Chapter 6

Interacting systems

So far we have almost exclusively[1] focused on ideal systems in which the units composing the system did not interact with each other via interparticle potentials. This simplification helped us more clearly understand the structure of our statistical descriptions of macroscopic systems (and, helpfully, let us solve everything analytically) – and for quantum mechanical systems we even saw that non-interacting Bose and Fermi systems can exhibit rich/interesting behaviors.

However. Interactions are responsible for the amazing variety of phases of matter and material behaviors! Since most physical systems that we encounter cannot be described without considering interactions, in this chapter and the next we'll start building up ways of incorporating interactions into our statistical mechanical formalism. This chapter will focus on systematic expansions, in which an idealized, non-interacting system serves as a useful starting point. Implicitly, for instance, throughout the next sections you can imagine that we're trying to describe the properties of a dilute gas.

6.1 From cumulant expansions...

6.1.1 Moment expansion

Let's return to the idea of a classical system[2] and start with a general Hamiltonian in the absence of an external potential:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \mathcal{U}\left(\{\boldsymbol{r}\}\right),$$

where we've written a general interaction potential, $\mathcal{U}$, which could be an arbitrary function involving the spatial coordinates of the particles.

[1] With the exception of introducing some interactions in Chapter 3 to get to the Boltzmann equation

[2] With our corrected phase-space measure

In the canonical ensemble the partition function would be

$$\begin{aligned} Z(N,V,T) &= \frac{1}{N!h^{3N}} \int \left(\prod_i \mathrm{d}^3\boldsymbol{p}_i \mathrm{d}^3\boldsymbol{r}_i \right) \exp\left(-\beta \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} \right) e^{-\beta \mathcal{U}(\{\boldsymbol{r}\})} \\ &= \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \int \prod_i \frac{\mathrm{d}^3\boldsymbol{r}_i}{V} e^{-\beta \mathcal{U}(\{\boldsymbol{r}\})}, \end{aligned} \tag{6.1}$$

where in the second line we've done the integral over momenta and taken the liberty of multiplying and dividing by N copies of the system volume V. We've done this because now we see terms directly related to ideal, non-interacting quantities. The prefactor is just the ideal gas partition function, and the integral is like doing an average over particle positions where there are no correlations between the particle positions – exactly as if the positions were those from an ideal gas with no interactions. Using the notation where a superscript (0) refers to these ideal-gas like quantities or averages, we can write the canonical partition function as

$$Z(N,V,T) \equiv Z^{(0)}(N,V,T) \left\langle e^{-\beta \mathcal{U}(\{\boldsymbol{r}\})} \right\rangle^{(0)} \tag{6.2}$$

$$= Z^{(0)} \sum_l \frac{(-\beta)^l}{l!} \left\langle \mathcal{U}^l \right\rangle^{(0)}. \tag{6.3}$$

This looks like a moment-based perturbative description of a system: when $\mathcal{U} = 0$ we recover the ideal gas which we know how to solve, and when $\mathcal{U}$ is solve we can calculate corrections systematically. As we'll see shortly, this direct moment-based expansion is often not especially useful: at short ranges there are often strong repulsions (Pauli exclusion, or hard-core repulsion between particles, or...), so the moments of $\mathcal{U}$ need not be small. Nevertheless, working with this will lead us to an expansion which *is* useful.

6.1.2 Cumulant expansion

We know that what we often want to work with is the log of the partition function, so let's replace our moment expansion with a cumulant expansion: we see above that Z is acting like a generator of moments, so taking the log gives us a generator of cumulants:

$$\log Z = \log Z^{(0)} + \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \left\langle \mathcal{U}^l \right\rangle_c^{(0)}. \tag{6.4}$$

At this point we specialize the form of the interparticle potential away from complete generality, and study potentials, ϕ that are pairwise in nature,

$$\mathcal{U} = \sum_{i<j} \phi\left(\boldsymbol{r}_i - \boldsymbol{r}_j\right) \equiv \phi\left(\boldsymbol{r}_{ij}\right), \tag{6.5}$$

where we've introduce the notation $\boldsymbol{r}_{ij}$ to represent vector separations between pairs of particles, which we'll be seeing a lot of in the next sections.

Writing out the first few terms of this cumulant expansion, we have

$$\log Z = \log Z^{(0)} - \beta \left\langle \mathcal{U} \right\rangle^{(0)} + \frac{\beta^2}{2} \left(\left\langle \mathcal{U}^2 \right\rangle^{(0)} - \left(\left\langle \mathcal{U} \right\rangle^{(0)} \right)^2 \right) + \cdots \tag{6.6}$$

Let's evaluate these first few cumulants for our pairwise potential.

First cumulant

The first cumulant is quite straightforward, recognizing that for each pair of particles we pick as the interacting pair we're going to get copies of the same result:

$$\begin{aligned}\langle \mathcal{U} \rangle^{(0)} &= \sum_{i<j} \int \left(\prod_{\alpha} \frac{\mathrm{d}^3 \boldsymbol{r}_\alpha}{V} \right) \phi(\boldsymbol{r}_i - \boldsymbol{r}_j) \\ &= \frac{N(N-1)}{2} \int \frac{\mathrm{d}^3 \boldsymbol{r}_1}{V} \frac{\mathrm{d}^3 \boldsymbol{r}_2}{V} \cdots \frac{\mathrm{d}^3 \boldsymbol{r}_N}{V} \phi(\boldsymbol{r}_1 - \boldsymbol{r}_2) \\ &= \frac{N(N-1)}{2V} \int \mathrm{d}^3 \boldsymbol{r} \phi(\boldsymbol{r}), \end{aligned} \tag{6.7}$$

where in the last line we've let $\boldsymbol{r} = \boldsymbol{r}_{12}$. There you go: someone hands you a particular interparticle potential (Lennard-Jones, or screened Coulomb, or...), and you go off, calculate an integral, and you've got the first term in the cumulant expansion.

