Notes for Lecture 9

Interacting particles (cont.)

In the last class, a perturbation theory was used to derive the useful result – namely the van der Waals equation of state. Please read that lecture note to notice what the real perturbation parameter was.

In this lecture, we will explore the same method but with a more systematic method. Our goal here is to arrive at a diagrammatic expansion, which is called Mayer cluster expansion.

9.1 Mayer cluster expansion

We spent a fair amount of time in class deriving this result. While the mathematical steps are interesting and definitely need to be understood, they do not need to be repeated here. You can read your lecture notes plus Section T5.2.

Here we summarize the goal and the results. The goal is to obtain virial coefficients $B_2(T)$, $B_3(T)$, etc. in

$$\frac{P}{k_B T} \;=\; n + B_2(T) n^2 + B_3(T) n^3 + ... \tag{9.1}$$

where $n = N/V$. Note that, by definition, virial coefficients can be functions of only T, since they must be intensive, and they cannot depend on n.

The Mayer cluster cluster expansion is given by

$$\log \mathcal{Q} \;=\; \sum_{k=1}^{\infty} z^k \, \frac{b_k}{k!} \tag{9.2}$$

where z is the fugacity

$$z \;=\; \frac{e^{\beta\mu}}{\lambda^3}$$

as defined in Eq. 8.20, with $\lambda(T) = h/\sqrt{2\pi m k_B T}$.

Using Eq. 7.42 on the above result, we get

$$N \;=\; \sum_{k=1}^{\infty} z^k \, \frac{b_k}{(k-1)!} \tag{9.3}$$

As $\log \mathcal{Q} = -\mathcal{G}\beta = PV\beta$, the last assuming the extensivity, and as b_k is proportional to the volume V (see near the end of this section), we can re-write the above two results as

$$\frac{P}{k_B T} \;=\; \sum_{k=1}^{\infty} z^k \, \frac{\mathfrak{b}_k}{k!} \qquad\qquad \mathfrak{b}_k \equiv b_k/V \tag{9.4}$$

$$n \;=\; \sum_{k=1}^{\infty} z^k \, \frac{\mathfrak{b}_k}{(k-1)!} \tag{9.5}$$

These two equations can be combined by eliminating z, to arrive at the virial expansion

$$\frac{P}{k_B T} \;=\; n + \sum_{k=2}^{\infty} B_k n^k \tag{9.6}$$

$$B_k \;=\; \frac{(1-k)}{k!}\, \mathfrak{d}_k \qquad\qquad B_k = \text{virial coefficient, } k \geq 2 \tag{9.7}$$

For instance, we worked out in class that

$$B_2(T) \;=\; -\frac{\mathfrak{b}_2}{2} \tag{9.8}$$

$$B_3(T) \;=\; \mathfrak{b}_2^2 - \frac{\mathfrak{b}_3}{3} \equiv -\frac{1}{3}\mathfrak{d}_3 \tag{9.9}$$

The symbols b_k and $\mathfrak{d}_k$ must be explained. The symbol b_k stands for the sum of integrals, each of which is diagrammatically represented by a linked cluster of k dots. The i-th dot represents the integration variable $\vec{q}_i$. Each pair of dots ("bond") may be connected or not connected. A linked cluster means that all dots are connected to one another. The integrand is 1 for an unconnected bond, and $f_{ij} = \exp(-\beta U_{ij}) - 1$ for a connected bond, where $U_{ij} = U(\vec{q}_i, \vec{q}_j)$ is the pair potential. As all dots are connected in any diagram of b_k, it follows that there is one and only one free variable that can

be integrated out to give a factor of V for any diagram of b_k. And so, any diagram contributing to b_k is of order V. This is why we defined above $\mathfrak{b}_k(T) \equiv b_k/V$: $\mathfrak{b}_k(T)$ is now independent of V and so is a function of T only. The symbol $\mathfrak{d}_k$ stands for the sum of of integrals that correspond to a special subset – the *one particle irreducible* diagrams – of those diagrams for $\mathfrak{b}_k$. The one particle irreducible diagrams are those diagrams that cannot be separated into two disjoint diagrams by removing one dot. See the four diagrams in page T131 for b_3 – only the last one is one particle irreducible and contributes to B_3.

