Assignment 6

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April 5, 2010

1 Kadar Ch. 5 Problem 6

Model a section of a polyelectrolyte as a charged cylinder surrounded by ions who are dispersed in a solvent. The total system charge is neutral. There are N ions. If we ignore the Coulomb interactions between ions and say they each only interact with the charged rod by the potential

$$U(r) = -2\frac{Ne^2}{L}\ln\left(\frac{r}{L}\right) \tag{1}$$

then the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + 2e^2 n \ln\left(\frac{r_i}{L}\right)\right] \tag{2}$$

where $n = N/L$ is the number density, L is the height of the cylinder, r the radial coordinate, R the radius of the container, a the radius of the rod and e unit charge.

1.1 Part a)

To find the canonical partition function, we consider the momentum of the ions to be an ideal **but** we can not pull it out of the radial/coordinate-space integral since it has an r dependence. I repeat $Z \neq Z_0 Z_{\text{int}}$ if Z is the total partition function, Z_0 the ideal partition funtion and Z_int the interaction term to the partition function. With that said

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

where we've used the ideal gas result **but** without the volume term V^N because we haven't integrated over spatial coordinates yet. Notice also that U really only depends on the radial position not the index so

$$
\begin{aligned}
Z &= \frac{1}{N!}\int \left(\frac{1}{\lambda^3}\right)^N \exp\left[-\beta N U\right]\left\{d^3\vec{q}\right\}^N \\
&= \frac{1}{N!}\left(\frac{1}{\lambda^3}\right)^N \left[\int_{\ell=0}^{L}\int_{\theta=0}^{2\pi}\int_{r=a}^{R} r dr d\theta d\ell \exp\left[-\beta U\right]\right]^N \\
&= \frac{1}{N!}\left(\frac{1}{\lambda^3}\right)^N \left[2\pi L\int_{r=a}^{R} r dr \exp\left[-\beta U\right]\right]^N \\
&= \frac{1}{N!}\left(\frac{2\pi L}{\lambda^3}\right)^N \left[\int_{r=a}^{R} r dr \exp\left[-\beta 2ne^2 \ln\left(\frac{r}{L}\right)\right]\right]^N \\
&= \frac{1}{N!}\left(\frac{2\pi L}{\lambda^3}\right)^N \left[\int_{r=a}^{R} r dr \left(\frac{r}{L}\right)^{\left[-2\beta ne^2\right]}\right]^N \\
&= \frac{1}{N!}\left(\frac{2\pi L}{\lambda^3}\right)^N L^{2N\beta ne^2}\left[\int_{r=a}^{R} r^{1-2\beta ne^2} dr\right]^N \\
&= \frac{1}{N!}\left(\frac{2\pi L}{\lambda^3}\right)^N L^{2N\beta ne^2}\left\{\left[\frac{r^{-2\beta ne^2+2}}{2\left(1-\beta ne^2\right)}\right]_{r=a}^{R}\right\}^N
\end{aligned}
$$

$$
\boxed{Z = \frac{1}{N!}\left(\frac{2\pi L}{\lambda^3}\right)^N L^{2N\beta ne^2}\left[\frac{R^{2\left(1-\beta ne^2\right)} - a^{2\left(1-\beta ne^2\right)}}{2\left(1-\beta ne^2\right)}\right]^N}. \tag{3}
$$

1.2 Part b)

Find the probability of being at a certain radial position r. Notice this is not the probability of being in a state $p(r,v)$ but just of being at a radial position, *i.e.* we don't care about the momentum.

$$
\begin{aligned}
p(r) &= p(q_i|p_i) \\
&= \frac{p(q_i,p_i)}{p(p_i)} \\
&= \frac{e^{-\beta\mathcal{H}}/Z}{e^{-\beta\mathcal{H}_0}/Z_0}
\end{aligned}
$$

where $\mathcal{H}_0$ and Z_0 are respectively the Hamiltonian and partition function for an ideal gas.

$$
\begin{aligned}
p(r) &= \frac{e^{-\beta(\mathcal{H}_0+U)}/Z}{e^{-\beta\mathcal{H}_0}/Z_0} \\
&= \frac{Z_0}{Z}e^{-\beta(U)}.
\end{aligned}
$$

Remember $Z \neq Z_0 Z_U$ in this particular case. So the Z_0 will cancel out all the pesky coefficients in Z and all we will have is the integrand that we had in Z divided by the integral:

$$\begin{aligned} p(r) &= \frac{r\exp\left[-\beta U\right]}{\int_{r=a}^{R} r\exp\left[-\beta U\right]dr} \\ &= \frac{r^{1-2\beta ne^2}}{\int_{r=a}^{R} r^{1-2\beta ne^2}dr} \\ &= r^{1-2\beta ne^2}\left[\frac{R^{2\left(1-\beta ne^2\right)} - a^{2\left(1-\beta ne^2\right)}}{2\left(1-\beta ne^2\right)}\right]^{-1} \end{aligned}$$

$$\boxed{p(r) = 2\left(1-\beta ne^2\right)\frac{r^{1-2\beta ne^2}}{R^{2(1-\beta ne^2)} - a^{2(1-\beta ne^2)}}}. \tag{4}$$