Second cumulant

Let's write out the second cumulant as

$$\left\langle \mathcal{U}^2 \right\rangle_c^{(0)} = \sum_{\substack{i<j \\ k<l}} \left[\langle \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{kl}) \rangle^{(0)} - \langle \phi(\boldsymbol{r}_{ij}) \rangle^{(0)} \langle \phi(\boldsymbol{r}_{kl}) \rangle^{(0)} \right]. \tag{6.8}$$

This is a sum over $\left(\frac{N(N-1)}{2}\right)^2$ total terms, and it is helpful to divide those into three classes of terms:

All particle labels are distinct, i.e., i, j, k, l are all different indices. In this case we can look at the second moment and see

$$\begin{aligned}\langle \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{kl}) \rangle^{(0)} &= \int \left(\prod_{\alpha} \frac{\mathrm{d}^3 \boldsymbol{r}_\alpha}{V} \right) \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{kl}) \\ &= \left(\int \frac{\mathrm{d}^3 \boldsymbol{r}_i}{V} \frac{\mathrm{d}^3 \boldsymbol{r}_j}{V} \phi(\boldsymbol{r}_{ij}) \right) \left(\int \frac{\mathrm{d}^3 \boldsymbol{r}_k}{V} \frac{\mathrm{d}^3 \boldsymbol{r}_l}{V} \phi(\boldsymbol{r}_{kl}) \right) \\ &= \langle \phi(\boldsymbol{r}_{ij}) \rangle^{(0)} \langle \phi(\boldsymbol{r}_{kl}) \rangle^{(0)}. \end{aligned} \tag{6.9}$$

Thus, these terms do not make any contribution to $\langle \mathcal{U}^2 \rangle^{(0)}$.

One particle label is shared i.e., we have $i, j, k = i, l$ as the four labels. We can make a similar argument for neglecting this class of terms, too. We first write

$$\langle \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{il}) \rangle^{(0)} = \int \frac{\mathrm{d}^3 \boldsymbol{r}_i \mathrm{d}^3 \boldsymbol{r}_j \mathrm{d}^3 \boldsymbol{r}_l}{V^3} \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{il}), \tag{6.10}$$

and then change variables in the integration from $\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_l$ to $\boldsymbol{r}_i, \boldsymbol{r}_{ij}, \boldsymbol{r}_{il}$. This leaves us with

$$\langle \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{il}) \rangle^{(0)} = \int \frac{\mathrm{d}^3 \boldsymbol{r}_i \mathrm{d}^3 \boldsymbol{r}_{ij} \mathrm{d}^3 \boldsymbol{r}_{il}}{V^3} \phi(\boldsymbol{r}_{ij}) \phi(\boldsymbol{r}_{il}) = \langle \phi(\boldsymbol{r}_{ij}) \rangle^{(0)} \langle \phi(\boldsymbol{r}_{il}) \rangle^{(0)}, \tag{6.11}$$

which again means these terms do not contribute to $\langle \mathcal{U}^2 \rangle^{(0)}$.

The same pair is considered twice i.e., $i = k, j = l$. Well, the second cumulant doesn't vanish, and these are the remaining terms which we do need to keep track of. There are $\frac{N(N-1)}{2}$ terms of this form, and they all contribute identically. Thus, our complete expression for the second cumulant is

$$\left\langle \mathcal{U}^2 \right\rangle_c^{(0)} = \frac{N(N-1)}{2} \left[\int \frac{\mathrm{d}^3 \boldsymbol{r}_{ij}}{V} \phi^2(\boldsymbol{r}_{ij}) - \left(\int \frac{\mathrm{d}^3 \boldsymbol{r}_{ij}}{V} \phi(\boldsymbol{r}_{ij}) \right)^2 \right]. \tag{6.12}$$

So far, we have the following expansion for the log of the partition function:

$$\log Z = \log Z^{(0)} + \frac{N(N-1)}{2} \left[-\beta \int \frac{\mathrm{d}^3 \boldsymbol{r}}{V} \phi(\boldsymbol{r}) + \frac{\beta^2}{2} \left(\int \frac{\mathrm{d}^3 \boldsymbol{r}}{V} \phi^2(\boldsymbol{r}) - \left(\int \frac{\mathrm{d}^3 \boldsymbol{r}}{V} \phi(\boldsymbol{r}) \right)^2 \right) + \cdots \right]. \tag{6.13}$$

We now consider the thermodynamic limit, $V, N \to \infty$, and we find

$$\log Z \approx N \log \left(\frac{Ve}{N\lambda^3} \right) + \frac{N^2}{2V} \left[-\beta \int \mathrm{d}^3 \boldsymbol{r} \phi(\boldsymbol{r}) + \frac{\beta^2}{2} \int \mathrm{d}^3 \boldsymbol{r} \phi^2(\boldsymbol{r}) + \cdots \right]. \tag{6.14}$$

If we now, for instance, want to know the pressure of our system, we take the appropriate derivative and find

$$\begin{aligned} \beta P &= \frac{\partial \log Z}{\partial V} \\ &= \frac{N}{V} - \frac{1}{2} \left(\frac{N}{V} \right)^2 \left[-\beta \int \mathrm{d}^3 \boldsymbol{r} \phi(\boldsymbol{r}) + \frac{\beta^2}{2} \int \mathrm{d}^3 \boldsymbol{r} \phi^2(\boldsymbol{r}) + \cdots \right] + \mathcal{O}\left(\left(\frac{N}{V} \right)^3 \right). \end{aligned} \tag{6.15}$$

What have we done? We've basically written the equation of state of the system as a perturbation organized in powers of density, where the contribution at each order in density is a sum over a series of terms involving integrals of powers of the pairwise potential.