9.2 Perturbation parameter

In the last lecture note, it was pointed out that N itself is a perturbation parameter. In this lecture, we see that $B_2 n$ can be taken as a perturbation parameter, since $P\beta \approx n(1 + B_2 n)$. We have evaluated B_2 already for a simplified potential (Eqs. 8.14 and 8.22):

$$B_2 n \;=\; -\frac{\mathfrak{b}_2}{2} n \;=\; \frac{1 - \beta u_0}{2}\, \Omega\, n \tag{9.10}$$

Note that the expression for $\mathfrak{b}_2$ was obtained assuming high temperature $\beta u_0 \ll 1$, and so we see that the perturbation parameter is Ωn, which is about $1/1000$, since $\Omega \sim 1/n_{liquid}$. We can see that the perturbation theory will not be good if the density is high or the temperature is low. If the temperature is low, then the above expression cannot be used, and $\mathfrak{b}_2$ must be re-evaluated.

In any case, the information contained in the previous paragraph may be good starting information with which to figure out the answer for the "cluster expansion paradox" as posed on-line at the forum site.

9.3 Van der Waals theory as a mean field theory, phase transition

Note that the total volume excluded by the hard core repulsion is given by $N(N-1)\Omega/2 \approx N^2\Omega/2$. So, it is $N\Omega/2$ per particle.

Note that from, Eq. 8.2,

$$Z(N,T,V) \;=\; \frac{1}{N!\lambda^{3N}} \int d\vec{\mathbf{q}} \exp\left(-\sum_{i<j} \beta U_{ij} \right) \tag{9.11}$$

A mean field approach can be taken to replace the potential energy with an average potential energy for the attractive part. Then, the integrand is simply a number, and the integral becomes $V(V-\Omega)...(V-(N-1)\Omega)$ due to the excluded volume. By taking the log and approximating (using $\Omega/V \ll 1$) and then re-exponentiating, we get

$$V(V-\Omega)...(V-(N-1)\Omega) \;\approx\; (V-N\Omega/2)^N \tag{9.12}$$

which basically reflects our observation above that the excluded volume is $N\Omega/2$ per particle.

Now, let us look at the mean-field approximation for the potential energy

$$\overline{\sum_{i<j} U_{ij}} \;=\; \frac{1}{2}n^2 \int_{\text{attractive part}} d^3\vec{x}_1 d^3\vec{x}_2 U(\vec{x}_1,\vec{x}_2) \tag{9.13}$$

$$\;=\; \frac{1}{2}n^2\, V\, 4\pi \int_{r_0}^{\infty} dr r^2 \left(-u_0 \frac{r_0^6}{r^6}\right) \tag{9.14}$$

using the same approximate model as in the previous lecture. The integral is elementary, and we get

$$\overline{\sum_{i<j} U_{ij}} \;=\; -\frac{1}{2}\, nN\, \Omega u_0 \tag{9.15}$$

Thus, the partition function is given by

$$Z(N,T,V) \;=\; \frac{1}{N!\lambda^{3N}} \left[\left(V - N\frac{\Omega}{2}\right) \exp\left(\frac{n\beta\Omega u_0}{2}\right)\right]^N \tag{9.16}$$

We can compare this equation with the partition function for an ideal gas (Eq. 7.32)

$$Z_0(N,T,V) \;=\; \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

Clearly, it indicates that the reduction of volume by $N\Omega/2$. Also, note that

$$P \;=\; -\frac{\partial F}{\partial V} \;=\; k_B T \frac{\partial \log Z}{\partial V} \tag{9.17}$$

$$\;=\; \left[\frac{Nk_BT}{V - N\frac{\Omega}{2}} - \frac{u_0\Omega n^2}{2}\right] \tag{9.18}$$

$$\;=\; \left[\frac{Nk_BT}{V-bN} - an^2\right] \qquad a \equiv u_0\Omega/2,\; b \equiv \Omega/2 \tag{9.19}$$

$$(P+an^2)(V-bN) \;=\; Nk_BT \tag{9.20}$$

So, the van der Waals equation of state can be derived as a mean field theory where the average attraction energy per particle $-n\Omega u_0/2 = -an$ reduces the pressure (see detailed discussions in Section T5.3) and the core repulsion reduces the volume by bN.

