}}{\lambda_T^{3N} N!}\\ &= \frac{1}{\Xi_1(V_1,T,\mu_1)} \frac{1}{\beta} \frac{\partial}{\partial\mu_1} \sum_N \frac{V_1^N e^{N\beta\alpha} e^{\beta\mu_1 N}}{\lambda_T^{3N} N!}\\ &= \frac{1}{\beta} \frac{\partial \log \Xi_1(V_1,T,\mu_1)}{\partial\mu_1}\\ &= \frac{V_1 e^{\beta(\alpha+\mu_1)}}{\lambda_T^3}.\end{aligned}$$

In the same way we find

$$\begin{aligned}\langle N_2\rangle &= \frac{1}{\beta} \frac{\partial \log \Xi_2(V_2,T,\mu_2)}{\partial\mu_2}\\ &= \frac{V_2 e^{\beta\mu_2}}{\lambda_T^3}.\end{aligned}$$

Now imposing that these are equal to those computed in b) we have

$$\begin{aligned}N \frac{V_1 e^{\beta\alpha}}{V_1 e^{\beta\alpha} + V_2} &= \frac{V_1 e^{\beta(\alpha+\mu_1)}}{\lambda_T^3},\\ N \frac{V_2}{V_1 e^{\beta\alpha} + V_2} &= \frac{V_2 e^{\beta\mu_2}}{\lambda_T^3}.\end{aligned}$$

Dividing the left side of one equation by the left side of the other we find

$$1 = e^{\beta(\mu_1-\mu_2)},$$

so we must have $\mu_1 = \mu_2$.

2.21 Arrhenius law

3 Interacting Systems

3.1 Hard Rods

The momentum part of the integral can easily be calculated so we see

$$Z_N = \frac{1}{N!\lambda_T^N} \int \Phi(x_1, \dots, x_N) \prod_i dx_i,$$

where $\lambda_T = \frac{h\sqrt{\beta}}{\sqrt{2\pi m}}$.

We order the particles from left to right, such that x_1 is outermost left, x_2 right from x_1 and so forth with x_N outermost right. This ordering isn't arbitrary, the positions of the particles may as well be interchanged. So we introduce a factor $N!$ to correct this

$$Z_N = \frac{1}{\lambda_T^N} \int_{\sigma/2}^{L-\sigma/2} dx_1 \int_{\sigma/2}^{L-\sigma/2} dx_2 \dots \int_{\sigma}^{L-\sigma/2} dx_N \prod_i A_{i-1,i}$$

where we have introduced $A_{i-1,i}$ which is zero when $|x_i - x_{i-1}| < \sigma$ and equal to one when $|x_i - x_{i-1}| \geq \sigma$. Now the first particle has to leave room for $N-1$ other particles, this means that its upper bound is $L - N\sigma + \sigma/2$. The k-th particle has to leave room for $N-k$ other particles so its upper bound is $L - (N-k+1)\sigma + \sigma/2$. The k-th particle has to have a distance larger than σ from the (k-1)-th particle so its lower bound is $x_{k-1} + \sigma$. We see

$$Z_N = \frac{1}{\lambda_T^N} \int_{\sigma/2}^{L-N\sigma+\sigma/2} dx_1 \dots \int_{x_k+\sigma}^{L-(N-k-1/2)\sigma+\sigma/2} dx_{k+1} \dots \int_{x_{N-1}+\sigma}^{L-\sigma/2} dx_N$$

Using the change of variable $y_{k+1} = x_{k+1} - \sigma(k+1/2)$ we see

$$\begin{aligned} Z_N &= \frac{1}{\lambda_T^N} \int_0^{L-N\sigma} dy_1 \int_{y_1}^{L-N\sigma} dy_2 \dots \int_{y_{N-1}}^{L-N\sigma} dy_N \\ &= \frac{1}{\lambda_T^N} \int_0^{L-N\sigma} \frac{(L-N\sigma-x)^{N-1}}{(N-1)!} \\ &= \frac{(L-N\sigma)^N}{\lambda_T^N N!}. \end{aligned}$$

First we calculate the internal energy as follows

$$\begin{aligned} E &= -\frac{\partial \log Z_N}{\partial \beta} \\ &= N\frac{\partial \log \lambda_T}{\partial \beta} \\ &= \frac{N}{2\beta} \\ &= \frac{Nk_BT}{2} \end{aligned}$$

so we have for the specific heat $c_L = \frac{Nk_b}{2}$.

b)

The pressure is now given by

$$\begin{aligned} p &= -\frac{\partial F}{\partial L} \\ &= \frac{1}{\beta}\frac{\partial(N \log \frac{L-N\sigma}{\lambda_T} - N\log N + N)}{\partial L} \\ &= \frac{1}{\beta(L-N\sigma)} \\ &= \frac{k_BT}{L-N\sigma} \end{aligned}$$

3.2 Hard Disks

a)

The first disk that is placed in the area has the total area of S available, if we neglect the area that is lost at the boundary. The second disk has again an area of S available minus the area of a circle of radius σ. So the effective area available is $A_2 = S^2 - \pi\sigma^2 S$.

b)

