

## 8.2: Perturbation Theory

### 8.2.1 Fluids in the canonical ensemble

The partition function for a fluid is

$$Z(T, V, N) = \frac{1}{h^{3N} N!} \int d\Gamma e^{-\beta H(\Gamma)} \quad (8.2.1)$$

where

$$H(\Gamma) = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2 + U_N(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (8.2.2)$$

The momentum integrals can be performed precisely as they were for the ideal gas, giving

$$Z(T, V, N) = \frac{1}{\lambda^{3N}(T) N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (8.2.3)$$

where  $\lambda(T)$  is the thermal de Broglie wavelength. It is useful to define the “configurational partition function”

$$Q_N(T, V) = \frac{1}{N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)}. \quad (8.2.4)$$

For example, in a three-particle system with spherically symmetric pair potential  $u(r)$ , the configurational partition function is

$$Q_3(T, V) = \frac{1}{6} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \int_V d\mathbf{r}_3 e^{-\beta[u(|\mathbf{r}_1 - \mathbf{r}_2|) + u(|\mathbf{r}_1 - \mathbf{r}_3|) + u(|\mathbf{r}_2 - \mathbf{r}_3|)]}. \quad (8.2.5)$$

Every other time in this book that we have encountered a complicated partition function, like the one above, it has factorized into the product of many similar terms. (This happened even in our treatment of harmonic lattice vibrations, through the use of normal coordinates.) The expression above does not factorize in this neat way. With considerable diligence and patience, it is possible to evaluate  $Q_N(T, V)$  for  $N = 3$ . But you can see that doing it for cases of interest, such as  $N = 6.02 \times 10^{23}$ , is simply out of the question. Instead we attempt to use perturbation theory by expanding about an already solved problem, namely the ideal gas. Such an approximation will be a good one at low densities, where the gas is “nearly ideal”. The obvious thing to do is to expand  $Q_N(T, V)$  in the small parameter  $\rho = N/V$ , the number density. But how can we do that? The quantity  $\rho$  doesn’t appear in these formulas!

### 8.2.2 The search for a small parameter

We cannot expand  $Q_N(T, V)$  in terms of  $\rho$ , but we do know that at low densities all fluids behave like an ideal gas, and that for an ideal gas the chemical potential is

$$\mu = k_B T \ln \left( \frac{\rho}{1/\lambda^3(T)} \right), \quad (8.2.6)$$

so that as  $\rho \rightarrow 0$ ,  $\mu \rightarrow -\infty$  and  $e^{\beta\mu} \rightarrow 0$ . So here is a second small parameter. You might object that  $e^{\beta\mu}$  doesn’t appear in the partition function any more than  $\rho$  does, but it does appear in the grand canonical partition function!

### 8.2.3 Fluids in the grand canonical ensemble

The grand canonical partition function is

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T, V, N) \quad (8.2.7)$$

$$= \sum_{N=0}^{\infty} \left( \frac{e^{\beta\mu}}{\lambda^3(T)} \right)^N Q_N(T, V) \quad (8.2.8)$$

$$= \sum_{N=0}^{\infty} z^N Q_N(T, V) \quad (8.2.9)$$

$$= 1 + Q_1(T, V)z + Q_2(T, V)z^2 + Q_3(T, V)z^3 + \mathcal{O}(z^4), \quad (8.2.10)$$

where we have the *activity*

$$z \equiv \frac{e^{\beta\mu}}{\lambda^3(T)}. \quad (8.2.11)$$

The activity is the small parameter upon which perturbation theory relies. (For an ideal gas, it is equal to the number density  $\rho$ .)

Note that in this approach we still have to calculate  $Q_N$  coefficients, but we will probably stop at  $N = 4$  or 5 rather than  $N = 6.02 \times 10^{23}$ . I will write down the first two coefficients:

$$\begin{aligned} Q_1(T, V) &= \int_V d\mathbf{r}_1 e^{-\beta 0} = V \\ Q_2(T, V) &= \frac{1}{2} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{-\beta u(|\mathbf{r}_1 - \mathbf{r}_2|)}. \end{aligned} \quad (8.2.12)$$

Because the interactions are short-ranged, most of the time  $u(|\mathbf{r}_1 - \mathbf{r}_2|)$  nearly vanishes, so  $Q_2$  is pretty close to  $V^2/2$ . It is neither intensive nor extensive.