From the partition function, the Helmholtz free energy can be written down as (using Sterling's formula)

$$\frac{F(N,T,V)}{-k_BT} = N\log\left(V - N\frac{\Omega}{2}\right) + \frac{Nn\beta\Omega u_0}{2} - N\log N + N - 3N\log\lambda \quad (9.21)$$

$$= N\log\left(\frac{V}{N} - \frac{\Omega}{2}\right) + \frac{Nn\beta\Omega u_0}{2} + N(1 - 3\log\lambda) \quad (9.22)$$

Note that, within the grand canonical ensemble, the number N is determined as that value of $\mathcal{N}$ that minimizes the would-be[1] grand potential $\mathcal{G}_{\mathcal{N}}(\mu,T,V) = F(\mathcal{N},T,V) - \mu\mathcal{N}$ (lecture 7), where, as in LN 8, $\mathcal{N}$ means a random variable while N is its ensemble average. Since V is fixed in this minimization, we might as well divide by V. Also, diving by $-k_BT$ as above for F, we get

$$\frac{\mathcal{G}_{\mathcal{N}}(\mu,T,V)}{-k_BTV} = x\log\left(x^{-1} - \frac{\Omega}{2}\right) + \frac{\beta\Omega u_0}{2}x^2 + (1 - 3\log\lambda + \beta\mu)x \quad (9.23)$$

$$= x\log\left(x^{-1} - b\right) + \beta a x^2 + (1 - 3\log\lambda + \beta\mu)x \quad (9.24)$$

Here, $x = \mathcal{N}/V$. Due to the division by a negative number, we would need to maximize this function of x, and $x_{max} = n$, the average particle density.

The above function has either one x_{max} or two maxima and one minimum. When the latter happens at low temperature and the two maxima correspond to the density of the gas phase and the density of the liquid phase. This is a great discovery of the van der Waals theory! While the theory is not quantitatively correct (most mean field theories aren't!), the theory is able to qualitatively predict (most mean filed theories do!) that there *is* a phase transition.

As a function of T, the thermodynamic potential develops a non-analytic behavior – a singularity. Just above T^*, the transition temperature, the grand potential is lower in the gas phase, so the density n_{gas} prevails. Just below T^*, the liquid density n_{liquid} prevails, since the liquid phase is lower in the grand potential. So, the density is discontinuous! Or, by the van der Waals equation of state, the pressure is discontinuous! Note that $\mathcal{G} = -PV$, and so it means that G is discontinuous. The reason for the singularity is not to be found in the non-analyticity of the expression Eq. 9.24, which

[1]This is not the grand potential just yet. It becomes the grand potential when we have found $\mathcal{N}$ that minimizes it. So, the subscript $\mathcal{N}$. For this reason, $\mathcal{G}_{\mathcal{N}} \neq -PV$. In other words, μ here is not a function of $\mathcal{N}$ at all, but is a function of N.

is analytical in the physical domain. In fact, since all thermodynamic potentials are nice integrals and they seem to have no reason to be non-analytic. If you see the argument above for the non-analyticity, you realize that the non-analyticity comes from the rule of large numbers. **So, a phase transition is possible only in the thermodynamic limit** ($N, V \to \infty$). We have no problem accepting it – we surely know that phase transitions occur predictably when we boil water, for example, and also know that the water in a pot has a lot of molecules. Here, we find that these two facts are inseparable.

Just as the concious "I" is the result of an extremely large number of molecules, and just as the classical "particle" becomes distinguishable only due to the large number of molecules that make up a classical "particle" like a baseball or a planet, a sure emergent behavior like a phase transition or, in fact, the *existence* of a phase at all owes it to the very simple fact that there are very many molecules involved.