Using the same approximation as before, we try to find the approximate area A_N available for N particles. Let us put the particles in S in a particular order. Then for the first particle there's an area of S available, the second has $S - \pi\sigma^2$, the third $S - 2\pi\sigma^2$ and so forth. Multiplying this we get $a_N = \prod_{i=0}^{N}(S - i\pi\sigma^2)$. Notice we have the following recursion relation

$$\begin{aligned} a_N &= S a_{N-1} - N\pi\sigma^2 a_{N-1} \\ &= -a_{N-1}\pi\sigma^2 \left(N - \frac{S}{\pi\sigma^2}\right). \end{aligned}$$

To which the solution is

$$a_N = \frac{(-\pi\sigma^2)^N \Gamma\left(N + 1 - \frac{S}{\pi\sigma^2}\right)}{\Gamma\left(1 - \frac{S}{\pi\sigma^2}\right)}.$$

Now because we placed the particles in a particular order, we have to introduce a factor of $N!$ to account for all the orders the particles might come in. So $A_n = N! a_n$. The momentum part of the partition function is easily integrated, it is simply $\left(\frac{2\pi m}{\beta h^2}\right)^N$. So the total partition function is

$$\begin{aligned} Z_n &= \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^N A_n \\ &= \frac{(-\pi\sigma^2)^N \Gamma\left(N + 1 - \frac{S}{\pi\sigma^2}\right)}{\Gamma\left(1 - \frac{S}{\pi\sigma^2}\right)} \left(\frac{\beta h^2}{2\pi m}\right)^N \end{aligned}$$

The approximation is good for small σ. Then the area lost at the boundary will be negligible.

c)

Now if we take A_N to be the exact available area. Now because A_n doesn't depend on β we see

$$\begin{aligned} E &= -\frac{\partial \log Z_N}{\partial \beta} \\ &= N\frac{\partial \log \beta}{\partial \beta} \\ &= \frac{N}{\beta} \\ &= N k_B T \end{aligned}$$

so the specific heat is $c_V = N k_B$. This result is exact, since we didn't approximate A_N here.

3.3 Virial expansion for Hard Spheres

a)

We know

$$f(\mathbf{q}) = \begin{cases} 0 & |\mathbf{q}| \geq \sigma_0 \\ -1 & |\mathbf{q}| < \sigma_0 \end{cases}$$

so $f(\mathbf{q}) = g(\mathbf{q}) - 1$.
The second virial coefficient we calculate as follows

$$\begin{aligned} b_2(T) &= -\frac{1}{2} \int d\mathbf{q} f(\mathbf{q}) \\ &= \frac{1}{2} \int_{S(0,\sigma_0)} d\mathbf{q} \\ &= \frac{2\pi\sigma_0^3}{3}, \end{aligned}$$

where we used $S(0, \sigma_0)$ to denote a sphere with radius σ_0 and center 0.

b)

The third virial coefficient we calculate as follows

$$\begin{aligned} b_3(T) &= -\frac{1}{3} \int d\mathbf{q}_1 \int d\mathbf{q}_2 f(\mathbf{q}_1) f(\mathbf{q}_2) f(\mathbf{q}_{12}) \\ &= -\frac{1}{3} \int_{S(0,\sigma_0)} d\mathbf{q}_1 \int_{S(0,\sigma_0)} d\mathbf{q}_2 f(\mathbf{q}_{12}). \end{aligned}$$

First fix some $\mathbf{q}_1$, and we calculate the following integral

$$-\int_{S(0,\sigma_0)} d\mathbf{q}_2 f(\mathbf{q}_{12}) = \int_{S(0,\sigma_0) \cap S(\mathbf{q}_1,\sigma_0)} d\mathbf{q}_2.$$

Notice that this is precisely the volume in the intersection between a sphere with center 0 and radius σ_0 and a sphere with center $\mathbf{q}_1$ and radius σ_0. This volume is also equal to the volume of a spherical cap of the first sphere plus the volume of a spherical cap of the second sphere. So first we will figure out the volume of a spherical cap.

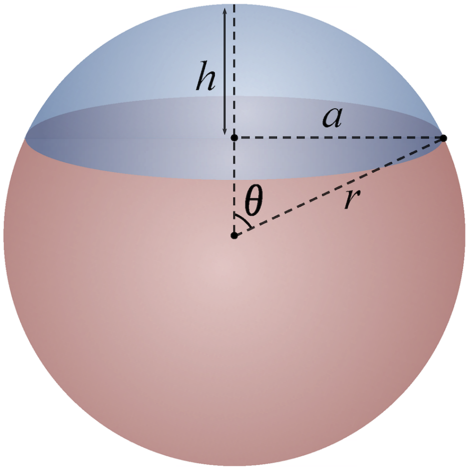

Figure 1: *The parts in blue and red are both spherical caps.*

A spherical cap is a portion of the sphere cut off by a plane. The volume of the spherical cap is given by [5]

$$V_{\text{cap}} = \frac{\pi h^2(3r-h)}{3}.$$

For the first sphere take h as described in figure 1 to be h_1 and for the second h_2. By symmetry h_1 must be equal to h_2 and $h = \sigma_0 - \frac{|\mathbf{q}_1|}{2}$. Now the volume of the two spherical caps is given by

$$\begin{aligned} V_{\text{cap}} &= \frac{\pi}{3}\left(h_1^2(3\sigma_0 - h_1) + h_2^2(3\sigma_0 - h_2)\right) \\ &= \frac{2\pi(2\sigma_0 - |\mathbf{q}_1|)^2}{12}(2\sigma_0 + \frac{|\mathbf{q}_1|}{2}) \\ &= \frac{\pi(2\sigma_0 - |\mathbf{q}_1|)^2}{12}(4\sigma_0 + |\mathbf{q}_1|). \end{aligned}$$

Finally we can calculate the third virial coefficient as follows

$$b_3(T) = \frac{1}{3}\int_{S(0,\sigma_0)} d\mathbf{q}_1 \frac{\pi(2\sigma_0 - |\mathbf{q}_1|)^2}{12}(4\sigma_0 + |\mathbf{q}_1|)$$

---

[5] You can see this by taken the volume of the spherical wedge described by θ and subtracting the volume of the cone with the circle with radius a as base.