As written, this sort of cumulant expansion is still not very helpful. Why? Because for typical interactions there are large forces keeping molecules apart. For instance, one common potential is the Lennard-Jones potential:

$$\phi(\boldsymbol{r}) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \tag{6.16}$$

where ε is related to the depth of the potential well and σ to the range over which the repulsion is felt. Where do these sorts of potential come from? The attractive r^{-6} part comes from fluctuating dipoles of electrically neutral atoms. Recall that if there were two interacting permanent dipole moments, p_1 and p_2, the potential energy would scale as $p_1 p_2 / r^3$. There are no permanent dipoles for neutral atoms, but atoms can acquire transient dipoles through quantum fluctuations. If the first atom has a transient dipole p_1 it will induce an electric field, which will in turn induce a dipole in the second atom $p_2 \sim E \sim p_1 / r^3$. The resulting energy thus scales as $p_1 p_2 / r^3 \sim r^{-6}$; this is typically called the van der Waals attraction. The r^{-12} term is meant to reflect the rapid transition to strong repulsion as the atoms get very close. The exact form is not so important, and the common choice of a term like r^{-12} is simply a mathematical convenience.

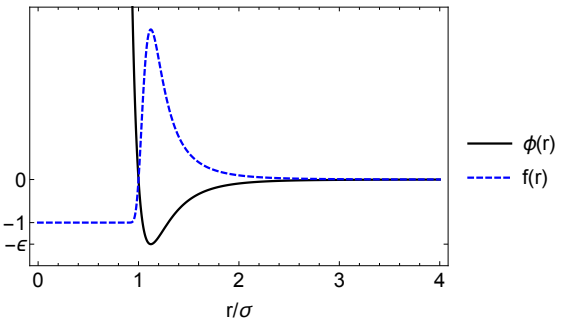

Figure 6.1: **Lennard-Jones potential and the corresponding Mayer f-function** The potential, ϕ, is shown as a solid black line and the corresponding $f = \exp(-\beta\phi) - 1$ is shown as a dashed blue line.

With such a potential, we see that *each integral in the series of series we wrote about diverges*! This is, on its face, not such a good perturbation theory. Before we integrate each term and despair, though, let's do two things. First, let's assume that the perturbative series in *density* is still okay; for a dilute gas we'll go ahead and truncate at order $\left(\frac{N}{V}\right)^2$. Second, lets sum the series first:

$$\begin{aligned} -\beta \int \mathrm{d}^3\boldsymbol{r}\phi(\boldsymbol{r}) + \frac{\beta^2}{2}\int \mathrm{d}^3\boldsymbol{r}\phi^2(\boldsymbol{r}) + \cdots &= \int \mathrm{d}^3\boldsymbol{r}\left[-\beta\phi + \frac{\beta^2}{2}\phi^2 - \frac{\beta^3}{3!}\phi^3 + \cdots\right] \\ &= \int \mathrm{d}^3\boldsymbol{r}\left[e^{-\beta\phi(\boldsymbol{r})} - 1\right] \\ &\equiv \int \mathrm{d}^3\boldsymbol{r} f(\boldsymbol{r}), \end{aligned} \tag{6.17}$$

where in the final line we defined a new function (the *Mayer f function*) to stand for the combination $e^{-\beta\phi(\boldsymbol{r})} - 1$. In Figure 6.1 I show a plot of the Lennard-Jones potential together with the associated $f(\boldsymbol{r})$: At short distances (where the potential is diverging) the f functions converges to a value of -1, and at large distances (where the potential is vanishing) the f function converges to 0. Indeed, for reasonable potentials integrals over these f functions are perfectly well behaved, and we see that in our cumulant expansion we wrote down a series in which every term individually diverges, but the sum of the series is something we can evaluate!

Surveying our work in this section, we see that we tried to write down *cumulant expansion* – a perturbative expansion in the potential – but that for reasonable potentials we ended up having to re-express our result in terms of these Mayer f functions. It seems lie we would have been better off – and could perhaps have made more systematic progress – had we been able to *expand in powers of f*, rather than in powers of ϕ. The *cluster expansion* introduced in the next section allows us to do exactly that!

6.2 ...to cluster expansions!

Now that we have a *reason* that we might want to find an expansion of the partition function in powers of these f functions, let's do so. We continue working with our Hamiltonian with

only pairwise interparticle potential,

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} \phi(\boldsymbol{r}_{ij}),$$

for which the canonical partition function is

$$Z(N,V,T) = \frac{1}{N!\lambda^{3N}} \int \left(\prod_{\alpha} \mathrm{d}^3\boldsymbol{r}_\alpha \right) \prod_{i<j} e^{-\beta\phi(\boldsymbol{r}_{ij})}. \tag{6.18}$$

In order to understand how to manipulate this expression into a useful expansion, our initial goal of this section is going to be to transcribe Eq. 6.18 from math to pictures. We begin by introducing the additional bit of notation, writing the Mayer f functions as

$$f_{ij} \equiv f(\boldsymbol{r}_{ij}) = e^{-\beta\phi(\boldsymbol{r}_i - \boldsymbol{r}_j)} - 1.$$

Using this notation, let's organize the terms in Z by how many powers of f they contain:

$$\begin{aligned} Z(N,V,T) &= \frac{1}{N!\lambda^{3N}} \int \left(\prod_{\alpha} \mathrm{d}^3\boldsymbol{r}_\alpha \right) \prod_{i<j} (1 + f_{ij}) \\ &= \frac{1}{N!\lambda^{3N}} \int \left(\prod_{\alpha} \mathrm{d}^3\boldsymbol{r}_\alpha \right) \left[1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j \\ k<l}} f_{ij} f_{kl} + \cdots \right] \end{aligned} \tag{6.19}$$

6.2.1 Diagrammatic representation of the canonical partition function

To help us organize the many terms that appear in Eq. 6.19, let's start representing integrals with diagrams[3]. The way we'll draw these diagrams is by (1) drawing N points, and then

[3]Recall, from the section on probability, how we used a similar approach to deal with the combinatorics of relating cumulants to moments.