The average radial position is found in the standard way

$$\begin{aligned} <r> &= \int_{r=a}^{R} rp(r)dr \\ &= \int_{r=a}^{R} r2\left(1-\beta ne^2\right)\frac{r^{1-2\beta ne^2}}{R^{2(1-\beta ne^2)} - a^{2(1-\beta ne^2)}}dr \\ &= \frac{2\left(1-\beta ne^2\right)}{R^{2(1-\beta ne^2)} - a^{2(1-\beta ne^2)}}\int_{r=a}^{R} r^{2-2\beta ne^2}dr \\ &= \frac{2\left(1-\beta ne^2\right)}{R^{2(1-\beta ne^2)} - a^{2(1-\beta ne^2)}}\frac{R^{3-2\beta ne^2} - a^{3-2\beta ne^2}}{3-2\beta ne^2} \\ &= \frac{2-2\beta ne^2}{3-2\beta ne^2}\frac{R^{3-2\beta ne^2} - a^{3-2\beta ne^2}}{R^{2-2\beta ne^2} - a^{2-2\beta ne^2}} \end{aligned}$$

$$\boxed{<r> = \left(\frac{1-1\beta ne^2}{\frac{3}{2}-\beta ne^2}\right)\left(\frac{R^{3-2\beta ne^2} - a^{3-2\beta ne^2}}{R^{2-2\beta ne^2} - a^{2-2\beta ne^2}}\right)}. \tag{5}$$

1.3 Part c)

Here we investigate the limits of high and low temperatures. For this exercise we assume $R \gg a$. We have only two types of energy here:

1. thermal energy $k_{\mathrm{B}}T$
2. electrostatic energy ne^2.

We see the ratio of the two (as βne^2) in every result we found in Sections 1.1 to 1.2.

So very qualitatively, if the electrostatic energy is greater than the thermal energy, we expect the ions to be attracted to the charged rod and thus *condense* on it. But on the other hand, if the thermal energy is much greater than the electrostatic attraction, the motion of the ions will be randomized and they will act like an ideal gas.

When the two energies are comparable the behaviour will be the most complex because the ions' behaviour will be transitioning between the two limiting cases. The transition temperature is then when the two energies balance or

$$\boxed{T_c \sim \frac{ne^2}{k_{\rm B}}}. \tag{6}$$

Let's look at the two limits:

Low Temperatures: In this case,

$$\frac{ne^2}{k_{\rm B}T} > 1$$

and remembering $R \gg a$ such that $R^{-\frac{ne^2}{k_{\rm B}T}} \ll a^{-\frac{ne^2}{k_{\rm B}T}}$ which means the radial probability distribution from Eq. 4 becomes

$$\begin{aligned}
p(r) &= 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{r^{1-2\frac{ne^2}{k_{\rm B}T}}}{R^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)} - a^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)}} \\
&\approx -2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{r^{1-2\frac{ne^2}{k_{\rm B}T}}}{a^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)}}
\end{aligned}$$

$$\boxed{p(r) \approx 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\frac{1}{a}\left(\frac{r}{a}\right)^{1-2\frac{ne^2}{k_{\rm B}T}}} \qquad \text{for } \frac{ne^2}{k_{\rm B}T} > 1 \text{ and } R \gg a \tag{7}$$

With this limit of the probability density, the mean radial position is

$$\begin{aligned}
<r> &= \int_a^R p r dr \\
&\approx \int_a^R 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\frac{1}{a}\left(\frac{r}{a}\right)^{1-2\frac{ne^2}{k_{\rm B}T}} r dr \\
&= 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\int_a^R \left(\frac{r}{a}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} dr \\
&= 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\left(\frac{1}{a}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \int_a^R r^{2-2\frac{ne^2}{k_{\rm B}T}} dr \\
&= 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\left(\frac{1}{a}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \left[r^{3-2\frac{ne^2}{k_{\rm B}T}}\right]_a^R \\
&= 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\left(\frac{1}{a}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \left[a^{3-2\frac{ne^2}{k_{\rm B}T}} - R^{3-2\frac{ne^2}{k_{\rm B}T}}\right] \\
&\approx 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\left(\frac{1}{a}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \left[a^{3-2\frac{ne^2}{k_{\rm B}T}} - 0\right] \\
&\approx 2\left(\frac{ne^2}{k_{\rm B}T} - 1\right)\left(\frac{a^{3-2\frac{ne^2}{k_{\rm B}T}}}{a^{2-2\frac{ne^2}{k_{\rm B}T}}}\right)
\end{aligned}$$

$$\boxed{< r > \approx 2a\frac{ne^2}{k_{\rm B}T}} \qquad \text{for } \frac{ne^2}{k_{\rm B}T} > 1 \text{ and } R \gg a \tag{8}$$

The key is $< r > \propto a$ and doesn't go off to infinity. The ions have condensed on to the polyelectrolyte.

High Temperatures: Now

$$\frac{ne^2}{k_{\rm B}T} < 1$$

and still $R \gg a$ so now $R^{-\frac{ne^2}{k_{\rm B}T}} \gg a^{-\frac{ne^2}{k_{\rm B}T}}$ which means the radial probability distribution Eq. 4 becomes

$$\begin{aligned} p(r) &= 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{r^{1-2\frac{ne^2}{k_{\rm B}T}}}{R^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)} - a^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)}} \\ &\approx 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{r^{1-2\frac{ne^2}{k_{\rm B}T}}}{R^{2\left(1-\frac{ne^2}{k_{\rm B}T}\right)}} \end{aligned}$$

$$\boxed{p(r) \approx 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{1}{R}\left(\frac{r}{R}\right)^{1-2\frac{ne^2}{k_{\rm B}T}}} \qquad \text{for } \frac{ne^2}{k_{\rm B}T} < 1 \text{ and } R \gg a \tag{9}$$