Switching to spherical coordinates we find

$$\begin{aligned}
b_3(T) &= \frac{4\pi^2}{3\cdot 12}\int_0^{\sigma_0} r^2(2\sigma_0 - r)^2(4\sigma_0 + r)dr \\
&= \frac{\pi^2}{9}\frac{5\sigma_0^6}{2} \\
&= \frac{5}{8}\left(\frac{2\pi\sigma_0^3}{3}\right)^2 \\
&= \frac{5}{8}b_2(T)^2
\end{aligned}$$

3.4 Second virial coefficient and the Boyle temperature

a)

We see that

$$e^{-\beta\phi(r)} - 1 = \begin{cases} -1 & 0 < r < \sigma \\ e^{\beta\epsilon} - 1 & \sigma < r < 2\sigma \\ 0 & r > 2\sigma \end{cases}$$

The second virial coefficient is equal to

$$\begin{aligned}
b_2(T) &= -2\pi\int_0^{+\infty} drr^2\left(e^{-\beta\phi(r)} - 1\right) \\
&= -2\pi\left(\int_0^{\sigma}(-r^2)dr + \left(e^{\beta\epsilon} - 1\right)\int_\sigma^{2\sigma} r^2 dr\right) \\
&= 2\pi\left(\int_0^{2\sigma} r^2 dr - e^{\beta\epsilon}\int_\sigma^{2\sigma} r^2 dr\right) \\
&= \frac{2}{3}\pi\left(8\sigma^3 - e^{\beta\epsilon}(8\sigma^3 - \sigma^3)\right) \\
&= \frac{2\pi\sigma^3}{3} + \frac{14\pi\sigma^3}{3}\left(1 - e^{\beta\epsilon}\right).
\end{aligned}$$

Here the first term is due to the hard sphere potential and the second term due to the attractive part of the potential.

b)

Denote with T_b the Boyle temperature. So we have

$$\begin{aligned}
0 &= b_2(T_b) \\
&= \frac{16\pi\sigma^3}{3} - \frac{14\pi\sigma^3}{3}e^{\frac{\epsilon}{k_B T_b}}.
\end{aligned}$$

This gives us

$$e^{\frac{\epsilon}{k_B T_b}} = \frac{8}{7}.$$

So the Boyle temperature is $T_b = \frac{\epsilon}{k_B \log(8/7)}$. Considering that $b_2(T)$ is an increasing function we have that $b_2(T)$ is positive for $T > T_b$ and negative for $b_2(T)$ for $T < T_b$.

3.5 Virial coefficient

The second virial coefficient is given by

$$\begin{aligned} b_2(T) &= -2\pi \int_0^{+\infty} dr r^2 \left(e^{-\beta\phi(r)} - 1\right) \\ &= \frac{2\pi\sigma^3}{3} - 2\pi \int_\sigma^{+\infty} dr \left(e^{\frac{\beta\epsilon}{r^6}} - 1\right) r^2. \end{aligned}$$

Expanding the exponential we find

$$\begin{aligned} b_2(T) &= \frac{2\pi\sigma^3}{3} - 2\pi \sum_{n=1}^{\infty} \int_\sigma^{+\infty} dr r^2 \left(\frac{\beta\epsilon}{r^6}\right)^n \\ &\approx \frac{2\pi\sigma^3}{3} - 2\pi\beta\epsilon \int_\sigma^{+\infty} \frac{1}{r^4} dr \\ &\approx \frac{2\pi\sigma^3}{3} - \frac{2}{3\sigma^3}\pi\beta\epsilon. \end{aligned}$$

So we have

$$P = nk_B T \left(1 + bn - \frac{an}{k_B T}\right)$$

where $b = \frac{2\pi\sigma^3}{3}$ and $a = \frac{2\pi}{3\sigma^3}\epsilon$ which looks like the low desnity expansion of the van der Waals equation.

3.6 Second virial coefficient of Argon

a)

We calculate the second virial coefficient for the potential $\phi(r)$.

$$\begin{aligned}
b_2(T) &= -2\pi \int_0^\infty dr \left(e^{-\beta\phi(r)} - 1\right) r^2 \\
&= -2\pi \left(-\int_0^\sigma drr^2 + \int_\sigma^{\sigma'} \left(e^{\beta\epsilon} - 1\right) r^2 dr \right) \\
&= \frac{2\pi\sigma^3}{3} - \frac{2\pi(\sigma'^3 - \sigma^3)}{3} \left(e^{\beta\epsilon} - 1\right).
\end{aligned}$$