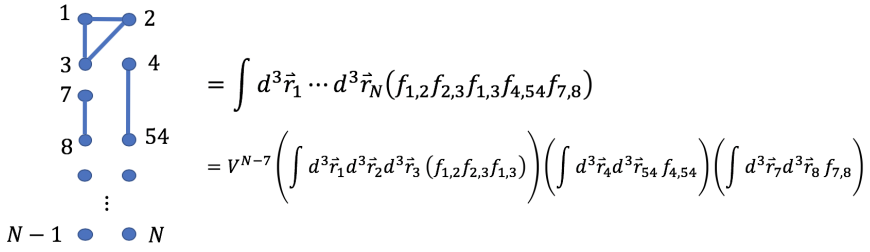

Figure 6.2: **The contribution of a graph is a product of the linked clusters,** where each unlinked point gives a factor of the volume.

(2) representing f_{ij} by a line connecting points i and j. According to this prescription, an nth-order term in f corresponds to diagrams with n lines drawn.

An example of a diagram with 5 copies of f is shown in Fig. 6.2. An important observation is that the contribution of a particular diagram can be written as the product of the linked clusters it contains (and where each point without a connecting line contributes one power of the volume, V). Another important observation is that every diagram with the same structure contributes identically, i.e., independently of the *labels*; we only need to care about the number of 1-clusters, 2-clusters, triangles, etc., in a diagram.

We now have a prescription for writing the terms in Eq. 6.19 as pictures, and now we will *organize* those pictures in a particular way. We define *cluster integrals*,

$$b_l \equiv \text{Sum over contributions of } \textit{all} \text{ linked clusters of } l \text{ points.} \tag{6.20}$$

Ultimately, these b_l are the namesake of the *cluster expansion* we will construct by the end of this section. The first few cluster integrals are shown in Fig. 6.3:

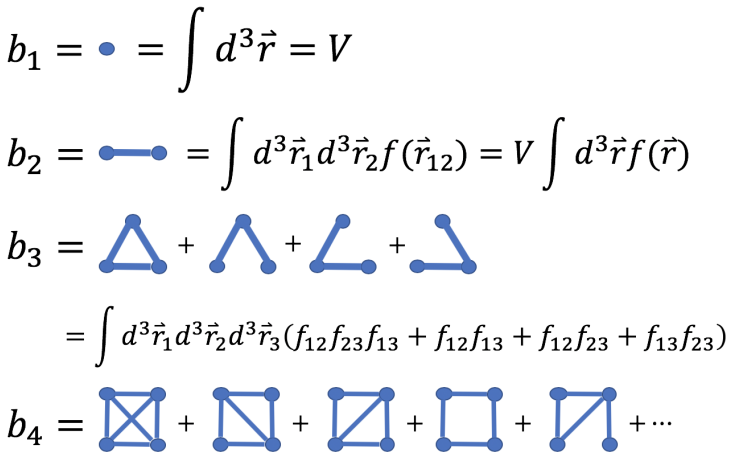

Figure 6.3: **Graphical representations of the first few cluster integrals**

6.2.2 The cluster expansion

Let's see why we care about these b_l. First, consider a diagram in which we take N points and partition it into n_1 clusters of size 1, n_2 clusters of size 2, and so forth (so, in the example in Fig. 6.2, we would have $n_1 = N - 7$, $n_2 = 2$, $n_3 = 1$, and $n_4 = n_5 = \cdots = n_N = 0$). This defines a set of numbers of clusters of different sizes, $\{n_l\}$. We noted above, though, that every diagram that looks the same contributes the same amount, regardless of the labels on the f's, so we are interested in the number of ways of choosing these sets of clusters of various sizes[4]. Let's call this number $W(\{n_l\})$, which we can compute as

$$W(\{n_l\}) = \frac{N!}{\prod_l n_l!(l!)^{n_l}}. \tag{6.21}$$

[4]Note that this problem of partitioning a large number, N, into sets of integers is an interesting math problem. Look up, for instance, the Hardy-Ramanujan Asymptotic Partition Formula if you're interested.

How did we arrive at this expression? Our strategy was essentially to first pick any particular partitioning into $\{n_l\}$ l-cluster. We first *overcount everything* by considering every possible permutation of the labels, giving us the $N!$ in the numerator above. Having overcounted, we now divide out to account for diagram symmetries. First, for each individual l-cluster, we note that the permutations of labels within that cluster give the same diagram (e.g., a line from point 1 to point 2 is unchanged when the labels 1 and 2 are permuted); this gives us a factor of $(l!)$ for each of the n_l clusters of size l. Additionally, we have to consider permutations of labels that replace all of the labels of one cluster of size l with a different cluster of size l (e.g., a line from point 1 to 2 and from 5 to 6is unchanged when labels (1 and 5) and (2 and 6) are permuted); this gives us the additional factor of $n_l!$ in the denominator.

I highly encourage you to get a feel for this by playing around. Try drawing, say, 5 or 6 points, break them up into clusters of different sizes, and get a feel for the combinatorics.

With this counting of the number of different types of diagrams, we can write the canonical partition function as

$$Z = \frac{1}{N!\lambda^{3N}} \sum_{\{n_l\}_{\text{restricted}}} W(\{n_l\}) \prod_l b_l^{n_l}, \tag{6.22}$$

where the restriction is that every point has to be in a cluster, $\sum_l l n_l = N$. From the last chapter, this situation should feel quite familiar: we have another case where a constrained sum in the canonical ensemble is making our life difficult. In exactly the same way as before, this difficulty is lifted by moving to the grand canonical ensemble.