## 8.2.4 The Mayer expansion

Now we go from the partition function to an experimentally measurable master function, namely pressure:

$$\frac{p(T, z)}{k_B T} = \frac{1}{V} \ln \Xi \quad (8.2.13)$$

$$= \frac{1}{V} \ln [1 + Q_1 z + Q_2 z^2 + Q_3 z^3 + \mathcal{O}(z^4)] \quad (8.2.14)$$

Employing

$$\ln(1 + \epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \frac{1}{3}\epsilon^3 + \mathcal{O}(\epsilon^4) \quad (8.2.15)$$

we obtain

$$\frac{p(T, z)}{k_B T} = \frac{1}{V} \left[ Q_1 z + Q_2 z^2 + Q_3 z^3 - \frac{1}{2} (Q_1 z + Q_2 z^2)^2 + \frac{1}{3} (Q_1 z)^3 + \mathcal{O}(z^4) \right] \quad (8.2.16)$$

$$= \frac{1}{V} Q_1 z + \frac{1}{V} \left( Q_2 - \frac{1}{2} Q_1^2 \right) z^2 + \frac{1}{V} \left( Q_3 - Q_1 Q_2 + \frac{1}{3} Q_1^3 \right) z^3 + \mathcal{O}(z^4) \quad (8.2.17)$$

$$= \sum_{\ell=1}^{\infty} b_{\ell} z^{\ell}. \quad (8.2.18)$$

The last line above defines the “Mayer expansion”. The expansion coefficients  $b_{\ell} = b_{\ell}(T)$  are intensive functions of temperature (in contrast to the coefficients  $Q_N(T, V)$ ). Using equations (8.14) it is easy to show that  $b_1 = 1$  and that

$$\begin{aligned} b_2 &= \frac{1}{2V} \left( \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{-\beta u(|\mathbf{r}_1 - \mathbf{r}_2|)} - \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 1 \right) \\ &= \frac{1}{2V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \left( e^{-\beta u(|\mathbf{r}_1 - \mathbf{r}_2|)} - 1 \right). \end{aligned} \quad (8.2.19)$$

In contrast to the situation with equation (8.14), the integrand above is nearly always zero, which makes it much easier to work with. (The same is true for all the the Mayer coefficients.) Indeed, a little more work will show that

$$b_2 = 2\pi \int_0^{\infty} dr r^2 \left( e^{-u(r)/k_B T} - 1 \right). \quad (8.2.20)$$

Specialists in the statistical mechanics of fluids spend a lot of time calculating  $b_{\ell}$  coefficients for a given potential energy of interaction  $u(r)$ . We will instead emphasize what to do with the  $b_{\ell}$ s once they are calculated.

## 8.2.5 Expansion for the density

To obtain the number density  $\rho = N/V$  from the Mayer expansion, use the thermodynamic connection between  $\rho$  and  $p$ :

$$\rho = \left( \frac{\partial p}{\partial \mu} \right)_T = \frac{\partial z}{\partial \mu} \left( \frac{\partial p}{\partial z} \right)_T = z \left( \frac{\partial (\beta p)}{\partial z} \right)_T. \quad (8.2.21)$$

Thus

$$\rho(T, z) = \sum_{\ell=1}^{\infty} \ell b_{\ell} z^{\ell}. \quad (8.2.22)$$

### 8.2.6 Eliminating the activity: the virial expansion

Now we have two expansions, (8.20) and (8.24), in terms of the activity:

$$\beta p(z) = z + b_2 z^2 + b_3 z^3 + \mathcal{O}(z^4) \quad (8.2.23)$$

$$\rho(z) = z + 2b_2 z^2 + 3b_3 z^3 + \mathcal{O}(z^4) \quad (8.2.24)$$

(The temperature dependence of  $p$ ,  $\rho$ , and the  $b_{\ell}$ s is not shown explicitly.) What we would really like, however, would be the traditional (and experimentally accessible) equation of state,  $p(\rho)$ . In other words, we want to eliminate the  $z$ s between the two expansions above. To this end we will invert the expansion for  $\rho(z)$  to find  $z(\rho)$ , and plug that expression into the expansion (8.25) for  $p(z)$ . In the appendix we perform the inversion to find, correct to third order,

$$z(\rho) = \rho - 2b_2 \rho^2 + (8b_2^2 - 3b_3) \rho^3 + \mathcal{O}(\rho^4). \quad (8.2.25)$$