Expanding $e^{\beta\epsilon} - 1$ we find

$$\begin{aligned}
b_2(T) &\approx \frac{2\pi\sigma^3}{3} - \frac{2\pi(\sigma'^3 - \sigma^3)}{3} \left(\beta\epsilon + \beta^2\epsilon^2\right) \\
&\approx \frac{2\pi\sigma^3}{3} - \frac{2\pi\epsilon(\sigma'^3 - \sigma^3)}{3k_B} \frac{1}{T} - \frac{2\pi\epsilon^2(\sigma'^3 - \sigma^3)}{3k_B^2} \frac{1}{T^2}.
\end{aligned}$$

So we find

$$\begin{aligned}
A &= \frac{2\pi\sigma^3}{3} \\
B &= \frac{2\pi\epsilon(\sigma'^3 - \sigma^3)}{3k_B} \\
C &= \frac{2\pi\epsilon^2(\sigma'^3 - \sigma^3)}{3k_B^2}.
\end{aligned}$$

Inverting these relations we find

$$\begin{aligned}
\sigma &= \left(\frac{3A}{2\pi}\right)^{1/3} \\
\sigma' &= \left(\frac{3}{2\pi}(A + B^2/C)\right)^{1/3} \\
\epsilon &= k_B \frac{C}{B}.
\end{aligned}$$

b)

3.8.12 is simply a quadratic equation in $1/T$ so we find

$$\frac{1}{T_b} = \frac{B + \sqrt{B^2 + 4AC}}{2A}.$$

We only consider the positive solutions, because we can't have any negative temperatures (in Kelvin that is). So for the Boyle temperatur we find

$$T_b = \frac{2A}{B + \sqrt{B^2 + 4AC}}.$$

3.7 The Flory exponent of a polymer

Differentiating the expression 3.8.14 with respect to V gives $-k_B T n - k_B T b_2 n^2$ which corresponds precisely to the virial expansion.
Now we can find the minimum of F given by 3.8.15 as follows

$$\begin{aligned} 0 &= \frac{\partial F}{\partial R} \\ &= k_B T \left(\frac{3R}{Na^2} - d\frac{b_2 N^2}{R^{d+1}} \right). \end{aligned}$$

This equation is satisfied for

$$R^{d+2} = \frac{d b_2 a^2}{3} N^3,$$

and so $R \sim N^{\frac{3}{d+2}}$.

3.8 The mean field theory of non-ideal gases

a)

Calculating the partition function for the system described by $\mathcal{H}_0$ we see

$$Z_0 = e^{-\beta N \lambda} Z_I$$

where Z_I is the partition function of the ideal gas which is $Z_I = \frac{V^N}{N! \lambda_T^{3N}}$. So the free energy of this system is

$$\begin{aligned} F_0(\lambda) &= -\frac{\log Z_0}{\beta} \\ &= N\lambda + \frac{-N \log V + N - N \log N + 3N \log \lambda_T}{\beta}. \end{aligned}$$

We also see that

$$\begin{aligned}\langle \mathcal{H}_1(\lambda)\rangle_0 &= \frac{1}{N!h^{3N}Z_0}\int d\Gamma e^{-\beta(K(\Gamma)+N\lambda)}\left(\sum_{i<j}\Phi(|\mathbf{r}_i-\mathbf{r}_j|)-N\lambda\right)\\ &= \frac{N(N-1)V^{N-1}}{2N!Z_0\lambda_T^{3N}}e^{-\beta N\lambda}\int d\mathbf{r}\Phi(|\mathbf{r}|)-N\lambda\\ &= \frac{N(N-1)}{V}a-N\lambda\\ &\approx -\frac{N^2}{V}a-N\lambda\end{aligned}$$

where $a=-\frac{1}{2}\int d\mathbf{r}\Phi(|\mathbf{r}|)$.
Now we see that

$$\mathcal{F}(\lambda)=fracN^2Va+\frac{-N\log V+N-N\log N+3N\log\lambda_T}{\beta},$$

which is already minimal so

$$\widetilde{\mathcal{F}}=-\frac{N^2}{V}a+\frac{-N\log V+N-N\log N+3N\log\lambda_T}{\beta}.$$

b)

From this we find the following equation of state

$$\begin{aligned}P &= -\frac{\partial\widetilde{\mathcal{F}}}{\partial V}\\ &= \frac{\partial\left(\frac{N^2}{V}a+Nk_BT\log V\right)}{\partial V}\\ &= \frac{Nk_BT}{V}-\frac{aN^2}{V^2}.\end{aligned}$$

This method cannot work if the pair potential is slowly decaying because then the integral $\int d\mathbf{r}\Phi(|\mathbf{r}|)$ diverges. It also can not contain a hard repulsive core, because then $\Phi(r)$ diverges at zero, making the integral diverge too.

