3 Interacting Gases and the Liquid-Gas Phase Transition

> *"yeah my distraction is my defense*
> *against this lack of inspiration*
> *against this slowly deflation*
> *yeah the further the horizon you know*
> *the more it warps my gaze*
> *the foreground's out of focus*
> *but you know I kinda hope it's*
> *just a phase, just a phase*
> *just a phase, just a phase*
> *just a phase, just a phase*
> *just a phase" - A. Difranco*

3.1 Virial Expansion

The virial expansion is defined as an expansion of the pressure in powers of the density,

$$P = \rho T\left[A_1 + \sum_{n=2}^{\infty} A_n\left(\frac{\rho}{\rho_0}\right)^{n-1}\right], \quad \rho_0 \equiv \frac{(2j+1)}{(2\pi\hbar)^3}\int d^3p\, e^{-\epsilon_p/T}. \tag{1}$$

The leading term is always $A_1 = 1$, as low density matter always behaves as an ideal gas. The contribution from interactions to the second order term, A_2, is negative for attractive interactions and positive for repulsive interactions. Quantum statistics also affects A_2. For bosons, the contribution is negative, while for fermions it is negative. The negative contribution for bosons can be understood by considering the Bose-Einstein form for the phase-space occupancy, which provides a relatively stronger enhancement to low-momentum particles. This lowers the average momentum of particles colliding with the boundaries, which lowers the pressure relative to $P = \rho T$. Similarly, the contribution is positive for fermions, as the average momentum of a particle in a Fermi gas is lowered by quantum statistics.

Like perturbation theory, virial expansions are only justifiable in the limit that they are unimportant, i.e., either only the first few terms matter, or the expansion does not converge. For that reason, the second-order coefficient is often calculated carefully from first principles, but subsequent coefficients are often inserted phenomenologically. The virial expansion will be considered more rigorously in Chapter 6, where coefficients will be expressed in terms of phase shifts (only second order) and perturbation theory.

3.2 The Van der Waals Eq. of State

All equations of state, $P(\rho, T)$, should behave as $P = \rho T$ at low density. The second-order virial coefficient is usually negative, as long-range interactions are usually attractive and dominate at low density. For molecules, the long range interaction usually originates from induced dipoles attracting one another and falls off as $1/r^6$ at large r. At high densities, particles tend to run out of space and repel one another. At some density, the contribution to the pressure from interactions tends to rise once again.

The Van der Waals parameterization of the equation of state incorporates both an attractive component for low density and repulsion at high density,

$$P = \frac{\rho T}{1 - \rho/\rho_s} - a\rho^2. \tag{2}$$

Here, the second order virial coefficient is

$$A_2 = \frac{\rho_0}{\rho_s} - \frac{a\rho_0}{T}, \tag{3}$$

and as long as a is large enough, the correction to the pressure to order ρ^2 is negative. However, at high density, the first term will dominate, and in fact $P \to \infty$ as $\rho \to \rho_s$. The quantity ρ_s is the saturation density, as it is the highest density one can obtain before the pressure jumps to infinity. As the temperature goes to zero, a system will approach the saturation density if there is no pressure. The inverse of ρ_s is often referred to as the excluded volume. The Van der Waals equation of state thus implies a hard-core interaction.

EXAMPLE:
Using the Maxwell relation,

$$\left.\frac{\partial(P/T)}{\partial\beta}\right|_{N,V} = -\left.\frac{\partial E}{\partial V}\right|_{N,T},$$

derive the energy per particle E/N for a Van der Waals equation of state, as a function of ρ and T.

First,

$$\frac{\partial}{\partial\beta}\left(\frac{P}{T}\right) = \frac{\partial}{\partial\beta}\left(\frac{\rho}{1-\rho/\rho_s} - \beta a\rho^2\right) = -a\rho^2.$$

Beggining with $E/N = 3/2T$ at $\rho = 0$,

$$\frac{E}{N} = \frac{3}{2}T + \frac{1}{N}\int_\infty^V dV\ a\rho^2 = \frac{3}{2}T - \int_0^\rho \frac{1}{\rho^2}d\rho\ a\rho^2 = \frac{3}{2}T - a\rho.$$

Remarkably, the energy per particle is independent of ρ_s.

