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Homework 1

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Statistical Physics

Contents

1 Critical exponent for the coexistence boundary

(a) Consider a thermodynamical system described by the a Helmotz free energy F depending on temperature T, volume V and particle number N. Pressure is related to T, V at fixed N with $P = -\frac{\partial F}{\partial V}\big|_{T,N} = f(T,V)$ where the function f forms a state equation. We assume the state equation is consistent with a second order phase transition at T_c, V_c, P_c (highest pressure inflexion point of P, V isotherms). Furthermore, in a P, V diagram, this point is taken to join the first order phase transition lines of liquid-coexistence and coexistence-gas transitions. These lines respectively mark the end of a lower volume liquid phase and higher volume gas phase at pressures $P < P_c$. For $P > P_c$ there is no distinction between the liquid and gas phases. In what follows, volume dependance is replaced by reduced volume $v = V/V_c$ and we also use reduced temperature $t = T/T_c$. We are interested in the behavior of the liquid-coexistence transition volume v_l and gas-coexistence transition volume v_g on $t \sim 1$ isotherms. We can express v_l and v_g with their respective deviation from $v = 1$ as $v_l = 1 - x$ and $v_g = 1 + y$ with $x, y \geq 0$ (only moving to sides of the coexistence region where pressure is smooth). Suposing x, y are small, we perform a reduced volume Taylor expansion of the pressure on an isotherm with temperature $T \sim T_c$ to write

$$P(T, v) = P(T, 1) + a(T)(v - 1) + b(T)(v - 1)^2 + c(T)(v - 1)^3 + O((v - 1)^4)$$

where $a(T), b(T) \neq 0$. The defining caracteristic of the transition lines is that their points at a given temperature have the same pressure and chemical potential μ. Expressing the chemical potential with the Gibbs free energy $G = \mu N$, we have

$$P(T, v_l) = P(T, v_g) \quad \& \quad \frac{G}{N}\bigg|_{T, v = v_l, N} = \frac{G}{N}\bigg|_{T, v = v_g, N}$$

where the pressure dependance of the Gibbs free energy is formally replaced with volume dependance using the state equation. Using the above taylor expansion truncated from $O((v - 1)^4)$, the pressure constraint reads

$$P(T, v_l) = P(T, 1) + a(T)(1 - x - 1) + b(T)(1 - x - 1)^2 + c(T)(1 - x - 1)^3$$
$$= P(T, 1) + a(T)(1 + y - 1) + b(T)(1 + y - 1)^2 + c(T)(1 + y - 1)^3 = P(T, v_g)$$
$$\iff 0 = a(T)(x + y) + b(T)(y^2 - x^2) + c(T)(y^3 + x^3). \tag{$\star$}$$

To relate chemical potential μ to pressure and volume, we use the fact temperature should not vary on the isotherms. At fixed N and T, the free energy differential reduces to $dG = V\,dP$. To ensure that the chamical potentials are the same at v_l and v_g, there has to be no change in G/N between those volumes. Integrating the change on an isotherm (the change in a thermodynamic potential between two points is path independant) yields

$$0 = \frac{G}{V_c N}\bigg|_{T, v = v_l, N} - \frac{G}{V_c N}\bigg|_{T, v = v_g, N} = \frac{1}{N}\int_{P(T, v_l)}^{P(T, v_g)} v\,dP$$
$$= \frac{1}{N}\int_{v_l}^{v_g} v\,\frac{\partial P}{\partial v}\bigg|_{T, N} dv = \frac{1}{N}[P(T, v)v]_{v_l}^{v_g} - \frac{1}{N}\int_{v_l}^{v_g} P(T, v)\,dv$$
$$= \frac{1}{N}\left[P(T, v)v - P(T, 1)v - \frac{1}{2}a(T)(v - 1)^2 - \frac{1}{3}b(T)(v - 1)^3 + O((v - 1)^4)\right]_{v_l}^{v_g}$$
$$\iff 0 = (P(T, 1) - P(T, 1))(v_g - v_l) + a(T)(x + y) + b(T)(y^2 - x^2) + c(T)(y^3 + x^3)$$
$$\quad - (a(T)(-x) + b(T)(-x)^2 + c(T)(-x)^3)(-x) + (a(T)y + b(T)y^2 + c(T)y^3)(+y) - \frac{1}{2}a(T)(y^2 - x^2) - \frac{1}{3}b(T)(y^3 + x^3)$$
$$= a(T)(x + y) + \left(b(T) + \frac{1}{2}a(T)\right)(y^2 - x^2) + \left(c(T) + \frac{2}{3}b(T)\right)(y^3 + x^3) \tag{$\star\star$}$$