3.9 The critical exponents of a van der Waals fluid

3.10 One dimensional Ising model

a)

The partition function is given by

$$\begin{aligned} Z &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta h \sum_{i=1}^N s_i + \beta J \sum_{i=1}^N s_i s_{i+1}} \\ &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{i=1}^N e^{\beta h s_i + \beta J s_i s_{i+1}} \\ &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{i=1}^N T_{s_i, s_{i+1}} \end{aligned}$$

with

$$T = \begin{pmatrix} e^{\beta J - \beta h} & e^{-\beta J - \beta h} \\ e^{-\beta J + \beta h} & e^{\beta J + \beta h} \end{pmatrix}.$$

Now notice that

$$\begin{aligned} Z &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} T_{s_1,s_2} T_{s_2,s_3} \dots T_{s_N,s_1} \\ &= \sum_{s_1=\pm 1} (T^N)_{s_1,s_1} \\ &= \mathrm{Tr}(T^N). \end{aligned}$$

Now the trace of a matrix is equal to the sum of its eigenvalues. If $\lambda_\pm$ are the eigenvalues of T then $\lambda_\pm^N$ are the eigenvalues of T^N so we have

$$Z = \lambda_+^N + \lambda_-^N.$$

The eigenvalues $\lambda_\pm$ satisfy the characteristic equation

$$\left(e^{\beta J - \beta h} - \lambda\right)\left(e^{\beta J + \beta h} - \lambda\right) - e^{-2\beta J} = 0.$$

This is equivalent to

$$\lambda^2 - 2e^{\beta J} \cosh(\beta h)\lambda + 2\sinh(\beta J) = 0,$$

which has the following solution

$$
\begin{aligned}
\lambda_\pm &= e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}\cosh^2(\beta h) - 2\sinh(\beta J)} \\
&= e^{\beta J}\cosh(\beta h) \pm \sqrt{\frac{e^{2\beta J}}{4}\left(1 + e^{2\beta h} + e^{-2\beta h}\right) - e^{\beta J} + e^{-\beta J}}.
\end{aligned}
$$

3.11 The Infinite-range Ising-model

a)

Calculating the partition function using 3.8.28 we find

$$
\begin{aligned}
Z &= e^{-\beta\epsilon/2}\sum_{\{s_i\}}\exp\left(\frac{\beta\epsilon}{2N}\left(\sum_i s_i\right)^2\right) \\
&= \frac{e^{-\beta\epsilon/2}}{\sqrt{2\pi}}\sum_{\{s_i\}}\int dy\,\exp\left(-\frac{1}{2}y^2 + \sqrt{\frac{\beta\epsilon}{N}}\sum_i s_i y\right).
\end{aligned}
$$

Switching the sum and the integral and using the fact that

$$
\begin{aligned}
\sum_{\{s_i\}}\exp\left(\sqrt{\frac{\beta\epsilon}{N}}\sum_i s_i\right) &= \sum_{\{s_i\}}\prod_i e^{\sqrt{\frac{\beta\epsilon}{N}}s_i} \\
&= \left(\sum_{s=\pm 1} e^{\sqrt{\frac{\beta\epsilon}{N}}s}\right)^N \\
&= \left[2\cosh\left(\sqrt{\frac{\beta\epsilon}{N}}\right)\right]^N,
\end{aligned}
$$

we see that

$$
\begin{aligned}
Z &= \frac{e^{-\beta\epsilon/2}}{\sqrt{2\pi}}\int dy e^{-\frac{1}{2}y^2}\left[2\cosh\left(\sqrt{\frac{\beta\epsilon}{N}}\right)\right]^N \\
&= e^{-\beta\epsilon/2}\left[2\cosh\left(\sqrt{\frac{\beta\epsilon}{N}}\right)\right]^N
\end{aligned}
$$

b)

Now the free energy is given by

$$F = \frac{\epsilon}{2} - Nk_BT\log\left(2\cosh\left(\sqrt{\frac{\beta\epsilon}{N}}\right)\right).$$

3.12 The mean field solution of the Ising model

4 Quantum Statistical Mechanics

4.1 Quantum Harmonic Oscillators

a)

The classical partition function, as calculated in 2.3, is given by

$$Z(N,V,T) = \left(\frac{2\pi}{\omega\beta h^3}\right)^N .$$

Now the internal energy is given by

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial \beta} \\ &= Nk_BT, \end{aligned}$$

and the specific heat

$$c_V = Nk_B.$$

b)

The energy of a quantum harmonic oscillator is given by $\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right)$. So the quantum partition function can be calculated as follows

$$\begin{aligned} Z(N,V,T) &= \sum_{\{n_i\}} \exp\left(-\beta\hbar\omega \sum_{i=1}^{N}\left(n_i + \frac{1}{2}\right)\right) \\ &= \left(e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}\right)^N \\ &= \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}\right)^N \\ &= \left(2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)^{-N} . \end{aligned}$$

Now the internal energy is given by

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial \beta} \\ &= \frac{N\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right), \end{aligned}$$

and the specific heat by

$$\begin{aligned} c_V &= \frac{\partial E}{\partial T} \\ &= \frac{\hbar^2\omega^2}{4k_BT^2}\frac{1}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}. \end{aligned}$$

Now expanding for example the expression for E we find

$$\begin{aligned} E &= N\hbar\omega\frac{1+\frac{\beta^2\hbar^2\omega^2}{8}+\dots}{\frac{\beta\hbar\omega}{2}+\frac{\beta^3\hbar^3\omega^3}{8\cdot 6}+\dots} \\ &= Nk_BT\frac{1+\frac{\beta^2\hbar^2\omega^2}{8}+\dots}{1+\frac{\beta^2\hbar^2\omega^2}{24}+\dots}. \end{aligned}$$

Now for temperatures such that $\frac{\hbar\omega}{k_BT} << 1$ or $T >> \frac{\hbar\omega}{k_B}$, the energy reduces to $E = Nk_BT$ which is the classical energy for the harmonic oscillator.

