PHYSICS 140A : STATISTICAL PHYSICS
HW SOLUTIONS #3

(1) The entropy for a peculiar thermodynamic system has the form

$$S(E,V,N) = N k_B \left\{ \left(\frac{E}{N\varepsilon_0}\right)^{1/3} + \left(\frac{V}{N v_0}\right)^{1/2} \right\} ,$$

where ε_0 and v_0 are constants with dimensions of energy and volume, respectively.

(a) Find the equation of state $p = p(T,V,N)$.

(b) Find the work done along an isotherm in the (V,p) plane between points A and B in terms of the temperature T, the number of particles N, and the pressures p_A and p_B.

(c) Find $\mu(T,p)$.

Solution :

(a) We have

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{k_B T}{2v_0}\left(\frac{V}{N v_0}\right)^{-1/2} .$$

We use the result of part (a) to obtain

$$W_{AB} = \int_A^B p\, dV = N k_B T \left(\frac{V}{N v_0}\right)^{1/2} \Bigg|_A^B = \frac{N (k_B T)^2}{2v_0}\left(\frac{1}{p_B} - \frac{1}{p_A}\right) .$$

We have

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\tfrac{2}{3} k_B T \left(\frac{E}{N\varepsilon_0}\right)^{1/3} - \tfrac{1}{2} k_B T \left(\frac{V}{N v_0}\right)^{1/2} .$$

The temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{k_B}{3\varepsilon_0}\left(\frac{E}{N\varepsilon_0}\right)^{-2/3} .$$

Thus, using

$$\frac{E}{N\varepsilon_0} = \left(\frac{k_B T}{3\varepsilon_0}\right)^{3/2} \quad , \quad \frac{V}{N v_0} = \left(\frac{k_B T}{2p\, v_0}\right)^2 ,$$

we obtain

$$\mu(T,p) = -\frac{2(k_B T)^{3/2}}{3\sqrt{3}\,\varepsilon_0^{1/2}} - \frac{(k_B T)^2}{4 p v_0} .$$

(2) The Dieterici equation of state is

$$p\,(v-b) = RT\,e^{-a/vRT} \quad ,$$

with v the molar volume and with a and b constants.

(a) Wha are the dimensions of a and b?

(b) Find the coefficient of isobaric volume expansion, $\alpha_p = v^{-1}(\partial v/\partial T)_p$

(c) Find the conditions for the inversion temperature of throttling, $T\alpha_p = 1$ in terms of T and v.

(d) Define the temperature and pressure scales $RT_0 \equiv 2a/b$ and $p_0 \equiv 2a/b^2$. Define also the dimensionless temperature $\tau \equiv T/T_0$ and dimensionless pressure $\pi \equiv p/p_0$. Find and sketch the inversion curve $\pi(\tau)$.

Solution :

(a) Since $[R] = \text{J/mol}\cdot\text{K}$ and $[v] = \text{L/mol}$, we have $[a] = \text{L}\cdot\text{J/mol}^2$ or $\text{L}^2\,\text{bar/mol}$. Then $[b] = \text{L/mol}$.

(b) From

$$p = \frac{RT}{v-b}\,e^{-a/vRT}$$

we have

$$\begin{aligned} dp &= \left\{\left[\frac{R}{v-b} + \frac{RT}{v-b}\cdot\frac{a}{vRT^2}\right]dT + \left[-\frac{RT}{(v-b)^2} + \frac{RT}{v-b}\cdot\frac{a}{v^2RT}\right]dv\right\}e^{-a/vRT} \\ &= \frac{a+vRT}{v(v-b)T}\,dT + \frac{v^2RT - a(v-b)}{v^2(v-b)^2}\,dv \quad . \end{aligned}$$

Set $dp = 0$ to obtain

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T}\cdot\frac{(a+vRT)(v-b)}{v^2RT - a(v-b)} \quad .$$

(c) After some algebra, the equation for the inversion temperature, $T\alpha_p = 1$, yields the simple expression

$$RT = \frac{2a}{b}\cdot\frac{v-b}{v} \quad .$$

(d) With the definition $RT_0 = 2a/b$ and $\tau \equiv T/T_0$, we have $\tau = 1 - u^{-1}$, where $u \equiv v/b$. We also have, from the equation of state,

$$\pi = \frac{p}{p_0} = \frac{RTb^2/2a}{v-b}\,e^{-1/vRT} = \frac{\tau}{u-1}\,e^{-1/2u\tau} \quad ,$$

