Assignment 3

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October 27, 2010

1 Harden Problem 1

Model a polymer chain as a 1D random walk of N steps of length b in $\pm\hat{x}$. The total end-to-end distance is $R \leq Nb$.

1.1 Problem 1.a

Find the entropy

Let us have n_+ steps to the right (or $+\hat{x}$) and n_- steps to the left (or $-\hat{x}$). We can find both of these values from the fact that $N = n_+ + n_-$ and that the total length is

$$\begin{aligned} R &= n_+ b - n_- b \\ &= n_+ b - (N - n_+) b \\ &= 2n_+ b - Nb \end{aligned}$$

$$\boxed{n_+ = \frac{R + Nb}{2b}} \tag{1a}$$

$$\begin{aligned} R &= n_+ b - n_- b \\ &= (N - n_-) b - n_- b \\ &= Nb - 2n_- b \end{aligned}$$

$$\boxed{n_- = \frac{Nb - R}{2b}} \tag{1b}$$

We know that the definition of entropy is

$$S = k_{\mathrm{B}} \ln \Omega \tag{2}$$

and we realize that Ω is the number of different ways to get R from N steps or

$$\Omega = \frac{N!}{n_+! n_-!} = \frac{N!}{\left(\frac{R+Nb}{2b}\right)! \left(\frac{Nb-R}{2b}\right)!}. \tag{3}$$

Therefore, the entropy is (and we use Sterling's approximation)

$$\begin{aligned}
S = k_\mathrm{B} \ln \Omega = k_\mathrm{B} \ln \left[\frac{N!}{\left(\frac{R+Nb}{2b}\right)! \left(\frac{Nb-R}{2b}\right)!} \right] \\
&= k_\mathrm{B} \left[\ln N! - \ln \left(\frac{R+Nb}{2b} \right)! - \ln \left(\frac{Nb-R}{2b} \right)! \right] \\
&\approx k_\mathrm{B} \left[N \ln N - N - \left(\frac{R+Nb}{2b} \right) \ln \left(\frac{R+Nb}{2b} \right) + \left(\frac{R+Nb}{2b} \right) \right. \\
&\qquad \left. - \left(\frac{Nb-R}{2b} \right) \ln \left(\frac{Nb-R}{2b} \right) + \left(\frac{Nb-R}{2b} \right) \right] \\
&= k_\mathrm{B} \left[N \ln N - \left(\frac{R+Nb}{2b} \right) \ln \left(\frac{R+Nb}{2b} \right) - \left(\frac{Nb-R}{2b} \right) \ln \left(\frac{Nb-R}{2b} \right) \right] \\
&= k_\mathrm{B} \left[N \ln N - \frac{N}{2} \left(\frac{R}{Nb} + 1 \right) \ln \left(\frac{N}{2} \left(\frac{R}{Nb} + 1 \right) \right) \right. \\
&\qquad \left. - \frac{N}{2} \left(1 - \frac{R}{Nb} \right) \ln \left(\frac{N}{2} \left(1 - \frac{R}{Nb} \right) \right) \right] \\
&= \frac{k_\mathrm{B} N}{2} \left[2 \ln N - \left(1 + \frac{R}{Nb} \right) \ln \left(1 + \frac{R}{Nb} \right) - \left(1 - \frac{R}{Nb} \right) \ln \left(1 - \frac{R}{Nb} \right) \right. \\
&\qquad \left. - \left(1 + \frac{R}{Nb} \right) \ln \left(\frac{N}{2} \right) - \left(1 - \frac{R}{Nb} \right) \ln \left(\frac{N}{2} \right) \right] \\
&= \frac{k_\mathrm{B} N}{2} \left[2 \ln N - \left(1 + \frac{R}{Nb} \right) \ln \left(1 + \frac{R}{Nb} \right) - \left(1 - \frac{R}{Nb} \right) \ln \left(1 - \frac{R}{Nb} \right) - 2 \ln \left(\frac{N}{2} \right) \right]
\end{aligned}$$

$$\boxed{S = \frac{k_\mathrm{B} N}{2} \left[2 \ln 2 - \left(1 + \frac{R}{Nb} \right) \ln \left(1 + \frac{R}{Nb} \right) - \left(1 - \frac{R}{Nb} \right) \ln \left(1 - \frac{R}{Nb} \right) \right]} \tag{4a}$$

or

$$\boxed{S = -k_\mathrm{B} N \left[\left(\frac{1}{2} + \frac{R}{2Nb} \right) \ln \left(\frac{1}{2} + \frac{R}{2Nb} \right) + \left(\frac{1}{2} - \frac{R}{2Nb} \right) \ln \left(\frac{1}{2} - \frac{R}{2Nb} \right) \right]}. \tag{4b}$$

The nice thing about these forms is that we can easily take derivatives of it (as we will have to in the following parts).

