PHY 540 **Statistical Mechanics** Spring 2007

Homework 07 with Solution

Problem 7.1. Get as many analytical results as you possibly can for the temperature dependence of the phase-equilibrium pressure $p_0(T)$ and the latent heat $\Lambda(T)$ within the van der Waals model. In particular, explore the low-temperature limit ($T << T_C$), and the close vicinity of the critical point $\{P_C, V_C, T_C\}$.

Solution:

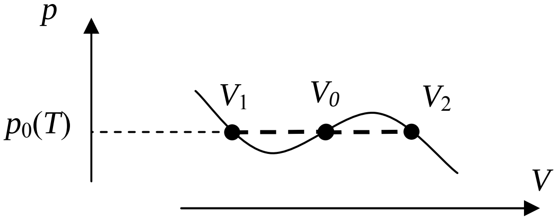
(a) $\boldsymbol{T \approx T_c}$. Let us expand the van der Waals function

$$p(V,T) = \frac{NT}{V - Nb} - a\frac{N^2}{V^2} \qquad (*)$$

into a Taylor series near the critical point

$$p_c = \frac{1}{27}\frac{a}{b^2}, \quad V_c = 3Nb, \quad T_c = \frac{8}{27}\frac{a}{b},$$

keeping only linear terms in T, but both the linear and cubic terms in V. (The last term is necessary to describe the hysteretic $V(p\,)$ dependence:



pertinent for the 1st order phase transitions. Using normalized variables

$$\tilde{p} \equiv \frac{p - p_c}{p_c}, \quad \tilde{v} \equiv \frac{V - V_c}{V_c}, \quad \tilde{t} \equiv \frac{T - T_c}{T_c},$$

the series has the form

$$\tilde{p} = 4\tilde{t} - 6\tilde{t}\tilde{v} - \frac{3}{2}\tilde{v}^3. \qquad (**)$$

Since this function is odd-symmetric in $\tilde{v}$, the phase equilibrium line $p = p_0(T)$ (the dashed line in Fig. above) passes through the point $\tilde{v} = 0$ (i.e. $V_0 = V_c$), and

$$\tilde{p}_0 = 4\tilde{t}, \quad \text{i.e.} \quad p_0(T) = p_c - 4p_c\frac{T_c - T}{T_c}.$$

Because of the same symmetry, the end points $V_{1,2}$ are on the equal distance from V_c:

$$V_2 - V_c = V_c - V_1 \equiv V_c\tilde{v}_0,$$

where according to Eq. (**), at $T < T_c$ ($\tilde{t} < 0$):

$$-6\tilde{t}\tilde{v}_0 - \frac{3}{2}\tilde{v}_0^3 = 0, \quad \text{i.e.} \quad \tilde{v}_0 = 2\sqrt{-\tilde{t}},$$

so that

$$V_2 - V_1 = 2V_c\tilde{v}_0 = 4V_c\left(\frac{T_c - T}{T_c}\right)^{1/2}.$$

Now using the Clapeyron-Clausius formula, for the latent heat (per one particle) we get

$$\Lambda(T) = \frac{T}{N}(V_2 - V_1)\frac{dp_0}{dT} \approx \frac{T_c}{N}4V_c\left(\frac{T_c - T}{T_c}\right)^{1/2} 4\frac{p_c}{T_c} = 16\frac{p_c V_c}{N}\left(1 - \frac{T}{T_c}\right)^{1/2}.$$

(b) ***T* << *T*$_c$**. Let us start with writing down Maxwell's equal-area rule for $p_0(T)$ in the following form:[1]

$$\int_{V_1}^{V_2}(p - p_0)dV = 0.$$

Plugging in the van der Waals equation (*) for p and integrating, we get the following relation (valid, so far, for any temperature)

$$NT\ln\frac{V_2 - Nb}{V_1 - Nb} + aN^2\left[\frac{1}{V_2} - \frac{1}{V_1}\right] = p_0(V_2 - V_1). \qquad (***)$$

In the limit $T \to 0$, $p_0(T)$ should tend to zero very fast, for the gas-phase Maxwell-rule area to be equal to the large liquid-phase area. (See, e.g., the numerical plot for $T/T_c = 0.3$ on the next page.) As a result, the gas-phase volume V_2 is much higher than not only the liquid-phase volume $V_1 \approx Nb$, but also the unstable-equilibrium volume $V_0 \sim aN/T >> Nb$ (at which both terms in the right-hand part of Eq. (*) are comparable). Hence for the definition of V_2 we can drop the terms with a and b in Eq. (*), so that V_2 is related to p_0 by the ideal gas law:

$$p_0 = \frac{NT}{V_2},$$

Also, the difference $V_1 - Nb$ is small and may be evaluated from Eq. (*) with $p \to 0$:

