2 Thermodynamics : Worked Examples

(2.1) ν moles of an ideal diatomic gas are driven along the cycle depicted in Fig. 1. Section AB is an adiabatic free expansion; section BC is an isotherm at temperature $T_A = T_B = T_C$; CD is an isobar, and DA is an isochore. The volume at B is given by $V_B = (1 - x) V_A + x V_C$, where $0 \leq x \leq 1$.

(a) Find an expression for the total work W_{cycle} in terms of ν, T_A, V_A, V_C, and x.

(b) Suppose $V_A = 1.0 \, \text{L}$, $V_C = 5.0 \, \text{L}$, $T_A = 500 \, \text{K}$, and $\nu = 5$. What is the volume V_B such that $W_{\text{cycle}} = 0$?

Solution :

(a) We have $W_{AB} = W_{DA} = 0$, and

$$W_{BC} = \int_B^C p \, dV = \nu R T_A \int_B^C \frac{dV}{V} = \nu R T_A \ln\left(\frac{V_C}{V_B}\right)$$

$$W_{CD} = \int_C^D p \, dV = p_C(V_D - V_C) = -\nu R T_A\left(1 - \frac{V_A}{V_C}\right) \quad .$$

Thus,

$$W_{\text{CYC}} = \nu R T_A\left[\ln\left(\frac{V_C}{V_B}\right) - 1 + \frac{V_A}{V_C}\right] \quad .$$

(b) Setting $V_B = (1 - x) V_A + x V_C$, and defining $r \equiv V_A/V_C$, we have

$$W_{\text{CYC}} = \nu R T_A\left(- \ln\left(x + (1 - x)\, r\right) + 1 - r\right) \quad ,$$

and setting $W_{\text{CYC}} = 0$ we obtain $x = x^*$, with

$$x^* = \frac{e^{r-1} - r}{1 - r} \quad .$$

For $V_A = 1.0 \, \text{L}$ and $V_C = 5.0 \, \text{L}$, we have $r = \frac{1}{5}$ and $x^* = 0.31$, corresponding to $V_B = 2.2 \, \text{L}$.
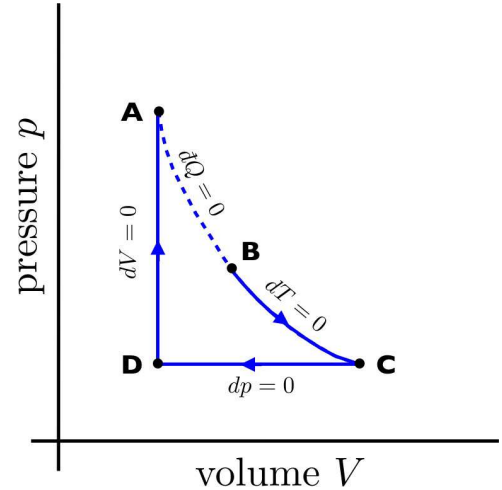

Figure 1: Engine cycle for problem 1, consisting of adiabatic free expansion (AB), isotherm (BC), isobar (CD), and isochore (DA).

(2.2) A strange material obeys the equation of state $E(S, V, N) = a\, S^7/V^4 N^2$, where a is a dimensionful constant.

(a) What are the SI dimensions of a?

(b) Find the equation of state relating p, T, and $n = N/V$.

(c) Find the coefficient of thermal expansion $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$. Express your answers in terms of p and T.

(d) ν moles of this material execute a Carnot cycle between reservoirs at temperatures T_1 and T_2. Find the heat Q and work W for each leg of the cycle, and find the cycle efficiency η.

Solution :

(a) Clearly $[a] = \mathrm{K}^7\, \mathrm{m}^{12}/\mathrm{J}^6$ where K are Kelvins, m are meters, and J are Joules.

(b) We have

$$T = +\left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{7aS^6}{N^2 V^4}$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{4aS^7}{N^2 V^5} \quad .$$

We must eliminate S. Dividing the second of these equations by the first, we find $S = 7pV/4T$, and substituting this into either equation, we obtain the equation of state,

$$p = c \cdot \left(\frac{N}{V}\right)^{1/3} T^{7/6} \quad ,$$

with $c = \frac{6}{7^{7/6}} a^{-1/6}$.

Figure 2: The Carnot cycle.

(c) Taking the logarithm and then the differential of the above equation of state, we have

$$\frac{dp}{p} + \frac{dV}{3V} - \frac{7\, dT}{6T} - \frac{dN}{3N} = 0 \quad .$$

Thus,

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{7}{2T} \quad , \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{3}{p} \quad .$$

(d) From the results of part (b), we have that $dS = 0$ means $d(N^2 V^4 T) = 0$, so with N constant the equation for adiabats is $d(TV^4) = 0$. Thus, for the Carnot cycle of Fig. 2, we have

$$T_2\, V_\mathsf{A}^4 = T_1\, V_\mathsf{D}^4 \quad , \qquad T_2\, V_\mathsf{B}^4 = T_1\, V_\mathsf{C}^4 \quad .$$

We shall use this relation in due time. Another relation we shall use is obtained by dividing out the S^7 factor common in the expressions for E and for p, then substituting for p using the equation of state:

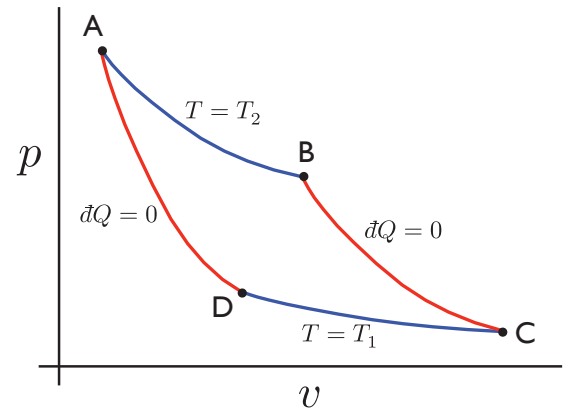$$E = \tfrac{1}{4}pV = \tfrac{1}{4}c\, N^{1/3}\, V^{2/3}\, T^{7/6} \quad .$$