4.2 Low temperature limit of a quantum partition function

The internal energy is given by

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial\beta} \\ &= \frac{e^{-\beta E_1}\left(E_1+E_2e^{-\beta\Delta E}\right)}{e^{-\beta E_1}\left(1+e^{-\beta\Delta E}\right)} \\ &= \frac{E_1+(E_1+\Delta E)e^{-\beta\Delta E}}{1+e^{-\beta\Delta E}}. \end{aligned}$$

The specific heat is then given by

$$\begin{aligned} c_V &= \frac{\partial E}{\partial T} \\ &= -\frac{1}{k_BT^2}\frac{\partial E}{\partial\beta} \\ &= -\frac{1}{k_BT^2}\frac{-\Delta E(E_1+\Delta E)e^{-\beta\Delta E}\left(1+e^{-\beta\Delta E}\right)+\left(E_1+(E_1+\Delta E)e^{-\beta\Delta E}\right)\Delta Ee^{-\beta\Delta E}}{\left(1+e^{-\beta\Delta E}\right)^2} \\ &= \frac{1}{k_BT^2}\frac{\Delta E^2e^{-\beta\Delta E}}{\left(1+e^{-\beta\Delta E}\right)^2} = \frac{\Delta E^2}{k_BT^2}\cosh\left(\frac{\beta\Delta E}{2}\right)^{-2}. \end{aligned}$$

At low temperatures $1+e^{-\beta\Delta E}\approx 1$ so $c_V = \frac{\Delta E^2}{k_BT^2}e^{-\frac{\Delta E}{k_BT}} \sim e^{-\frac{\Delta E}{k_BT}}$.

4.3 Ideal gas with internal degrees of freedom

i)

The kinetic energy of a particle enclosed in a volume $V = L^3$ is given by

$$E_{\mathrm{kin}} = \frac{h^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2),$$

where n_x, n_y and n_z are integers. The quantum partition function is then given by

$$\begin{aligned}
Z(N,V,T) &= \sum_{\{(n_{i,x}, n_{i,y}, n_{i,z})\}} \exp\left(-\beta \frac{h^2}{2mL^2} \sum_{i=1}^{N} (n_{x,i}^2 + n_{y,i}^2 + n_{z,i}^2)\right) \\
&= \left(\sum_{n=-\infty}^{\infty} \exp\left(-\beta \frac{h^2}{2mL^2} n^2\right)\right)^{3N} \\
&\approx \left(L \int_{-\infty}^{\infty} \exp\left(-\beta \frac{h^2}{2m} x^2\right) dx\right)^{3N} \\
&= \left(L \frac{\sqrt{2m\pi}}{\sqrt{\beta} h}\right)^{3N}
\end{aligned}$$

where we have approximated the sum by an integral. Now the energy is equal to

$$\begin{aligned}
E &= -\frac{\partial \log Z}{\partial \beta} \\
&= \frac{3N}{2} k_B T,
\end{aligned}$$

and the heat capacity $c_V = \frac{3N}{2} k_B$.

ii)

The partition function for molecules with vibrational degrees of freedom is given by

$$\begin{aligned} Z &= \sum_{\{n_i\}} e^{-\beta\hbar\omega \sum_{i=1}^{N}(n_i+1/2)} \\ &= \left(e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}\right)^N \\ &= \left(e^{-\beta\hbar\omega/2} \frac{1}{1-e^{-\beta\hbar\omega}}\right)^N \\ &= \left(2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)^{-N}. \end{aligned}$$

The energy is now given by

$$E = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right),$$

and the specific heat

$$\begin{aligned} c_V &= \frac{\partial E}{\partial T} \\ &= \frac{\hbar^2\omega^2}{4k_BT^2}\frac{1}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}. \end{aligned}$$

As calculated in 4.1. Now the heat capacity at low temperatures goes to zero and for high temperatures reduces to

$$\lim_{\beta\to 0} c_V = Nk_B.$$

4.4 When are quantum effects important?

4.5 Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann statistics

If the particles obey Bose-Einstein statistics or Maxwell-Boltzmann[6] statistics, all nine configurations are permitted, that is particle 1 can take on any

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[6] This isn't mentioned in the course notes but section 7.5 in the book by Sethna deals with this.

value of $0, \epsilon$ or 2ϵ and so can particle 2. If the particles obey Fermi-Dirac statistics, only six configurations are permitted, that is where the energy level of particle 1 and particle 2 differ.

The partition functions are

$$Z_{BE} = \left(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2$$
$$Z_{MB} = \frac{\left(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2}{2!}$$
$$Z_{FD} = \left(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2 - 1 - e^{-2\beta\epsilon} - e^{-4\beta\epsilon} = 2e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + 2e^{-3\beta\epsilon}.$$

The internal energies are then given by

$$E_{MB} = E_{BE} = 2\epsilon e^{-\beta\epsilon}\frac{1 + 2e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}}$$
$$E_{FD} = \epsilon + \epsilon e^{-\beta\epsilon}\frac{1 + 2e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}}.$$

For $T \to 0$, $\beta \to \infty$ and so $E_{MB} = E_{BE} \to 0$ but $E_{FD} \to \epsilon$. For $T \to \infty$, $\beta \to 0$ and so $E_{MB} = E_{BE} \to 2\epsilon$ and $E_{FD} \to 2\epsilon$.

