

Physics 614 Homework 7

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1. Gibbs free energy of the van der Waals gas

- i. The Helmholtz free energy of the van der Waals gas has the form

$$F(T, V, N) = -Nk_B T \ln\left(\frac{V}{N} - b\right) - \frac{N^2 a}{V} + Nf(T) \quad (1)$$

for some function f . Recall, the Helmholtz free energy and the Gibbs free energy are related via

$$G = F + PV \quad (2)$$

So we can write G as

$$G(P, T, N, V) = -Nk_B T \ln\left(\frac{V}{N} - b\right) - \frac{N^2 a}{V} + Nf(T) + PV \quad (3)$$

Dividing by N to get the chemical potential per particle, we have

$$\mu(P, T; v) = -k_B T \ln(v - b) - \frac{a}{v} + Pv + f(T) \quad (4)$$

where $v = V/N$.

- ii. Dropping f from Eq. (4), and differentiation with respect to v to minimize μ gives

$$\begin{aligned} \frac{\partial \mu}{\partial v} &= -k_B T \frac{1}{v - b} + \frac{a}{v^2} + P \\ 0 &= -k_B T \frac{1}{v - b} + \frac{a}{v^2} + P \\ \implies P + \frac{a}{v^2} &= k_B T \frac{1}{v - b} \end{aligned} \quad (5)$$

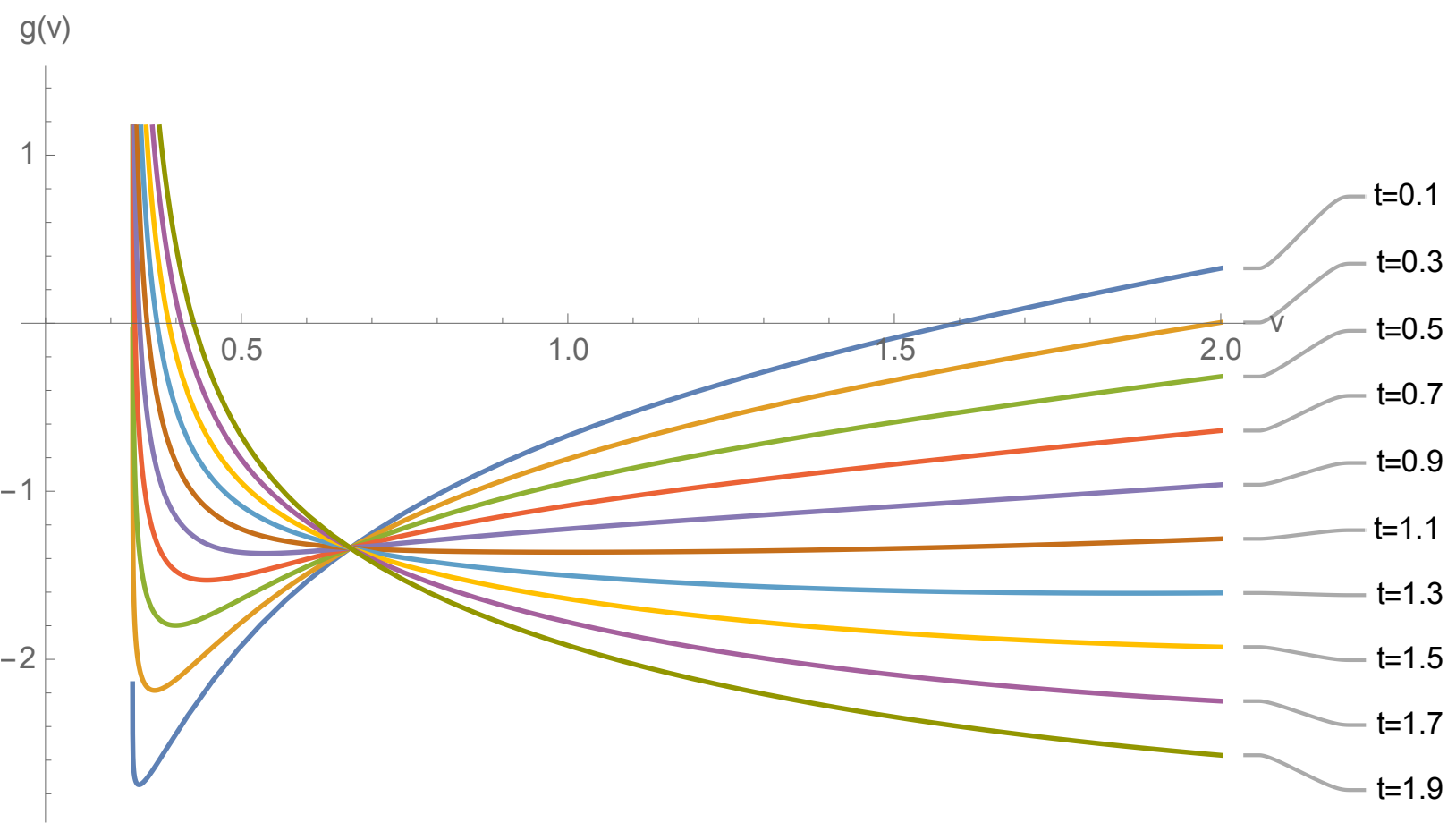
which is indeed the Van der Waals equation of state.