1.2 Problem 1.b

We find the Helmholtz free energy by realizing that there is no energy only entropy in the random walk so

$$\begin{aligned}
F &= E - TS = -TS \\
&= k_\mathrm{B} T \frac{N}{2} \left[\left(1 + \frac{R}{Nb} \right) \ln \left(1 + \frac{R}{Nb} \right) + \left(1 - \frac{R}{Nb} \right) \ln \left(1 - \frac{R}{Nb} \right) - 2 \ln 2 \right]
\end{aligned} \tag{5}$$

1.3 Problem 1.c

Since the change in free energy is related to the entropy and the tension by

$$dF = SdT + \tau dR$$

we know that

$$\begin{aligned}
\tau &= \left.\frac{\partial F}{\partial R}\right|_T \\
&= k_{\mathrm{B}}T\frac{N}{2}\left[\left(\frac{1}{Nb}\right)\ln\left(1+\frac{R}{Nb}\right)+\frac{1+\frac{R}{Nb}}{1+\frac{R}{Nb}}\left(\frac{1}{Nb}\right)\right. \\
&\qquad \left.+\left(-\frac{1}{Nb}\right)\ln\left(1-\frac{R}{Nb}\right)+\frac{1-\frac{R}{Nb}}{1-\frac{R}{Nb}}\left(-\frac{1}{Nb}\right)+0\right] \\
&= k_{\mathrm{B}}T\frac{N}{2}\left[\frac{1}{Nb}\ln\left(1+\frac{R}{Nb}\right)+\frac{1}{Nb}-\frac{1}{Nb}\ln\left(1-\frac{R}{Nb}\right)-\frac{1}{Nb}\right] \\
&= \frac{k_{\mathrm{B}}T}{2b}\left[\ln\left(1+\frac{R}{Nb}\right)-\ln\left(1-\frac{R}{Nb}\right)\right] \\
&= \frac{k_{\mathrm{B}}T}{2b}\left[\ln\left(\frac{1+\frac{R}{Nb}}{1-\frac{R}{Nb}}\right)\right]
\end{aligned}$$

$$\boxed{\tau = \frac{k_{\mathrm{B}}T}{2b}\ln\left(\frac{Nb+R}{Nb-R}\right)}. \tag{6}$$

For those people that chose to make approximations (like large N so that $\lim_{N\to\infty}\Omega \propto \exp\left[-R^2/2Nb^2\right]$ or chosing to expand the logarithms in S) we can check their approximation by approximating the exact (less Sterling's approximation) solution Eq. (6)

$$\begin{aligned}
\tau &= \frac{k_{\mathrm{B}}T}{2b}\ln\left(\frac{Nb+R}{Nb-R}\right) \\
&= \frac{k_{\mathrm{B}}T}{2b}\left[\ln\left(1+\frac{R}{Nb}\right)-\ln\left(1-\frac{R}{Nb}\right)\right] \\
&\approx \frac{k_{\mathrm{B}}T}{2b}\left[\left\{\frac{R}{Nb}-\frac{1}{2}\left(\frac{R}{Nb}\right)^2+\dots\right\}+\left\{\frac{R}{Nb}+\frac{1}{2}\left(\frac{R}{Nb}\right)^2+\dots\right\}\right] \\
&= \frac{k_{\mathrm{B}}T}{b}\frac{R}{Nb} = k_{\mathrm{B}}T\frac{R}{Nb^2}.
\end{aligned}$$

2 Harden Problem 2

Consider mixing a gas of species A and B in a closed system of total energy E, volume V and number of atoms $N = N_A + N_B$. Initially, all the A-type atoms (of mass m_A) are in a subvolume V_A and likewise all the B-atoms are in $V_B = V - V_A$. They are then allowed to mix and occupy the total volume V. Both the monatomic gases A and B and the mixture behave as ideal gases.

