

PH4211 Statistical Mechanics

Problem Sheet 3 — Answers

1 Show that the Joule-Kelvin coefficient is zero for an ideal gas.

The Joule-Kelvin coefficient is given by

$$\mu_J = \frac{1}{c_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\}.$$

For an ideal gas we have $pV = NkT$, so upon differentiating:

$$\left. \frac{\partial V}{\partial T} \right|_p = \frac{Nk}{p}$$

so that

$$\mu_J = \frac{1}{c_p} \left\{ T \frac{Nk}{p} - V \right\}.$$

And since $pV = NkT$, the bracket is zero. Thus the Joule-Kelvin coefficient is zero.

2 Derive the second virial coefficient expression for the Joule-Kelvin coefficient

$$\mu_J = \frac{2T}{5k} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}$$

and find the inversion temperature for the square well potential gas.

In the limit of small $B_2(T)$ we have the equivalent expression for the virial expansion

$$V = \frac{NkT}{p} + NB_2(T).$$

And we have

$$\mu_J = \frac{1}{c_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\}.$$

So differentiating the expression for V gives

$$\left. \frac{\partial V}{\partial T} \right|_p = \frac{Nk}{p} + N \frac{dB_2(T)}{dT}.$$

We substitute this into the expression for μ_J to give

$$\mu_J = \frac{NT}{c_p} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}.$$

Now for an ideal gas the thermal capacity at constant volume is given by

$$c_p = \frac{5}{2} Nk$$

and we adopt this as an acceptable approximation in this weakly interacting case. We then obtain the result

$$\mu_j = \frac{2T}{5k} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}.$$

The second virial coefficient for the square well gas is given by

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

To find the inversion temperature we require to solve the equation

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0$$

for T . Now using the square-well expression for B will result in an insoluble equation. A numerical solution can be found if R is specified, or an approximate solution may be found. We shall look for a solution for the inversion temperature in the (realistic) limiting case where there is a long-range, but weak interaction. In other words we are considering the case where R is large and ε is small. When R is very much greater than unity then B may be approximated by

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

and if ε is small then we may expand the exponential so that

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

This expansion is valid for temperatures T much greater than ε/k . This will be justified *a posteriori*.

This expression for $B_2(T)$ is actually equivalent to that obtained for the van der Waals gas; the general behaviour is

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

We can then quote the result (derived in the next Problem)

$$\begin{aligned} T_1 &= \frac{2a}{bk} \\ &= \frac{2}{k} R^3 \varepsilon. \end{aligned}$$

This satisfies the requirement on the expansion of the exponential, that $kT \gg \varepsilon$ since R is assumed to be large.

3 For the van der Waals gas show that $T_B = \frac{a}{bk}$ and $T_1 = \frac{2a}{bk}$.

We obtained the second virial coefficient for the van der Waals gas to be

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

The Boyle temperature is that for which $B_2(T) = 0$. So solving the above expression for zero gives

$$T_B = \frac{a}{bk}.$$

The inversion temperature is that for which

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0.$$

Now differentiating $B_2(T)$ gives

$$\frac{dB_2(T)}{dT} = \frac{a}{kT^2}$$

so that we now require to solve

$$\frac{a}{kT^2} = \frac{b}{T} - \frac{a}{kT^2}.$$

This has solution

$$T_1 = \frac{2a}{bk}.$$

4 Show that for a van der Waals fluid the critical parameters are given by

$V_c = 3Nb$, $p_c = \frac{a}{27b^2}$, $kT_c = \frac{8a}{27b}$. Express these critical quantities in terms of the microscopic interaction (Lennard-Jones) parameters ϵ and σ .

The van der Waals equation of state is

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

and this can be rearranged to give

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

Then differentiating this gives

$$\frac{\partial p}{\partial V} = \frac{2aN^2}{V^3} - \frac{NkT}{(V - Nb)^2} = 0$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2NkT}{(V - Nb)^3} - \frac{6aN^2}{V^4} = 0.$$

Solve the simultaneous equations to give T_c and V_c : $kT_c = 8a/27b$, $V_c = 3Nb$ and then substitute in to get $p_c = a/27b^2$.

In the mean field discussion the repulsive and the attractive parts of the inter-particle interaction were treated separately. Within the spirit of this let us consider how the two parameters of the van der Waals equation might be related to the two parameters of the Lennard-Jones inter-particle interaction potential. The repulsion is strong; particles are correlated when they are very close together. We accounted for this by saying that there is zero probability of two particles being closer together than σ . Then, as in the hard core discussion of Section 3.2.1, the region of co-ordinate space is excluded, and the form of the potential in the excluded region ($U(r)$ very large) does not enter the discussion. Thus just as in the discussion of the hard core model, the excluded volume will be

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

one half of the total hard core volume.

