Problem and solution Huang Chapter 4 Introduction to Statistical Mechanics Masatsugu Sei Suzuki, SUNY at Binghamton (Date: November 10, 2019)

4.6 Sketch the Gibbs potential G(P, T) of the van der Waals gas as a function of P at constant T. In particular, show the behavior in the transition region. Derive the Maxwell construction using the principle of minimization of G

((Solution))

Maxwell construction for the pr vs vr phase diagram



Fig.1 The phase diagram of v_r vs p_r at $t_r = 0.96$.



Fig. Gibbs free energy at $t_r = 0.96$.

At $t_r = t_1$,

$$g(t_r = t_1, p_r) = g(t_1, p_a) + \int_{p_a}^{p} v_r(p_r, t_1) dp_r ,$$

We assume that $p_0 = p_e$ (the pressure at the point *e*). Then we have

$$g(t_r = t_1, p_e) = g(t_1, p_a) + \int_{abc} v_r(p_r, t_1) dp_r + \int_{cde} v_r(p_r, t_1) dp_r ,$$

Since $g(t_1, p_a) = g(t_1, p_e)$, we have

$$\int_{abc} v_r(p_r,t_1)dp_r + \int_{cde} v_r(p_r,t_1)dp_r = 0,$$

or

$$\int_{ed} v_r(p_r, t_1) dp_r + \int_{dc} v_r(p_r, t_1) dp_r = \int_{ab} v_r(p_r, t_1) dp_r + \int_{bc} v_r(p_r, t_1) dp_r \,.$$

We note that

$$\int_{ed} v_r(p_r, t_r) dp_1 > 0, \qquad \int_{dc} v_r(p_r, t_1) dp_r = -\int_{cd} v_r(p_r, t_1) dp_r$$

and

$$\int_{bc} v_r(p_r, t_1) dp_r > 0, \qquad \int_{ab} v_r(p_r, t_1) dp_r = -\int_{ba} v_r(p_r, t_1) dp_r .$$

Then we have

$$\int_{ed} v_r(p_r, t_1) dp_r - \int_{cd} v_r(p_r, t_1) dp_r = \int_{bc} v_r(p_r, t_1) dp_r - \int_{ba} v_r(p_r, t_1) dp_r \, dp_r \,$$

which means that the area of the region e-d-c is the same as that of the region a-b-c. Note that

$$p_a = p_c = p_e = p_1.$$

It is only after the nominal (non-monotonic) isotherm has been truncated by this equal area construction that it represents a true physical isotherm.

In summary, In the p_r vs v_r phase diagram,

- (i) The a-c-e- is the coexistence line ($p_r = p_1$ and $t_r = t_1$) of the liquid phase and the gas phase.
- (ii) The area (a-b-c-a) is the same as the area (c-d-e-c) [Maxwell construction].
- (iii) K is the critical point $(p_r = v_r = t_r = 1)$.
- (iv) The line KA and the line AB are the spinodal lines.

4.7

(a) Calculate the free energy *A*(*V*, *T*) for 1 mol of a van der Waals gas.

Hint: Integrate - 1 *PdV* along an isotherm. Determine the unknown additive function of *T* by requiring A(V, T) to approach that of an ideal gas as $V \rightarrow \infty$, given in Problem 3.2.

(b) Show that C_V of a van der Waals gas is a function of T only.

Hint: Use $C_V = -T(\partial^2 A/\partial T^2)_V$ (Problem 3.1). Show $(\partial C_V/\partial V)_T = 0$.

((Solution))

For ideal gas, the partition function is given by

$$Z_1 = n_Q V$$

so the free energy F is calculated as

$$F = -k_B T \ln(\frac{Z_1^N}{N!})$$

= $-k_B T (N \ln Z_1 - \ln N!)$
 $\approx -k_B T (N \ln Z_1 - N \ln N + N)$
= $-k_B T N [\ln(\frac{Z_1}{N}) + 1]$
= $-k_B T N [\ln(\frac{n_Q}{n}) + 1]$

where $n = \frac{N}{V}$, and n_Q is the quantum concentration;

$$n_{Q} = \left(\frac{mk_{B}T}{2\pi\hbar^{2}}\right)^{3/2} = \left[\frac{mk_{B}T}{2\pi\frac{h^{2}}{4\pi^{2}}}\right]^{3/2} = \left[\frac{2\pi mk_{B}T}{h^{2}}\right]^{3/2} = \frac{\left(2\pi mk_{B}T\right)^{3/2}}{h^{3}},$$

where *m* is a mass of atom.

$$f = \frac{F}{N} = -k_B T \{ \ln[n_Q(v-b)] + 1 \} - \frac{a}{v}$$
$$= -k_B T \ln(v-b) - \frac{a}{v} - k_B T [\ln(n_Q) + 1]$$
$$= -k_B T \ln(v-b) - \frac{a}{v} + \Phi(T)$$

where

$$\Phi(T) = -k_B T [\ln(n_Q) + 1]$$

= $-k_B T \{\ln[\frac{(2\pi n k_B T)^{3/2}}{h^3}] + 1\}$
= $-k_B T \{\ln T^{3/2} + \ln \frac{(2\pi n k_B)^{3/2}}{h^3} + 1\}$
= $-k_B T (\ln T^{3/2} + \ln \alpha + 1)$
= $-k_B T (\frac{3}{2} \ln T + \ln \alpha + 1)$

with the constant α

$$\alpha = \frac{\left(2\pi m k_B\right)^{3/2}}{h^3}$$

In summary the Helmholtz free energy is obtained as

$$f = -\frac{a}{v} - k_B T [\ln(v-b) + \frac{3}{2} \ln T + \ln \alpha + 1].$$

The pressure P is obtained as

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial f}{\partial v}\right)_{T,N} = \frac{k_B T}{v - b} - \frac{a}{v^2},$$

or more simply,

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

or

$$P = -\frac{a}{v^2} + \frac{k_B T}{v - b}.$$

Since $v = \frac{V}{N}$, the above van der Waals equation can be rewritten as

$$(P+\frac{N^2a}{V^2})(V-bN)=Nk_BT.$$

(b) The heat capacity

$$\frac{C_V}{N} = -T \left(\frac{\partial^2 f}{\partial T^2} \right)_V = \frac{3k_B}{2}, \quad \text{which is constant.}$$

or

$$C_V = \frac{3Nk_B}{2}$$

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