## Chapter 3 Non-ideal Gases

## 3.1 Statistical Mechanics





#### **3.1.1** The partition function

We are now considering gases where the interactions between the particles cannot be ignored. Our starting point is that everything can be found from the partition function. We will work, initially, in the classical framework where the energy function of the system is

$$H(p_{i},q_{i}) = \sum_{i} \frac{p_{i}^{2}}{2m} + \sum_{i < j} U(q_{i},q_{j})$$

Because of the interaction term  $U(q_i,q_j)$  the partition function can no longer be factorised into the product of single-particle partition functions. The many-body partition function is

$$Z = \frac{1}{N!h^{3N}} \int e^{-\left(\sum_{i} \frac{p_i^2}{2m} + \sum_{i < j} U(q_i, q_j)\right)/kT} d^{3N}p d^{3N}q$$

where the factor 1/N! is used to account for the particles being indistinguishable.



While the partition function cannot be factorised into the product of single-particle partition functions, we can factor out the partition function for the non-interacting case since the energy is a sum of a momentum-dependent term (kinetic energy) and a coordinate-dependent term (potential energy). The non-interacting partition function is

$$Z_{\rm id} = \frac{V^N}{N!h^{3N}} \int e^{-\sum_i \frac{p_i^2}{2mkT}} \mathrm{d}^{3N}p$$

where the V factor comes from the integration over the  $q_i$ . Thus the interacting partition function is

$$Z = Z_{\rm id} \frac{1}{V^N} \int e^{-\left(\sum_{i < j} U(q_i, q_j)\right)/kT} d^{3N} q$$

The "correction term" is referred to as the configuration integral.

We denote this by Q



$$Q = \frac{1}{V^N} \int e^{-\left(\sum_{i < j} U(q_i, q_j)\right)/kT} \mathrm{d}^{3N} q.$$

\* Different authors have different pre-factors such as *V* or *N*!, but that is not important. The partition function for the interacting system is then

$$Z = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N Q$$

and the attention now focuses on evaluation / approximation of the configuration integral Q.

\* Our convention means that the non-interacting Z is factored out.



### **Configuration integral**

$$Q = \frac{1}{V^N} \int e^{-\left(\sum_{i< j} U(q_i, q_j)\right) / kT} \mathrm{d}^{3N} q.$$

#### **3.1.2** Cluster expansion

We need a "small quantity" in terms of which to perform an expansion. To this end we define

$$f_{ij} = e^{-U(q_i, q_j)/kT} - 1$$

so that  $f_{ij}$  is only appreciable when the particles are close together. In terms of this the configuration integral is

$$Q = \frac{1}{V^N} \int \prod_{i < j} \left( 1 + f_{ij} \right) \mathrm{d}^{3N} q_i$$

where the exponential of the sum has been factored into the product of exponentials.



Next we expand the product as:

$$\prod_{i < j} (1 + f_{ij}) = 1 +$$
no interactions  

$$+ f_{12} + f_{13} + f_{23} + f_{14} + \dots$$
particle pairs  

$$+ f_{12} f_{23} + f_{13} f_{34} + f_{12} f_{24} + \dots$$
particle triples  

$$+ \dots$$
particle quadruples  

$$\vdots$$
i  

$$\prod_{i < j} particle pairs$$

$$\int_{i < j} particle pairs$$

$$\int_{i < j} particle triples$$

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The terms in the second line are significant whenever pairs of particles are close together. Terms in the third line require triples of particles to be close together, in the fourth line we require sets of four particles etc. etc. The general expansion in this way is called a "cluster expansion".

To be precise there are also terms in the third line such as  $f_{12}f_{34}$  which will be significant when two different pairs of particles are *simultaneously* close together. In the limit of large N these terms are a negligible fraction of the third line terms and they may be neglected. Similar arguments apply to later lines as well.

A more rigorous treatment of the cluster expansion is given in the AJP article by W. Mullin.