AB: Consider the AB leg of the Carnot cycle. We use the equation of state along the isotherm to find

$$W_{AB} = \int_{V_A}^{V_B} dV \, p = \tfrac{3}{2} c \, N^{1/3} \, T_2^{7/6} \big(V_B^{2/3} - V_A^{2/3} \big) \quad .$$

Since E depends on volume, unlike the case of the ideal gas, there is a change in energy along this leg:

$$(\Delta E)_{AB} = E_B - E_A = \tfrac{1}{4} c \, N^{1/3} \, T_2^{7/6} \big(V_B^{2/3} - V_A^{2/3} \big) \quad .$$

Finally, the heat absorbed by the engine material during this leg is

$$Q_{AB} = (\Delta E)_{AB} + W_{AB} = \tfrac{7}{4} c \, N^{1/3} \, T_2^{7/6} \big(V_B^{2/3} - V_A^{2/3} \big) \quad .$$

BC: Next, consider the BC leg. Clearly $Q_{BC} = 0$ since BC is an adiabat. Thus,

$$W_{BC} = -(\Delta E)_{BC} = E_B - E_C = \tfrac{1}{4} c \, N^{1/3} \big(T_2^{7/6} \, V_B^{2/3} - T_1^{7/6} \, V_C^{2/3} \big) \quad .$$

But the fact that BC is an adiabat guarantees $V_C^{2/3} = (T_2/T_1)^{1/6} \, V_B^{2/3}$, hence

$$W_{BC} = \tfrac{1}{4} c \, N^{1/3} \, V_B^{2/3} \, T_2^{1/6} (T_2 - T_1) \quad .$$

CD: For the CD leg, we can apply the results from AB, *mutatis mutandis*. Thus,

$$W_{CD} = \tfrac{3}{2} c \, N^{1/3} \, T_2^{7/6} \big(V_D^{2/3} - V_C^{2/3} \big) \quad .$$

We now use the adiabat conditions $V_C^{2/3} = (T_2/T_1)^{1/6} \, V_B^{2/3}$ and $V_D^{2/3} = (T_2/T_1)^{1/6} \, V_A^{2/3}$ to write W_{CD} as

$$W_{CD} = \tfrac{3}{2} c \, N^{1/3} \, T_1 \, T_2^{1/6} \big(V_A^{2/3} - V_B^{2/3} \big) \quad .$$

We therefore have

$$Q_{CD} = \tfrac{7}{4} c \, N^{1/3} \, T_1 \, T_2^{1/6} \big(V_A^{2/3} - V_B^{2/3} \big) \quad .$$

Note that both W_{CD} and Q_{CD} are negative.

DA: We apply the results from the BC leg, *mutatis mutandis*, and invoke the adiabat conditions. We find $Q_{DA} = 0$ and

$$W_{DA} = \tfrac{1}{4} c \, N^{1/3} \, V_A^{2/3} \, T_2^{1/6} (T_2 - T_1) \quad .$$

For the cycle, we therefore have

$$W_{cyc} = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \tfrac{7}{4} c \, N^{1/3} \, T_2^{1/6} (T_2 - T_1) \big(V_B^{2/3} - V_A^{2/3} \big) \quad .$$

and thus

$$\eta = \frac{W_{cyc}}{Q_{AB}} = 1 - \frac{T_1}{T_2} \quad .$$

This is the same result as for an ideal gas, as must be the case as per the Second Law of Thermodynamics.

(2.3) For each of the following situations, explain clearly and fully why it is or is not thermodynamically possible.

(a) Energy function $E(S, V, N) = a\,S\,V\,N$ with a constant.

(b) Equation of state $V = a\,N\,p\,T$ with a constant.

(c) A system where $\left(\frac{\partial V}{\partial T}\right)_{p,N} < 0$ over some range of T and p.

(d) The phase diagram for a single component system depicted in Fig. 3 (left panel). (You only need know that a superfluid is a distinct thermodynamic phase.)

(e) The phase diagram for a single component system in Fig. 3 (right panel). (You only need know that BCC, HCP, and FCC solids are distinct phases.)

(f) $E(S, V, N) = a\,N^2\,V^{-1}\,\exp(S/Nb)$ with a and b constant.

(g) 15 Joules of heat energy are required to raise the temperature of a system by $\Delta T = 1°C$ at constant volume. 10 Joules of heat energy are required to raise the temperature of the same system by $\Delta T = 1°F$ at constant pressure.

(h) A heat engine operating between reservoirs at temperatures $T_1 = 400\,K$ and $T_2 = 600\,K$. During each cycle, the engine does work $W = 300\,J$ and the entropy of the upper reservoir decreases by $2.00\,J/K$.
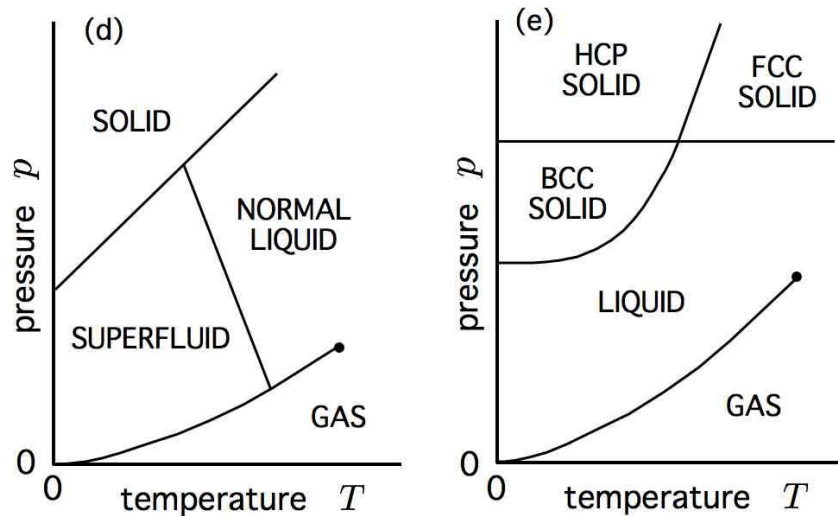

Figure 3: Phase diagrams for parts (d) and (e) of problem 3.