where the integral was evaluated using the taylor expansion of P.

(b) Substracting ($\star$) from ($\star\star$), we get

$$0 = \frac{1}{2}a(T)(y^2 - x^2) + \frac{2}{3}b(T)(y^3 + x^3) \iff 0 = 3a(T)(y^2 - x^2) + 4b(T)(y^3 + x^3). \tag{$\star\star\star$}$$

We can now assume the deviation x, y for a fixed pressure can be related by a temperature dependant Taylor expansion of y in terms of x. To preserve the validity of our previous truncations, we need to have $y \propto x$ (x and y are close deviations) so that all the terms pushed beyond $O(x^3)$ stay truncated. A constant term in the expansion of y would shift terms from higher orders to our truncated expansion and ($\star\star\star$) would not hold. We can also conclude $y \propto x$ from the fact $x = 0 \implies y = 0$ since the two transition lines are joined at the critical point. Substituting $y = d(T)x + e(T)x^2 + f(T)x^3 + O(x^4)$ in a second order expansion in x of ($\star\star\star$) yields

$$0 = 3a(T)(d(T)^2 x^2 - x^2) \iff d(T) = \pm 1.$$

Since x being positive, we can find a neighborhood of $v = 1$ where the linear term in the expansion of y dominates and impose $d(T) = 1$. We finally have $y = x + O(x^2)$ which translates to $|v_g - 1| \sim |v_l - 1|$ for $t \to 0^-$.

2 | Dietrici equation of state

(a) To investigate the universality of critical exponents caracterising phase transitions, we consider the Dietrici equation of states

$$P(v-b) = kT \exp\left(-\frac{a}{kTv}\right), \quad a, b > 0$$

describing a gas with pressure P and volume v per particle at temperature T. Figure 1 represents caracteristic isotherms associated to this equation of states.
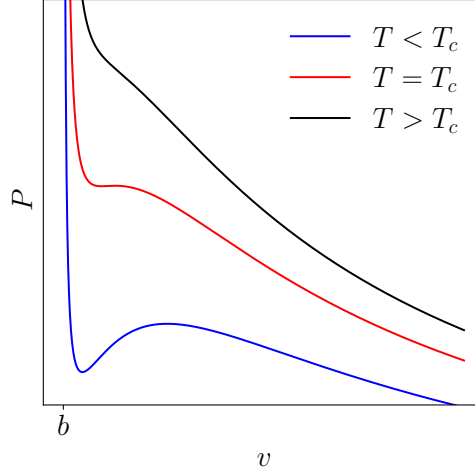

Figure 1: Sketch of the three types of isotherms found in the P, v diagram of the Dietrici equation of states. For $T = T_c$ is the temperature at which a signe vanishing derivative point apears in the isoterms (it is also an inflexion point). Higher temperatures have no such point and lower temperatures have two local extrema. Globally, these caracteristic are analogous to the isotherm structure of the Van der Waals equation of states.

