

FYS4130 – 2014 – Problem set 6
Phase coexistence in the van der Waals system

This problem set was given in FYS2160 at UiO in the Fall 2013 semester as oblig 7. It was found to be one of the best assignments in that course, and so we reuse it here.

In this problem we will study the van der Waals fluid. You will learn how to find the Gibbs free energy for the system and how to use the Gibbs free energy to find the equilibrium state of the system, also in the case when both a liquid and a gas phase are present simultaneously.

The van der Waals fluid is a mean field theory of a gas. It is a model system, just as the ideal gas, but it includes more features of realistic gases. The van der Waals gas includes two of the main effects of an attractive two-particle interaction between particles in the gas: a repulsive interaction that keeps particles apart, and an attractive long-range interaction that pulls particles together. These two effects lead to two changes in the Helmholtz free energy of the gas, as compared to an ideal gas: Instead of the volume V we introduce the effective volume, $V - Nb$, where the volume b is the excluded volume per particle, and we introduce an average binding energy, $-a(N/V)^2$. The Helmholtz free energy for the van der Waals gas is¹

$$F_{wdW} = -NkT \left(\ln \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V}. \quad (1)$$

(a) Show that the pressure $p(N, V, T)$ of the van der Waals gas is

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

This is the equation of state for the van der Waals gas.

We define the quantities

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

so that we can introduce dimensionless quantities

$$\hat{p} = p/p_c, \quad \hat{V} = V/V_c, \quad \hat{T} = T/T_c, \quad (4)$$

and for the density

$$\hat{\rho} = 1/\hat{V} = \rho/\rho_c, \quad \rho_c = \frac{1}{3b}. \quad (5)$$

(b) Show that the pressure of the van der Waals gas can be written as

$$\hat{p} = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}. \quad (6)$$

(c) Plot the pressure \hat{p} as a function of \hat{V} for \hat{V} in the range from 0.4 to 20 for $\hat{T} = 1.15, 1.0, \text{ and } 0.85$.

Notice that there is a range of values where the volume is not a unique function of the pressure. This means that we generally cannot find $\hat{V}(\hat{p})$.

¹ n_Q is the inverse of the thermal volume of a particle, $n_Q = \Lambda^{-3}$, where $\Lambda = \frac{h}{\sqrt{2\pi mkT}}$ is the thermal wavelength.

- (d) Show that the pressure can also be expressed using the density instead of the volume and is

$$\hat{p} = \frac{8\hat{\rho}\hat{T}}{3 - \hat{\rho}} - 3\hat{\rho}^2 . \quad (7)$$

- (e) Plot the pressure \hat{p} as a function of $\hat{\rho}$ for $\hat{\rho}$ in the range from 0.0 to 2.0 for $\hat{T} = 1.15, 1.0, \text{ and } 0.85$.

- (f) Based on your plot, for what temperature does the density become a non-unique function of the pressure?

- (g) Based on your plot, when does the isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_{T,N} \quad (8)$$

become negative?

A negative compressibility would mean that the system was unstable. This is an unphysical situation. Let us now discuss the thermodynamic equilibrium and stability of the system by analyzing its Gibbs free energy.

- (h) Show that the Gibbs free energy of the system in dimensional quantities is

$$G(T, V, N) = \frac{NkTV}{V - Nb} - \frac{2aN^2}{V} - NkT (\ln(n_Q(V - Nb)/N) + 1) , \quad (9)$$

Unfortunately, we cannot insert $V(p)$ into this relation to get $G(T, p, N)$, which are the natural variables for G , because V is not a unique function of p . Let us therefore instead study Gibbs free energy as a function of V as V is lowered. This gives a unique pressure p for every value of V even though the reverse is not true.

- (i) Argue that Gibbs free energy can be written as

$$G = -NkT \ln(V - Nb) - \frac{aN^2}{V} + pV + NkTc(T) , \quad (10)$$

where $c(T)$ is a function of temperature alone.

It is now convenient to introduce a dimensionless Gibbs free energy by introducing $G_c = 3kT_c/8$.

- (j) Show that the Gibbs free energy per particle is

$$\hat{g} = \frac{G/G_c}{N} = -3\hat{\rho} - \frac{8}{3}\hat{T} \ln\left(\frac{3}{\hat{\rho}} - 1\right) + \frac{\hat{p}}{\hat{\rho}} , \quad (11)$$

if you only include terms that depend on \hat{p} or $\hat{\rho}$.

- (k) For $\hat{T} = 0.9$ plot \hat{p} as a function of $\hat{\rho}$ for $\hat{\rho}$ from 0.2 to 2.0. Then plot \hat{V} as a function of \hat{p} for the same data, using that $\hat{V} = 1/\hat{\rho}$. Finally, plot \hat{g} as a function of \hat{p} for the same data. Comment on the curve you get for Gibbs free energy. You may want to plot all three plots in three subfigures and highlight some points along the curves in order to be able to relate the values in the three plots.

- (l) Argue that we can find the minimum of Gibbs free energy if we can determine where the curve $\hat{g}(\hat{p}(\hat{\rho}))$ intersects itself.
- (m) You can find self-intersections in matlab using the program `selfintersect`². When you call `selfintersect` for this particular dataset ($\hat{T} = 0.9$), you will get a pair of indices. Plot the corresponding points – the two points corresponding to the intersection – in the plots for $\hat{p}(\hat{\rho})$ and for $\hat{V}(\hat{\rho})$. Draw a straight line between the two points. Comment on the results.
- (n) What do you think really happens in the system between the two intersections?
- (o) Make a systematic study, where you plot the line between the two intersection points in the $\hat{p}(\hat{V})$ plots for \hat{T} varying from 1.0 down to 0.85. Comment on (or simply marvel at) the results.

We return to the expression for Gibbs free energy:

$$\hat{g} = -3\hat{\rho} - \frac{8}{3}\hat{T} \ln\left(\frac{3}{\hat{\rho}} - 1\right) + \frac{\hat{p}}{\hat{\rho}}. \quad (12)$$

We can interpret this equation in the following way: For a given pair of \hat{p} and \hat{T} we can find the equilibrium density $\hat{\rho}$ as the value that gives a minimum value for \hat{g} .

- (p) For $\hat{T} = 0.9$ generate a series of plots of \hat{g} as a function of $\hat{\rho}$ for \hat{p} in the range from 0.4 to 0.8. Discuss what happens during this change in pressure. (Good question for class discussion).

End of problem set 6

²<http://www.mathworks.com/matlabcentral/fileexchange/13351-fast-and-robust-self-intersections/content/selfintersect.m>