#### **3.1.3** Low density approximation

In the case of a dilute gas, we only need to consider the effect of pairwise interactions – the first two lines. Then we have

$$\prod_{i < j} \left( 1 + f_{ij} \right) \approx 1 + \sum_{i < j} f_{ij}$$

so that, within this approximation,

$$Q = \frac{1}{V^N} \int \left\{ 1 + \sum_{i < j} f_{ij} \right\} d^{3N} q_i$$
$$= 1 + \int \sum_{i < j} f_{ij} d^{3N} q_i.$$



There are N(N-1)/2 terms in the sum since we take all pairs without regard to order. Since the particles are identical, each integral in the sum will be the same, so that

$$Q = 1 + \frac{N(N-1)}{2V} \int f_{12} d^3 r_{12} \, .$$

The  $V^N$  in the denominator has now become *V* since the integration over  $i, j \neq 1, 2$  gives a factor  $V^{N-1}$  in the numerator.

Finally, then, we have the partition function for the interacting gas:

$$Z = Z_{\rm id} \left\{ 1 + \frac{N(N-1)}{2V} \int \left[ e^{-U(\mathbf{r})/kT} - 1 \right] d^3r \right\}$$

and on taking the logarithm, the free energy is the sum of the noninteracting gas free energy and the new term



$$F = F_{\rm id} - kT \ln \left\{ 1 + \frac{N(N-1)}{2V} \int \left[ e^{-U(\mathbf{r})/kT} - 1 \right] \mathrm{d}^3 r \right\}.$$

In this low density approximation the second term in the logarithm, which accounts for pairwise intractions, is much less than the first term. – Otherwise the third and higher-order terms would also be important. But if the second term is small then the logarithm can be expanded. Also, obviously the (N-1) can be approximated by N. Thus we obtain

$$F = F_{\rm id} - kT \frac{N^2}{2V} \int \left[ e^{-U(\mathbf{r})/kT} - 1 \right] \mathrm{d}^3 r$$



#### **3.1.4 Equation of state**

The pressure is found by differentiating the free energy:

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N}$$
$$= \frac{NkT}{V} - \frac{N^2kT}{2V^2} \int \left[e^{-U(\mathbf{r})/kT} - 1\right] \mathrm{d}^3 r \, .$$

We see that the effect of the interaction U(r) can be regarded as modifying the pressure from the ideal gas value. The net effect can be either attractive or repulsive; decreasing or increasing the pressure. This will be considered, for various model interaction potentials U(r).

However before that we consider a systematic way of generalising the gas equation of state.



# 3.2 The Virial Expansion

#### **3.2.1** Virial coefficients

At low densities we know that the equation of state reduces to the ideal gas equation. A systematic procedure for generalising the equation of state would therefore be as a power series in the number density N/V. Thus we write

$$\frac{p}{kT} = \frac{N}{V} + B_2 \left(T\right) \left(\frac{N}{V}\right)^2 + B_3 \left(T\right) \left(\frac{N}{V}\right)^3 + K$$

The *B* factors are called *virial coefficients*. And  $B_n$  is called the  $n^{\text{th}}$  virial coefficient. By inspecting the equation of state derived above, we see that this is equivalent to an expansion up to the second virial coefficient. We see that the second virial coefficient is given by

$$B_2(T) = -\frac{1}{2} \int \left[ e^{-U(\mathbf{r})/kT} - 1 \right] \mathrm{d}^3 r$$



Since  $U(\mathbf{r})$  is spherically symmetric we can integrate over the angular coordinates, giving

$$B_2(T) = -2\pi \int_0^\infty r^2 \left[ e^{-U(r)/kT} - 1 \right] \mathrm{d}r$$

which should be "relatively" easy to evaluate once the form of the interparticle interaction U(r) is known. It is also possible to evaluate higher order virial coefficients, but it becomes more difficult.



#### **3.2.2 Hard core potential**

(See Reichl's book for details of the models in the next three sections) The hard core potential is specified by  $U(\mathbf{r})$ 

$$U(r) = \infty \quad r < \sigma$$
$$= 0 \quad r > \sigma$$

Here the single parameter 
$$\sigma$$
 is the hard core diameter. This is really modelling the particles as "billiard balls". There is

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core diameter. This is really modelling  
the particles as "billiard balls". There is  
no interaction when the particles' centres are separated greater than  $\sigma$   
and they are prevented, by the interaction, from getting closer than  $\sigma$ . It  
should, however, be noted that this model interaction is somewhat  
unphysical since it only considers the repulsive part; there is no

attraction at any separation.