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

$$\begin{aligned} \langle E_1 \rangle &= \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^2 U(r) dr \\ &= \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^2 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} dr = -\frac{8\pi\sigma^3}{3V} \epsilon. \end{aligned}$$

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

$$\begin{aligned} \langle E \rangle &= \langle E_1 \rangle N/2 \\ &= -\frac{4\pi\sigma^3}{3} \frac{N}{V} \epsilon. \end{aligned}$$

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

$$N \frac{d\langle E \rangle}{dV} = \frac{4}{3} \pi \sigma^3 \left(\frac{N}{V} \right)^2 \epsilon.$$

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

$$\begin{aligned} a &= \frac{4}{3} \pi \sigma^3 \epsilon \\ b &= \frac{2}{3} \pi \sigma^3. \end{aligned}$$

5 Show that, for a van der Waals fluid, the combination of critical parameters $p_c V_c / N k T_c$ takes the universal value $3/8$.

The critical parameters for the van der Waals equation are given by

$$V_c = 3Nb, \quad p_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b}.$$

Then $p_c V_c / N k T_c$ is given by

$$\begin{aligned} \frac{p_c V_c}{N k T_c} &= \frac{a}{27b^2} 3Nb \frac{1}{N} \frac{27b}{8a} \\ &= 3/8. \end{aligned}$$

6 Show that for the Dieterici fluid the critical parameters are given by

$V_c = 2Nb$, $p_c = \frac{a}{4b^2 e^2}$, $kT_c = \frac{a}{4b}$, and the universal combination $p_c V_c / N k T_c$ has the value $2/e^2 = 0.271$.

The Dieterici equation of state is

$$p(V - Nb) = NkTe^{-\frac{Na}{kTV}}$$

and this can be arranged to give

$$p = \frac{NkTe^{-\frac{Na}{kTV}}}{V - Nb}.$$

Then differentiating this gives

$$\frac{\partial p}{\partial V} = \frac{Ne^{-\frac{Na}{kTV}}}{V^2(V - Nb)^2} \{aN(V - Nb) - kTV^2\}$$

and

$$\frac{\partial^2 p}{\partial V^2} = \frac{Ne^{-\frac{Na}{kTV}}}{kTV^4(V - Nb)^3} \{2k^2T^2V^4 + N^2a^2(V - Nb)^2 - 2NakTV(N^2b^2 - 3NbV + 2V^2)\}.$$

For the critical point, these must be set equal to zero and the equations solved to give T_c and V_c . Solution of the equations thus gives

$$kT_c = \frac{a}{4b}, \quad V_c = 2Nb$$

and we then substitute these into the equation of state to give:

$$p_c = \frac{a}{4b^2e^2}.$$

Using these values for the critical parameters we then find $p_c V_c / NkT_c$ is given by

$$\begin{aligned} \frac{p_c V_c}{NkT_c} &= \frac{a}{4b^2e^2} 2Nb \frac{1}{N} \frac{4b}{a} \\ &= 2/e^2 \approx 0.271. \end{aligned}$$

7 Show that the partition function for an interacting gas may be expressed as

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

where Z_{id} is the partition function for a non-interacting gas. In terms of this expression explain why the partition function of a *hard sphere* gas might be approximated by

$$Z = Z_{\text{id}} \left(\frac{V - Nb}{V} \right)^N.$$

The partition function for an interacting gas is given by

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

This may be factorised, separating the p and q integrations:

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

But the ideal gas partition function is

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

so that Z may then be written as

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

If the interaction energy $U(q_i, q_j)$ were zero, then the integral would become V^N as one is simply integrating (unity) over the $3N$ dimensional space. Now for the hard sphere interaction the integrand is unity so long as the particles do not approach closer than the dimension σ . But if the particles did approach closer then the interaction energy would be infinite and the integrand would be zero. So when the q integrals are performed over all space the effect of this interaction *appears* simply to remove the hard core volume. And in this way the integral would be $(V - Nb)^N$ so that the partition function would then be

$$Z = Z_{\text{id}} \left(\frac{V - Nb}{V} \right)^N.$$

8 Show that the approximate partition function for the hard sphere gas in the previous question leads to the equation of state $p(V - Nb) = NkT$. This is sometimes called the Clausius equation of state. Give a physical interpretation of this equation.

Show that the first few virial coefficients are given by $B_2(T) = b$, $B_3(T) = b^2$, $B_4(T) = b^3$, etc. These virial coefficients are independent of temperature. Discuss whether this is a fundamental property of the hard sphere gas, or whether it is simply a consequence of the *approximated* partition function.