Solution :

(a) No! $E(\lambda S, \lambda V, \lambda N) = \lambda^3 E(S, V, N)$ is homogeneous of degree 3 – not extensive.

(b) No! The isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -1/p$ is negative, which violates $\kappa_T > \kappa_S > 0$.

(c) Yes! Many systems, such as water, contract upon a temperature increase over some range of temperature.

(d) No! This one is tricky. From the Clapeyron equation, we have $\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{\Delta s}{\Delta v}$. Nernst's law says that the entropy of both the solid and superfluid phases must vanish at $T = 0$. Therefore all coexistence curves which intersect the pressure axis at $T = 0$ must do so with zero slope.

4

(e) No! The Gibbs phase rule $d = 2 + \sigma - \varphi$ gives the dimension of thermodynamic space over which φ distinct phases among σ species can coexist. For $\sigma = 1$ we have $\varphi \leq 3$, since $d \geq 0$. So four phase coexistence with a single component is impossible.

(f) Yes! E is properly extensive and convex. One can derive $E = pV = NbT$, which is the ideal gas law with k_{B} replaced by b.

(d) Yes! The heat capacity at constant volume is $C_V = \left(\frac{dQ}{dT}\right)_V = 15\,\mathrm{J/K}$. The heat capacity at constant pressure is $C_p = \left(\frac{dQ}{dT}\right)_p = 10\,\mathrm{J}/\frac{5}{9}\mathrm{K} = 18\,\mathrm{J/K}$. Stability requires $C_p > C_V$, which is satisfied.

(h) Yes! The only possible obstacle here is whether the engine's efficiency is greater than that of the corresponding Carnot cycle, for which $\eta_{\mathrm{C}} = 1 - \frac{T_1}{T_2} = \frac{1}{3}$. We have $\eta = \frac{W}{Q_2}$ and $\Delta S_2 = -\frac{Q_2}{T_2}$. Thus, $\eta = W/\left[T_2(-\Delta S_2)\right] = 300\,\mathrm{J}/\left[(600\,\mathrm{K})(2.00\,\mathrm{J/K})\right] = \frac{1}{4} < \eta_{\mathrm{C}}$.

(2.4) Using the chain rule from multivariable calculus (see §2.17 of the lecture notes), solve the following:

(a) Find $(\partial N / \partial T)_{S,p}$ in terms of T, N, S, and $C_{p,N}$.

(b) Experimentalists can measure $C_{V,N}$ but for many problems it is theoretically easier to work in the grand canonical ensemble, whose natural variables are (T, V, μ). Show that

$$C_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,z} - \left(\frac{\partial E}{\partial z} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,z} \bigg/ \left(\frac{\partial N}{\partial z} \right)_{T,V} \quad ,$$

where $z = \exp(\mu / k_{\mathrm{B}} T)$ is the fugacity.

Solution :

(a) We have

$$\left(\frac{\partial N}{\partial T} \right)_{S,p} = \frac{\partial(N,S,p)}{\partial(T,S,p)} = \frac{\partial(N,S,p)}{\partial(N,T,p)} \cdot \frac{\partial(N,T,p)}{\partial(T,S,p)} = -\frac{N C_{p,N}}{TS} \quad .$$

(b) Using the chain rule,

$$\begin{aligned}
C_{V,N} &= \frac{\partial(E,V,N)}{\partial(T,V,N)} = \frac{\partial(E,V,N)}{\partial(T,V,z)} \cdot \frac{\partial(T,V,z)}{\partial(T,V,N)} \\
&= \left[\left(\frac{\partial E}{\partial T} \right)_{V,z} \left(\frac{\partial N}{\partial z} \right)_{T,V} - \left(\frac{\partial E}{\partial z} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,z} \right] \cdot \left(\frac{\partial z}{\partial N} \right)_{T,V} \\
&= \left(\frac{\partial E}{\partial T} \right)_{V,z} - \left(\frac{\partial E}{\partial z} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,z} \bigg/ \left(\frac{\partial N}{\partial z} \right)_{T,V} \quad .
\end{aligned}$$

(2.5) The entropy of a thermodynamic system $S(E, V, N)$ is given by

$$S(E, V, N) = r\, E^\alpha\, V^\beta\, N^\gamma \quad ,$$

where r is a dimensionful constant.

(a) Extensivity of S imposes a condition on (α, β, γ). Find this constraint.

(b) Even with the extensivity condition satisfied, the system may violate one or more stability criteria. Find the general conditions on (α, β, γ) which are thermodynamically permissible.

Solution :

(a) Clearly we must have $\alpha + \beta + \gamma = 1$ in order for S to be extensive.

(b) The Hessian is

$$Q = \frac{\partial^2 S}{\partial X_i\, \partial X_j} = \begin{pmatrix} \alpha(\alpha - 1)\, S/E^2 & \alpha\beta\, S/EV & \alpha\gamma\, S/EN \\ \alpha\beta\, S/EV & \beta(\beta - 1)\, S/V^2 & \beta\gamma\, S/VN \\ \alpha\gamma\, S/EN & \beta\gamma\, S/VN & \gamma(\gamma - 1)\, S/N^2 \end{pmatrix} \quad .$$

As shown in the notes, for any 2×2 submatrix of Q, obtained by eliminating a single row and its corresponding column, and written $\begin{pmatrix} a & b \\ b & c \end{pmatrix}$, we must have $a < 0$, $c < 0$, and $ac > b^2$. For example, if we take the upper left 2×2 submatrix, obtained by eliminating the third row and third column of Q, we have $a = \alpha(\alpha-1)S/E^2$, $b = \alpha\beta\, S/EV$, and $c = \beta(\beta - 1)S/V^2$. The condition $a < 0$ requires $\alpha \in (0, 1)$. Similarly, $b < 0$ requires $\beta \in (0, 1)$. Finally, $ac > b^2$ requires $\alpha + \beta < 1$. Since $\alpha + \beta + \gamma = 1$, this last condition requires $\gamma > 0$. Obviously we must have $\gamma < 1$ as well, else either α or β would have to be negative. An examination of either of the other two submatrices yields the same conclusions. Thus,

$$\alpha \in (0, 1) \qquad , \qquad \beta \in (0, 1) \qquad , \qquad \gamma \in (0, 1) \quad .$$

(2.6) Consider the equation of state,

$$p = \frac{R^2 T^2}{a + vRT} \quad,$$

where $v = N_{\mathrm{A}} V/N$ is the molar volume and a is a constant.