Plugging into (8.25) gives

$$\beta p(\rho) = z + b_2 z^2 + b_3 z^3 + \mathcal{O}(z^4) \quad (8.2.26)$$

$$= [\rho - 2b_2 \rho^2 + (8b_2^2 - 3b_3) \rho^3] + b_2 [\rho - 2b_2 \rho^2]^2 + b_3 [\rho]^3 + \mathcal{O}(\rho^4) \quad (8.2.27)$$

$$= [\rho - 2b_2 \rho^2 + (8b_2^2 - 3b_3) \rho^3] + b_2 [\rho^2 - 4b_2 \rho^3] + b_3 [\rho]^3 + \mathcal{O}(\rho^4) \quad (8.2.28)$$

$$= \rho - b_2 \rho^2 + (4b_2^2 - 2b_3) \rho^3 + \mathcal{O}(\rho^4). \quad (8.2.29)$$

This last expression is called the “virial expansion”, and it is usually written (with the temperature dependence put back in) as

$$\frac{p(T, \rho)}{k_B T} = \rho + B_2(T) \rho^2 + B_3(T) \rho^3 + \mathcal{O}(\rho^4). \quad (8.2.30)$$

### 8.2.7 Appendix: Inverting $\rho(z)$ to find $z(\rho)$

Begin with

$$\rho(z) = z + 2b_2 z^2 + 3b_3 z^3 + \mathcal{O}(z^4), \quad (8.2.31)$$

then use

$$\begin{aligned} z &= \rho + \mathcal{O}(z^2) & z^2 &= (\rho + \mathcal{O}(z^2)) (\rho + \mathcal{O}(z^2)) & z^3 &= (\rho^2 + \mathcal{O}(z^3)) (\rho + \mathcal{O}(z^2)) \\ &= \rho^2 + 2\rho \mathcal{O}(z^2) + \mathcal{O}(z^4) & &= \rho^3 + \mathcal{O}(z^4) \\ &= \rho^2 + \mathcal{O}(z^3) & &= \rho^3 + \mathcal{O}(z^4) \end{aligned}$$

$$z = \rho - 2b_2 z^2 + \mathcal{O}(z^3)$$

$$\begin{aligned} z &= \rho - 2b_2 \rho^2 + \mathcal{O}(z^3) = (\rho - 2b_2 \rho^2 + \mathcal{O}(z^3)) (\rho - 2b_2 \rho^2 + \mathcal{O}(z^3)) \\ &= \rho^2 - 4b_2 \rho^3 + 4b_2^2 \rho^4 + \rho \mathcal{O}(z^3) \\ &= \rho^2 - 4b_2 \rho^3 + \mathcal{O}(z^4) \end{aligned}$$

$$z = \rho - 2b_2 z^2 - 3b_3 z^3 + \mathcal{O}(z^4)$$

$$z = \rho - 2b_2 [\rho^2 - 4b_2 \rho^3 + \mathcal{O}(z^4)] - 3b_3 [\rho^3 + \mathcal{O}(z^4)] + \mathcal{O}(z^4)$$

to find

$$z(\rho) = \rho - 2b_2 \rho^2 + (8b_2^2 - 3b_3) \rho^3 + \mathcal{O}(\rho^4). \quad (8.2.32)$$

## Problems

### 8.4 Virial expansion for the ideal gas

Find  $Q_1$ ,  $Q_2$ ,  $Q_3$ , etc. for an ideal gas. Hence show that the virial equation of state for an ideal gas is  $pV = Nk_B T$ .

### 8.5 General properties of expansion coefficients

a. Show that  $Q_1 = V$ , whence  $b_1 = 1$ .

b. Show (informally) that the  $b_\ell$  Mayer coefficients, as well as the  $B_n(T)$  virial coefficients, are intensive.

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