For this potential we have

$$e^{-U(r)/kT} = 0$$
  $r < \sigma$   
= 1  $r > \sigma$ 

so that the expression for  $B_2(T)$  is

$$B_2(T) = 2\pi \int_0^\sigma r^2 \mathrm{d}r$$

 $=\frac{2}{3}\pi\sigma^3$ . ~ the volume of a particle

In this case we see that the second virial coefficient is independent of temperature, and it is always positive. The equation of state, in this case, is

$$pV = NkT\left\{1 + \frac{2}{3}\pi\sigma^3\frac{N}{V}\right\}$$



which indicates that the effect of the hard core is to increase the pV product over the ideal gas value.

It is instructive to rearrange this equation of state. Writing it as

$$pV\left\{1+\frac{2}{3}\pi\sigma^3\frac{N}{V}\right\}^{-1}=NkT,$$

we note that the correction term  $\frac{2}{3}\pi\sigma^3 N/V$  is small within the validity of the derivation; it is the hard core volume of a particle divided by the total volume per particle. So performing a binomial expansion we find to the same leading power of density

$$pV\left\{1-\frac{2}{3}\pi\sigma^3\frac{N}{V}\right\} = NkT$$





or

$$p\left\{V-\frac{2}{3}N\pi\sigma^3\right\}=NkT$$

In this form we see that the effect of the hard core can be interpreted as simply reducing the available volume of the system.



Volume of space excluded by particle 1, 2 pair is  $\frac{4}{3}\pi\sigma^3$  so volume per particle excluded is half of this. Then volume excluded by *N* particles is

$$V_{\rm ex} = \frac{2}{3} N \pi \sigma^3.$$

*Four times* the actual volume of the particles.



#### **3.2.3 Square-well potential**

The square-well potential somewhat more realistic than the hard core by including a region of attraction as well as the repulsive hard core. The potential is specified by

$$U(r) = \infty \quad 0 < r < \sigma$$

$$= -\varepsilon \quad \sigma < r < R\sigma$$

$$= 0 \quad R\sigma < r$$
so we see that it depends on three parameters:  $\sigma$ ,  $\varepsilon$  and  $R$ .
$$U(r)$$

$$\longleftrightarrow$$

$$F_{\sigma} \rightarrow F_{\sigma}$$

$$\Leftrightarrow$$

$$f_{\varepsilon}$$

$$\downarrow$$

S





For this potential we have

$$e^{-U(r)/kT} = 0 \qquad 0 < r < \sigma$$
$$= e^{\varepsilon/kT} \quad \sigma < r < R\sigma$$
$$= 1 \qquad R\sigma < \sigma$$

so that the expression for  $B_2(T)$  is

$$B_{2}(T) = -2\pi \left\{ (-1) \int_{0}^{\sigma} r^{2} dr + (e^{\varepsilon/kT} - 1) \int_{\sigma}^{R\sigma} r^{2} dr \right\}$$
$$= \frac{2}{3}\pi\sigma^{3} \left\{ 1 - (R^{3} - 1)(e^{\varepsilon/kT} - 1) \right\}.$$

In this case, using the more realistic potential, we see that the second virial coefficient depends on temperature. At low temperatures, where  $B_2(T)$  is negative, this indicates that the attractive part of the potential is dominant and the pressure is reduced compared with the ideal gas case.



And at higher temperatures, where it is intuitive that the small attractive part of the potential will have negligible,  $B_2(T)$  will be positive and the pressure will be increased, as in the hard sphere case. The temperature at which  $B_2(T)$  goes through zero is called the *Boyle temperature*, denoted by  $T_{\rm B}$ . At very high temperatures we see from the expression for  $B_2(T)$  that it will saturate at the hard core value  $2\pi\sigma^3/3$ . Thus the general form of the second virial coefficient is as shown in the figure.