The average radial position is easy to find just like in the low temperature limit:

$$\begin{aligned} < r > &= \int_a^R prdr \\ &\approx \int_a^R 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\frac{1}{R}\left(\frac{r}{R}\right)^{1-2\frac{ne^2}{k_{\rm B}T}} rdr \\ &= 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\left(\frac{1}{R}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \int_a^R r^{2-2\frac{ne^2}{k_{\rm B}T}} dr \\ &= 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\left(\frac{1}{R}\right)^{2-2\frac{ne^2}{k_{\rm B}T}} \left[r^{3-2\frac{ne^2}{k_{\rm B}T}}\right]_a^R \\ &\approx 2\left(1 - \frac{ne^2}{k_{\rm B}T}\right)\left(\frac{R^{3-2\frac{ne^2}{k_{\rm B}T}}}{R^{2-2\frac{ne^2}{k_{\rm B}T}}}\right) \end{aligned}$$

$$\boxed{< r > \approx 2R\left(1 - \frac{ne^2}{k_{\rm B}T}\right)} \qquad \text{for } \frac{ne^2}{k_{\rm B}T} < 1 \text{ and } R \gg a. \tag{10}$$

Here $< r > \propto R$, the container size, as expected for a gas.

1.4 Part d)

The counter-ions exert a pressure on the container walls. What is it? The pressure is the change in free energy with volume.

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} \\ &= k_{\mathrm{B}} T \frac{\partial \ln Z}{\partial V}. \end{aligned}$$

In this question, we haven't been varying anything but the radial component of the volume so then in cylindrical coordinates $\partial V = 2\pi L R \partial R$. Then the pressure is

$$\begin{aligned} P &= k_{\mathrm{B}} T \frac{\partial \ln Z}{\partial V} \\ &= k_{\mathrm{B}} T \frac{\partial R}{\partial V} \frac{\partial \ln Z}{\partial R} \\ &= k_{\mathrm{B}} T \frac{1}{2\pi L R} \frac{\partial \ln Z}{\partial R} \\ &= k_{\mathrm{B}} T \frac{1}{2\pi L R} \frac{\partial}{\partial R} \ln \left(\frac{1}{N!} \left(\frac{2\pi L}{\lambda^3} \right)^N L^{2N\beta n e^2} \left[\frac{R^{2\left(1-\beta n e^2\right)} - a^{2\left(1-\beta n e^2\right)}}{2\left(1-\beta n e^2\right)} \right]^N \right) \\ &= k_{\mathrm{B}} T \frac{1}{2\pi L R} \left(0 + 0 + 0 + N \frac{\partial}{\partial R} \ln \left[R^{2\left(1-\beta n e^2\right)} - a^{2\left(1-\beta n e^2\right)} \right] - 0 \right) \\ &= \frac{N k_{\mathrm{B}} T}{2\pi L R} \frac{1}{R^{2(1-\beta n e^2)} - a^{2(1-\beta n e^2)}} 2(1-\beta n e^2) R^{1-2\beta n e^2} \\ &= \frac{N k_{\mathrm{B}} T}{\pi L R} (1-\beta n e^2) \frac{R^{-1}}{1-\left(\frac{a}{R}\right)^{2(1-\beta n e^2)}} \\ &= \frac{N k_{\mathrm{B}} T}{V} (1-\beta n e^2) \frac{1}{1-(a/R)^{2(1-\beta n e^2)}}. \end{aligned}$$

Notice what we have there: the ideal gas law with two correction terms:

$$\boxed{PV = N k_{\mathrm{B}} T \left(1 - \frac{n e^2}{k_{\mathrm{B}} T} \right) \left(1 - \left[\frac{a}{R} \right]^{2\left(1-\frac{n e^2}{k_{\mathrm{B}} T}\right)} \right)^{-1}}. \tag{11}$$

If we continue to assume that $R \gg a$ then the second correction term approaches one and we have a nice clean

$$PV \approx N k_{\mathrm{B}} T \left(1 - \frac{n e^2}{k_{\mathrm{B}} T} \right)$$

but Eq. 11 allows for the fact that even if the polyelectrolyte is quite weak but in a very confined space the ions will have a correction term of approximately

$$PV \approx N k_{\mathrm{B}} T \left(\frac{R^2}{R^2 - a^2} \right)$$

1.5 Part e)

To try to account for the interaction between counter-ions (previously considered non-interacting) we simply say that the number of ions N can be broken up into two populations: N_1 ions are condensed on the rod and the other $N_2 = N - N_1$ ions are free out in the solvent. We say that the N_2 free ions are still non-interacting but the N_1 do some shielding of the charged rod and lower it's electrostatic potential making the modified Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N_1} \left[\frac{p_i^2}{2m} + 2e^2 n_2 \ln\left(\frac{r_i}{L}\right) \right]. \tag{12}$$

Argue without calculating anything what the equalibrium number of N_2 should be (or equivalently n_2).

We know at high enough temperatures $N_1 \to 0$ and $N_2 \to N$ meaning all the counter-ions are free. At very low temperatures, they all condense and $N_2 \to 0$ and $N_1 \to N$. The equalibrium value of n_2 will be the value that balances the electrostatic energy with the thermal energy so

$$\boxed{n_2^* = \frac{k_{\mathrm{B}}T}{e^2}}. \tag{13}$$

When we happen to have $n_2 < n_2^*$ (*i.e.* many condensed ions and few free ions) then too much of the electrostatic potential is shielded and less ions condense and more are able to leave the area around the rod meaning n_2 will be lowered towards n_2^*. On the other hand, if we happen to have $n_2 > n_2^*$ (*i.e.* many free ions and few condensed ions) the electrostatic energy is momentarily higher than the thermal energy and more ions are attracted to the rod meaning n_2 will be increased towards n_2^*. The system is always driven towards n_2^*.

