Notes for Lecture 8

Interacting particles

So far, we have been working under the assumption that molecules in gas do not interact. This is clearly not the case, in reality. Consideration of interactions leads to fascinating results. This will be the topic of interest for the later part of this course.

Generally, interactions make problems extremely difficult. One way to say this is that we do not have a general, reliable way of calculating the properties of a liquid or a solid from first principles, i.e. starting from the N body Hamiltonian. For a low-density gas, we do have a systematic way of doing it, namely the Mayer cluster expansion, as we will see here. The difference between gas and liquid/solid is that in a gas there is a very small chance that a gas molecule belongs in a small "cluster" of molecules. Essentially, the gas molecule spends most of the time as a lone molecule (cluster of size 1), while occasionally colliding with other molecules forming a cluster of size 2 or 3 or more, with an increasingly smaller probability to do so as the cluster size increases. In a liquid or a solid, this idea fails completely, since the specimen is so dense that the "cluster" that a molecule belongs is always the total group of *all* the molecules.

8.1 Nature of the problem

Let us start by reminding ourselves of the result of the non-interacting problem (Eq 7.32).

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

where $\lambda(T) = h/\sqrt{2\pi m k_B T}$ is the thermal Debye wavelength. This partition function resulted from the non-interacting Hamiltonian, $\sum_i p_i^2/(2m)$. Now, let us add the interaction term

$$H_{int}(\vec{q}) \;=\; \sum_{i>j} U(\vec{q}_i - \vec{q}_j) \;\equiv\; \sum_{i>j} U_{ij} \;=\; \frac{1}{2}\sum_{i\neq j} U_{ij} \tag{8.1}$$

What would be the change to the partition function? Since this interaction term does not depend on the momentum variables at all, we get

$$Z(N,T,V) \;=\; Z_0(N,T,V)\,\frac{R(N,T,V)}{V^N} \tag{8.2}$$

$$R(N,T,V) \;=\; \int \prod_{i=1}^{N} d^3\vec{q}_i \,\exp\left(-\beta H_{int}\right) \tag{8.3}$$

The integral of H_{int} is impossible to do, in general.

One way to think about R is that R/V^N is the expectation value of $\exp(-\beta H_{int})$ in the non-interacting state. That is,

$$\frac{R}{V^N} \;=\; \langle \exp(-\beta H_{int}) \rangle^0 \tag{8.4}$$

where the superscript 0 is used for the expectation value in the non-interacting state. Written this way, it is clear that R/V^N is the characteristic function of the probability distribution of the canonical ensemble for the non-interacting system, with a complex "wave number," $k = i\beta$. Thus, it follows that

$$\log R - N\log V \;=\; \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!}\,\langle H_{int}^n \rangle_c^0 \tag{8.5}$$

Taking this approach, the cumulants of H_{int} can be analyzed in terms of the cumulants of U_{ij}, as is done in the textbook (Section T5.1). However, we would not need the results of that section at all.

8.2 Perturbative treatment of the grand partition function

This section is a short summary of what Sriram taught in the class.

The grand partition function can be written as

$$\mathcal{Q}(\mu,T,V) \;=\; \sum_{\mathcal{N}=0}^{\infty} \exp(\beta\mu\mathcal{N}) Z(\mathcal{N},T,V) \tag{8.6}$$

where, for $\mathcal{N} = 0$, $Z = 1$ (you must convince yourself why this must be!).

Also, note that, assuming the extensivity,

$$\mathcal{G}(\mu, T, V) \equiv -k_B T \log \mathcal{Q} = E - TS - \mu N = -PV \tag{8.7}$$

where the assumption of the extensivity is used in the last step (Section 2.5.1: $E = TS + Jx + \mu N$).

We will also use the following very useful relation (from Eq. 7.42)

$$N = \frac{1}{\beta} \left. \frac{\partial \log \mathcal{Q}}{\partial \mu} \right|_{T,V}$$

Note that, in terms of the notation, N is used as the ensemble average for $\mathcal{N}$.

8.2.1 First order

Let us see what the $\mathcal{N} = 1$ term looks like. Using Eqs. 8.2,8.3 and the first equation of this note, we get

$$\begin{aligned} Z(\mathcal{N} = 1, T, V) &= \frac{1}{\lambda^3} \int d^3\vec{q} && \text{since } H_{int} = 0 \text{ for } N \leq 1 \qquad (8.8) \\ &= \frac{V}{\lambda^3} && \text{same as } Z_0(N = 1, T, V) \qquad (8.9) \end{aligned}$$