- iii. Define the dimensionless variables, $g := \mu/k_B T$, $p := P/p_c$, $\nu := v/v_c$, and $t := T/T_c$, where T_c , P_c , and v_c are the values of the corresponding variables at the critical point. From the lecture notes, we know that $k_B T_c = 8a/27b$, $p_c = a/27b^2$, and $v_c = 3b$. Substituting these values in Eq. (4) yields

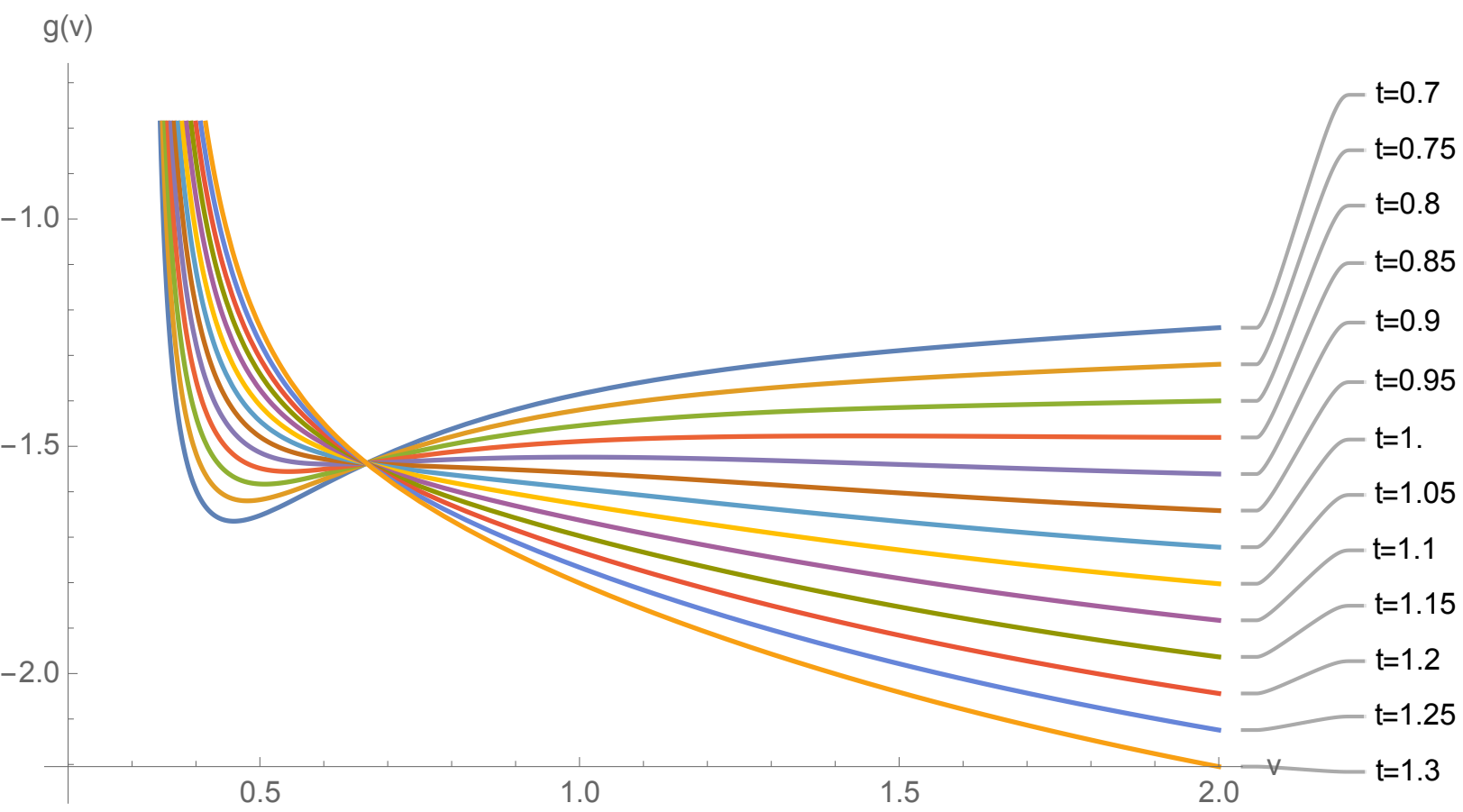
$$\begin{aligned} \mu(P, T; v) &= -k_B T \ln(v - b) - \frac{a}{v} + Pv \\ \rightsquigarrow \frac{\mu(P, T; v)}{k_B T_c} &= -t \ln(3b\nu - b) - \frac{27b}{8a} \frac{a}{3b\nu} + \frac{27b}{8a} \frac{a}{27b^2} p 3b\nu \\ g(p, t; \nu) &= -t \ln(3\nu - 1) - \frac{9}{8\nu} + \frac{3p\nu}{8} \end{aligned} \quad (6)$$

where the term which did not depend on p or ν has been dropped.

- iv. On the next page is a plot of $g(\nu)$ for $p = 1.4$ and t taking a range of values. Each curve has at most one minimum which corresponds to the existence of an inflection point on the plot of the Van der Waals gas in the PT -plane.



- v. Below is a similar plot but for $p = 0.6$ and over a smaller range so that we can estimate the value of t , for which the phase transition from gas to liquid occurs, more precisely. This seems to occur at approximately $t = 1.05$.



2. Dieterici equation of state

We consider a gas whose equation of state is

$$P = \frac{k_B T}{v - b} \exp\left(-\frac{a}{k_B T v}\right) \quad (7)$$

- i. This is where profound apathy set in and I decided I was happy taking the proverbial “L” on this assignment. Apologies for the boring assignment submission.

Below is a plot of $P(v)$ for several values of $k_B T$. The plots with vertical asymptotes are of $P(v)$ with $a = 1$ and $b = 1$, while the plots with maxima are with $a = 1$ and $b = 0.1$. This suggests that the critical behavior of this gas is more dependent of a and b than on T . One would like to find a condition on a and b such that $P(v)$ experiences a gas-liquid phase transition. This might be found by requiring that, for some T , $\partial P/\partial v =$ and $\partial^2 P/\partial v^2 = 0$.