2 Kadar Ch. 5 Problem 7

Consider an ensemble of hard rods of length 2ℓ. Account for their interactions by making an excluded volume. This question is very similar to the hard sphere problems already considered.

2.1 Part a)

If each rod has some excluded volume ω (you can thank me for my better notation than the book's Ω next time you see me) than we expect the number of states Ω to go like

$$\Omega \propto \left(V - \frac{\omega N}{2}\right)^N.$$

in the exact same way as the hard spheres did. We also expect an indistinguishablity term

$$\Omega \propto \frac{1}{N!}.$$

And finally unlike a sphere which has no rotational degrees of freedom, we expect there to be some number of states associated with each rod's ability to take some number of orientations. Kadar calls this

$$\Omega \propto A^N$$

but we know that A should be proportional to the arch length formed from the restricting angle θ (we arbitrarily call the proportionality constant a)

$$\Omega \propto A^N = (a\ell\theta)^N . \tag{14}$$

So putting these three together

$$\Omega \propto \frac{1}{N!}\left(V - \frac{\omega N}{2}\right)^N (a\ell\theta)^N \tag{15}$$

and so the entropy (as always defined only up to an arbitrary constant) is

$$\begin{aligned} S &= k_\mathrm{B} \ln \Omega \\ &= k_\mathrm{B} \ln \left(\frac{1}{N!}\left(V - \frac{\omega N}{2}\right)^N A^N \right) \\ &\approx k_\mathrm{B} \left[\ln A^N + \ln \left(V - \frac{\omega N}{2}\right)^N - N \ln N + N \right] \end{aligned}$$

$$\boxed{S = N k_\mathrm{B} \left[\ln A + \ln \left(\frac{1}{n} - \frac{\omega}{2} \right) + 1 \right]} \tag{16}$$

where $n \equiv N/V$ is the number density of rods and we have used Stirling's approximation.

2.2 Part c)

I'm doing the first part of **Part c)** before **Part b)** because it makes the most sense that way.

The rotational motion is restricted to an angle θ so as shown in Kadar's figure, the area is made up of two equalateral triangle and two pizza slices. The area of each slice is $\alpha = \int_0^\theta \int_0^\ell r dr = \theta \ell^2/2$ and the area of each triangle is $\alpha' = \ell^2 \sin\theta/2$. This means the excluded area is

$$\boxed{\omega = \ell^2 (\theta + \sin\theta)} \tag{17}$$

2.3 Part b)

In equalibrium the entropy must be at an extrema. Use this fact to find the density as a function of restriction angle.

$$\begin{aligned}
\frac{\partial S}{\partial \theta} &= N k_{\mathrm{B}} \frac{\partial}{\partial \theta}\left[\ln A + \ln\left(\frac{1}{n} - \frac{\omega}{2}\right) + 1\right] \\
&= N k_{\mathrm{B}} \left[\frac{\frac{\partial A}{\partial \theta}}{A} + \frac{-\frac{1}{2}\frac{\partial \omega}{\partial \theta}}{\left(\frac{1}{n} - \frac{\omega}{2}\right)} + 0\right] \\
&= N k_{\mathrm{B}} \left[\frac{A'}{A} - \frac{\omega'}{\left(\frac{2}{n} - \omega\right)}\right] \\
&= 0
\end{aligned}$$

where $'$ denotes the derivative with respect to θ. Therefore,

$$\begin{aligned}
\frac{A'}{A} &= \frac{\omega'}{\left(\frac{2}{n} - \omega\right)} \\
n &= \frac{2}{\frac{\omega' A}{A'} + \omega} \\
&= \frac{2A'}{\omega' A + \omega A'}.
\end{aligned}$$

We've already said $A = a\ell\theta$ and $\omega = \ell^2\left(\theta + \sin\theta\right)$ so then

$$\begin{aligned}
n &= \frac{2A'}{\omega' A + \omega A'} \\
&= \frac{2a\ell}{\ell^2\left(1 + \cos\theta\right) a\ell\theta + \ell^2\left(\theta + \sin\theta\right) a\ell}
\end{aligned}$$

$$\boxed{n = \frac{2}{\ell^2}\frac{1}{2\theta + \theta\cos\theta + \sin\theta}} \tag{18}$$

which is plotted in Fig. 1.

2.4 Part d)

- What's the equalibrium state at high densities?
  - Referring to Fig. 1, we see high density only occurs at small θ which is to say, all the rods are aligned. If we consider small θ ($\ll 1$) then the density goes like

    $$\begin{aligned}
    n &= \frac{2}{\ell^2}\frac{1}{2\theta + \theta\cos\theta + \sin\theta} \\
    &\approx \frac{2}{\ell^2}\frac{1}{2\theta + \theta\left(1 + \ldots\right) + \left(\theta + \ldots\right)} \\
    &= \frac{1}{2\ell^2\theta}
    \end{aligned}$$

    as the rods approach close-packing.