Second virial coefficient as a function of temperature





Figure 3.4: Second virial coefficient of nitrogen as a function of temperature with the square well functional form Eq. (3.2.14). Square well parameters  $\varepsilon/k = 88.3 \,\mathrm{K}, \, \sigma = 3.27 \,\mathrm{\AA}, \, \mathrm{and} \, R = 1.62.$ 



#### **3.2.4 Lennard-Jones potential**

The Lennard-Jones potential is a very realistic representation of the inter-atomic interaction. It comprises an attractive  $1/r^6$  term with a repulsive  $1/r^{12}$  term. The form of the attractive part is well-justified as a description of the attraction arising from fluctuating electric dipole

moments. The repulsive term is simply a power law approximation to the effect of the overlap of electronic orbit. We write the Lennard-Jones potential as

$$U(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}$$

which depends on the two parameters:  $\varepsilon$  and  $\sigma$ .





The integral for the second virial coefficient is

$$B_2(T) = -2\pi \int_0^\infty r^2 \left[ e^{-\frac{4\varepsilon}{kT} \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right\}} - 1 \right] \mathrm{d}r$$

which can be expressed as

$$B_2(T) = \frac{2}{3}\pi\sigma^3\sqrt{2\pi}\left(\frac{\varepsilon}{kT}\right)^{1/4} H_{\frac{1}{2}}\left(-\sqrt{\frac{\varepsilon}{kT}}\right).$$

Here H is a Hermite *function*.

The figure below shows the second virial coefficient as calculated from the Lennard-Jones potential with the nitrogen data. Observe the reduction from the hard core value at high temperatures: with L-J, energetic collisions can cause the atoms to come even closer together.





Figure 3.6: Second virial coefficient of nitrogen plotted with the Lennard-Jones functional form, Eq. (3.2.19). Lennard-Jones parameters  $\varepsilon/k = 95.5$  K,  $\sigma = 3.76$  Å.



#### **3.2.5 Sutherland potential**

The Sutherland potential treats the short-distance repulsion as a hard core and the attractive tail is described by the conventional dipolar  $r^{-6}$  law.





As with the Lennard-Jones potential, this has a universal form, scaled with an energy parameter  $\varepsilon$  and a distance parameter  $\sigma$ .



The second virial coefficient is given by

$$B_{2}(T) = -2\pi \int_{0}^{\infty} r^{2} \left( e^{-U(r)/kT} - 1 \right) dr$$

so using the mathematical form for U(r), the integral splits into two parts

$$B_{2}(T) = 2\pi \int_{0}^{\sigma} r^{2} dr - 2\pi \int_{\sigma}^{\infty} r^{2} \left( e^{\frac{\varepsilon}{kT} \left( \frac{\sigma}{r} \right)^{6}} - 1 \right) dr$$
$$= \frac{2}{3}\pi \sigma^{3} - 2\pi \int_{\sigma}^{\infty} r^{2} \left( e^{\frac{\varepsilon}{kT} \left( \frac{\sigma}{r} \right)^{6}} - 1 \right) dr.$$

We substitute  $x = r/\sigma$  so that

$$B_{2}(T) = \frac{2}{3}\pi\sigma^{3} \left\{ 1 - 3\int_{1}^{\infty} x^{2} \left( e^{\varepsilon/kTx^{6}} - 1 \right) dx \right\}.$$



It is possible to express  $B_2(T)$  in terms of the imaginary error function Erfi, as

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \left( e^{\varepsilon/kT} - \sqrt{\pi}\sqrt{\frac{\varepsilon}{kT}} \operatorname{Erfi}\sqrt{\frac{\varepsilon}{kT}} \right).$$





Figure 3.8: Second virial coefficient of nitrogen plotted with the Sutherland functional form, Eq. (3.2.19). Sutherland parameters  $\varepsilon/k = 274.2$  K,  $\sigma = 3.16$  Å.