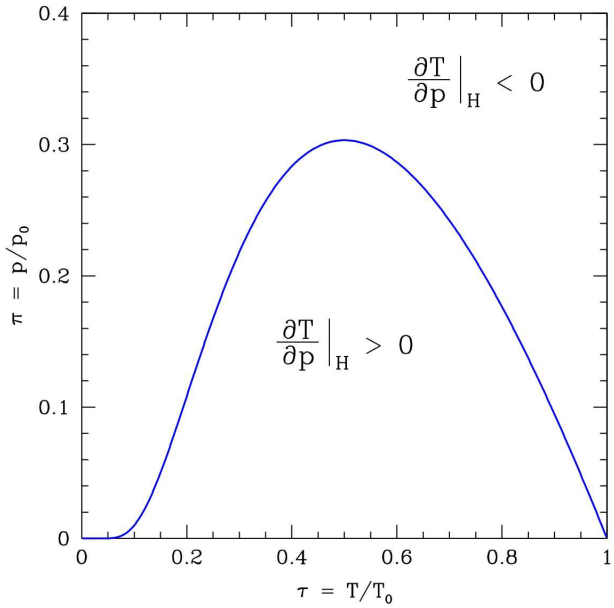

Figure 1: Inversion temperature *versus* pressure (dimensionless) for the Dieterici equation of state.

and with $u^{-1} = 1 - \tau$, we have $\tau/(u-1) = 1 - \tau$, and thus

$$\pi(\tau) = (1-\tau)\exp\Big[-\tfrac{1}{2}\big(\tau^{-1} - 1\big)\Big] \quad .$$

(3) Consider the analog of the van der Waals equation of state for a gas if diatomic particles with *repulsive* long-ranged interactions,

$$p = \frac{RT}{v-b} + \frac{a}{v^2} \quad ,$$

where v is the molar volume.

(a) Find the molar energy $\varepsilon(T, v)$.

(b) Find the coefficient of volume expansion $\alpha_p = v^{-1}(\partial v/\partial T)_p$ as a function of v and T.

(c) Find the adiabatic equation of state in terms of v and T. If at temperature T_1 a volume $v_1 = 3b$ of particles undergoes reversible adiabatic expansion to a volume $v_2 = 5b$, what is the final temperature T_2?

Solution :

(a) We have

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad ,$$

where we have invoked a Maxwell relation based on $dF = -S\,dT - p\,dV$, we have

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = -\frac{a}{v^2} \quad ,$$

whence $\varepsilon(T,v) = \omega(T) + \frac{a}{v}$. In the $v \to \infty$ limit, we recover the diatomic ideal gas, hence $\omega(T) = \frac{5}{2}RT$ and

$$\varepsilon(T,v) = \tfrac{5}{2}RT + \frac{a}{v} \quad .$$

(b) To find α_p, set $dp = 0$, where

$$dp = \frac{R}{v-b}\,dT - \left[\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right] dv \quad .$$

We then have

$$\alpha_p(T,v) = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{R(v-b)v^2}{RTv^3 + 2a(v-b)^2} \quad .$$

Note that we recover the ideal gas value $\alpha_p = T^{-1}$ in the $v \to \infty$ limit. We may also evaluate the isothermal compressibility,

$$\kappa_T(T,v) = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{(v-b)^2 v^2}{RTv^3 + 2a(v-b)^2} \quad .$$

In the limit $v \to \infty$, we have $\kappa_T = v/RT$. Since $pv = RT$ in this limit, $\kappa_T(T, v \to \infty) = 1/p$, which is the ideal gas result.

(c) Let $s = N_A S/N$ be the molar entropy. Then

$$\begin{aligned} ds &= \frac{1}{T}\,d\varepsilon + \frac{p}{T}\,dv \\ &= \tfrac{1}{2} f R\,\frac{dT}{T} + \left(\frac{R}{v-b}\right) dv \\ &= d\left[\tfrac{1}{2} f R \ln T + R\ln(v-b)\right] \quad . \end{aligned}$$

Writing $-a/TV = R\ln\exp(-a/RTv)$, we have that the adiabatic equation of state is

$$(v-b)\,T^{f/2} = \text{constant} \quad .$$

Thus, an adiabatic free expansion from v_1 to v_2 entails

$$(v_1 - b)\,T_1^{f/2} = (v_2 - b)\,T_2^{f/2} \quad .$$

Substituting in $v_1 = 3b$ and $v_2 = 5b$ results in

$$T_2 = \left(\frac{v_1 - b}{v_2 - b}\right)^{2/f} T_1 = 2^{-2/5}\,T_{\mathrm{f}} \quad .$$

(My original solution was correct!)