4.6 Quantum Corrections in a Bose ideal gas

We write

$$\frac{P}{nk_BT} = \sum_{n=0}^{\infty} a_n x^n,$$

where $x = n\lambda_T^3$. According to 4.2.12 and 4.2.13 we have

$$\sum_{n=0}^{\infty} a_n x^{n+1} = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}},$$
$$x = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}.$$

Filling in the second equation into the first, and working out for the first few orders of z we find

$$za_0 + z^2\left(a_0\frac{1}{2\sqrt{2}} + a_1\right) + z^3\left(a_0\frac{1}{3\sqrt{3}} + a_1\frac{1}{\sqrt{2}} + a_2\right) = z + z^2\frac{1}{4\sqrt{2}} + z^3\frac{1}{9\sqrt{3}} + \ldots$$

Since equal power series must have equal coefficients, we have

$$\begin{aligned} &a_0 = 1, \\ &a_0 \frac{1}{2\sqrt{2}} + a_1 = \frac{1}{4\sqrt{2}}, \\ &a_0 \frac{1}{3\sqrt{3}} + a_1 \frac{1}{\sqrt{2}} + a_2 = \frac{1}{9\sqrt{3}}. \end{aligned}$$

Now these equations have the solutions $a_0 = 1$, $a_1 = -\frac{1}{4\sqrt{2}}$ and $a_2 = \frac{1}{8} - \frac{1}{\sqrt{3}}\frac{2}{9}$. [7]

4.7 Bose-Einstein condensation in two dimensions?

The quantum partition function is given by

$$\log \Xi = -\sum_{\mathbf{p}} \log\left(1 - e^{\beta\mu - \beta p^2/(2m)}\right).$$

Now using 4.2.9 and $z = e^{\beta\mu}$ we have

$$\begin{aligned} \log \Xi &= \sum_{\mathbf{p}} \sum_{l=1}^{\infty} \frac{z^l}{l} e^{-\beta p^2 l/(2m)} \\ &\approx \frac{A}{h^2} \int d\mathbf{p} \sum_{l=1}^{\infty} \frac{z^l}{l} e^{-\beta p^2 l/(2m)} \\ &= \frac{A}{\lambda_T^2} \sum_{l=1}^{\infty} \frac{z^l}{l^2}. \end{aligned}$$

where the sum over $\mathbf{p}$ is replace by an integral. Now we also find

$$\begin{aligned} N &= \sum_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle \\ &= \frac{z}{1-z} + \sum_{\mathbf{p} \neq 0} \frac{z}{e^{\beta p^2/(2m)} - z}. \end{aligned}$$

---

[7] In the notes there's a different answer, but I fed this into maple, and it gave the same answer as my solution. If you find another solution that corresponds to the one in the notes or an error in this solution, please let me know.

Now integrating gives

$$
\begin{aligned}
N &= \frac{\lambda_T^2}{A}\frac{z}{1-z} + \sum_{l=1}^{\infty}\frac{z^l}{l} \\
&= \frac{\lambda_T^2}{A}\frac{z}{1-z} - \log(1-z).
\end{aligned}
$$

4.8 Bose condensation in a band

UNDER CONSTRUCTION (any solutions you have for the following exercises, I'll happily receive)

4.9 Bose-Einstein condensation in a harmonic potential

The energy levels are given by $\epsilon(n_x, n_y) = \hbar\omega(n_x + n_y + 1)$. For any given energy ϵ, the area described by $n_x + n_y < \frac{\epsilon}{\hbar\omega} - 1$ is a triangle in the n_x, n_y plane with area $N(\epsilon) = \frac{1}{2}\left(\frac{\epsilon}{\hbar\omega} - 1\right)^2$.
Now the density of states is given by $g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = \frac{\epsilon - \hbar\omega}{\hbar^2\omega^2}$. Given a chemical potential μ, the amount of particles in the system is equal to

$$
N(\mu) = \int_0^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1} dx.
$$

The maximal value is

$$
\begin{aligned}
N_{\text{max}} &= \frac{1}{\hbar^2\omega^2}\int_0^\infty \frac{(x - \hbar\omega)}{e^{\beta x} - 1} dx \\
&= \frac{1}{\hbar^2\omega^2}\frac{1}{\beta^2}\frac{\pi^2}{6}.
\end{aligned}
$$

So the amount of particles in this approximation is bounded, if there are more particles in the system than this maximum value the system becomes a Bose-Einstein condensate.
In one dimension the energy is given by $\epsilon(n) = \hbar\omega\left(n + \frac{1}{2}\right)$, so the density of states is given by $g_{1D}(\epsilon) = \frac{1}{\hbar\omega}$. Now the amount of particles,

$$
N(\mu) = \frac{1}{\hbar\omega}\int_0^\infty \frac{dx}{e^{\beta(x-\mu)} - 1}
$$

isn't bounded, so Bose-Einstein condensation does not occur.

4.10 Photons and phonons are bosons

A quantum harmonic oscillator with frequency ω has the energy $\epsilon = \hbar\omega\left(n + \frac{1}{2}\right)$, shifting the zero of this energy, gives $\epsilon = \hbar\omega n$. The canonical partition function for a quantum harmonic oscillator of frequency ω is then

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\ &= \frac{1}{1 - e^{-\beta\hbar\omega}} \end{aligned}$$

The grand canonical partition function for bosons filling a single state with energy $\hbar\omega$ is

$$\Xi(\mu) = \frac{1}{1 - e^{\beta(\mu - \hbar\omega)}}.$$

Now we see that $\Xi(0) = Z$.

