

Problem 1

Kittel & Kroemer, Chapter 10, problem 1 [Entropy, energy, and enthalpy of van der Waals gas.]

In this problem, all results are given to first order in the van der Waals correction terms a , b .

(a): 1 point

Show that the entropy of the van der Waals gas is

$$\sigma = N(\ln[n_Q(V - Nb)/N] + 5/2).$$

We can start from the free energy

$$F = -N\tau[\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1] - N^2a/V.$$

Then the entropy is given by

$$\begin{aligned}\sigma &= -(\partial F/\partial\tau)_{N,V} = N[\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1] + N\tau\frac{\partial}{\partial\tau}[\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1] \\ &= N[\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1] + \frac{3}{2}N \\ &= N[\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 5/2].\end{aligned}$$

(a): 1 point

(b): 1 point

Show that the energy is

$$U = \frac{3}{2}N\tau - N^2a/V.$$

From $F = U - \tau\sigma$ and our result in part (a), we directly see that

$$U = F + \tau\sigma = \frac{3}{2}N\tau - N^2a/V$$

(b): 1 point

(c): 1 point

Show that the enthalpy $H \equiv U + pV$ is

$$H(\tau, V) = \frac{5}{2}N\tau + N^2b\tau/V - 2N^2a/V$$

$$H(\tau, p) = \frac{5}{2}N\tau + Nbp - 2Nap/\tau.$$

Equation (39) gives the pressure of the van der Waals gas as

$$p = \frac{N\tau}{V - Nb} - \frac{N^2a}{V^2},$$

from which we see that

$$pV = \frac{NV\tau}{V - Nb} - \frac{N^2a}{V}.$$

Then

$$H(\tau, V) = \frac{3}{2}N\tau - N^2a/V + pV$$

$$= \frac{3}{2}N\tau + \frac{NV\tau}{V - Nb} - 2N^2a/V.$$

To move forward we need to Taylor expand $\frac{NV\tau}{V - Nb}$ for small b . When we Taylor expand it is wise to make a dimensionless small parameter; here we can divide the top and bottom by V to get $\frac{N\tau}{1 - Nb/V}$, and we can see that Nb/V is our dimensionless small parameter. We now use the fact that the Taylor expansion of $1/(1 - x)$ for small x is $1/(1 - x) = 1 + x + \mathcal{O}(x^2)$, so that $\frac{N\tau}{1 - Nb/V} = N\tau + N^2\tau b/V + \mathcal{O}(b^2)$. Using this above, we see that, to first order in our small parameters,

$$H(\tau, V) = \frac{3}{2}N\tau + N\tau + N^2\tau b/V - 2N^2a/V$$

$$= \frac{5}{2}N\tau + N^2\tau b/V - 2N^2a/V.$$

To change variables to p , notice that the van der Waals equation of state is an expansion around the ideal gas equation of state: $pV = N\tau + (\text{terms linear in } a, b) + \dots$. In our above equation, volume shows up in terms that are *already* linear in a, b . This means that we can simply use the ideal gas law equation of state, since including the higher-order terms would lead to terms quadratic in our small parameters, which we are dropping. So we can substitute in $V = N\tau/p$ above to get

$$H(\tau, p) = \frac{5}{2}N\tau + Nbp - 2Nap/\tau,$$

to first order in our small parameters.

(c): 1 point

Problem 2

Kittel & Kroemer, Chapter 10, problem 4 [Gas-solid equilibrium.]

Consider a version of the example (26)-(32) in which we let the oscillators in the solid move in three dimensions.

(a): 1 point

Show that in the high temperature regime ($\tau \gg \hbar\omega$) the vapor pressure is

$$p \simeq \left(\frac{M}{2\pi}\right)^{3/2} \frac{\omega^3}{\tau^{1/2}} e^{-\epsilon_0/\tau}$$

We will attempt to follow the logic of the 1D example in the book, adapting it to 3D where necessary. The energies of the oscillator are still $n\hbar\omega - \epsilon_0$, but now $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ with $n_x, n_y, n_z = 0, 1, 2, \dots$. The partition function for a single oscillator in the solid is then

$$\begin{aligned} Z_s &= \sum_{n_x, n_y, n_z} e^{-(n\hbar\omega - \epsilon_0)/\tau} \\ &= e^{\epsilon_0/\tau} \sum_{n_x, n_y, n_z} e^{-\hbar\omega \sqrt{n_x^2 + n_y^2 + n_z^2}/\tau}. \end{aligned}$$

We can no longer exactly evaluate this sum as a geometric series. In the high-temperature limit, we can attempt to turn it into an integral, as we have done many times before in this class:

$$\begin{aligned} Z_s &= e^{\epsilon_0/\tau} \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-\hbar\omega \sqrt{n_x^2 + n_y^2 + n_z^2}/\tau} \\ &= \frac{1}{8} (4\pi) e^{\epsilon_0/\tau} \int_0^\infty dn n^2 e^{-\hbar\omega n/\tau} \\ &= \frac{\pi}{2} e^{\epsilon_0/\tau} \frac{\tau^3}{\hbar^3 \omega^3} \int_0^\infty dx x^2 e^{-x}. \end{aligned}$$