So, we write down the grand partition function, noting that the sum over all possible N of a restricted sum on the $\{n_l\}$ is equivalent to performing an *unrestricted sum* over the $\{n_l\}$:

$$\begin{aligned}
\mathcal{Q} &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \\
&= \sum_{\{n_l\}} \frac{1}{N!\lambda^{3N}} \left(e^{\beta\mu}\right)^{\sum_l l n_l} N! \prod_l \frac{b_l^{n_l}}{n_l!(l!)^{n_l}} \\
&= \prod_l \sum_{n_l=0}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l n_l} \frac{b_l^{n_l}}{n_l!(l!)^{n_l}}.
\end{aligned} \tag{6.23}$$

In the last line we recognize that we have written something like

$$\prod_l \sum_{n_l} \frac{1}{n_l!} [\cdots]^{n_l},$$

which is just the expansion of an exponential. Thus, we find[5]

$$\mathcal{Q} = \prod_l \exp\left[\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^l \left(\frac{b_l}{l!}\right)\right], \tag{6.24}$$

[5] if you're comparing these expression with Pathria, or other texts, please note that different authors use slightly different conventions in the definitions of the cluster integrals; in particular, sometimes the b_l account for the factors of $l!$ in that divide it in the expressions I'm writing.

i.e.,

$$\boxed{\Rightarrow \log \mathcal{Q} = \sum_{l=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^l \left(\frac{b_l}{l!}\right)} \tag{6.25}$$

Before we make use of this expression for the grand canonical partition function, it is worth thinking for a moment about the graphical expressions we wrote for cumulants and moments. The graphical interpretation of the above result is that the log of the sum over all graphs is equivalent to the sum over only the connected clusters.

6.3 Virial expansion for a dilute gas

We consider, now, a dilute gas, and our goal for this section is to write a *virial expansion* for the equation of state of the dilute gas, i.e., something of the form

$$\beta P = B_1(T)\frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \cdots, \tag{6.26}$$

where we've written temperature-dependent coefficients B_i for the powers of density. For a dilute gas we can certainly exploit the extensivity condition to write the grand potential as

$$-\beta\mathcal{G} = \log \mathcal{Q} = -\beta\left(E - TS - \mu N\right) = \beta P V. \tag{6.27}$$

Just as in Chapter 4 when we discussed the ideal gas in the grand canonical ensemble, we see that the grand potential is proportional to the volume; comparing with Eq. 6.25 we see that in fact each cluster integral $b_l \propto V$. We thus define a version of the cluster integrals with this volume dependence removed,

$$\text{ƀ}_l \equiv \frac{b_l}{V},$$

in terms of which we can write the pressure as

$$\beta P = \sum_l \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^l \frac{\text{ƀ}_l}{l!}. \tag{6.28}$$

At the same time, we know that, specifying the chemical potential μ in the grand canonical ensemble we can compute the expected number density of particles as

$$n = \frac{N}{V} = \frac{1}{V}\frac{\partial \log \mathcal{Q}}{\partial\left(\beta\mu\right)} = \sum_l l\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^l \frac{\text{ƀ}_l}{l!}. \tag{6.29}$$

Simplifying the notation by writing a dimensional version of the fugacity, $x \equiv e^{\beta\mu}/\lambda^3$, we arrive at the equation of state for a dilute gas:

$$\begin{aligned} \beta P &= \sum_l x^l \frac{\text{ƀ}_l}{l!} \\ n &= \sum_l l x^l \frac{\text{ƀ}_l}{l!}. \end{aligned} \tag{6.30}$$

This is... not exactly what we typically want. Just as in the chapter on quantum statistical mechanics, what we want is the pressure as a function of density, but what we have is the pressure as a function of fugacity together with a separate equation relating the number density to the fugacity. We encountered this exact situation in looking at ideal quantum gases, and we resolve it in the same way.

So, we write out the series expansion for n,

$$n = b_1 x + b_2 x^2 + \frac{b_3}{2} x^3 + \cdots \tag{6.31}$$

Rearranging this (and noting that $b_1 = 1$), we have

$$x = n - b_2 x^2 - \frac{b_3}{2} x^3 - \cdots , \tag{6.32}$$

which we can self-consistently solve to any desired order by substituting the ith-order solution for x into the $(i+1)$th-order expression. Starting with the first order approximation $x_1 \approx n$, we get

$$\begin{aligned} x_1 &= n + \mathcal{O}\left(n^2\right) \\ x_2 &= n - b_2 n^2 + \mathcal{O}\left(n^3\right) \\ x_3 &= n - b_2 \left(n - b_2 n^2\right)^2 - \frac{b_3}{2}\left(n - b_2 n^2\right)^3 + \mathcal{O}\left(n^4\right) \\ &= n - b_2 n^2 + \left(2b_2^2 - \frac{b_3}{2}\right) n^3 + \mathcal{O}\left(n^4\right), \end{aligned} \tag{6.33}$$

and so on. We can now substitute this into the equation for the pressure; to get an expansion correct to order i we use the x_i expression obtained by the above procedure. So, for instance, to third order we write (collecting all terms up to third order in the number density)

$$\begin{aligned} \beta P &= b_1 x + \frac{b_2}{2} x^2 + \frac{b_3}{3!} x^3 \\ &= n - b_2 n^2 + \left(b_2^2 - \frac{b_3}{3}\right) n^3 + \mathcal{O}\left(n^4\right). \end{aligned} \tag{6.34}$$

