Van der Waals Model and Phase Transitions

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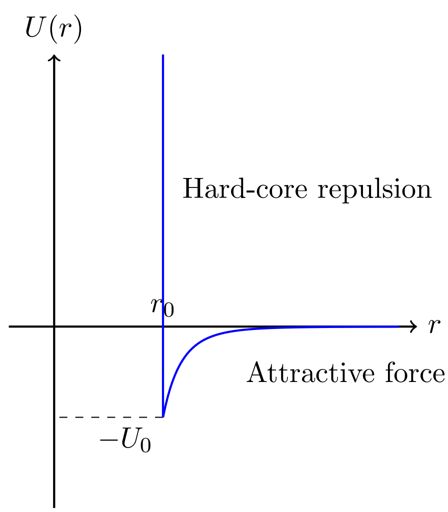
1 The Van der Waals Equation of State

Last time, we computed the partition function for a weakly interacting gas with an interatomic potential given by:

$$U(r) = \begin{cases} \infty & \text{for } r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & \text{for } r \geq r_0 \end{cases} \tag{1}$$



At leading order, we obtained the **van der Waals Equation of State (EOS)**:

$$\boxed{P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}} \tag{2}$$

where the constants are:

- $b = \frac{2\pi r_0^3}{3} \sim$ one atom's volume. The hard-core repulsion *increases* the pressure by reducing the effective volume available to the gas.
- $a = bU_0$. The attractive force *decreases* the pressure by pulling atoms together.

By construction, we must always have $V > Nb$. We can plot this equation of state at fixed temperatures in the P vs. V/N plane. Notice that the pressure is entirely a function of the specific volume $v = V/N$:

$$P(v) = \frac{k_BT}{v - b} - \frac{a}{v^2} \tag{3}$$

2 Isotherms and the Critical Point

When we plot P as a function of V/N for different temperatures, we see three distinct behaviors:

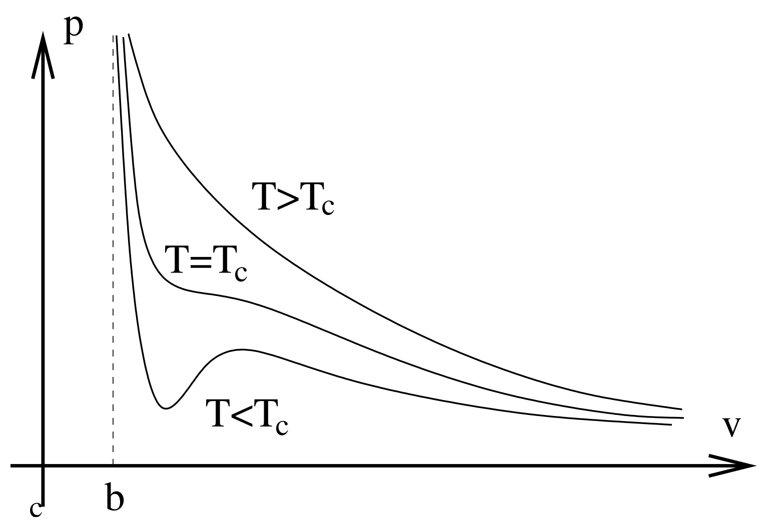


Figure 1: Isotherms of the van der Waals equation of state

For high temperatures ($T > T_c$), the curve is monotonically decreasing, similar to an ideal gas. As we lower the temperature, a **critical temperature** T_c is reached where the isotherm develops an inflection point. At this critical point:

$$\left.\frac{\partial P}{\partial V}\right|_{T_c} = 0 \quad \text{and} \quad \left.\frac{\partial^2 P}{\partial V^2}\right|_{T_c} = 0 \tag{4}$$

In the homework, you will derive the critical temperature by solving these equation. It is equal to $k_B T_c = 8a/27b = 8U_0/27$.