(a): 1 point

We can look up this integral; it equals 2. Thus

$$Z_s = \frac{\pi \tau^3}{\hbar^3 \omega^3} e^{\epsilon_0/\tau}.$$

From here we can find the Helmholtz free energy per particle: $F_s = -\tau \ln Z_s$, and we can also write down the Gibbs free energy per particle: $G_s = F_s + p_s v_s = -\tau \ln Z_s + p_s v_s$, where v_s is the volume per particle in the solid phase and p_s is the pressure in the solid phase. The Gibbs free energy per particle for a single species of particle is simply the chemical potential μ_s , so that we have

$$\mu_s = -\tau \ln Z_s + p_s v_s.$$

The solid and gas should be in diffusive equilibrium when their chemical potentials are equal. From an earlier chapter, the chemical potential of an ideal gas is $\mu_g = \tau \ln(n/n_Q) = \tau \ln(N/n_Q V) = \tau \ln(p/\tau n_Q)$, so our condition for coexistence is $\mu_s = \mu_g$, or

$$-\tau \ln Z_s + p v_s = \tau \ln(p/\tau n_Q).$$

The volume per particle v_s in the solid phase is very small, so we can drop the term pv_s , and then our equation can be solved for p to find

$$\begin{aligned} p &= \tau n_Q / Z_s \\ &= \tau \left(\frac{M\tau}{2\pi\hbar^2} \right)^{3/2} \frac{\hbar^3 \omega^3}{\pi \tau^3} e^{-\epsilon_0/\tau} \\ &= \left(\frac{M}{2\pi} \right)^{3/2} \frac{\omega^3}{\tau^{1/2}} e^{-\epsilon_0/\tau}. \end{aligned}$$

(a): 1 point

(b): 1 point

Explain why the latent heat per atom is $\epsilon_0 - \frac{1}{2}\tau$.

The latent heat per atom is the difference in enthalpy per particle between the two phases. For the gas phase, the enthalpy per particle is $H_g = U_g + pv_g = \frac{3}{2}\tau + \tau = \frac{5}{2}\tau$, where we used the equation of state $pv_g = \tau$ for an ideal gas. For the solid, the enthalpy per particle is essentially just the energy per particle, since the volume per particle is so small. By the equipartition theorem, the energy per particle for the oscillators is $6 \times \frac{1}{2}\tau = 3\tau$; since there is also a binding energy, this is reduced by ϵ_0 compared to the gas phase, so that the enthalpy per particle for the solid is $H_s = 3\tau - \epsilon_0$. Thus

$$L = H_g - H_s = \frac{5}{2}\tau - (3\tau - \epsilon_0) = \epsilon_0 - \frac{1}{2}\tau.$$

(b): 1 point

We were not able to use our results from part (a) to answer this, since that result was only the limiting case of high temperature.

Problem 3

Kittel & Kroemer, Chapter 10, problem 5 [Gas-solid equilibrium.]

Consider the gas-solid equilibrium under the extreme assumption that the entropy of the solid may be neglected over the temperature range of interest. Let $-\epsilon_0$ be the cohesive energy of the solid, per atom. Treat the gas as ideal and monatomic. Make the approximation that the volume accessible to the gas is the volume V of the container, independent of the much smaller volume occupied by the solid.

(a): 1 point

Show that the total Helmholtz free energy of the system is

$$F = F_s + F_g = -N_s\epsilon_0 + N_g\tau[\ln(N_g/Vn_Q) - 1],$$

where the total number of atoms, $N = N_s + N_g$ is constant.

In the case that the entropy of the solid can be neglected, the Helmholtz free energy $F = U - \tau\sigma$ of the solid is equal to its internal energy; if each atom in the solid has $-\epsilon_0$ energy (relative to a free atom at rest), then the total internal energy of the solid is $-N_s\epsilon_0$. For the gas, if it occupies a volume V , we have shown that the Helmholtz free energy is $F_g = N_g\tau[\ln(N_g/Vn_Q) - 1]$, so we immediately have

$$F = F_s + F_g = -N_s\epsilon_0 + N_g\tau[\ln(N_g/Vn_Q) - 1].$$

(a): 1 point

(b): 1 point

Find the minimum of the free energy with respect to N_g ; show that in the equilibrium condition

$$N_g = n_Q V e^{-\epsilon_0/\tau}.$$

We must write $N_s = N - N_g$ to find this minimum, in which case the free energy looks like

$$F = -(N - N_g)\epsilon_0 + N_g\tau[\ln(N_g/Vn_Q) - 1].$$

Then the condition for minimum is

$$\begin{aligned} 0 = \frac{\partial F}{\partial N_g} &= \epsilon_0 + \tau[\ln(N_g/Vn_Q) - 1] + N_g \frac{\partial}{\partial N_g} \tau[\ln(N_g/Vn_Q) - 1] \\ &= \epsilon_0 + \tau[\ln(N_g/Vn_Q) - 1] + \tau \\ &= \epsilon_0 + \tau \ln(N_g/Vn_Q). \end{aligned}$$

Solving this for N_g , we find

$$N_g = n_Q V e^{-\epsilon_0/\tau}$$

is the value of N_g for which F is minimized.