In general, we have a result of the form

$$\beta P = n + \sum_{l=2}^{\infty} B_l(T) n^l, \tag{6.35}$$

as desired! The first term, $B_1 = 1$, reproduces the ideal gas result. The second term is

$$B_2(T) = -\frac{b_2}{2} = -\frac{1}{2}\int \mathrm{d}^3\boldsymbol{r}\left[e^{-\beta\phi(\boldsymbol{r})} - 1\right], \tag{6.36}$$

which diagrammatically is $-1/2$ times what we drew as a line between two points. We calculate the third term diagrammatically, as illustrated in Fig. 6.4, and find

$$B_3(T) = -\frac{1}{3}\int \mathrm{d}^3\boldsymbol{r}_{12}\mathrm{d}^3\boldsymbol{r}_{13} f(\boldsymbol{r}_{12}) f(\boldsymbol{r}_{13}) f(\boldsymbol{r}_{12} - \boldsymbol{r}_{13}) \tag{6.37}$$

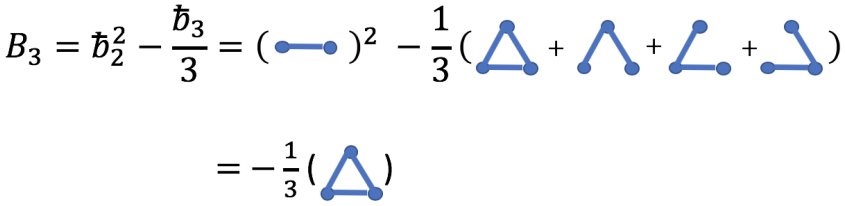

Figure 6.4: **Diagrammatic calculation of the third virial coefficient**

That calculation shows the general result, that in these terms all of the "1-particle reducible diagrams" – in which the removal of one point leads to disjoint clusters in the diagram – cancel; the general result (consider working through the B_4 term to verify your understanding) is

$$B_l(T) = -\frac{l-1}{l!}\đ_l, \tag{6.38}$$

where $\đ_l$ represents a sum over all 1-particle irreducible clusters of size l. In the next section we'll evaluate these sorts of virial coefficients for a "typical" gas, i.e., one governed by a potential similar to a Lennard-Jones form.

6.4 The van der Waals equation

To see how (or if!) the sort of virial expansion we just worked out is useful, let's consider just the first correction to the ideal gas equation of state – the term involving $B_2(T)$ – for the Lennard-Jones potential,

$$\phi(\boldsymbol{r}) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{6.39}$$

which, again, is a simple but reasonable approximation to the interaction between two neutral molecules separated by some distance r.

6.4.1 The second virial coefficient for a Lennard-Jones interaction

The most straightforward approach is just to jump from the potential to the definition of the second virial coefficient that we derived in the last section,

$$\begin{aligned} B_2(T) &= \frac{-1}{2}\int \mathrm{d}^3\boldsymbol{r}\left(e^{-\beta\phi(r)} - 1\right) \\ &= -2\pi\int \mathrm{d}r\; r^2\left(e^{-\beta\phi(r)} - 1\right) \end{aligned} \tag{6.40}$$

That integral looks unfamiliar, but one can express the answer in terms of the Kummer confluent hypergeometric function[6] ${}_1F_1(a;b;z)$, and the Gamma function:

$$B_2(T) = \frac{-\pi\sigma^3\,(\beta\varepsilon)^{1/4}}{3\sqrt{2}}\left[\Gamma\left(\frac{-1}{4}\right){}_1F_1\left(\frac{-1}{4};\frac{1}{2};\beta\varepsilon\right) + 2\sqrt{\beta\varepsilon}\,\Gamma\left(\frac{1}{4}\right){}_1F_1\left(\frac{1}{4};\frac{3}{2};\beta\varepsilon\right)\right] \quad (6.41)$$

Is this helpful? This is, indeed, what you get by plugging things into, e.g., Mathematica, and you could plot the behavior of this second virial coefficient as you vary the temperature for various values of the Lennard-Jones parameters. This "plug-and-chug" approach, while technically correct, obscures the physical picture of how we expect a dilute gas to behave.

6.4.2 Approximate but physical treatment of B_2

Let's do a better job of capturing the physics by making a *rougher* approximation to the molecular interactions. In particular, let's replace the Lennard-Jones potential with the function

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon\left(\frac{\sigma}{r}\right)^6 & r > \sigma \end{cases}. \quad (6.42)$$

This approximate potential captures the following main features of the Lennard-Jones potential: it has the van der Waals r^{-6} at large distances, it has an attractive well of depth ε at short distances, and it is strongly (in fact, *infinitely*!) repulsive within a characteristic size of the molecular core. Note that this simpler form makes it clear that σ is like the characteristic *diameter* of one of the interacting molecules.

With this simpler potential we can compute the second virial coefficient as

$$\begin{aligned} B_2(T) &= -\frac{1}{2}\int \mathrm{d}^3\boldsymbol{r}\left(e^{-\beta\phi(r)} - 1\right) \\ &= -\frac{1}{2}\left[-\frac{4\pi\sigma^3}{3} + 4\pi\int_\sigma^\infty \mathrm{d}r\; r^2\left(e^{\beta\varepsilon\left(\frac{\sigma}{r}\right)^6} - 1\right)\right]. \end{aligned} \quad (6.43)$$

The first term above reflects an *excluded volume* in the potential we have written down. Keeping in mind that we are trying to describe a dilute gas at reasonably high temperatures, let's further approximate the second term by assuming $\beta\varepsilon \ll 1$, that is, that we are at high T relative to the well depth. We will use this approximation to write a series expansion for the exponential of the potential:

$$e^{\beta\phi} \approx \beta\varepsilon\left(\frac{\sigma}{r}\right)^6 + \mathcal{O}\left(\beta\varepsilon\right)^2.$$

With this approximation, the integral can be easily carried out:

$$\begin{aligned} B_2(T) &= -\frac{1}{2}\left[\left(-\frac{4\pi\sigma^3}{3}\right) + \frac{4\pi\sigma^3}{3}\beta\varepsilon\right] \\ &= \frac{\Omega}{2}\left[1 - \beta\varepsilon\right], \quad \text{where } \Omega = \frac{4\pi\sigma^3}{3}. \end{aligned} \quad (6.44)$$

[6] As a series expansion, ${}_1F_1(a;b;z) = \sum_{n=0}^{\infty}\frac{a^{(n)}z^n}{b^{(n)}n!}$, where $a^{(n)}$ is the "rising factorial," $a^{(0)} = 1$, $a^{(1)} = a$, $a^{(n)} = a(a+1)\cdots(a+n-1)$, etc.

