

PHYS 301

Thermodynamics and Statistical Mechanics

Worksheet #15
Thursday April 16 2026

Question 1.

Below a certain critical temperature T_c , the van der Waals equation of state predicts isotherms (curves of constant temperature in the $P - V$ plane) that have inflection points, as shown in Fig. 1 below. This means that for a given temperature and pressure, there are multiple solutions for the volume (or density) of the system (labeled in the figure by 1, 2, and 3). The goal of this worksheet is to understand what each of these solutions is telling us about the state of the system.

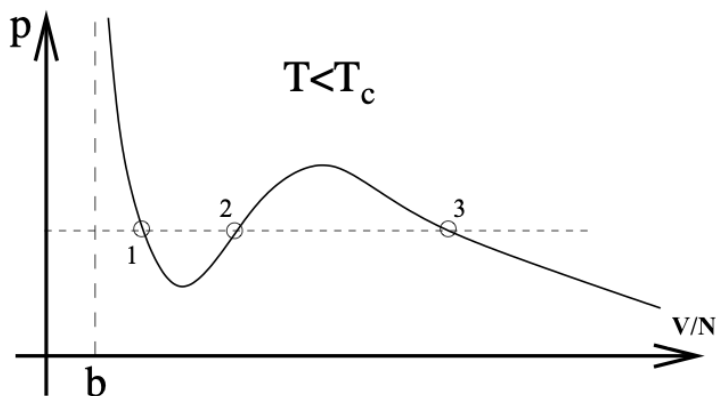


Figure 1: Isotherm for the van der Waals model at a temperature below T_c .

- (a) Let's first consider the solution labeled "2" in Fig. 1. From the slope of the isotherm there, we know that

$$\left. \frac{\partial P}{\partial V} \right|_T > 0. \quad (1)$$

If this is the case, what happens to the pressure of this system if it is compressed ($dV < 0$) a little bit? What about if I expand the volume ($dV > 0$) by a small amount? Given this, could this be a stable physical state of the system?

- (b) Now, let's look at the solution labeled "1". This state has $V/N \sim b$, where b is essentially the volume a single atom. What does this tell you about the density of this state? Also, from the slope of the graph, we see that $|\frac{\partial P}{\partial V}|$ is very large there. What does this tell you about how easy (or difficult) it is to compress ($dV < 0$) this state? What is the nature of this state?
- (c) Finally, let's look at the solution labeled "3". This one has $V/N \gg b$ and a relatively small and negative $\partial P/\partial V$. What does this tell you about the density and compressibility of this state? Is this a familiar state of matter?