Problem Sheet 6

I. VIRIAL EXPANSION AND VDW EQUATION

In the last exercise from the virial expansion you found

$$P = T(n + B_2(T)n^2 + B_3(T)n^3 ...) \tag{1.1}$$

with

$$B_2 = \frac{1}{2}\int d^3r(1 - \exp(-\beta V_{int}(r))) \tag{1.2}$$

for the second virial coefficient.

What is B_2 in the van der Waals theory? (Rewrite the vdW equation in a form which matches the above!)

Consider in particular the Lennard-Jones potential:

$$V_{int}(r) = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right] \tag{1.3}$$

Compare the exact result (at low denisty) of the virial expansion with the one from the phenomenological vdW equation. To do this, split the integral for B_2 into two parts: (i) short distances, $r < r_{\min}$: approximate the potential $V_{int}(r < r_{\min})$ as infinitely large (where $r_{\min}$ is the location of the minimum of V_{int}.

(ii) long distances ($r > r_{\min}$): make a high temperature expansion (expansion in $\beta V_{int} \ll 1$) to obtain the lowest terms in a power series in β. Putting the two parts together and compare with the van der Waals equation. What are the parameters a and b which you would extract from the virial expansion?

II. ALTERNATIVE DERIVATION OF THE VDW EQUATION

In principle, the clean way to obtain the equation of state consists in finding the free energy $F(T, V)$ and writing $P = -\partial F/\partial V$. This requires always certain approximations or expansions, one of them being the virial expansion, which works well at small density.

Here we take another root which potentially should work also for higher n. We determine a Gibbs free energy, subject to the constraint of a given density $n = N/V$, that is we impose a given volume V. In the end we minimize over V, considering that G should be minimal at fixed T, p, N.

a) Motivate the form of the Gibbs free energy, ($G = U - TS = PV$)

$$G(T,P,N;V) = \frac{3}{2}NT + \frac{1}{2}\langle\sum_{i\neq j} V_{LJ}(|\mathbf{r}_i - \mathbf{r}_j|)\rangle - T\log((V/v_0)!/(V/v_0 - N)!N!) + PV, \tag{2.1}$$

where $v_0 \equiv 1/n_0 \equiv r_0^3$, and the sum is over all pairs of particles. (Sloppily we write $X! \equiv \Gamma(X+1)$ as an approximation for the factorial of the closest integer to X. But this does not matter since $X \gg 1$.)

Instead of V, take $n \equiv N/V$ as independent inhibition parameter and show that

$$\frac{G}{N} \approx -nW + T[\log(n/n_0) - (1 - n_0/n)\log(1 - n/n_0)] + P/n + const.(T) \tag{2.2}$$

where

$$W \approx -\frac{1}{2}\int_{r>r_0} d^3r V_{LJ}(r) \equiv c\epsilon r_0^3 \tag{2.3}$$

and try to give a reason for the latter approximation. Calculate the constant c.

b) It is convenient to introduce $T_0 \equiv c\epsilon$ and $P_0 \equiv c\epsilon n_0$ and the reduced quantities $t \equiv T/T_0$, $p \equiv P/P_0$ and $\rho \equiv n/n_0$. With those one obtains the dimensionless chemical potential

$$g(t,p,\rho) \equiv \frac{G(T,P,N;V)}{T_0 N} = -\rho + t\left[\log(\rho) - (1 - 1/\rho)\log(1-\rho)\right] + p/\rho + const.(t). \tag{2.4}$$

which is still inhibited by a constraint on ρ. Draw $g(t,p,\rho)$ as a function of the dimensionless density ρ in the interval $[0,1]$, for various t and p. (Hint consider especially t and p a little below the critical point t_c and p_c determined below in point (c).)

How many minima are there? (Remember that g has to be minimized with respect to the inhibition parameter ρ!) How do you interpret them? (Think of the $P-T$ diagram of the liquid-gas system! Where do you find one phase, where do you find two phases?)

c) How does the critical point show up in this description? Show that it corresponds to the point where

$$\frac{\partial}{\partial\rho}g(t_c,p_c,\rho_c) = 0; \quad , \frac{\partial^2}{\partial\rho^2}g(t_c,p_c,\rho_c) = 0; \quad , \frac{\partial^3}{\partial\rho^3}g(t_c,p_c,\rho_c) = 0. \tag{2.5}$$

(Characterize first how you expect the critical point to manifest itself in a curve $g(t_c,p_c,\rho)$ as a function of ρ!)

Find the solution to these equations explicitly!

d) Argue that the equation of state results immediately from the condition

$$\left(\frac{\partial G}{\partial n}\right)_{T,P,N} = 0, \tag{2.6}$$

or equivalently

$$\left(\frac{\partial g}{\partial n}\right)_{T,P} = 0, \tag{2.7}$$

Obtain the equation of state, and make it resemble as much as possible the vdW equation! You should obtain the form

$$p + \rho^2 = -t \log(1 - \rho). \tag{2.8}$$

Expand the last logarithm into powers of ρ and obtain thus the virial expansion (within the present approximation). Truncate the expansion of the logarithm at the appropriate order, such that you recover exactly the form of vdW's equation. Extract the constants a and b and compare with the first section of this sheet!

e) Explain with the help of the inhibited potential $g(t, p, \rho)$ what it means to supercool a gas, or to superheat the liquid! What do these metastable states correspond to in $g(t, p, \rho)$? Explain what the Maxwell construction means in terms of $g(t, p, \rho)$! What is the condition for coexistence of two phases? Sketch qualitatively the P, T diagram with the equilibrium vapor-liquid line and the two spinodals! Formulate the mathematical conditions which determine the three lines!