This is a nice, compact expression for the second virial coefficient: we see a small perturbative correction that comes in at high temperatures, with an overall scale set by the excluded volume of the molecules.

A few comments are in order, directed at the question of "*when should this approximation be reasonable?*" Two obvious conditions stand out.

First, this is clearly meant to be a low-density expansion, but what we do mean by "low" in this context? As with any series expansion, we want the ratio of consecutive terms to be small, and the ratio of the correction to the ideal term is $\sim B_2 \frac{\rho^2}{\rho} \sim \frac{\Omega}{\rho^{-1}}$. Note that Ω is close to an atomic volume, so one can think of the above ratio as $\sim \frac{\rho_{gas}}{\rho_{liquid}}$. That is, when the density of the system is such that the gas is close to liquifying, we should assume our series approximation is insufficient.

Second, in our expansion of the attractive tail, we assumed that $\beta\varepsilon \ll 1$. If $\beta\varepsilon \gtrsim 1$ for these attractive potentials, we could not have done a reasonable series expansion in the first place. In general, for low temperatures the ground state of a system with attractive interactions is not a gas, but a dense collection of molecules sticking together.

There is an additional consideration, which speaks to our ability to factor out the Ω term in the series expansion we wrote. The fact that we could do this speaks to the sense that the *short-ranged* part of the potential dominates the integral we had to do. In this context there is a sense in which potentials which fall of faster than r^{-3} are "short ranged;" for potentials like $\phi \sim r^{-3}$ there are terms which are logarithmic in the size of the system, and for even longer-ranged potentials the whole expansion fails.

6.4.3 The van der Waals equation

Finally, we can write down the equation of state based on our approximate treatment of the second virial coefficient:

$$\begin{aligned} \beta P &= n + \frac{n^2}{2}\Omega\left(1 - \beta\varepsilon\right) \\ \Rightarrow \beta\left(P + \frac{n^2\Omega}{2}\varepsilon\right) &= n\left(1 + \frac{n\Omega}{2} + \cdots\right). \end{aligned} \tag{6.45}$$

Since we're only being accurate to order n^2 in the above expression, we're free to re-write the right-hand side as

$$n\left(1 + \frac{n\Omega}{2} + \cdots\right) \approx \frac{n}{1 - \frac{n\Omega}{2}} + \cdots .$$

Using this rearranging, we arrive at the van der Waals equation of state:

$$\boxed{P = \frac{Nk_BT}{V - \frac{N\Omega}{2}} - \frac{\varepsilon\Omega}{2}\left(\frac{N}{V}\right)^2,} \tag{6.46}$$

which is often presented as

$$\left(P + a\left(\frac{N}{V}\right)^2\right)(V - bN) = Nk_BT.$$

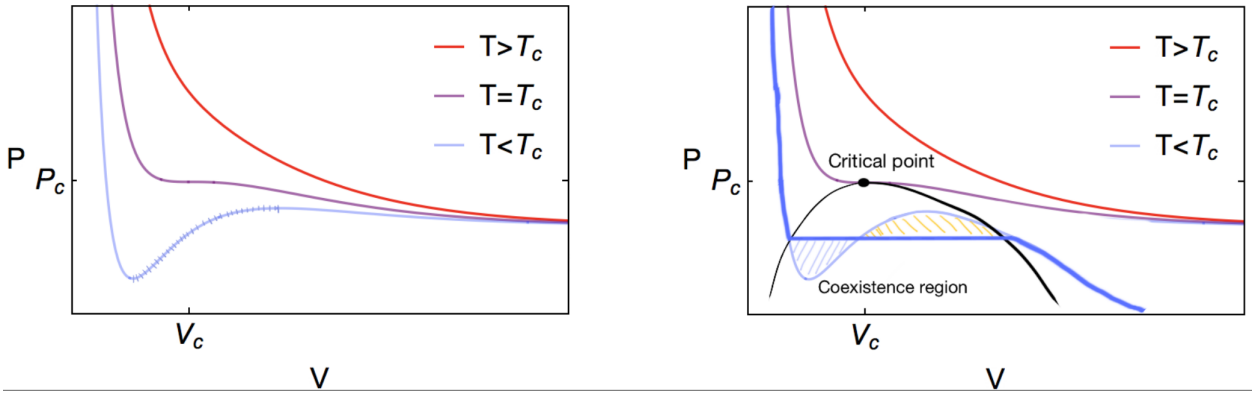

Figure 6.5: **van der Waals equation of state** (Left) The van der Waals equation of state for a dilute gas above, at, and below the critical temperature. (Right) The Maxwell equal-area construction for finding the coexistence region.

The van der Waals equation does a reasonable job of describing dilute gases, which is certainly how we derived it, but ultimately we would like to be able to describe *dense* phases of matter (going from weakly interacting systems to strongly interacting ones). To that end, and as an introduction to the phase transition material to come, we spend a bit more time thinking about what the van der Waals equation says.