(b): 1 point

(c): 1 point

Find the equilibrium vapor pressure.

In equilibrium, N_g is given as above, and the gas still obeys the ideal gas law $pV = N_g\tau$, so

$$p = \frac{N_g\tau}{V} = n_Q\tau e^{-\epsilon_0/\tau}.$$

This matches the high-temperature limit of (31) from the textbook, where the temperature is high enough that the energy level spacing $\hbar\omega$ of the solid atoms is negligible.

(c): 1 point

Problem 4

Kittel & Kroemer, Chapter 10, problem 8 [First order crystal transformation.]

Consider a crystal that can exist in either of two structures, denoted by α and β . We suppose that the α structure is the stable low temperature form and the β structure is the stable high temperature form of the substance. If the zero of the energy scale is taken as the state of separated atoms at infinity, then the energy density $U(0)$ at $\tau = 0$ will be negative. The phase stable at $\tau = 0$ will have the lower value of $U(0)$: thus $U_\alpha(0) < U_\beta(0)$. If the velocity of sound v_β in the β phase is lower than v_α , in the α phase, corresponding to lower values of the elastic moduli for β , then the thermal excitations in the β phase will have larger amplitudes than in the α phase. The larger the thermal excitation, the larger the entropy and the lower the free energy. Soft systems tend to be stable at high temperatures, hard systems at low.

(a): 1 point

Show from Chapter 4 that the free energy density contributed by the phonons in a solid at a temperature much less than the Debye temperature is given by $-\pi^2\tau^4/30v^3\hbar^3$, in the Debye approximation with v taken as the velocity of all phonons.

Chapter 4 gives the low-temperature heat capacity of the phonons as (Equation 4.47a))

$$C_V = \frac{12\pi^4 N \tau^3}{5k_B^3 \theta^3},$$

where $\theta \equiv (\hbar v/k_B)(6\pi^2 N/V)^{1/3}$ is the Debye temperature. Plugging in that definition, we see that

$$\begin{aligned} C_V &= \frac{12\pi^4 N \tau^3}{5\hbar^3 v^3} \frac{V}{6\pi^2 N} \\ &= \frac{2\pi^2 \tau^3 V}{5\hbar^3 v^3}. \end{aligned}$$

The heat capacity and Helmholtz free energy are related by $C_V = -\tau(\partial^2 F/\partial T^2)_{V,N}$. Thus we should be able to integrate $-C_V/\tau$ twice to get the Helmholtz free energy. From above,

$$-C_V/\tau = -\frac{2\pi^2 V}{5\hbar^3 v^3} \tau^2.$$

Integrating this twice brings down a factor of $3 \times 4 = 12$, so that the Helmholtz free energy is

$$F = -\frac{\pi^2 V}{30\hbar^3 v^3} \tau^4.$$

Then the free energy density of the phonons is

$$f \equiv F/V = -\frac{\pi^2}{30\hbar^3 v^3} \tau^4$$

We know that the constant of integration is zero, since in Chapter 4 we also saw that the total energy of the phonons went to zero as $\tau \rightarrow 0$.

(a): 1 point

(b): 1 point

Show that at the transformation temperature

$$\tau_c^4 = (30\hbar^3/\pi^2)[U_\beta(0) - U_\alpha(0)]/(v_\beta^{-3} - v_\alpha^{-3}),$$

where U is now the total energy contained in unit volume. There will be a finite real solution if $v_\beta < v_\alpha$. This example is a simplified model of a class of actual phase transformations in solids.

If we have two phases coexisting, with V_α the volume occupied by the α phase and $V_\beta = V - V_\alpha$ the volume occupied by the β phase, the total free energy will be

$$F = V_\alpha(f_\alpha + U_\alpha(0)) + V_\beta(f_\beta + U_\beta(0)) = V_\alpha(U_\alpha(0) - \frac{\pi^2\tau^4}{30\hbar^3v_\alpha^3}) + (V - V_\alpha)(U_\beta(0) - \frac{\pi^2\tau^4}{30\hbar^3v_\beta^3}).$$

At the transformation temperature τ_c , the free energy will be minimized with respect to V_α :

$$0 = \partial F / \partial V_\alpha = (U_\alpha(0) - \frac{\pi^2\tau_c^4}{30\hbar^3v_\alpha^3}) - (U_\beta(0) - \frac{\pi^2\tau_c^4}{30\hbar^3v_\beta^3}).$$

We can now rearrange to solve for the transition temperature, and indeed we find

$$\tau_c^4 = (30\hbar^3/\pi^2)[U_\beta(0) - U_\alpha(0)]/(v_\beta^{-3} - v_\alpha^{-3}).$$

(b): 1 point