(a) Find an expression for the molar energy $\varepsilon(T, v)$. Assume that in the limit $v \to \infty$, where the ideal gas law $pv = RT$ holds, that the gas is ideal with $\varepsilon(v \to \infty, T) = \frac{1}{2} f RT$.

(b) Find the molar specific heat $c_{V,N}$.

Solution :

(a) We fix N throughout the analysis. As shown in §2.11.2 of the lecture notes,

$$\left(\frac{\partial E}{\partial V} \right)_{T,N} = T \left(\frac{\partial p}{\partial T} \right)_{V,N} - p \quad.$$

Defining the molar energy $\varepsilon = E/\nu = N_{\mathrm{A}} E/N$ and the molar volume $v = V/\nu = N_{\mathrm{A}} V/N$, we can write the above equation as

$$\left(\frac{\partial \varepsilon}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p = p \left[\left(\frac{\partial \ln p}{\partial \ln T} \right)_v - 1 \right] \quad.$$

Now from the equation of state, we have

$$\ln p = 2 \ln T - \ln(a + vRT) + 2 \ln R \quad,$$

hence

$$\left(\frac{\partial \ln p}{\partial \ln T} \right)_v = 2 - \frac{vRT}{a + vRT} \quad.$$

Plugging this into our formula for $\left(\frac{\partial \varepsilon}{\partial v} \right)_T$, we have

$$\left(\frac{\partial \varepsilon}{\partial v} \right)_T = \frac{a\, p}{a + vRT} = \frac{aR^2 T^2}{(a + vRT)^2} \quad.$$

Now we integrate with respect to v at fixed T, using the method of partial fractions. After some grinding, we arrive at

$$\varepsilon(T, v) = \omega(T) - \frac{aRT}{(a + vRT)} \quad.$$

In the limit $v \to \infty$, the second term on the RHS tends to zero. This is the ideal gas limit, hence we must have $\omega(T) = \frac{1}{2} f RT$, where $f = 3$ for a monatomic gas, $f = 5$ for diatomic, *etc.* Thus,

$$\varepsilon(T, v) = \frac{1}{2} f RT - \frac{aRT}{a + vRT} = \frac{1}{2} f RT - \frac{a}{v} + \frac{a^2}{v(a + vRT)} \quad.$$

(b) To find the molar specific heat, we compute

$$c_{V,N} = \left(\frac{\partial \varepsilon}{\partial T} \right)_v = \frac{1}{2} f R - \frac{a^2 R}{(a + vRT)^2} \quad.$$

(2.7) A diatomic gas obeys the equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^2} + \frac{cRT}{v^3} \quad,$$

where a, b, and c are constants.

   (a) Find the adiabatic equation of state relating temperature T and molar volume v.

   (b) What is the internal energy per mole, $\varepsilon(T,v)$?

   (c) What is the Helmholtz free energy per mole, $f(T,v)$?

Solution :

(a) Let ε be the molar internal energy and v the molar volume. We have already shown (see Lecture Notes, §2.11.2)

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

Thus, for our system,

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = \frac{a}{v^2} \quad\Rightarrow\quad \varepsilon(T,v) = \tfrac{5}{2}RT - \frac{a}{v} \quad,$$

where the first term is the result for the rarefied limit $v \to \infty$, where the gas presumably becomes ideal. Now if $s = S/\nu$ is the molar entropy ($\nu = N/N_\mathsf{A}$ is the number of moles), then

$$T\,ds = d\varepsilon + p\,dv = \tfrac{5}{2}R\,dT + RT\,\frac{dv}{v-b} + cRT\,\frac{dv}{v^3} \quad.$$

Dividing by T and then integrating, we have

$$s(T,v) = R\ln\left[T^{5/2}(v-b)\,e^{-c/2v^2}\right] + \text{const.} \quad.$$

Thus, the equation of the adiabat is

$$T^{5/2}(v-b)\,e^{-c/2v^2} = \text{const.}$$

(b) We have already obtained the result

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

(c) From $f = \varepsilon - Ts$, where $f = F/\nu$ is the Helmholtz free energy per mole, we have

$$f(T,v) = \tfrac{5}{2}RT - \frac{a}{v} - \tfrac{5}{2}RT\ln\left(\frac{bRT}{a}\right) - RT\ln\left(\frac{v-b}{b}\right) + \frac{cRT}{2v^2} - Ts_0 \quad.$$

Here we have inserted constants with the proper dimensions in order to render our expression for f with the appropriate dimensions. Thus, the constant s_0 has dimensions of $\mathrm{J/mol \cdot K}$, the same as the gas constant R. Since c/b^2 is dimensionless, there is more than one way to do this. Any resulting differences will show up in a different expression for s_0.

(2.8) A van der Waals gas undergoes an adiabatic free expansion from initial volume V_i to final volume V_f. The equation of state is given in §2.11.3 of the lecture notes. The number of particles N is held constant.

   (a) If the initial temperature is T_i, what is the final temperature T_f?

   (b) Find an expression for the change in entropy ΔS of the gas.