We start with the left side of Fig. 6.5, which shows the isotherms predicted by the van der Waals equation for three different temperatures. For high temperatures we see curves that are basically the same as the ideal gas isotherms we encountered back when we were thinking about thermodynamics as a phenomenological theory. The pressure diverges not at $V = 0$ but at some finite value of V, thanks to the excluded volume effects, but otherwise this looks quite familiar. On the other hand, at lower temperatures the isotherms look very strange, developing a minimum at small volumes; precisely at a critical temperature there is part of the corresponding isotherm where the curve is flat.

Clearly, the low-temperature curves, with $T < T_c$, are unphysical (and they are, after all, in a parameter regime we did not expect our theory to work), which we can see in two ways. Early on, we argued in a problem set that thermodynamic stability requires $\delta P \delta V < 0$, which is violated on portions of an isotherm where $\frac{\partial P}{\partial V} > 0$. One can also see this using our our statistical mechanical relations. We recall that

$$\langle N \rangle = \frac{\partial \log \mathcal{Q}}{\partial(\beta\mu)} = V \left.\frac{\partial P}{\partial \mu}\right|_{T,v},$$

and

$$\left\langle N^2 \right\rangle = \frac{\partial^2 \log \mathcal{Q}}{\partial(\beta\mu)^2} = \frac{\partial \langle N \rangle}{\partial(\beta\mu)} = k_B T \left.\frac{\partial N}{\partial \mu}\right|_{T,v}.$$

Dividing these expressions we get the ratio of the number fluctuations to the mean and relate that ratio to the isothermal compressibility:

$$\frac{\langle N^2 \rangle}{\langle N \rangle} = \frac{1}{\beta V} \left.\frac{\partial N}{\partial P}\right|_{T,V} = \frac{-1}{\beta V} \left.\frac{\partial N}{\partial V}\right|_{P,T} \left.\frac{\partial V}{\partial P}\right|_{N,T} = \frac{N}{V} k_B T \kappa_T. \tag{6.47}$$

For a stable system the compressibility should be positive, and since $\kappa_T = \frac{-1}{V}\frac{\partial V}{\partial P}\Big|_T$, we see again that the van der Waals curves for $T < T_c$ are unphysical.

Maxwell construction

So, our equation contains obviously unphysical features, but it also schematically *does* remind us of the phase behavior of real fluids, schematically illustrated on the right of Fig. 6.5. Can we make some ad hoc changes to the theory to get at the right answer? One reason for hope is that qualitatively our theory both gives the right behavior for $T \geq T_c$ *and* gives us a clear indication that it needs help for $T < T_c$ – theories that have this self-consistent limitation on their regime of validity often contain important clues to system behavior even outside of where they technically work.

To motivate the Maxwell construction which attempts to correct the van der Waals picture, let's consider changes in the chemical potential as we move along an isotherm below the critical temperature. From the above we know $N = V\frac{\partial P}{\partial \mu}\Big|_T$, giving us $d\mu = \frac{V}{N}dP$ at constant T. Integrating this up, starting from some reference point A, we have

$$\mu(T,P) = \mu(T,P_A) + \int_{P_A}^{P} dP' \frac{V(T,P')}{N}.$$

The qualitative behavior of the chemical potential as the isotherm is traversed is schematically illustrated in Fig. 6.6. There are some portions where the curves is well-behaved, but there are a range (determined by an *equal-area consideration*) over which the function μ is multi-valued!

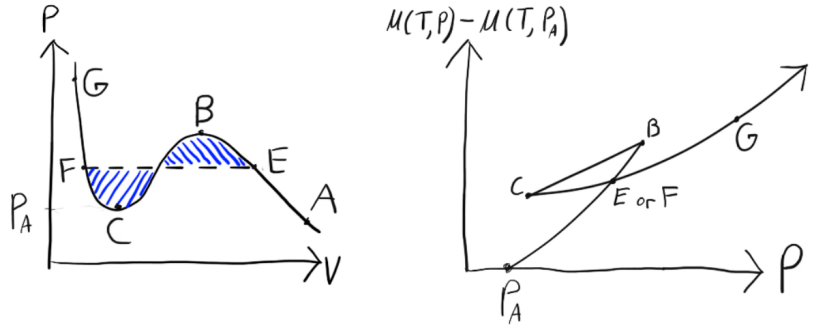

Figure 6.6: **Moving along an isotherm** from a reference point at state point A through the sequence $A \to B \to C \to G$, we calculate the chemical potential relative to that at the starting point. In addition to $B \to C$ being thermodynamically unstable, we see the portions $E \to B$ and $C \to F$ are metastable. In equilibrium, the system will have the minimum μ, and follow the path $A \to E \to F \to G$.

In equilibrium the number of particles N_α in phase α will adjust so as to minimize the Gibbs free energy $\sum_\alpha \mu_\alpha N_\alpha$, and so when confronted with a multi-valued set of possible chemical potentials we *choose the lowest one*. In the figure, the isotherm $A \to B \to C \to G$ gets replaced by the isotherm $A \to E \to F \to G$, corresponding to the straight line we drew in the coexistence region in Fig. 6.5. Notice, by the way, that the part of the original isotherm

which gets replaced is *not* just the part where the thermodynamic stability condition was violated, but is actually a larger region! In these additional parts of the isotherm the system is *metastable*, rather than being strictly stable or unstable.

This Maxwell construction qualitatively succeeds, in that it now gives us largely the correct physical behavior, but it certainly feels weird! It required us to start with an approximate theory, consider regions of that theory where the behavior was clearly unphysical, and then try to sweep any unpleasantness under the rug. This was all done, additionally, in a regime where it is not at all clear that simply doing a better job with our perturbative expansion would be of any help. In the next chapter we'll take a more principled approach to these issues.