2.1 Problem 2.a

Calculate the entropy of mixing ΔS from the entropy of the initial and final states.

From the text we know

$$S\left(E,V,N\right) = Nk_{\mathrm{B}}\ln\left[V\left(\frac{4\pi emE}{3N}\right)^{3/2}\right] \tag{7}$$

so the initial entropy of the A-gas is

$$\begin{aligned} S_{A,i} &= N_A k_{\mathrm{B}}\ln\left[V_A\left(\frac{4\pi em_A E_A}{3N_A}\right)^{3/2}\right] \\ &= N_A k_{\mathrm{B}}\ln\left[V_A\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}\right] \end{aligned} \tag{8a}$$

where we took advantage of

$$\boxed{\frac{3}{2}k_{\mathrm{B}}T = \frac{E_A}{N_A} = \frac{E_B}{N_B}}. \tag{8b}$$

Likewise the entropy of the B-gas is initially

$$\begin{aligned} S_{B,i} &= N_B k_{\mathrm{B}}\ln\left[V_B\left(\frac{4\pi em_B E_B}{3N_B}\right)^{3/2}\right] \\ &= \left(N-N_A\right)k_{\mathrm{B}}\ln\left[\left(V-V_A\right)\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}\right]. \end{aligned} \tag{8c}$$

The total initial entropy is

$$S_i = S_{A,i} + S_{B,i} \tag{8d}$$

The gases are ideal so the entropies after mixing are

$$S_{A,f} = N_A k_{\mathrm{B}}\ln\left[V\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}\right] \tag{9a}$$

$$S_{B,f} = \left(N-N_A\right)k_{\mathrm{B}}\ln\left[V\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}\right] \tag{9b}$$

$$S_f = S_{A,f} + S_{B,f} \tag{9c}$$

So then the entropy is of mixing is the difference

$$\begin{aligned} \Delta S &= S_f - S_i = S_{A,f} + S_{B,f} - S_{A,i} - S_{B,i} \\ &= N_A k_{\mathrm{B}}\ln\left[V\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}\right] + \left(N-N_A\right)k_{\mathrm{B}}\ln\left[V\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}\right] \\ &\qquad - N_A k_{\mathrm{B}}\ln\left[V_A\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}\right] - \left(N-N_A\right)k_{\mathrm{B}}\ln\left[\left(V-V_A\right)\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}\right] \\ &= N_A k_{\mathrm{B}}\ln\left[\frac{V\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}}{V_A\left(2\pi em_A k_{\mathrm{B}}T\right)^{3/2}}\right] + \left(N-N_A\right)k_{\mathrm{B}}\ln\left[\frac{V\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}}{\left(V-V_A\right)\left(2\pi em_B k_{\mathrm{B}}T\right)^{3/2}}\right] \\ &= N_A k_{\mathrm{B}}\ln\left[\frac{V}{V_A}\right] + \left(N-N_A\right)k_{\mathrm{B}}\ln\left[\frac{V}{V-V_A}\right] \end{aligned}$$

$$\boxed{\Delta S = N_A k_\mathrm{B} \ln\left[\frac{V}{V_A}\right] + N_B k_\mathrm{B} \ln\left[\frac{V}{V_B}\right]} \tag{10a}$$

which by the way can take the really nice forms

$$\boxed{\Delta S = N k_\mathrm{B} \ln V - N_A k_\mathrm{B} \ln V_A - N_B k_\mathrm{B} \ln V_B} \tag{10b}$$

or

$$\boxed{\Delta S = k_\mathrm{B} \ln\left(\frac{V^N}{V_A^{N_A} V_B^{N_B}}\right)}. \tag{10c}$$