The interesting point about the Sutherland potential is that it gives the high-temperature behaviour of the  $B_2(T)$  as

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3 \left(1 - \frac{\varepsilon}{kT} - \ldots\right);$$

the limiting value at high temperatures is the hard core  $2\pi\sigma^3/3$ , while the leading deviation goes as  $T^{-1}$ .

Compare with square well potential:

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3 \left(1 - \frac{\left(R^3 - 1\right)\varepsilon}{kT} - \dots\right).$$





Again the limiting high temperature value is the hard core expression and the leading deviation goes as  $T^{-1}$ . Note *R* is dimensionless, greater than unity. And  $\varepsilon$  is different in the two cases, i.e.

$$\varepsilon_{\rm S} = (R^3 - 1)\varepsilon_{\rm sw}$$





Figure 3.9: Second virial coefficient of nitrogen compared with fits corresponding to the square well, Lennard-Jones and Sutherland potentials.





Figure 3.10: Square well, Lennard-Jones and Sutherland potentials corresponding to second virial coefficient fits.



#### **Corresponding States -- Scaling**



Figure 3.11: Reduced second virial coefficient of helium, argon, krypton and xenon, with Lennard-Jones form.



## 3.4 Van der Waals Equation of State

#### **3.4.1** Approximating the Partition Function

Rather than perform an exact calculation in powers of a small parameter (the density), we shall adopt a different approach by making an approximation to the partition function, which should be reasonably valid at *all* densities.

The approximation is based on the single-particle partition function.

Shall obtain an equation of state approximating behaviour of real gases. Originally proposed by van der Waals in his Ph. D. Thesis in 1873. In the absence of interactions the single-particle partition function is

$$z = \frac{V}{\Lambda^3}$$

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Recall: factor V comes from integration over the position coordinates.

► How to treat inter-particle interactions – in an approximate way?

#### Interaction U(r) comprises:

i ) a strong repulsive core at short separationsii) a weak attractive tail at large separations.

The key is to treat these two parts separately/differently:

i) The repulsive core effectively excludes regions of space from the integration over position coordinates. This may be accounted for by replacing V by  $V - V_{ex}$  where  $V_{ex}$  is the volume excluded by the hard core.

ii) The attractive long tail is accounted for by including a factor in the expression for z of the form

 $e^{-\langle E \rangle/kT}$ 

where  $\langle E \rangle$  is some average of the attractive part of the potential.

► Thus we arrive at the approximation

$$z = \frac{V - V_{\text{ex}}}{\Lambda^3} e^{-\langle E \rangle/kT}$$



We have approximated the interaction by a *mean field* assumed to apply to individual particles.

This allows us to keep the simplifying feature of the free-particle calculation where the many-particle partition function factorizes into a product of single-particle partition functions.

Accordingly, this is referred to as a mean field calculation.



#### **3.4.2 Van der Waals Equation**

The equation of state is found by differentiating the free energy expression:

$$p = kT \frac{\partial \ln Z}{\partial V} \bigg|_{T,N} = NkT \frac{\partial \ln Z}{\partial V} \bigg|_{T}.$$

Now the logarithm of z is

$$\ln z = \ln \left( V - V_{\rm ex} \right) - 3 \ln \Lambda - \left\langle E \right\rangle / kT$$

so that

$$p = NkT \frac{\partial \ln z}{\partial V} \bigg|_{T} = \frac{NkT}{V - V_{\text{ex}}} - N \frac{d\langle E \rangle}{dV}$$

since we allow the average interaction energy to depend on volume (density). This equation may be rearranged as

$$p + N \frac{\mathrm{d}\langle E \rangle}{\mathrm{d}V} = \frac{NkT}{V - V_{\mathrm{ex}}}$$

or

$$\left(p + N\frac{\mathrm{d}\langle E\rangle}{\mathrm{d}V}\right)\left(V - V_{\mathrm{ex}}\right) = NkT$$

This is similar to the ideal gas equation except that the pressure is increased and the volume decreased from the ideal gas values. These are characteristic parameters. They account, respectively, for the attractive long tail and the repulsive hard core in the interaction. Conventionally we express the parameters as  $aN^2/V^2$  and Nb, so that the equation of state is

$$\left(p+a\frac{N^2}{V^2}\right)(V-Nb) = NkT$$

and this is known as the van der Waals equation of state.