(a) This part is done for you in §2.10.5 of the notes. One finds

$$\Delta T = T_f - T_i = \frac{2a}{fR}\left(\frac{1}{v_f} - \frac{1}{v_i}\right) \quad .$$

(b) Consider a two-legged thermodynamic path, consisting first of a straight leg from (T_i, V_i) to (T_i, V_f), and second of a straight leg from (T_i, V_f) to (T_f, V_f). We then have

$$\Delta S = \overbrace{\int_{V_i}^{V_f} dV \left(\frac{\partial S}{\partial V}\right)_{T_i,N}}^{\Delta S_1} + \overbrace{\int_{T_i}^{T_f} dT \left(\frac{\partial S}{\partial T}\right)_{V_f,N}}^{\Delta S_2} \quad .$$

Along the first leg we use

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{R}{v - b}$$

and we then find

$$\Delta S_1 = R\ln\left(\frac{v_f - b}{v_i - b}\right) \quad .$$

Along the second leg, we have

$$\Delta S_2 = \int_{T_i}^{T_f} dT \left(\frac{\partial S}{\partial T}\right)_{V_f,N} = \int_{T_i}^{T_f} dT \frac{C_{V_f,N}}{T} = \tfrac{1}{2}fR\int_{T_i}^{T_f}\frac{dT}{T} = \tfrac{1}{2}fR\ln\left(\frac{T_f}{T_i}\right) \quad .$$

Thus,

$$\Delta S = R\ln\left(\frac{v_f - b}{v_i - b}\right) + \tfrac{1}{2}fR\ln\left[1 + \frac{2a}{fRT_i}\left(\frac{1}{v_f} - \frac{1}{v_i}\right)\right] \quad .$$

(2.9) Recall that a van der Waals gas obeys the equation of state

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

where v is the molar volume. We showed that the energy per mole of such a gas is given by

$$\varepsilon(T, v) = \tfrac{1}{2}fRT - \frac{a}{v} \quad,$$

where T is temperature and f is the number of degrees of freedom per particle.

(a) For an ideal gas, the adiabatic equation of state is $v\, T^{f/2} = \text{const.}$ Find the adiabatic equation of state (at fixed particle number) for the van der Waals gas.

(b) One mole of a van der Waals gas is used as the working substance in a Carnot engine (see Fig. 1). Find the molar volume at v_C in terms of v_B, T_1, T_2, and constants.

(c) Find the heat Q_{AB} absorbed by the gas from the upper reservoir.

(d) Find the work done per cycle, W_{cyc}. *Hint: you only need to know Q_{AB} and the cycle efficiency η.*

Solution :

(a) We have

$$\begin{aligned}
0 = T\, ds &= d\varepsilon + p\, dv \\
&= \tfrac{1}{2}fR\, dT + \left(p + \frac{a}{v^2}\right) dv \\
&= \tfrac{1}{2}fR\, dT + \frac{RT\, dv}{v - b} = \tfrac{1}{2}fRT\, d\ln\!\left[(v - b)\, T^{f/2}\right] \quad,
\end{aligned}$$

where $s = N_A S/N$ is the molar entropy. Thus, the adiabatic equation of state for the van der Waals gas is

$$ds = 0 \quad \Rightarrow \quad (v - b)\, T^{f/2} = \text{const.}$$

Setting $b = 0$, we recover the ideal gas result.

(b) Since BC is an adiabat, we have

$$(v_B - b)\, T_2^{f/2} = (v_C - b)\, T_1^{f/2} \quad \Rightarrow \quad v_C = b + (v_B - b)\left(\frac{T_2}{T_1}\right)^{f/2}$$

(c) We have, from the First Law,

$$\begin{aligned}
Q_{AB} &= E_B - E_A + W_{AB} \\
&= \nu\left(\frac{a}{v_A} - \frac{a}{v_B}\right) + \nu\int_{v_A}^{v_B} dv\, p \\
&= \nu\left(\frac{a}{v_A} - \frac{a}{v_B}\right) + \nu\int_{v_A}^{v_B} dv\left[\frac{RT_2}{v - b} - \frac{a}{v^2}\right] \quad,
\end{aligned}$$

hence

$$Q_{AB} = \nu RT_2 \ln\!\left(\frac{v_B - b}{v_A - b}\right)$$

11

with $\nu = 1$.

(d) Since the cycle is reversible, we must have

$$\eta = \frac{W_{\text{cyc}}}{Q_{\text{AB}}} \quad \Rightarrow \quad W_{\text{cyc}} = \nu R(T_2 - T_1) \ln\left(\frac{v_{\text{B}} - b}{v_{\text{A}} - b}\right)$$

(2.10) The *triple point* of a single component thermodynamic system is an isolated point $(T_\mathrm{t}, p_\mathrm{t})$ in the (T, p) plane where there is three phase coexistence between solid, liquid, and vapor. Consider three phase coexistence between a pure solid, a pure vapor, and a solution where the solute fraction is x. Find the shift $(\Delta T_\mathrm{t}, \Delta p_\mathrm{t})$ as a function of x, T_t, and the quantities $s_\mathrm{S,L,V}$ and $v_\mathrm{S,L,V}$, *i.e.* the molar entropies and volumes of the three respective phases.

Solution :

At the triple point, we have $\mu_\mathrm{S}(T_\mathrm{t}, p_\mathrm{t}) = \mu_\mathrm{L}(T_\mathrm{t}, p_\mathrm{t}) = \mu_\mathrm{V}(T_\mathrm{t}, p_\mathrm{t})$, which gives two equations for the two unknowns T_t and p_t. We write $T_\mathrm{t} = T_\mathrm{t}^0 + \Delta T$ and $p_\mathrm{t} = p_\mathrm{t}^0 + \Delta p$, and we solve

$$\mu_\mathrm{L}^0(T_\mathrm{t}^0 + \Delta T, p_\mathrm{t}^0 + \Delta p) - x k_\mathrm{B}(T_\mathrm{t}^0 + \Delta T) = \mu_\mathrm{V}^0(T_\mathrm{t}^0 + \Delta T, p_\mathrm{t}^0 + \Delta p)$$
$$\mu_\mathrm{V}^0(T_\mathrm{t}^0 + \Delta T, p_\mathrm{t}^0 + \Delta p) = \mu_\mathrm{S}^0(T_\mathrm{t}^0 + \Delta T, p_\mathrm{t}^0 + \Delta p) \quad,$$

where the 0 superscript indicates the value for a pure phase. We now expand in the notionally small quantities ΔT and Δp, and we use

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{p,T} = -\frac{s}{N_\mathrm{A}} \quad, \qquad \left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{p,T} = \frac{v}{N_\mathrm{A}} \quad,$$

where s and v are the molar entropy and molar volume, respectively. This yields the linear system,

$$\begin{pmatrix} s_\mathrm{V} - s_\mathrm{L} & v_\mathrm{L} - v_\mathrm{V} \\ s_\mathrm{S} - s_\mathrm{V} & v_\mathrm{V} - v_\mathrm{S} \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta p \end{pmatrix} = \begin{pmatrix} x R T_\mathrm{t}^0 \\ 0 \end{pmatrix} \quad.$$