To find the equation of state we must differentiate $kT \ln Z$ with respect to volume. Now the logarithm of approximate partition is

$$\ln Z = \ln Z_{\text{id}} + N \ln(V - Nb) - N \ln V.$$

For the ideal gas partition function we have

$$\ln Z_{\text{id}} = N \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve}{N} \right],$$

which may be written as

$$\ln Z_{\text{id}} = N \ln V + \text{terms independent of } V.$$

Then

$$\ln Z = N \ln(V - Nb) + \text{terms independent of } V$$

as the $N \ln V$ terms cancel. We then have for the pressure

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} = \frac{NkT}{V - Nb},$$

so that

$$p(V - Nb) = NkT$$

as required.

The physical interpretation of this is as an the equation of state for an ideal gas, but with a reduced volume available, because of the finite volume of the (otherwise non-interacting) particles.

In order to find the virial coefficients we must expand p/kT in powers of N/V . Now

$$\frac{p}{kT} = \frac{N}{V - Nb}.$$

(Observe that the right hand side is independent of temperature, so we know that the virial coefficients will be temperature-independent before we start.)

We write p/kT as

$$\frac{p}{kT} = \frac{N}{V} \left(1 - b \frac{N}{V} \right)^{-1}$$

and this is then expanded as

$$\frac{p}{kT} = \frac{N}{V} \left(1 + b \frac{N}{V} + b^2 \left(\frac{N}{V} \right)^2 + b^3 \left(\frac{N}{V} \right)^3 + \dots \right).$$

From this we identify directly

$$B_2(T) = b, B_3(T) = b^2, B_4(T) = b^3, \text{ etc.}$$

The argument about excluded volume in obtaining the partition function for the hard sphere gas is an approximation. In reality imposing the boundary condition $|q_i - q_j| > \sigma$ for all i and j is more complex. However, by examining the structure of the configuration integral

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

we note that the exponent is independent of temperature since U/kT is either zero or infinite. Thus Q_N is independent of temperature and from this it follows that the virial coefficients will be temperature-independent. In other words, the virial coefficients for the hard sphere gas will be temperature-independent, irrespective of any approximations made.

⌈ A full calculation of the virial coefficients of the hard sphere gas gives

$$B_2(T) = b, B_3(T) = \frac{5}{8} b^2, B_4(T) = 0.29 b^3$$

where $b = 2\pi\sigma^3/3$. So the precise values of the virial coefficients are not quite those predicted from the approximated Clausius equation of state. ⌋

9 For a general interatomic interaction potential $U(r)$ we may define an effective hard core dimension d by $U(d) = kT$. What is the significance of this definition? Show that for the Lennard-Jones potential of Section 3.2.4, d is given by

$$d = \sigma \left\{ \frac{2}{1 + \sqrt{1 + kT/\epsilon}} \right\}^{1/6}.$$

Plot this to demonstrate that d is a very slowly varying function of temperature.

If you have access to a symbolic mathematics system such as *Mathematica* or *Maple*, show that at low temperatures

$$d \sim \sigma \left(1 - \frac{1}{24} \frac{kT}{\epsilon} + \frac{19}{1152} \left(\frac{kT}{\epsilon} \right)^2 - \dots \right).$$

So how high must the temperature be so that d differs appreciably from its zero temperature value?

How does d vary for the hard core and the square well potentials of Sections 3.2.2 and 3.2.3?

With d defined by $U(d) = kT$, this corresponds to the distance of closest approach of particles with kinetic energy kT . So from equipartition, this is essentially the mean distance of closest approach of particles of a gas at the temperature T .

For the Lennard-Jones potential, d then satisfies

$$4\epsilon \left\{ \left(\frac{\sigma}{d} \right)^{12} - \left(\frac{\sigma}{d} \right)^6 \right\} = kT.$$

This may be solved for d by setting $x = (\sigma/d)^6$. Then x satisfies

$$x^2 - x - kT/4\epsilon = 0,$$

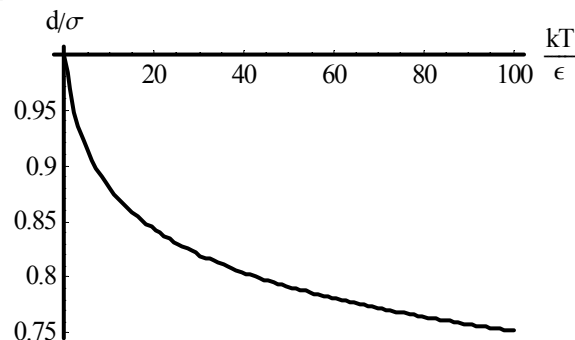
which has solution

$$x = \frac{1 \pm \sqrt{1 + kT/\epsilon}}{2}.$$

We must keep the positive square root since this gives a positive value for x . Then we find that

$$d = \sigma \left\{ \frac{2}{1 + \sqrt{1 + kT/\epsilon}} \right\}^{1/6}$$

as required. This is plotted below.