#### **3.4.3 Microscopic 'estimation' of Parameters**

In mean field, the repulsive and the attractive parts of the inter-particle interaction were treated separately.

How are the two parameters of the van der Waals equation related to the parameters of the Lennard-Jones inter-particle interaction?

i) The repulsion is strong. We accounted for this by saying that there is zero probability of two particles being closer than  $\sigma$ . Then that region of co-ordinate space is excluded; form of the potential in the excluded region (U(r) very large) does not enter the discussion.

Interaction  $\rightarrow$  boundary condition. Thus the excluded volume will be

$$V_{\rm ex} = \frac{2}{3} N \pi \sigma^3,$$

the total hard core volume.



ii) The attractive part of the potential is weak. Here there is very little correlation between the positions of the particles; we therefore treat their distribution as approximately uniform. The mean interaction for a single pair of particles  $\langle E_1 \rangle$  is then

$$E_{1} \rangle = \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^{2} U(r) dr$$
$$= \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^{2} 4\varepsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right\} dr = -\frac{32\pi\sigma^{3}}{9V} \varepsilon .$$

Now there are N(N-1)/2 pairs, each interacting through U(r), so neglecting the 1, the total mean energy per particle is

$$\langle E \rangle = \langle E_1 \rangle N / 2$$
  
=  $-\frac{16\pi\sigma^3}{9} \frac{N}{V} \varepsilon$ .



In the van der Waals equation it is the derivative of this quantity we require. Thus we find

$$N\frac{\mathrm{d}\langle E\rangle}{\mathrm{d}V} = \frac{16}{9}\pi\sigma^3\left(\frac{N}{V}\right)^2\varepsilon.$$

These results give the correct assumed *N* and *V* dependence of the parameters used in the previous section. So finally we identify the van der Waals parameters *a* and *b* as

$$a=\frac{16}{9}\pi\sigma^{3}\varepsilon, \quad b=\frac{2}{3}\pi\sigma^{3}.$$



#### **3.4.4 Virial Expansion**

It is a straightforward matter to expand the van der Waals equation as a virial series. We express p/kT as

$$\frac{p}{kT} = \frac{N}{V - Nb} - \frac{aN^2}{kTV^2}$$
$$= \left(\frac{N}{V}\right) \left(1 - b\frac{N}{V}\right)^{-1} - \frac{a}{kT} \left(\frac{N}{V}\right)^2.$$

and this may be expanded in powers of N/V to give

$$\frac{p}{kT} = \left(\frac{N}{V}\right) + \left(\frac{N}{V}\right)^2 \left(b - \frac{a}{kT}\right) + \left(\frac{N}{V}\right)^3 b^2 + \left(\frac{N}{V}\right)^4 b^3 + K$$

Thus we immediately identify the second virial coefficient as

$$B_2^{\rm VW}(T) = b - \frac{a}{kT}.$$



#### Comparison – Square well potential and van der Waals gas

Second virial coefficient for the van der Waals gas is

$$B_2^{\rm VW} = b - \frac{a}{kT} \,.$$

Second virial coefficient for square well potential is

$$B_2^{\rm sw} = \frac{2}{3}\pi\sigma^3 \left\{ 1 - (R^3 - 1)(e^{\varepsilon/kT} - 1) \right\}.$$

In the limit that  $R \gg 1$  and  $\varepsilon \ll kT$  we have

$$B_2^{\text{sw}} = \frac{2}{3}\pi\sigma^3 \left(1 - \frac{R^3\varepsilon}{kT}\right) \quad \text{or} \quad B_2^{\text{sw}} = \frac{2}{3}\pi\sigma^3 - \frac{2\pi\sigma^3R^3\varepsilon}{3kT}$$
  
So identify  $b = \frac{2}{3}\pi\sigma^3 \quad \text{and} \quad a = \frac{2}{3}\pi\sigma^3\frac{R^3\varepsilon}{kT}.$ 

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