9.4 Van der Waals theory as a variation solution

The variational principle provides a very useful approximate method.

Suppose that we are given the Hamiltonian H that is difficult to solve for the partition function. Suppose that a Hamiltonian H_0 based on the same degrees of freedom is easy to solve. Define

$$Z(\lambda) = \mathrm{tr}\left\{\exp(-\beta H(\lambda)\right\} \tag{9.25}$$

$$H(\lambda) \equiv H_0 + \lambda(H - H_0) \tag{9.26}$$

where "tr" means the operator $\int \frac{d\vec{\mathbf{p}}d\vec{\mathbf{q}}}{N!h^{3N}}$ for the current semi-classical case and the trace for the quantum statistical mechanics.

By differentiating with respect to λ twice (cf. Section 7.2.2), we see that

$$\frac{d^2 \log Z(\lambda)}{d\lambda^2} = \left\langle \beta^2 (H - H_0)^2 \right\rangle_c \geq 0 \tag{9.27}$$

for *any* λ value. This means that

$$\log Z(\lambda) \geq \log Z(0) + \lambda \left.\frac{d \log Z}{d\lambda}\right|_{\lambda=0} \tag{9.28}$$

As $\left.\frac{d \log Z}{d\lambda}\right|_{\lambda=0} = \beta \left\langle H_0 - H \right\rangle^0$, we get (by putting $\lambda = 1$),

$$\log Z \geq \log Z(0) + \beta \left\langle H_0 - H \right\rangle^0 \tag{9.29}$$

This is the *Gibbs inequality*.

The variation principle is then established by choosing an easy-to-solve H_0 that depends on certain variational parameters and maximizing the right hand side, which is easy to calculate, as a function of those parameters.

In the grand canonical ensemble, the same derivation applies, and leads to

$$\log \mathcal{Q} \geq \log \mathcal{Q}(0) + \beta \left\langle H_0 - H \right\rangle^0 \tag{9.30}$$

As shown in Section T5.6, this variable principle leads to the same equation, namely the minimization of the would-be grand potential, as we explored in the last section, if we take n as the variational parameter, H_0 as the kinetic energy plus the hard core repulsion, and $H - H_0$ as the attractive potential energy.

9.5 Van der Waals theory and phase transition

As derived using the cluster expansion, the van der Waals equation is not expected to be quantitatively valid at all near the gas-liquid phase transition where the temperature is low and the density is high. Nevertheless, this equation is historically the first equation to explain the gas-liquid phase transition, as it has the qualitative features to do so. We already saw this in Section 9.3.

Other typical discussion of the gas-liquid phase transition involves the Maxwell construction of the Gibbs free energy along an isotherm, and the Clapeyron equation at phase coexistence ($dP/dT = \Delta S/\Delta V$; $\Delta S = L/T$ is the entropy change (L being the latent heat), $\Delta V =$ the volume change across the transition).[2] These are elementary topics that are usually covered in undergraduate classes. So, I will leave this topic to reading (and possibly some homework problem).

The gas-liquid transition is a first order transition, as the latent heat is involved. However, as T is raised, the latent heat vanishes just when the gas-liquid phase transition disappears. The T_c, P_c values at which this transition just disappears define the critical point. At the critical point, the transition is a second order transition, since the latent heat vanishes (or more generally, since the first derivative of the Gibbs free energy is continuous).

A more aggressive application of van der Waals equation is to use it to quantitatively describe the behavior near this critical point, and generally to apply it to

[2] I believe that during the May 3 lecture I wrote, on the board, $\Delta S = LT$. That was a typo. It must read as above, $\Delta S = L/T$.

describe the phase transition quantitatively. However, this naive hope was not met with success. Instead, a proper way of dealing with critical phenomena is the renormalization group, which we will consider in a later part of this course. The description of the critical behaviors and the universality classes associated with them is one of the most important developments in the statistical physics in the latter half of the last century.