$$0 = \frac{NT}{V_1 - Nb} - a\frac{N^2}{(Nb)^2},$$

giving

$$V_1 = Nb + \frac{NTb^2}{a}.$$

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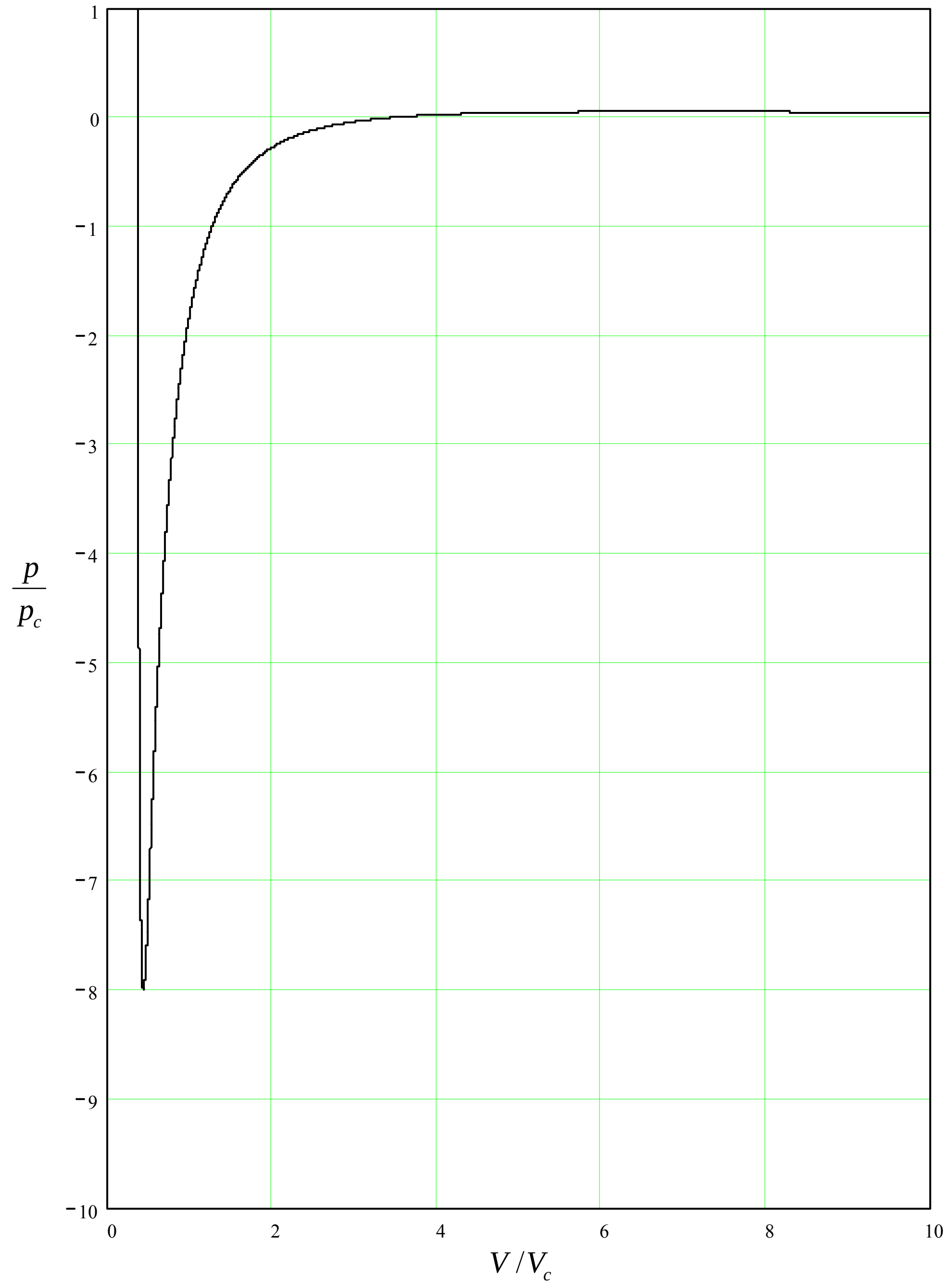
[1] In defining an area on a plane, the choice of integration direction is not important.



Plugging these relations into Eq. (***), we get a simple equation for V_2:

$$NT\ln\frac{aV_2}{NTb^2}-\frac{aN}{b}=NT,$$

which gives

$$V_2=\frac{NTb^2}{a}\exp\left\{\frac{a}{b}+1\right\}=\frac{NTb^2}{a}\exp\left\{\frac{27}{8}\frac{T_c}{T}+1\right\}\approx\frac{NTb^2}{a}\exp\left\{\frac{27}{8}\frac{T_c}{T}\right\}>>V_0,V_1,$$

thus justifying our assumptions. Finally, for the phase-equilibrium (the saturation vapor) pressure p_0 we get

$$p_0(T) = \frac{NT}{V_2} = \frac{a}{b^2}\exp\left\{-\frac{27}{8}\frac{T_c}{T}\right\} = 27\,p_c\exp\left\{-\frac{27}{8}\frac{T_c}{T}\right\} << p_c .$$

Note that the temperature dependence of p_0 follows the exponential "Arrhenius" law (with the activation energy $U = 27T_c/8$), in accordance with the basic physics of evaporation. (Physically, U is the molecular binding energy in the liquid phase.) It is amazing how well is this exponential law hidden inside the van der Waals equation of state (*).

Now, using the Clapeyron-Clausius law, for the latent heat of evaporation (per molecule) we get a temperature-independent value

$$\Lambda(T) = \frac{T}{N}\left(V_2 - V_1\right)\frac{dp_0}{dT} \to \frac{T}{N}\frac{NTb^2}{a}\frac{27}{8}\frac{T_c}{T^2} = \frac{27}{8}T_c = U,$$

which confirms the physical picture of evaporation, discussed in the last paragraph.