The critical temperature T_c is the temperature at which an isotherm features an inflexion point. At this point, the two extremas for $P(v)$ for isotherms with $T < T_c$ are brought together and the first derivative of $P(v)$ has only one degenerate root. This implies that

$$0 = \left.\frac{\partial P}{\partial v}\right|_{T_c, v_c} = \frac{-T_c k v_c^2 - a(b - v_c)}{v_c^2 (b - v_c)^2} e^{-\frac{a}{T_c k v_c}} \quad \text{with degenerate root} \implies a^2 - 4T_c kab = 0 \quad \text{discriminant} \implies T_c = \frac{a}{4kb}$$

where the derivative was computed using the following sympy code

```
1  import sympy as sp
2
3  T, a, b, v, k = sp.symbols("T a b v k")
4
5  P = k * T * sp.exp(-a/(k * T * v))/(v-b)
6
7  del1P = sp.diff(P, v, 1).simplify()
```

Solving for the critical volume v_c yields

$$0 = -\frac{a}{4kb} k v_c^2 - a(b - v_c) \iff 0 = v_c^2 + 4b^2 - 4v_c b = (v_c - 2b)^2 \iff v_c = 2b.$$

The associated critical pressure is obtaiuned by substituting the expression for v_c and T_c in $P(v)$. We get

$$P_c = \frac{ka}{4k(2b - b)b} \exp\left(-\frac{4kab}{2kab}\right) = \frac{a}{4b^2} \exp(-2).$$

To simplify further calculations we reexpress the equation of states with reduced pressure volume $v_r = v/v_c$, $P_r = P/P_c$ and $T_r = T/T_c$.

$$P_r = \frac{P}{P_c} = \frac{kT}{b(2v_r - 1)} \exp\left(-\frac{2a}{4bkTv_r}\right) \frac{4b^2}{a} \exp(+2) = \frac{T_r}{2v_r - 1} \exp\left(2 - \frac{2}{T_r v_r}\right).$$

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(b) Around the critical volume $v_r = 1$ and we can do an of the expansion of the reduced volume $v_r = 1 + x$. The pressure associated to the deviation x on the $T_r = 1$ isotherm is given by

$$P_r = \frac{T_r}{2(1+x)-1} \exp\left(2 - \frac{2}{T_r(1+x)}\right) \approx 1 - \frac{2x^3}{3} + O\left(x^4\right).$$

which is expected because at the inflexion point the first and second derivatives vanish. The previous expansion was computed uing the following sympy code

```
1  import sympy as sp
2
3  vr, x = sp.symbols("vr x")
4
5  P = sp.exp(2−2/vr)/(2*vr − 1)
6  P = P.subs({vr:1+x}).series(x, 0, 4)
```

Using the previous expansion, we can solve for x as a function of P_r leading to

$$x = v_r - 1 = -\frac{3}{2}(P_r - 1)^{1/3} \sim (P_r - 1)^{1/\delta}$$

leading to the critical same critical exponent $\delta = 3$ as in the Van der Waals model. We this result to extract the γ critical exponent describing the scaling of isothermal compressibility k_T at $T_r = 1$ as a function of P_r. We have

$$k_T = -\frac{1}{v_r}\left(\frac{\partial v_r}{\partial P_r}\right) \approx \frac{-\frac{3}{6}(P_r-1)^{-2/3}}{-\frac{3}{2}(P_r-1)^{1/3}} = -\frac{-\frac{3}{6}(P_r-1)^{-2/3}}{-\frac{3}{2}(P_r-1)^{1/3}} = -\frac{1}{3}(P_r-1)^{-1} \sim (P_r-1)^{-\gamma}$$

which is consistent with $\gamma = 1$.

(c) Below the critical point, the temperature is expanded as $T_r = 1 - t$ with a small positive deviation t. At fixed pressure on the liquid-coexistence and coexistence-gas transition lines, the volumes are respectively v_l and v_g. These volumes are expanded around $v_r = 1$ as $v_l = 1 - x$ and $v_g = 1 + y$ with respective positive deviations x and y associated with a small temperature shift t. Form the calculations of question 1, we know that $y = x + cx^2 + O(x^3)$ [1] is required by equality of chemical potential, pressure and critical temperature deviation t. With this in mind, we can relate the shifts x and t with the pressure equality condition. It reads

$$P_r(v_l, T_r) = P_r(v_g, T_r) \implies P_r(1+x, 1+t) = P_r(1-x+cx^2+O(x^3), 1+t)$$

3 | Acknowledgement

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[1] The quadratic term weighted by c is considered here because it appears in a third order expansion in x of $P_r(v_g, T_r)$, but it doesn't affect the critical exponent we find