2.2 Problem 2.b

Through the first law

$$dE = TdS - pdV + \mu dN \tag{11}$$

we know that

$$\begin{aligned}
\frac{1}{T} &= \left.\frac{\partial S_f}{\partial E}\right|_{V,N} \\
&= \left.\frac{\partial S_{A,f}}{\partial E}\right|_{V,N} + \left.\frac{\partial S_{B,f}}{\partial E}\right|_{V,N} \\
&= \frac{\partial}{\partial E} N_A k_\mathrm{B} \ln\left[V\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right]_{V,N} + \frac{\partial}{\partial E} N_B k_\mathrm{B} \ln\left[V\left(\frac{4\pi e m_B E_B}{3N_B}\right)^{3/2}\right]_{V,N} \\
&= \frac{\partial}{\partial E} N_A k_\mathrm{B} \ln\left(E_A^{3/2}\right) + \frac{\partial}{\partial E} N_B k_\mathrm{B} \ln\left(E_B^{3/2}\right) \\
&= N_A k_\mathrm{B} \frac{\partial E_A}{\partial E} \frac{\partial}{\partial E_A} \ln\left(E_A^{3/2}\right) + N_B k_\mathrm{B} \frac{\partial E_B}{\partial E} \frac{\partial}{\partial E_B} \ln\left(E_B^{3/2}\right)
\end{aligned}$$

Notice those Jacobians from the energy

$$\frac{E}{N} = \frac{E_A}{N_A} = \frac{E_B}{N_B} \quad \rightarrow \quad \frac{\partial E_A}{\partial E} = \frac{N_A}{N}, \frac{\partial E_B}{\partial E} = \frac{N_B}{N}.$$

So then

$$\begin{aligned}
\frac{1}{T} &= N_A k_\mathrm{B} \frac{N_A}{N} \frac{3}{2} \frac{1}{E_A} + N_B k_\mathrm{B} \frac{N_B}{N} \frac{3}{2} \frac{1}{E_B} \\
&= k_\mathrm{B} \frac{N_A}{N} \frac{3}{2} \frac{N}{E} + k_\mathrm{B} \frac{N_B}{N} \frac{3}{2} \frac{N}{E} \\
&= \frac{3}{2} k_\mathrm{B} \left[\frac{N_A}{E} + \frac{N_B}{E}\right] \\
&= \frac{3}{2} k_\mathrm{B} \left[\frac{N_A + N_B}{E}\right]
\end{aligned}$$

$$\boxed{E = \frac{3}{2} N k_\mathrm{B} T} \tag{12}$$

2.3 Problem 2.c

Calculate the chemical potential of A and B-type species. Use these to find the exchange potential $\Delta\mu = \mu_A - \mu_B$.

Using the initial entropy for the A-gas, we see

$$\begin{aligned}\mu_A &= -T \left.\frac{\partial S_{A,i}}{\partial N_A}\right|_{E_A,V_A} \\ &= -T\frac{\partial}{\partial N_A}\left[N_A k_\mathrm{B} \ln\left(V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right)\right]_{E_A,V_A} \\ &= -T\left[k_\mathrm{B}\ln\left(V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right) + N_A k_\mathrm{B}\left(-\frac{3}{2}\frac{1}{N_A}\right)\right]\end{aligned}$$

$$\boxed{\mu_A = -k_\mathrm{B}T\left[\ln\left(V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right) - \frac{3}{2}\right]}. \tag{13}$$

In exactly the same way

$$\boxed{\mu_B = -k_\mathrm{B}T\left[\ln\left(V_B\left(\frac{4\pi e m_B E_B}{3N_B}\right)^{3/2}\right) - \frac{3}{2}\right]}. \tag{14}$$

So then once again using Eq. (8b) , we find the exchange potential to be

$$\begin{aligned}\Delta\mu &= \mu_A - \mu_B \\ &= -k_\mathrm{B}T\left[\ln\left(V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right) - \frac{3}{2}\right] + k_\mathrm{B}T\left[\ln\left(V_B\left(\frac{4\pi e m_B E_B}{3N_B}\right)^{3/2}\right) - \frac{3}{2}\right] \\ &= k_\mathrm{B}T\left[-\ln\left(V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}\right) + \ln\left(V_B\left(\frac{4\pi e m_B E_B}{3N_B}\right)^{3/2}\right)\right] \\ &= k_\mathrm{B}T\ln\left(\frac{V_B\left(\frac{4\pi e m_B E_B}{3N_B}\right)^{3/2}}{V_A\left(\frac{4\pi e m_A E_A}{3N_A}\right)^{3/2}}\right) = k_\mathrm{B}T\ln\left(\frac{V_B\left(\frac{4\pi e m_B}{3}\frac{3}{2}k_\mathrm{B}T\right)^{3/2}}{V_A\left(\frac{4\pi e m_A}{3}\frac{3}{2}k_\mathrm{B}T\right)^{3/2}}\right)\end{aligned}$$

$$\boxed{\Delta\mu = k_\mathrm{B}T\ln\left(\frac{V_B m_B^{3/2}}{V_A m_A^{3/2}}\right)} \tag{15}$$