3 Maxwell Construction and Coexistence

For temperatures below the critical temperature ($T < T_c$), the van der Waals isotherm exhibits inflection points as shown in Fig. 2. This means that at a fixed pressure (and temperature since we are on an isotherm), there are multiple possible densities predicted by the equation of state. What are these different states?

- Starting with the state labeled "2" in Fig. 2, it has $\frac{\partial P}{\partial V} > 0$. This means that compressing the gas ($dV < 0$) would somehow decrease the pressure, making it easier to compress and decreasing the pressure further. The whole system would collapse on itself. Similarly, if I expand the gas ($dV > 0$), the pressure increases, making the system wanting to expand more, increasing the pressure further. The system explodes. This is clearly an unstable and unphysical state.

- The state labeled "1" in Fig. 2 has $v \sim b$, which means atoms are very tightly packed together. The density is thus high. Also, $|\frac{\partial P}{\partial V}|$ is very large and negative, implying that it is very difficult to compress this state: a tiny change in volume would lead to a huge change in pressure. This is a liquid.

- The state labeled "3" has $V/N \gg b$ (low density) and has a small and negative $|\frac{\partial P}{\partial V}|$. This is a gas.

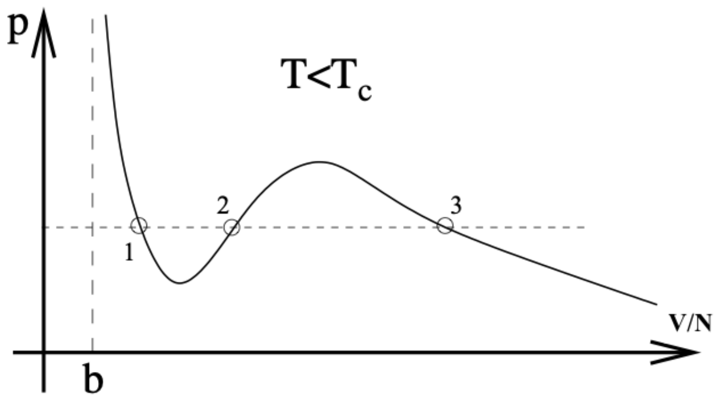


Figure 2: For $T < T_c$ and for a given pressure and temperature, the van der Waals model predict three different states of the system, characterized by difference densities and compressibility.

Thus, state 1 and 3 have clear physical realizations in the real world, but intermediate states between these two appear unphysical. What is going on? We are missing an important piece of physics: phase transformation and coexistence of multiple phases in the same volume. That is, between state 1 and state 3, the system undergoes a phase transition, separating into a **liquid** and a **gas**. To find the physical pressure at which coexistence occurs ($P_{\text{coexistence}}$), we use the **Maxwell Equal Area Construction**.