If one plots P vs. V, the behavior is no longer monotonic for low T as seen in Fig. 1. For these temperatures below the critical temperature,

$$T_c = \frac{8a\rho_s}{27}, \tag{4}$$

multiple densities can provide the same pressure. We refer to the inflection point as the critical point, at which $V_c = 3/\rho_s$, and $P_c = a\rho_s^2/27$.

A region of densities for $T < T_c$ is unstable to phase separation. To find the region we consider the conditions for phase co-existence.

$$T_{\rm gas} = T_{\rm liq}, \quad P_{\rm gas} = P_{\rm liq}, \quad \mu_{\rm gas} = \mu_{\rm liq}. \tag{5}$$

The first two conditions can be satisfied by taking any two points on the same isotherm in Fig. 1 that are at the same pressure. The third condition, that the chemical potentials are equal, can also be illustrated with the isotherm. Beginning with

$$TdS = dE + PdV - \mu dN, \quad TS = PV + E - \mu N, \tag{6}$$

one can solve for $Nd\mu$,

$$Nd\mu = -SdT + VdP. \tag{7}$$

Following along an isotherm, $dT = 0$, between two points illustrated in the upper panel of Fig. 1 the change in the chemical potential is

$$\mu_{\rm gas} - \mu_{\rm liq} = \int vdP = \int d(Pv) - \int Pdv = P_{\rm gas}v_{\rm gas} - P_{\rm liq}v_{\rm liq} - \int_{v_{\rm liq}}^{v_{\rm gas}} Pdv = 0. \tag{8}$$

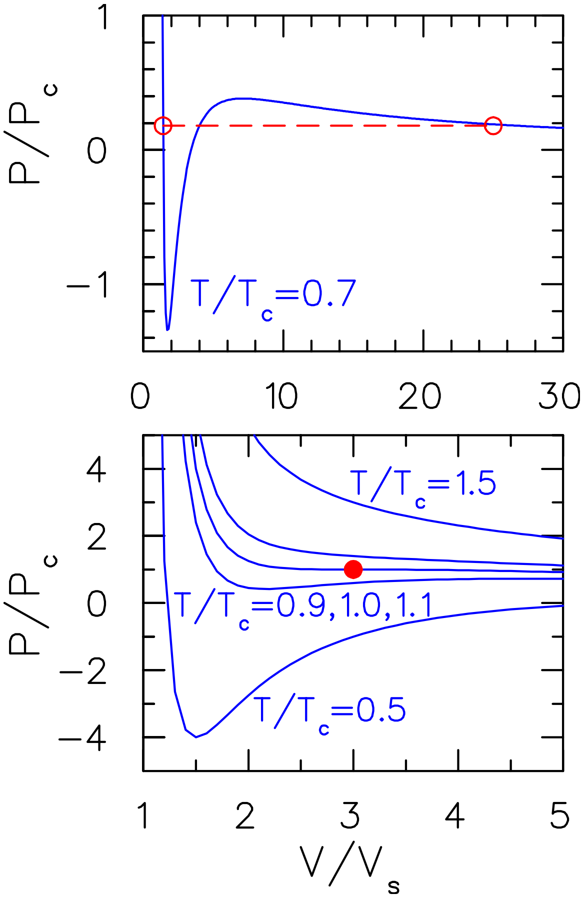

Figure 1: The lower panel illustrates P vs V for several isotherms for the Van der Waals equation of state. For $T < T_c$, the behavior is no longer monotonic and phase separation can occur. For T_c, there is an inflection point, where $d^2P/dV^2 = dP/dV = 0$. This is the critical point. In the upper panel, the $T = 0.7 \cdot T_c$ isotherm is shown along with the two points denoting the liquid and gas densities. Graphically, these points are found by requiring that the area between the isotherm and a horizontal line connecting between two points on the isotherm integrates to zero.