This yields

$$\Delta T = \frac{(v_\mathrm{V} - v_\mathrm{S}) \cdot x R T_\mathrm{t}^0}{s_\mathrm{V}(v_\mathrm{L} - v_\mathrm{S}) + s_\mathrm{L}(v_\mathrm{S} - v_\mathrm{V}) + s_\mathrm{S}(v_\mathrm{V} - v_\mathrm{L})}$$

$$\Delta p = \frac{(s_\mathrm{V} - s_\mathrm{S}) \cdot x R T_\mathrm{t}^0}{s_\mathrm{V}(v_\mathrm{L} - v_\mathrm{S}) + s_\mathrm{L}(v_\mathrm{S} - v_\mathrm{V}) + s_\mathrm{S}(v_\mathrm{V} - v_\mathrm{L})} \quad.$$

Note that we do not retain terms of order $x \Delta T$, because we have assumed x is small, *i.e.* a weak solution.

(2.11) A grocer starts his day with 4 boxes of pears, 5 boxes of oranges, and 6 boxes of apples. Each box contains 24 fruit and is initially completely filled.

- (a) At some time, the grocer notes that exactly half the pears, a third of the oranges, and a quarter of the apples have been sold. Assuming that customers take fruit from random positions in each of the boxes, find the dimensionless entropy $\ln W$ of the fruit distribution.

- (b) A clumsy customer then topples the table on which the fruit boxes rest, and all the fruit fall to the ground. The customer cleans up the mess, putting all the fruit back into the boxes, but into random locations. What is the entropy of the final state?

Solution :

(a) The grocer starts with 96 pears, 120 oranges, and 144 apples. By the time the grocer checks, 48 pears, 40 oranges, and 36 apples have been removed. The number of ways of doing this is

$$W = \binom{96}{48}\binom{120}{40}\binom{144}{36} = 8.303 \times 10^{93} \quad .$$

Thus, $\ln W = 216.3$.

(b) There are a total of $96 + 120 + 144 = 360$ slots for the fruit, which contain the remaining 48 pears, 120 oranges, and 108 apples. The rest of the slots, which amount to $360 - 48 - 120 - 108 = 84$ in total, are empty. Therefore,

$$W' = \frac{360!}{84! \cdot 48! \cdot 120! \cdot 108!} = 1.093 \times 10^{205} \quad ,$$

and the dimensionless entropy is $\ln W' = 472.1$.

(2.12) In a chemical reaction among σ species,

$$\zeta_1\,A_1 + \zeta_2\,A_2 + \cdots + \zeta_\sigma\,A_\sigma = 0 \quad,$$

where A_a is a chemical formula and ζ_a is a stoichiometric coefficient. When $\zeta_a > 0$, the corresponding A_a is a *product*; when $\zeta_a < 0$, A_a is a *reactant*. (See §2.13.1 of the Lecture Notes.) The condition for equilibrium is

$$\sum_{a=1}^{\sigma} \zeta_a\,\mu_a = 0 \quad,$$

where μ_a is the chemical potential of the ath species. The *equilibrium constant* for the reaction is defined as

$$\kappa(T,p) = \prod_{a=1}^{\sigma} x_a^{\zeta_a} \quad,$$

where $x_a = n_a / \sum_{b=1}^{\sigma} n_b$ is the fraction of species a.

(a) Working in the grand canonical ensemble, show that

$$\kappa(T,p) = \prod_{a=1}^{\sigma} \left(\frac{k_{\mathrm{B}} T\, \xi_a(T)}{p \lambda_a^3} \right)^{\zeta_a} \quad.$$

Note that the above expression does not involve any of the chemical potentials μ_a.

(b) Compute the equilibrium constant $\kappa(T,p)$ for the dissociative reaction $N_2 \rightleftharpoons 2\,N$ at $T = 5000\,\mathrm{K}$, assuming the following: the characteristic temperature of rotation and that of vibration of the N_2 molecule are $\Theta_{\mathrm{rot}} = 2.84\,\mathrm{K}$ and $\Theta_{\mathrm{vib}} = 3350\,\mathrm{K}$. The dissociation energy, including zero point contributions, is $\Delta = 169.3\,\mathrm{kcal\,mol^{-1}}$. The electronic ground state of N_2 has no degeneracy, but that of the N atom is 4 due to electronic spin.

Solution :

(a) In the GCE, we have

$$\Omega\big(T,V,\{\mu_a\}\big) = -k_{\mathrm{B}} T\, V \sum_{a=1}^{\sigma} \lambda_a^{-3}\, e^{\mu_a/k_{\mathrm{B}}T}\, \xi_a \quad,$$

where $\lambda_a = (2\pi\hbar^2/m_a k_{\mathrm{B}} T)^{1/2}$ the thermal wavelength for species a and $\xi_a(T)$ is the internal coordinate partition function for species a. We then have

$$n_a = -\frac{1}{V} \left(\frac{\partial \Omega}{\partial \mu_a} \right)_{T,V,\mu_{b\neq a}} = z_a\, \lambda_a^{-3}\, \xi_a \quad,$$

where $z_a = e^{\mu_a/k_{\mathrm{B}}T}$. OK, so we now define

$$x_a = \frac{n_a}{\sum_{b=1}^{\sigma} n_b} = \frac{z_a \lambda_a^{-3} \xi_a}{p/k_{\mathrm{B}}T} = \frac{k_{\mathrm{B}} T\, \xi_a\, z_a}{p\,\lambda_a^3} \quad,$$

since $\sum_b n_b = -\Omega/V k_{\mathrm{B}} T = p/k_{\mathrm{B}}T$. (Remember $\Omega = -pV$). Therefore

$$\kappa(T,p) \equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a}$$

$$= \prod_{a=1}^{\sigma} \left(\frac{k_{\mathrm{B}} T\, \xi_a}{p \lambda_a^3} \right)^{\zeta_a} \cdot \prod_{a=1}^{\sigma} z_a^{\zeta_a} \quad.$$

15

However,
$$\prod_{a=1}^{\sigma} z_a^{\zeta_a} = \prod_{a=1}^{\sigma} e^{\zeta_a \mu_a / k_{\mathrm{B}} T} = \exp\left(\frac{1}{k_{\mathrm{B}} T} \sum_{a=1}^{\sigma} \zeta_a\, \mu_a\right) = 1 \quad,$$
since $\sum_{a=1}^{\sigma} \zeta_a\, \mu_a = 0$.