So, it follows that, if we keep terms up to $\mathcal{N} = 1$, we get

$$\begin{aligned} \mathcal{Q}^{(1)} &= 1 + \frac{e^{\beta\mu} V}{\lambda^3} && (8.10) \\ PV &= k_B T \log \mathcal{Q}^{(1)} \;=\; k_B T \log \left(1 + \frac{e^{\beta\mu} V}{\lambda^3} \right) \\ &\approx k_B T \, \frac{e^{\beta\mu} V}{\lambda^3} \;=\; N k_B T && (8.11) \end{aligned}$$

where the last step is from

$$N = \frac{1}{\beta} \left. \frac{\partial \log \mathcal{Q}^{(1)}}{\partial \mu} \right|_{T,V} = \frac{e^{\beta\mu} V}{\lambda^3}$$

Two important things need to be noted. First, we just recovered the ideal gas equation of state. Second, we did this by assuming that a perturbation theory is possible, with

$$N \approx \frac{e^{\beta\mu} V}{\lambda^3} \ll 1 \tag{8.12}$$

Here, I use the $\approx$ sign rather than $=$, since the equality is valid only at this order of the perturbation.

8.2.2 Second order

$$Z(\mathcal{N}=2,T,V) \;=\; \frac{1}{2}\left(\frac{1}{\lambda^3}\right)^2 \int d^3\vec{q}_1 d^3\vec{q}_2 \exp\left(-\beta U(\vec{q}_1,\vec{q}_2)\right) \tag{8.13}$$

The integral here is defined as $V^2 + b_2$. Simplifying the potential to have a hard wall at $r = r_0$ and a van der Waals attraction $-u_0 r_0^6/r^6$ for $r > r_0$, the calculation is straightforward to do. Assuming that the temperature is high $\beta u_0 \ll 1$, one gets (cf. your notes taken during lectures 8, 9 or Section T5.3)

$$V^2 + b_2 \;=\; V^2 + V\,\Omega(\beta u_0 - 1) \tag{8.14}$$

where $\Omega = 4\pi r_0^3/3$ is the excluded volume due to the repulsive potential.

$$\begin{aligned}
\mathcal{Q}^{(2)} &= 1 + V\frac{e^{\beta\mu}}{\lambda^3} + \frac{V}{2}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 (V + \text{ƀ}_2) \qquad \text{ƀ}_2 \equiv b_2/V && (8.15)\\
PV &= k_B T \log \mathcal{Q}^{(2)} && (8.16)\\
&\approx k_B T\left[V\frac{e^{\beta\mu}}{\lambda^3} + \frac{V}{2}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 (V+\text{ƀ}_2) - \frac{1}{2}V^2\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2\right] && (8.17)\\
&= k_B T V\left[\frac{e^{\beta\mu}}{\lambda^3} + \frac{\text{ƀ}_2}{2}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2\right] && (8.18)\\
N &= \frac{1}{\beta}\left.\frac{\partial \log \mathcal{Q}^{(2)}}{\partial \mu}\right|_{T,V} = V\left[\frac{e^{\beta\mu}}{\lambda^3} + \text{ƀ}_2\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2\right] && (8.19)
\end{aligned}$$

Note here that all expressions PV and N are written up to order "$(e^{\beta\mu})^2$" only since we are doing the perturbation theory at second order here. Now the last equation can be inverted so that the fugacity

$$z \equiv \frac{e^{\beta\mu}}{\lambda^3} \tag{8.20}$$

can be expressed in terms of the density. Note from the previous section that N is in fact our perturbation parameter. This means that n is proportional to the perturbation parameter and so, we must keep z up to n^2 also. This is easy to do (by re-arranging the above equation as $z - n = -\text{ƀ}_2 z^2$ and using the method of iteration on it),

$$z \;=\; n - \text{ƀ}_2 n^2 \tag{8.21}$$

Plugging this into the PV equation above, we get

$$P\beta \;=\; n - \frac{\bar{b}_2}{2} n^2 \tag{8.22}$$

Here, $-\frac{\bar{b}_2}{2}$ is the so-called second virial coefficient. Since $\bar{b}_2 \;=\; \Omega(\beta u_0 - 1)$ (Eq. 8.14), we can re-arrange this equation as

$$\begin{aligned}
P\beta \;&=\; n - \frac{\Omega}{2} u_0 \beta n^2 + \frac{\Omega}{2} n^2 && (8.23)\\
\left(P + \frac{\Omega}{2} u_0 n^2\right) \;&=\; n k_B T \left(1 + \frac{n\Omega}{2}\right) && (8.24)\\
\left(P + \frac{\Omega}{2} u_0 n^2\right)\left(1 - \frac{n\Omega}{2}\right) \;&\approx\; n k_B T && (8.25)\\
\left(P + \frac{u_0 \Omega}{2} n^2\right)\left(V - \frac{N\Omega}{2}\right) \;&\approx\; N k_B T && (8.26)\\
\left(P + a n^2\right)\left(V - bN\right) \;&\approx\; N k_B T && (8.27)
\end{aligned}$$

So, we get the famous van der Waals equation of state, with $a \equiv \frac{u_0 \Omega}{2}$ and $b \equiv \Omega/2$.