Here, $v = V/N$ is the volume per particle. The condition that $\mu_{\text{liq}} = \mu_{\text{gas}}$ can then be stated graphically by stating that the integrated area between the P vs. V isotherm in the upper panel of Fig. 1 and the line between the two points is zero, i.e., there are equal amounts of area above and below the line.

As an example of coexistence, Fig. 2 shows how the coexistence region is remarkably similar for a variety of transitions when viewed after scaling the variables. Here, we make only a quick remark that the actual form of the coexistence curve, and the behavior of the matter, in the region near the critical point defies the simple Van der Waals picture. In that region, there are no longer two distinct phases and the density fluctuates wildly. Critical phenomena represents a field in itself, and will be discussed later in the course.

EXAMPLE:
Solve for T_c, P_c and V_c in the Van der Waals equation of state using the scaled variables, $p = P/a\rho_s^2$, $t = T/a\rho_s$, $v = \rho_s V/N = \rho_s/\rho$.

In terms of these variables,

$$p = \frac{t}{v-1} - \frac{1}{v^2}.$$

For $T < T_c$ there are two points where $dP/dV = 0$. At one of these points, $d^2P/dV^2 < 0$. At the critical point,

$$\frac{dp}{dv} = \frac{d^2p}{dv^2} = 0.$$

If the second derivative were not zero, P vs. V would not be monotonic. These relations become:

$$\frac{t_c}{(v_c-1)^2} = -2\frac{1}{v_c^3}, \qquad 2\frac{t_c}{(v_c-1)^3} = 6\frac{1}{v_c^4}.$$

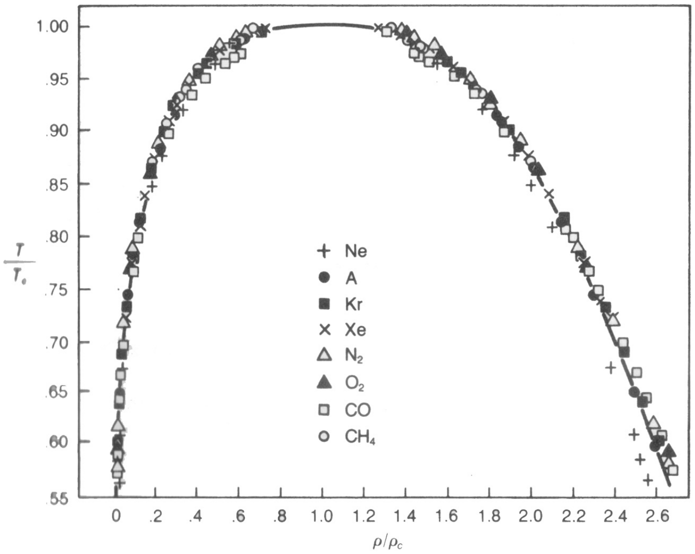

Figure 2: Phase coexistence for a variety of substances shows a remarkable universality after being scaled. The Van der Waals along with Maxwell constructions fails when working very close to T_c, but explains the behavior well for $T < T_c$. This figure was compiled by Guggenheim in 1945 (J.Chem).

This gives, $v_c = 3$ and $t_c = 8/27$. Plugging this into the expression for p, $p_c = 1/27$.

3.3 Clausius-Clapeyron Equation

The Clausius-Clapeyron equation allows us to plot the coexistence line in a P-V diagram if given the latent heat and the change of the volume per particle as one goes across the phase line.

$$\frac{dP}{dT} = \frac{L/T}{(V/N)_{\text{gas}} - (V/N)_{\text{liq}}} \tag{9}$$

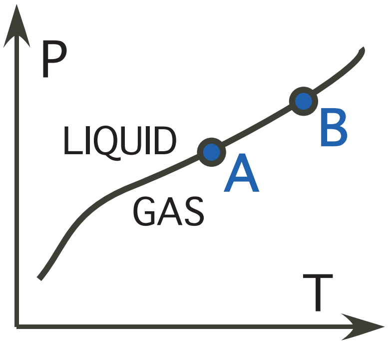

Figure 3: For phase coexistence, P, T and μ are continuous across the coexistence line. The requirement that $\mu^{(B)} - \mu^{(A)}$ is the same on both sides of the coexistence line is the starting point for proving the Clausius-Clapeyron equation.