(b) The internal partition function for N is just $\xi_{\mathrm{N}} = (2S+1)(2I+1)$, where $S = \frac{3}{2}$ is the total electronic spin from Hund's rules, and $I = 1$ is the nuclear spin. It turns out that we will never need to know the value of I. For N_2 the internal partition function is
$$\xi_{\mathrm{N}_2} = (2I+1)^2 \cdot \frac{T}{2\Theta_{\mathrm{rot}}} \cdot \frac{e^{\Delta/T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} \quad.$$

This formula requires some explanation. We appeal to Eqs. 4.292 in the Lecture Notes. Since $T \gg \Theta_{\mathrm{rot}}$, we have
$$\zeta_g \approx \zeta_u \approx \tfrac{1}{2} \int_0^{\infty} du\, e^{-u\Theta_{\mathrm{rot}}/T} = \frac{T}{2\Theta_{\mathrm{rot}}} \quad,$$

where the factor of $\frac{1}{2}$ comes from summing only over half the allowed L values, *i.e.* either all even or all odd, and where $u = L(L+1)$ so $du = (2L+1)\, dL$. We then have $\xi_{\mathrm{rot}} = (2I+1)^2 T / 2\Theta_{\mathrm{rot}}$ because $g_g + g_u = (2I+1)^2$. The vibrational partition function was derived to be $\xi_{\mathrm{vib}} = \frac{1}{2}\,\mathrm{csch}\,(\Theta_{\mathrm{vib}}/2T)$, however since we are including the zero point vibrational energy $\frac{1}{2}\hbar\omega_{\mathrm{vib}} = \frac{1}{2}k_{\mathrm{B}}\Theta_{\mathrm{vib}}$ in the dissociation energy, we get the above expression for ξ_{N_2}. According to our result from part (a), we have
$$\kappa(T,p) = 32 k_{\mathrm{B}} \Theta_{\mathrm{rot}} \cdot e^{-\Delta/T} \cdot \left(1 - e^{-\Theta_{\mathrm{vib}}/T}\right) \cdot \frac{\lambda_{\mathrm{N}_2}^3}{p\lambda_{\mathrm{N}}^6}$$
$$= 16\sqrt{2} \cdot \frac{k_{\mathrm{B}} \Theta_{\mathrm{rot}}}{p\lambda_{\mathrm{N}}^3} \cdot e^{-\Delta/T} \cdot \left(1 - e^{-\Theta_{\mathrm{vib}}/T}\right) \quad.$$

Now we need to evaluate some quantities. The gas constant is
$$R = N_{\mathrm{A}} k_{\mathrm{B}} = 8.314\,\mathrm{J/mol\cdot K} = 1.986 \times 10^{-3}\,\mathrm{kcal/mol\cdot K} \quad,$$
hence at $T = 5000\,\mathrm{K}$, we have
$$\frac{\Delta}{k_{\mathrm{B}} T} = \frac{(169.3\,\mathrm{kcal/mol})(4184\,\mathrm{J/kcal})}{(8.314\,\mathrm{J/mol\cdot K})(5000\,\mathrm{K})} = 17.0 \quad.$$

Furthermore, $\Theta_{\mathrm{vib}}/T = 0.670$. The thermal wavelength of N at this temperature is found to be
$$\lambda_{\mathrm{N}} = \left(\frac{2\pi \cdot (1.055 \times 10^{-27}\,\mathrm{g\,cm^2/s})^2}{(14\,\mathrm{g}/6.02 \times 10^{23}) \cdot (1.38 \times 10^{-16}\,\mathrm{erg/K}) \cdot 5000\,\mathrm{K}}\right)^{1/2} = 6.60\,\text{Å} \quad.$$

We also have
$$\frac{k_{\mathrm{B}} \Theta_{\mathrm{rot}}}{p\lambda_{\mathrm{N}}^3} = \frac{(1.38 \times 10^{-16}\,\mathrm{erg/K}) \cdot (2.84\,\mathrm{K})}{(1.013 \times 10^6\,\mathrm{g/cm\cdot s^2})(6.60 \times 10^{-8}\,\mathrm{cm})^3} \cdot \frac{p_0}{p} = \frac{1.35\,p_0}{p} \quad,$$
where $p_0 = 1.013 \times 10^5\,\mathrm{Pa}$ is atmospheric pressure. Putting it all together, we obtain
$$\kappa(T = 5000\,\mathrm{K}, p) = 6.2 \times 10^{-7} \cdot \frac{p_0}{p} \quad.$$

(2.13) The phase diagram for a binary *eutectic* system is depicted in Fig. 4. The liquid phase is completely miscible, but the solid phase separates into A-rich α and B-rich β phases over a broad range of temperatures and compositions. There is a single chemical composition which solidifies at a temperature lower than any other for this system - the eutectic composition. You are invited to model such a system using the Gibbs free energy densities

$$g_{\mathsf{L}}(T,p,x) = (1-x)\,\mu_{\mathsf{L}}^{\mathsf{A}}(T,p) + x\,\mu_{\mathsf{L}}^{\mathsf{B}}(T,p) + k_{\mathsf{B}}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_{\mathsf{L}}\,x(1-x)$$

$$g_{\mathsf{S}}(T,p,x) = (1-x)\,\mu_{\mathsf{S}}^{\mathsf{A}}(T,p) + x\,\mu_{\mathsf{S}}^{\mathsf{B}}(T,p) + k_{\mathsf{B}}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_{\mathsf{S}}\,x(1-x) \quad,$$

where $\lambda_{\mathsf{L}} < 0$ and $\lambda_{\mathsf{S}} > 0$. For simplicity, you may assume

$$\mu_{\mathsf{L}}^{\mathsf{A}}(T,p) \approx \mu_{\mathsf{L}}^{\mathsf{B}}(T,p) \equiv \mu_{\mathsf{L}}(T,p)$$
$$\mu_{\mathsf{S}}^{\mathsf{A}}(T,p) \approx \mu_{\mathsf{S}}^{\mathsf{B}}(T,p) \equiv \mu_{\mathsf{S}}(T,p) \quad,$$

with $\mu_{\mathsf{S}}(T,p) = \mu_{\mathsf{L}}(T,p) + rk_{\mathsf{B}}(T - T_0)$, where $r > 0$.