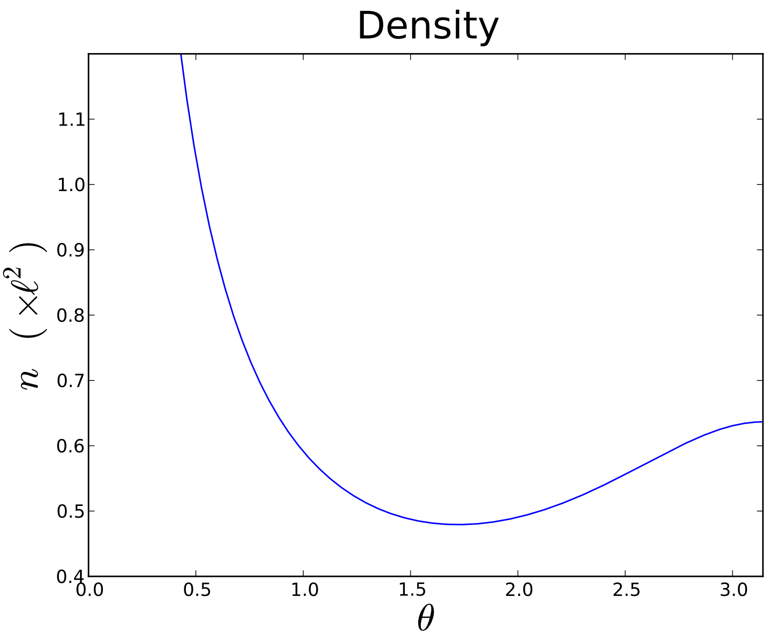

Figure 1: Density is a function of excluded volume and number of orientational states both of which are functions of θ. **Notice:** solutions of $\theta \geq \pi$ are nonsensical. If you allow $\theta = \pi$ you will find a second extrema (a local maxima).

- Is there a phase transition?
  - There is a density minimum which gives sort of critical angle θ_c. All other densities are higher than $n_c = n(\theta_c)$. The minimum is at

$$\frac{dn}{d\theta} = 0$$

but that's a pain to work with. The minimum is also when the denominator is maximized or

$$\frac{d}{d\theta}\left(2\theta + \theta\cos\theta + \sin\theta\right) = 0$$
$$2 + \cos\theta_c - \theta_c \sin\theta_c + \cos\theta_c = 0$$

$$\boxed{\frac{\theta_c \sin\theta_c}{1 + \cos\theta_c} = 2}. \tag{19}$$

This isn't an expression for θ_c but θ_c must satisfy the above equation. Numerically,

$$\theta_c = 1.72067. \tag{20}$$

3 Kadar Ch. 5 Problem 9

Say we have a equation of state

$$P = k_{\mathrm{B}}Tn - \frac{b}{2}n^2 + \frac{c}{6}n^3 \tag{21}$$

where $n = N/V$ is the density and b and c are positive constants.

3.1 Part a)

To find the critical temperature, density and pressure, we require

$$\frac{\partial P}{\partial n} = 0 \tag{22a}$$

$$\frac{\partial^2 P}{\partial n^2} = 0. \tag{22b}$$

The two derivatives area

$$\begin{aligned}\frac{\partial P}{\partial n} &= \frac{\partial}{\partial n}k_{\mathrm{B}}Tn - \frac{b}{2}n^2 + \frac{c}{6}n^3 \\ &= k_{\mathrm{B}}T - bn + \frac{cn^2}{2} \qquad (23a)\\ \frac{\partial^2 P}{\partial n^2} &= \frac{\partial}{\partial n}k_{\mathrm{B}}T - bn + \frac{cn^2}{2} \\ &= -b + cn \qquad (23b)\end{aligned}$$

Therefore, from the second derivative

$$\boxed{n_c = \frac{b}{c}} \tag{24}$$

and then from the first derivative

$$\begin{aligned}k_{\mathrm{B}}T_c - bn_c + \frac{cn_c^2}{2} &= 0\\ k_{\mathrm{B}}T_c - b\left(\frac{b}{c}\right) + \frac{c}{2}\left(\frac{b}{c}\right)^2 &= 0\\ k_{\mathrm{B}}T_c - \frac{b^2}{2c} &= 0\end{aligned}$$

$$\boxed{k_{\mathrm{B}}T_c = \frac{b^2}{2c}} \tag{25}$$

and then from the equation of state itself

$$\begin{aligned}P_c &= k_{\mathrm{B}}T_cn_c - \frac{b}{2}n_c^2 + \frac{c}{6}n_c^3\\ &= \left(\frac{b^2}{2c}\right)\left(\frac{b}{c}\right) - \frac{b}{2}\left(\frac{b}{c}\right)^2 + \frac{c}{6}\left(\frac{b}{c}\right)^3\end{aligned}$$

$$\boxed{P_c = \frac{b^3}{6c^2}}. \tag{26}$$

These critical values mean

$$\begin{aligned}
\frac{k_{\mathrm{B}} T_c n_c}{P_c} &= \frac{\frac{b^2}{2c}\frac{b}{c}}{\frac{b^3}{6c^2}} \\
&= \frac{b^2 b 6c^2}{2ccb^3}
\end{aligned}$$

$$\boxed{\frac{k_{\mathrm{B}} T_c n_c}{P_c} = 3}. \tag{27}$$

3.2 Part b)

Calculate the isothermal compressibility.