4.11 Black body radiation

a)

We know that $\mathbf{k} = \frac{\pi}{L}(n_x, n_y, n_z)$ where n_x, n_y and n_z are positive integers. Now the amount of photons in a volume element $d\mathbf{k}$ is $2\frac{L^3}{\pi^3}d\mathbf{k}$. Now the number of oscillators in $[\omega, \omega + d\omega]$ is

$$\frac{1}{8}2\frac{L^3}{\pi^3}4\pi k^2 dk = \frac{V}{\pi^2 c^3}\omega^2 d\omega = g(\omega)d\omega.$$

b)

The grand canonical partition function is now given by

$$\begin{aligned} \log \Xi &= \int_0^{\infty} d\omega g(\omega) \log\left(1 - e^{\beta(\mu - \hbar\omega)}\right) \\ &= \frac{V}{\pi^2 c^3}\int_0^{\infty} d\omega \omega^2 \log\left(1 - e^{\beta(\mu - \hbar\omega)}\right). \end{aligned}$$

c)

The pressure of the gas is given by

$$\begin{aligned} PV &= k_B T \log \Xi \\ &= \frac{k_B T V}{\pi^2 c^3}\int_0^{\infty} d\omega \omega^2 \log\left(1 - e^{-\beta\hbar\omega}\right). \end{aligned}$$

Using integration by parts, we find

$$\begin{aligned} PV &= \frac{V}{\pi^2 c^3} \frac{1}{3} \int_0^\infty d\omega \hbar \omega^3 \frac{1}{e^{\beta\hbar\omega} - 1} \\ &= \frac{E}{3}. \end{aligned}$$

d)

The average energy of the system is now given by

$$\begin{aligned} E &= \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V}{\pi^2 c^3} \frac{1}{\beta^4 \hbar^3} \int_0^\infty dx \frac{x^3}{e^x - 1} \\ &= \frac{V k_B^4 T^4}{15 \hbar^3 c^3}. \end{aligned}$$

e)

Notice that

$$\begin{aligned} E &= \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= V \int_0^\infty d\omega u(T, \omega), \end{aligned}$$

such that

$$\begin{aligned} u(T, \omega) &= \frac{g(\omega)}{V} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\beta\hbar\omega} - 1\right)}. \end{aligned}$$

f)

Now for $\beta\hbar\omega << 1$ we have $e^{\beta\hbar\omega} - 1 \approx \beta\hbar\omega$ such that

$$u(T, \omega) = \frac{\omega^2}{\pi^2 c^3} k_B T.$$

4.12 Phonons on a String

a)

4.13 Debye Model

4.14 Ideal Fermi gas in two dimensions

4.15 Landau Theory of diamagnetism

4.16 Pauli spin paramagnetism

a)

The magnetization is equal to

$$\begin{aligned} M &= \sum_{\{\mathbf{p}_i, s_i\}} \frac{1}{B} \left(\epsilon_{\mathbf{p}_i, s_i} - \frac{\mathbf{p}^2}{2m} \right) e^{-\beta \epsilon_{\mathbf{p}_i, s_i}} \\ &= \frac{E - \left\langle \frac{\mathbf{p}^2}{2m} \right\rangle}{B}. \end{aligned}$$

4.17 Particles in magnetic field

The canonical partition function is given by

$$\begin{aligned} Z &= \sum_{\{s_i\}} e^{-\beta \mu H \sum_{i=1}^N s_i} \\ &= \left(\sum_{s=\pm 1} e^{-\beta \mu H s} \right)^N \\ &= \left(2 \cosh(\beta \mu H)\right)^N . \end{aligned}$$

Now the internal energy is given by

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial \beta} \\ &= -N \mu H \tanh(\beta \mu H). \end{aligned}$$

And the entropy is given by

$$\begin{aligned} S &= \frac{E - F}{T} \\ &= N(k_B \log(2 \cosh(\beta \mu H)) - \frac{\mu H}{T} \tanh(\beta \mu H)) \end{aligned}$$

The specific heat is given by

$$
\begin{aligned}
c_V &= \frac{N}{k_B T^2} \frac{\partial \tanh(\beta\mu H)}{\partial \beta} \\
&= \frac{N\mu H}{k_B T^2 \cosh(\beta\mu H)^2}.
\end{aligned}
$$

The total magnetization is given by

$$
\begin{aligned}
M &= \left\langle \sum_{i=1}^{N} s_i \right\rangle \\
&= \frac{E}{\mu H}.
\end{aligned}
$$

Finally the magnetic susceptibility is

$$
\begin{aligned}
\chi &= \frac{\partial M}{\partial H} \\
&= -N \frac{\partial}{\partial H} \left(\frac{\sinh(\beta\mu H)}{\mu H \cosh(\beta\mu H)} \right) \\
&= -N\mu\beta^2 \frac{\partial}{\partial \gamma} \left(\frac{\sinh(\gamma)}{\gamma \cosh(\gamma)} \right) \qquad \text{with } \gamma = \beta\mu H \\
&= N\mu\beta^2 \frac{\sinh(\gamma) - \gamma}{\cosh(\gamma)^2}.
\end{aligned}
$$

4.18 High temperature specific heat of metals: a paradox?

4.19 Electronic contribution of specific heat

4.20 White dwarfs