(a) By sketching the free energies, show that the phase diagram is as shown in Fig. 4.

(b) Solve numerically for the eutectic temperature assuming $\lambda_{\mathsf{L}} = -1$, $\lambda_{\mathsf{S}} = +1$, and $k_{\mathsf{B}}T_0 = 1$, and $r = 0.8$.
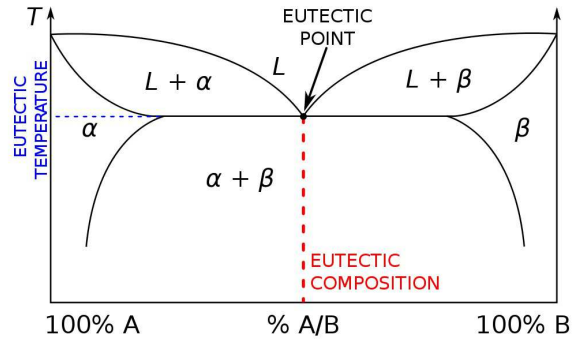

Figure 4: Eutectic phase diagram (from *Wikipedia*). L denotes the liquid phase, and α and β are two solid phases.

Solution :

(a) A set of curves illustrating the phenomenon is shown in Fig. 5. We have taken the valus in part (b) of the problem and varied the quantity $k_{\mathsf{B}}T$ (in dimensionless units). For our system, both the liquid and solid free energies are symmetric in x about the point $x = \frac{1}{2}$. At high temperatures, $g_{\mathsf{L}} < g_{\mathsf{S}}$ for all x, as shown in the upper left panel of Fig. 5. As the temperature is lowered, g_{S} starts to dip below g_{L} at the endpoints $x = 0, 1$. For our model and parameters, this happens for $k_{\mathsf{B}}T = k_{\mathsf{B}}T_0 = 1$. Because $\lambda_{\mathsf{L}} > \lambda_{\mathsf{S}}$, the curvature of $g_{\mathsf{L}}(x)$ is greater than that of $g_{\mathsf{S}}(x)$, which means that initially there will be two intersections where $g_{\mathsf{L}}(x) = g_{\mathsf{S}}(x)$, at $x = x^* < \frac{1}{2}$ and $x = 1 - x^* > \frac{1}{2}$. To guarantee thermodynamics stability, one must invoke the Maxwell construction which connects the solid curve at some point $x_1 < x^*$ to the liquid curve at point $x_2 > x^*$, with $x_2 < \frac{1}{2}$. A similar construction follows on the second half of the curve, between $g_{\mathsf{L}}(1 - x_2)$ and $g_{\mathsf{S}}(1 - x_1)$. These two phase regions represent mixtures of the liquid at intermediate concentration and a low or high concentration solid phase. Furthering lower the temperature, the solid curve develops a negative curvature at $x = \frac{1}{2}$ for $k_{\mathsf{B}}T < \frac{1}{2}\lambda_{\mathsf{S}}$. Eventually, the temperature gets so
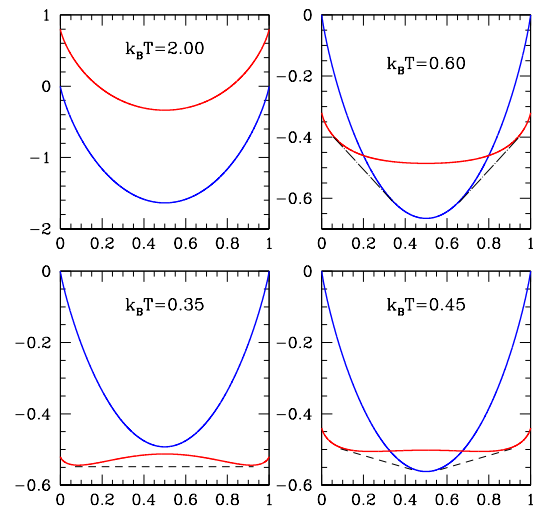

Figure 5: Gibbs free energies for liquid (blue) and solid (red) phases at different temperatures, with Maxwell constructions shown.

low that $g_{\mathsf{S}}(x)$ lies below $g_{\mathsf{L}}(x)$ for all $x \in [0, 1]$. The system is then in the solid phase, but one must nevertheless invoke a Maxwell construction, as shown in the lower left panel in Fig. 5, between a low-concentration solid at $x = x_3 < \frac{1}{2}$ and a high-concentration solid at $x = 1 - x_3 > \frac{1}{2}$. At such temperatures, the solid is in a homogeneous phase for $x < x_3$ or $x > 1 - x_3$, and in a mixed phase for $x_3 < x < 1 - x_3$.

(b) A crude numerical experiment is performed by successively lowering $k_{\mathsf{B}}T$ until the minima of the $g_{\mathsf{L}}(x)$ and $g_{\mathsf{S}}(x)$ curves cross, and then iterating to find the temperature where the minima coincide. In this manner, I find a eutectic temperature $k_{\mathsf{B}}T_{\mathsf{e}} = 0.3948$, as shown in Fig. 6.
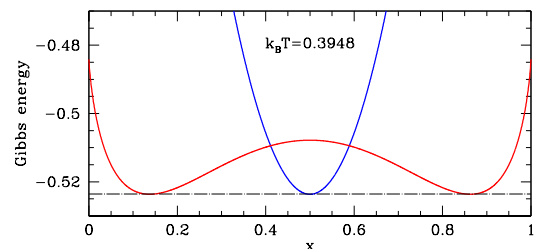

Figure 6: Gibbs free energies for the liquid (blue) and solid (red) phases at the eutectic temperature.