The isothermal compressibility is

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \tag{28}$$

which we want in terms of density. So we write

$$\begin{aligned}
\kappa_T &= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \\
&= -\frac{1}{N/n}\left.\frac{\partial N/n}{\partial P}\right|_T \\
&= -\frac{n}{N}N\left.\frac{\partial n^{-1}}{\partial P}\right|_T \\
&= -n\left(-\frac{1}{n^2}\right)\left.\frac{\partial n}{\partial P}\right|_T \\
&= \frac{1}{n}\left.\frac{\partial P}{\partial n}\right|_T^{-1} \\
&= \frac{1}{n}\left[k_{\mathrm{B}}T - bn + \frac{cn^2}{2}\right]^{-1}
\end{aligned}$$

$$\boxed{\kappa_T = \frac{1}{nk_{\mathrm{B}}T - bn^2 + \frac{cn^3}{2}}} \tag{29}$$

For $n = n_c$, the compressibility

$$\begin{aligned}
\kappa_T &= \frac{1}{n_c k_{\mathrm{B}}T - bn_c^2 + \frac{cn_c^3}{2}} \\
&= \frac{1}{\frac{b}{c}k_{\mathrm{B}}T - b\frac{b^2}{c^2} + \frac{cb^3}{2c^3}} \\
&= \frac{c}{b}\frac{1}{k_{\mathrm{B}}T - \frac{b^2}{2c}}
\end{aligned}$$

$$\boxed{\kappa_t = \left(\frac{1}{k_B n_c}\right)\left(\frac{1}{T - T_c}\right)} \tag{30}$$

diverges at T_c

3.3 Part c)

Find $P - P_c$ along the critical isotherm.

$$\begin{aligned}
P - P_c &= k_B T_c n - \frac{b}{2}n^2 + \frac{c}{6}n^3 - P_c \\
&= \frac{b^2}{2c}n - \frac{b}{2}n^2 + \frac{c}{6}n^3 - \frac{b^3}{6c^2} \\
&= \frac{c}{6}n^3 - \frac{b}{2}n^2 + \frac{b^2}{2c}n - \frac{b^3}{6c^2} \\
&= \frac{c}{6}\left[n^3 - 3\frac{b}{c}n^2 + 3\frac{b^2}{c^2}n - \frac{b^3}{c^3}\right] \\
&= \frac{c}{6}\left[n^3 - 3n_c n^2 + 3n_c^2 n - n_c^3\right]
\end{aligned}$$

$$\boxed{P - P_c = \frac{c}{6}\left[n - n_c\right]^3} \tag{31}$$

3.4 Part d)

The liquid and the gas phase separate into two different densities (n_+ and n_- respectively). For temperatures close to T_c, the densities of both should be close to n_c. We expect the differences to be symmetric and so say

$$n_\pm \approx n_c\left(1 \pm \delta\right). \tag{32}$$

Kadar gives a hint. Where does it come from? Recall the Gibbs-Duhem relation:

$$SdT - VdP + Nd\mu = 0.$$

Along an isotherm $dT = 0$ so this reduces to

$$\begin{aligned}
0 &= -VdP + Nd\mu \\
d\mu &= \frac{V}{N}dP \\
&= \frac{1}{n}dP \\
&= \frac{dn}{n}\left.\frac{\partial P}{\partial n}\right|_T \\
&= \frac{dn}{n}\left[k_B T - bn + \frac{cn^2}{2}\right].
\end{aligned} \tag{33}$$

Do we have any expectations about chemical potential? Yes. Because the two phase coexist, the chemical potentials must be equal $\mu(n_+) - \mu(n_-) = 0$. But

$\mu(n_+) - \mu(n_-)$ is just $\int_{n_-}^{n_+} d\mu$. So

$$\begin{aligned}
0 &= \mu(n_+) - \mu(n_-) \\
&= \int_{n_-}^{n_+} d\mu \\
&= \int_{n_-}^{n_+} \frac{dn}{n}\left[k_\mathrm{B}T - bn + \frac{cn^2}{2}\right] \\
&= \int_{n_-}^{n_+} \left(\frac{k_\mathrm{B}T}{n} - b + \frac{cn}{2}\right) dn \\
&= \left[k_\mathrm{B}T \ln n - bn + \frac{cn^2}{4}\right]_{n_-}^{n_+} \\
&= k_\mathrm{B}T \ln n_+ - bn_+ + \frac{cn_+^2}{4} - k_\mathrm{B}T \ln n_- + bn_- - \frac{cn_-^2}{4} \\
&= k_\mathrm{B}T \ln\left(\frac{n_+}{n_-}\right) - b\left(n_+ - n_-\right) + \frac{c}{4}\left(n_+^2 - n_-^2\right)
\end{aligned}$$

but we said $n_\pm = n_c\left(1 \pm \delta\right)$, $n_c = b/c$ and $k_\mathrm{B}T_c = \frac{b^2}{2c}$ so

$$\begin{aligned}
0 &= k_\mathrm{B}T \ln\left(\frac{n_c\left(1+\delta\right)}{n_c\left(1-\delta\right)}\right) - b\left(n_c\left(1+\delta\right) - n_c\left(1-\delta\right)\right) + \frac{c}{4}\left(n_c^2\left(1+\delta\right)^2 - n_c^2\left(1-\delta\right)^2\right) \\
&= k_\mathrm{B}T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2bn_c\delta + \frac{cn_c^2}{4}\left(\left(1+\delta\right)^2 - \left(1-\delta\right)^2\right) \\
&= k_\mathrm{B}T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2bn_c\delta + \frac{cn_c^2}{4}\left(4\delta\right) \\
&= k_\mathrm{B}T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2\delta\frac{b^2}{c} + \delta\frac{b^2}{c} \\
&= k_\mathrm{B}T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2k_\mathrm{B}T_c\delta
\end{aligned}$$

$$\boxed{\delta = \frac{1}{2}\frac{T}{T_c}\ln\left(\frac{1+\delta}{1-\delta}\right)}. \tag{34}$$