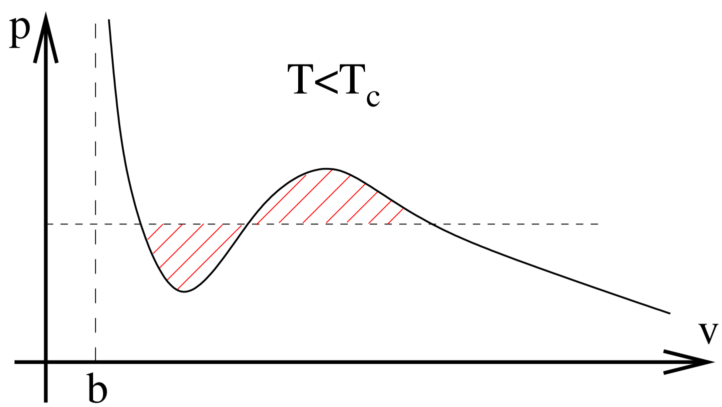


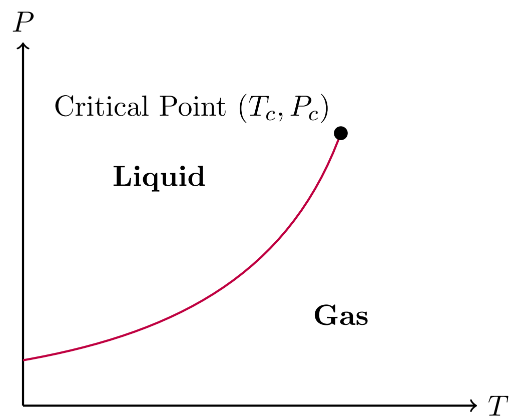
Figure 3: Maxwell construction for the pressure at which we have co-existence of liquid and gas. The co-existence pressure is determined by matching the two red hatched areas under the curve.

We draw a horizontal line at $P_{\text{coexistence}}$ such that the two hatched areas are equal in Fig. 3. The ends of this horizontal line represent the specific volume of the pure liquid phase (v_{liquid}) and the pure gas phase (v_{gas}). Physically, the coexistence pressure is determined by the condition of **chemical equilibrium**. For the liquid and gas to coexist in equilibrium at the same temperature and pressure, their chemical potentials must be equal:

$$\mu_{\text{liquid}} = \mu_{\text{gas}} \tag{5}$$

4 The Phase Diagram and the Clausius-Clapeyron Equation

We can summarize the phase behavior by determining the shape of the liquid-gas interface in the $P-T$ plane.



Along the interface curve, we have phase coexistence, so $\mu_{\text{liquid}} = \mu_{\text{gas}}$.
Remember that the Gibbs free energy is $G = \mu N$. The total Gibbs free energy is:

$$G = F + PV = \langle E \rangle - TS + PV \tag{6}$$

The fundamental thermodynamic identity for G is:

$$dG = -SdT + VdP + \mu dN \tag{7}$$

Let us define the Gibbs free energy per atom, $g = G/N$. Because G is extensive, $g = \mu$. Therefore, at the phase boundary:

$$g_{\text{liquid}} = g_{\text{gas}} \tag{8}$$

If we move infinitesimally along the phase boundary, the change in the specific Gibbs free energy must be the same for both phases ($dg_{\text{liquid}} = dg_{\text{gas}}$). From the total differential $dg = -sdT + vdP$ (where $s = S/N$ and $v = V/N$):

$$-s_{\text{liquid}}dT + v_{\text{liquid}}dP = -s_{\text{gas}}dT + v_{\text{gas}}dP \tag{9}$$

Rearranging to solve for the slope of the coexistence curve in the $P-T$ plane:

$$(v_{\text{gas}} - v_{\text{liquid}})dP = (s_{\text{gas}} - s_{\text{liquid}})dT \tag{10}$$

$$\frac{dP}{dT} = \frac{s_{\text{gas}} - s_{\text{liquid}}}{v_{\text{gas}} - v_{\text{liquid}}} \tag{11}$$

Finally, we define the **specific latent heat**, L, as the heat required to convert one particle from the liquid to the gas phase (or the heat released by condensing gas into liquid):

$$L = T(s_{\text{gas}} - s_{\text{liquid}}) \tag{12}$$

Substituting this into our slope equation yields the famous **Clausius-Clapeyron equation**:

$$\boxed{\frac{dP}{dT} = \frac{L}{T(v_{\text{gas}} - v_{\text{liquid}})}} \tag{13}$$

You will solve this equation for a simple case in the homework.

For the liquid-gas phase transition described above, we have the Gibbs free energy G is continuous across the coexistence curve. However, the entropy is generally discontinuous across this curve (otherwise $L = 0$). Since we have that

$$S = -\frac{\partial G}{\partial T}\bigg|_{P,N} \tag{14}$$

from Eq. (7) above, this means that the first derivative of G is discontinuous for the above phase transition. Such phase transitions are referred to as *first-order phase transitions.* First order phase transitions always involve the release of latent heat. In general, an nth order phase transition occurs when the nth derivative of the free energy is discontinuous across the coexistence curve. Most phase transitions are either first-order or second-order.