The figure shows that d varies quite slowly, particularly at high temperatures.

Series expansion of d gives

$$d \sim \sigma \left(1 - \frac{1}{24} \frac{kT}{\varepsilon} + \frac{19}{1152} \left(\frac{kT}{\varepsilon} \right)^2 - \dots \right)$$

so that T must be many times greater than ε/k for d to differ appreciably from its zero temperature value of σ .

For both the hard core and the square well potentials the effective hard core dimension d is a constant, equal to the actual the hard core dimension σ , independent of temperature.

10 The one dimensional analogue of the hard sphere gas is an assembly of rods constrained to move along a line (the Tonks model). For such a gas of N rods of length l confined to a line of length L , evaluate the configuration integral Q_N . Show that in the thermodynamic limit the equation of state is

$$f(L - Nl) = NkT$$

where f is the force, the one dimensional analogue of pressure.

Comment on the similarities and the differences from the hard sphere equation of state mentioned in Problem 3.8 (Clausius equation) and the van der Waals equation of state.

In one dimension the configuration integral is given by

$$Q_N = \frac{1}{L^N} \int e^{-\left(\sum_{i < j} U(x_i, x_j)\right)/kT} dx_1 dx_2 \dots dx_N.$$

This may be simplified through the change of variables $X_i = x_i - x_{i-1}$. This gives

$$Q_N = \frac{1}{L^N} \int e^{-\left(\sum_i U(X_i)\right)/kT} dX_1 dX_2 \dots dX_N$$

with an appropriate choice of boundary conditions (cyclic boundary conditions). But in this form the integrals over the different variables are independent; the exponential, and thus the integral, can be factorised. And since the integral over each X will be the same, we obtain

$$Q_N = \left(\frac{1}{L} \int e^{-U(X)/kT} dX \right)^N$$

When $X > l$ we have $U = 0$ so that the exponential is unity. And when $X < l$ then U is infinite so that the exponential is zero. So in this case the excluded volume argument holds true and

$$\int e^{-U(X)/kT} dX = L - Nl$$

so that

$$Q_N = \left(\frac{L - Nl}{L} \right)^N.$$

The partition function for the ideal one-dimensional gas is

$$Z_{\text{id}} = \frac{1}{N!} \left(\frac{L}{\Lambda} \right)^N$$

Then using the calculated configuration integral the partition function is

$$Z = \frac{1}{N!} \left(\frac{L - Nl}{\Lambda} \right)^N.$$

The logarithm of Z is

$$\ln Z = N \ln(L - Nl) + \text{terms independent of } L.$$

The force in the one dimensional gas is given by

$$f = kT \left. \frac{\partial \ln Z}{\partial L} \right|_{T, N}$$

and thus we find

$$f = \frac{NkT}{L - Nl}$$

or

$$f(L - Nl) = NkT.$$

This is the 1d analogue of the Clausius equation of state for the hard sphere gas in 3d. However this is an exact equation of state; the Clausius equation is an approximation. The van der Waals equation is similar. But in that case the long-distance attractive interactions also are taken into account by modifying the pressure.

11 Compare the square well and the van der Waals expressions for the second virial coefficient. Show that they become equivalent when the range of the square well potential tends to infinity while its depth tends to zero.

The square well second virial coefficient is given by

$$B_2^{\text{sq}}(T) = \frac{2}{3} \pi \sigma^3 \left\{ 1 - (R^3 - 1) (e^{\varepsilon/kT} - 1) \right\},$$

while that for the van der Waals equation is

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

When ε is small the exponential of the square well second virial coefficient can be expanded:

$$B_2^{\text{sq}}(T) \approx \frac{2}{3} \pi \sigma^3 \left\{ 1 - (R^3 - 1) \left(\frac{\varepsilon}{kT} + \frac{1}{2} \left(\frac{\varepsilon}{kT} \right)^2 + \dots \right) \right\}$$

at the same time the range of the well become large so that the 1 may be neglected in comparison with the R^3 . Then

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

In the limit that $\varepsilon \rightarrow 0$, $R \rightarrow \infty$, while $R^3 \sigma$ remains finite this then becomes

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

And this has the form of the square well second virial coefficient, where

$$b = \frac{2}{3} \pi \sigma^3, \quad a = \frac{2}{3} \pi \sigma^3 R^3 \epsilon.$$

Thus we have shown that the second virial coefficient of van der Waals equation of state is equivalent to that arising from the square well interaction in the limit of a long-range but weak attraction.