Since δ is pretty small, let's expand the logarithm to

$$\begin{aligned}
\delta &\approx \frac{1}{2}\frac{T}{T_c}2\left(\delta - \delta^3 \ldots\right) \\
\frac{T_c}{T} &= 1 - \delta^2
\end{aligned}$$

$$\boxed{\delta = \sqrt{1 - \frac{T_c}{T}}} \tag{35}$$

4 Harden 1

Explore the Ising model for 2D. Say we have a dimensionless magnetization

$$m = \frac{N_+ - N_-}{N} \tag{36}$$

where $N_\pm$ are the number of up and down spins so $N = N_+ + N_-$. We can say

$$N_+ = N\frac{1+m}{2} \tag{37a}$$

$$N_- = N\frac{1-m}{2}. \tag{37b}$$

4.1 Part a)

If the spins are independent (see the next section) then we can say that the number of states are

$$\Omega = \left(\begin{array}{c} N \\ N_+ \end{array} \right) = \frac{N!}{(N\frac{1+m}{2})!\,(N\frac{1-m}{2})!}. \tag{38}$$

Using Stirling's approximation, the entropy is

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

$$\boxed{S = -\frac{N k_\mathrm{B}}{2} \left[(1+m) \ln \left(\frac{1+m}{2} \right) + (1-m) \ln \left(\frac{1-m}{2} \right) \right]} \tag{39}$$

4.2 Part b)

What's the Hamiltonian?

$$\mathcal{H} = -\mu_B B \sum_i \sigma_i - \frac{J}{2} \sum_{\substack{i,j \\ NN}} \sigma_i \sigma_j \tag{40}$$

where NN denotes summing only over nearest neighbours, B is the external magnetic field, J is the exchange interaction, μ_B is the Bohr magneton and $\sigma_i = \frac{2s_{zj}}{\hbar} = \pm 1$ is the spin.

We want to let there be some mean field that represents the state of the entire ensemble of spins. In this way, we'll have non-interacting spins **but** in an effective field that they all created. So let's call $\overline{\sigma}$ the average spin. Let's add it to $\sigma_i\sigma_j$ in a way that we can get an estimate

$$\begin{aligned}
\sigma_i\sigma_j &= (\sigma_i + 0)(\sigma_j + 0) \\
&\approx (\sigma_i - \overline{\sigma} + \overline{\sigma})(\sigma_j - \overline{\sigma} + \overline{\sigma}) \\
&= \sigma_i(\sigma_j - \overline{\sigma} + \overline{\sigma}) - \overline{\sigma}(\sigma_j - \overline{\sigma} + \overline{\sigma}) + \overline{\sigma}(\sigma_j - \overline{\sigma} + \overline{\sigma}) \\
&= \sigma_i(\sigma_j - \overline{\sigma}) + \sigma_i\overline{\sigma} - \overline{\sigma}(\sigma_j - \overline{\sigma}) - \overline{\sigma}^2 + \overline{\sigma}(\sigma_j - \overline{\sigma}) + \overline{\sigma}^2 \\
&= \sigma_i(\sigma_j - \overline{\sigma}) + \overline{\sigma}(\sigma_i - \overline{\sigma}) - \overline{\sigma}(\sigma_j - \overline{\sigma}) + \overline{\sigma}(\sigma_j - \overline{\sigma}) + \overline{\sigma}^2 \\
&= \left[\overline{\sigma}(\sigma_i - \overline{\sigma}) + \overline{\sigma}(\sigma_j - \overline{\sigma}) + \overline{\sigma}^2\right] + \left[\sigma_i(\sigma_j - \overline{\sigma}) - \overline{\sigma}(\sigma_j - \overline{\sigma})\right] \\
&= \underbrace{\left[\overline{\sigma}(\sigma_i - \overline{\sigma}) + \overline{\sigma}(\sigma_j - \overline{\sigma}) + \overline{\sigma}^2\right]}_{\text{No } i,j \text{ terms}} + \underbrace{\left[(\sigma_i - \overline{\sigma})(\sigma_j - \overline{\sigma})\right]}_{Correlationterm}.
\end{aligned}$$

Since we are only considering the mean, we ignore any cross terms and so neglect the correlation term on the far right, saying

$$\boxed{\sigma_{i,j} \approx \overline{\sigma}(\sigma_i + \sigma_j - \overline{\sigma})} \tag{41}$$

which means that if we define z to be the number of nearest neighbours, the Hamiltonian is approximately

$$\begin{aligned}
\mathcal{H} &= -\mu_B B \sum_i \sigma_i - \frac{J}{2} \sum_{\substack{i,j \\ NN}} \sigma_i\sigma_j \\
&= -\mu_B B \sum_i \sigma_i - \frac{J\overline{\sigma}}{2} \sum_{\substack{i,j \\ NN}} (\sigma_i + \sigma_j - \overline{\sigma}) \\
&= -\mu_B B \sum_i \sigma_i - \frac{J\overline{\sigma}}{2} \left(\sum_{\substack{i \\ NN}} \sigma_i + \sum_{\substack{j \\ NN}} \sigma_j - \sum_{NN} \overline{\sigma} \right) \\
&= -\mu_B B \sum_i \sigma_i - \frac{J\overline{\sigma}}{2} \left(2z \sum_i \sigma_i - z\overline{\sigma} \right) \\
&= -(\mu_B B + zJ\overline{\sigma}) \sum_i \sigma_i - \frac{1}{2} zJ\overline{\sigma}^2
\end{aligned}$$