3 Harden Problem 3

Consider a classical, monotonic ideal gas of N indistinguishable atoms each of mass m in a semi-infinite column with cross-sectional area A. The gas is maintained at a temperature T and is subject to a gravitational field in the $-\hat{z}$ direction. Thus atoms at a height z have a potential energy

$$u(z) = mgz. \tag{16}$$

3.1 Problem 3.a

(Notice, unless otherwise stated all integrals are over $-\infty$ to ∞). Anyway, the Hamiltonian for such a gas is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + mgz_i. \tag{17}$$

The partition function is

$$\begin{aligned} Z &= \sum_{\mu} e^{-\beta\mathcal{H}} \\ &= \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{q}_i d^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + mgz_i\right)\right] \\ &= \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] d^3\vec{q}_i \exp\left[-\beta \sum_{i=1}^{N} mgz_i\right]. \end{aligned}$$

The momentum integral you should recognize as exactly the integral done in the text book for the ideal gas less the $\int \prod d^3\vec{q}_i = V^N$ term (so we'll just steal that answer at this point).

$$\begin{aligned} Z &= \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] d^3\vec{q}_i \exp\left[-\beta \sum_{i=1}^{N} mgz_i\right] \\ &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} \int \prod_{i=1}^{N} d^3\vec{q}_i \exp\left[-\beta \sum_{i=1}^{N} mgz_i\right] \\ &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} \int \prod_{i=1}^{N} dx_i dy_i dz_i \exp\left[-\beta \sum_{i=1}^{N} mgz_i\right] \\ &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} A^N \int \prod_{i=1}^{N} dz_i \exp\left[-\beta \sum_{i=1}^{N} mgz_i\right] \\ &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} A^N \left[\int dz \exp\left[-\beta mgz\right]\right]^N. \end{aligned}$$

One last thing and we have it. Unlike all the others, the height integral goes from 0 to ∞.

$$\begin{aligned} Z &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} A^N \left[\int_0^{\infty} dz \exp\left[-\beta mgz\right]\right]^N \\ &= \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} A^N \left(\frac{1}{\beta mg}\right)^N \end{aligned}$$

$$\boxed{Z = \frac{1}{N!} \left(\frac{2\pi mk_{\mathrm{B}}T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ak_{\mathrm{B}}T}{mg}\right)^N} \tag{18}$$

Another way to think about this is

$$Z_N = \frac{Z_1^N}{N!}. \tag{19}$$

This is almost the same thing as above but you don't have to worry about the sums.

3.2 Problem 3.b

The heat capacity is

$$C = \frac{\partial E}{\partial T}. \tag{20}$$

We can find E from Eq. (18) by

$$\begin{aligned}
E &= -\frac{\partial \ln Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta} \ln \left[\frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3N}{2}} \left(\frac{A}{\beta m g} \right)^N \right] \\
&= -\frac{\partial}{\partial \beta} \ln \left[\frac{1}{N!} \left(\frac{2\pi m}{h^2} \right)^{\frac{3N}{2}} \left(\frac{A}{m g} \right)^N \left(\frac{1}{\beta} \right)^{3N/2} \frac{1}{\beta^N} \right] \\
&= -\frac{\partial}{\partial \beta} \ln \left[\frac{1}{N!} \left(\frac{2\pi m}{h^2} \right)^{\frac{3N}{2}} \left(\frac{A}{m g} \right)^N \right] - \frac{\partial}{\partial \beta} \ln \left[\beta^{-5N/2} \right] \\
&= 0 + \frac{5N}{2} \frac{\partial}{\partial \beta} \ln \beta
\end{aligned}$$

$$\boxed{E = \frac{5N}{2\beta}} \tag{21}$$

So then applying Eq. (20) , we have

$$C = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \frac{5 N k_{\mathrm{B}} T}{2}$$

$$\boxed{C = \frac{5}{2} N k_{\mathrm{B}}}. \tag{22}$$

This should be compared to $C_V = 3Nk_{\mathrm{B}}/2$ for an ideal gas in a box.