To prove the relation consider the coexistence line in the P-V diagram sketched in Fig. 3. Since P, T and μ are continuous across the line,

$$\mu_{\text{liq}}^{(B)} - \mu_{\text{liq}}^{(A)} = \mu_{\text{gas}}^{(B)} - \mu_{\text{gas}}^{(A)}. \tag{10}$$

Since $Nd\mu = -SdT + VdP$,

$$\begin{aligned} -\left(\frac{S}{N}\right)_{\text{liq}} dT + \left(\frac{V}{N}\right)_{\text{liq}} dP &= -\left(\frac{S}{N}\right)_{\text{gas}} dT + \left(\frac{V}{N}\right)_{\text{gas}} dP, \\ \frac{dP}{dT} &= \frac{(S/N)_{\text{gas}} - (S/N)_{\text{liq}}}{(V/N)_{\text{gas}} - (V/N)_{\text{liq}}}. \end{aligned} \tag{11}$$

Given that the latent heat is $L = T\Delta S$, this proves the relation.

3.4 Problems

1. Consider a low density three-dimensional gas of non-relativistic spin-zero bosons of mass m at temperature $T = 1/\beta$ and chemical potential μ.

   (a) Find ρ_0 as defined in Eq. (1) in terms of m and T.

   (b) Expand the density ρ to second order in $e^{\beta\mu}$, i.e., to $e^{2\beta\mu}$. Express your answers for this part and the next two parts in terms of ρ_0.

   (c) Expand ρ^2 to second order in $e^{\beta\mu}$.

   (d) Expand $\delta P \equiv P - \rho T$ to second order in $e^{\beta\mu}$. (Hint: it is easier if you use the expression for P involving $\ln(1-f)$ where you expand the logarithm in powers of f)

   (e) Determine the second virial coefficient defined by Eq. (1).

2. Consider the Van der Waals equation of state in scaled variables,

$$p = \frac{t}{v-1} - \frac{1}{v^2},$$

   where $p = P/a\rho_s^2$, $v = V/V_s$, $t = T/a\rho_s$.

   (a) Derive the Maxwell relation,

$$\left.\frac{\partial(P/T)}{\partial\beta}\right|_{N,V} = -\left.\frac{\partial E}{\partial V}\right|_{N,T}.$$

   (b) Find the scaled energy per particle $e \equiv E/(a\rho_s N)$ as a function of v and t using the Maxwell relation above. Begin with the fact that $e = (3/2)t$ as $v \to \infty$.

   (c) Show that the change of entropy/particle $s = S/N$ between two values of v at a fixed temperature t is:

$$s_b - s_a = \ln[(v_b-1)/(v_a-1)].$$

   (d) Using the fact that $ts = e + pv - \mu$, show that

$$\mu_b - \mu_a = -\frac{2}{v_b} + \frac{2}{v_a} + t\left[\frac{v_b}{v_b-1} - \frac{v_a}{v_a-1}\right] - t\ln\left(\frac{v_b-1}{v_a-1}\right).$$

   (e) Show that as $t \to 0$, p_b will equal p_a if $v_b \to \infty$ and $v_a = 1+t$. Then, show that in the same limit, μ_a will equal μ_b if $v_b = te^{1/t}$.

   (f) Find the latent heat $L = t(s_b - s_a)$ for the small t limit. How does it compare with the minimum of e at $t = 0$?

   (g) At $t = 0$, the system will have $p = 0$ in order to minimize the energy. Using the Clausius-Clapeyron equation, find dp/dt along the coexistence line at $t = 0$.