$$\boxed{\mathcal{H} = -\mu_B B_{\text{eff}} \sum_i \sigma_i - \frac{1}{2} zJ\overline{\sigma}^2} \tag{42}$$

where $B_{\text{eff}} = B + zJ\overline{\sigma}/\mu_B$ is the effective field seen by the now non-interacting spins. In this mean field each spin can take an energy $\pm B_{\text{eff}}$ *i.e.* it's a classic two level system now. At this point we can calculate the partition function

$$Z = e^{-NzJ\overline{\sigma}^2/2k_{\mathrm{B}}T} \left(e^{\mu_B B_{\text{eff}}/k_{\mathrm{B}}T} + e^{-\mu_B B_{\text{eff}}/k_{\mathrm{B}}T} \right)^N$$

and then the free energy

$$F = k_{\mathrm{B}}T \ln Z$$

if we want.

Or we can take a step back and do this following the assignment instructions. Setting the effective external field to $B_{\text{eff}} = 0$ (*i.e.* the external field to $B = 0$ and make an even worse approximation for the mean field: $\sum_{\substack{i,j \\ NN}} \sigma_i \sigma_j \approx \overline{\sigma}^2$), the number of nearest neighbours to $z = 4$, $\overline{\sigma}^2 = Nm^2$ and using the notation $\mathcal{H} \to E$.

$$\boxed{E \approx -2JNm^2}. \tag{43}$$

Using this approximation for E and our previous result for S, the free energy ($F = E - TS$) is

$$\boxed{F \approx -2JNm^2 + \frac{Nk_{\text{B}}T}{2}\left[(1+m)\ln\left(\frac{1+m}{2}\right) + (1-m)\ln\left(\frac{1-m}{2}\right)\right]} \tag{44}$$

4.3 Part c)

Find an implicit equation for the magnetization m as a function of the derivative of the free energy $h = \frac{\partial f}{\partial m}\Big|_T$ where f is the free energy per spin ($f = F/N$). The derivative is

$$\begin{aligned}
h &= \frac{\partial f}{\partial m}\bigg|_T \\
&\approx \frac{\partial}{\partial m}\left\{-2Jm^2 + \frac{k_{\text{B}}T}{2}\left[(1+m)\ln\left(\frac{1+m}{2}\right) + (1-m)\ln\left(\frac{1-m}{2}\right)\right]\right\} \\
&= -4Jm + \frac{k_{\text{B}}T}{2}\left[\ln\left(\frac{1+m}{2}\right) + (1+m)\left(\frac{2}{1+m}\right)\left(\frac{1}{2}\right)\right. \\
&\qquad\qquad \left. - \ln\left(\frac{1-m}{2}\right) + (1-m)\left(\frac{2}{1-m}\right)\left(\frac{1}{2}\right)\right] \\
&= -4Jm + \frac{k_{\text{B}}T}{2}\left[\ln\left(\frac{1+m}{2}\right) + 1 - \ln\left(\frac{1-m}{2}\right) - 1\right] \\
&= -4Jm + \frac{k_{\text{B}}T}{2}\ln\left(\frac{1+m}{1-m}\right).
\end{aligned}$$

Rearranging the above we get

$$2\frac{h + 4Jm}{k_{\text{B}}T} = \ln\left(\frac{1+m}{1-m}\right).$$

For convenience, let's momentarily define $\chi \equiv 2\frac{h+4Jm}{k_{\text{B}}T}$ and see that

$$\begin{aligned}
e^{\chi} &= \left(\frac{1+m}{1-m}\right) \\
e^{\chi} - me^{\chi} &= 1 + m \\
m &= \frac{e^{\chi} - 1}{e^{\chi} + 1} \\
&= \tanh\frac{\chi}{2} \\
&= \tanh\left(\frac{h + 4Jm}{k_{\text{B}}T}\right).
\end{aligned}$$

If we define $T_c \equiv zJ/k_{\mathrm{B}}$ and $h' \equiv h/k_{\mathrm{B}}$ then we are left with

$$\boxed{m = \tanh\left(\frac{h' + mT_c}{T}\right)} \tag{45}$$

4.4 Part d)

For $h = 0$, what is a good approximation to the magnetization? Setting $h = 0$ and expanding the hyperbolic tangent, we see

$$\begin{aligned}
m &= \tanh\left(\frac{0 + mT_c}{T}\right) \\
&= m\frac{T_c}{T} - \frac{1}{3}\left(m\frac{T_c}{T}\right)^3 + \dots \\
1 &\approx \frac{T_c}{T} - \frac{m^2}{3}\left(\frac{T_c}{T}\right)^3 \\
m^2 &= 3\left(\frac{T}{T_c}\right)^3\left(\frac{T_c}{T} - 1\right) \\
m &= \pm\sqrt{3\left(\left(\frac{T}{T_c}\right)^2 - \left(\frac{T}{T_c}\right)^3\right)} \\
&= \pm\sqrt{3\frac{T^2}{T_c^2}\frac{T_c - T}{T_c}} \\
&= \pm\frac{T}{T_c}\sqrt{3\frac{T_c - T}{T_c}}.
\end{aligned}$$

If assume that $T \lesssim T_c$ (*i.e.* $T \approx T_c$ but also $T < T_c$ so that the root is real) then $T/T_c \approx 1$ and the magnetization is

$$\boxed{m \approx \pm\sqrt{3\frac{T_c - T}{T_c}}}. \tag{46}$$