

## 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

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

**(b): 1 point**

Show that the energy is

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

**(c): 1 point**

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

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

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

## 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

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

**(b): 1 point**

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

## 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.

**(b): 1 point**

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

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

**(c): 1 point**

Find the equilibrium vapor pressure.

## 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  $\alpha$  and  $\beta$ . We suppose that the  $\alpha$  structure is the stable low temperature form and the  $\beta$  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  $v_\beta$  in the  $\beta$  phase is lower than  $v_\alpha$ , in the  $\alpha$  phase, corresponding to lower values of the elastic moduli for  $\beta$ , then the thermal excitations in the  $\beta$  phase will have larger amplitudes than in the  $\alpha$  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.

**(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.

**(c): 1 point**

The latent heat of transformation is defined as the thermal energy that must be supplied to carry the system through the transformation. Show that the latent heat per unit volume for this model is

$$L = 4[U_\beta(0) - U_\alpha(0)].$$