

**20.110/2.772/5.601 Fall 2005**  
**Recitation # 10**  
**10/18/2005**

1. Derivations for  $\langle \epsilon \rangle$ , S, A,  $\mu$ , P

2.

**EXAMPLE 10.5 The Schottky two-state model.** Consider a system that has  $N$  distinguishable particles with two energy levels for each particle: a ground state with energy zero, and an excited state with energy  $\epsilon = \epsilon_0 > 0$ . This model is useful for describing many different problems: our polymer or dimer lattice models in Chapter 8, the behaviors of atoms or molecules that are excited by electromagnetic radiation, or the behavior of spins in magnetic fields (see Example 10.6).

Here we'll keep the model general and won't specify  $\epsilon_0$  in terms of any particular microscopic structure or property. We aim to find the average particle energy  $\langle \epsilon \rangle$ , the heat capacity  $C_V$ , the entropy, and the free energy per particle from the partition function. The partition function for a two-level system is the sum of two Boltzmann factors, one for each level,

$$q = 1 + e^{-\beta\epsilon_0}. \quad (10.43)$$

The partition function approaches one at low temperatures and two at high temperatures. The relative populations of the two states are given by the Boltzmann distribution, Equation (10.9):

$$p_1^* = \frac{1}{q}, \quad \text{and} \quad p_2^* = \frac{e^{-\beta\epsilon_0}}{q}. \quad (10.44)$$

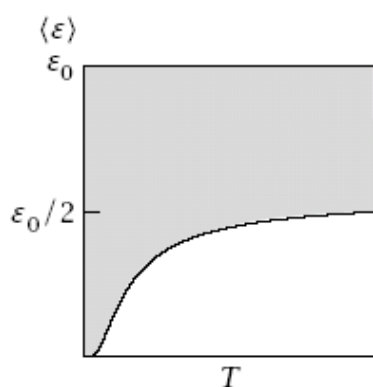
The average energy is found by taking the derivative in Equation (10.34):

$$\langle \epsilon \rangle = -\frac{1}{q} \left( \frac{\partial q}{\partial \beta} \right) = \frac{\epsilon_0 e^{-\beta\epsilon_0}}{1 + e^{-\beta\epsilon_0}} = \frac{\epsilon_0 e^{-\epsilon_0/kT}}{1 + e^{-\epsilon_0/kT}}. \quad (10.45)$$

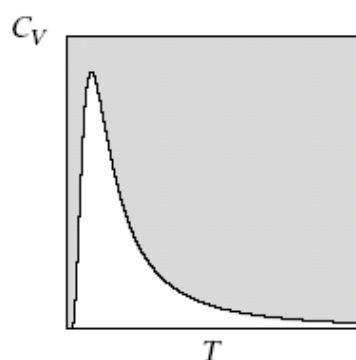
Figure 10.9(a) shows the energy of the two-state system as a function of temperature. At low temperatures, most molecules are in the ground state, so the system has low energy. As the temperature increases, the energy of the system increases and ultimately saturates at the value  $\epsilon_0/2$  per particle because energy levels 0 and  $\epsilon_0$  become equally populated.

To compute the heat capacity, use the definition  $C_V = (\partial \Delta U / \partial T)$  from thermodynamics. Using Equation (10.34) to convert the total energy to the average energy per particle,  $\Delta U = N \langle \epsilon \rangle$ , you have

(a) Average Energy



(b) Heat Capacity



**Figure 10.9** (a) The average energy per particle  $\epsilon$  for the Schottky model (Equation (10.45)) saturates at  $\epsilon_0/2$  as temperature  $T$  approaches infinity. (b) The two-state model has a peak in the heat capacity  $C_V$  as a function of temperature (Equation (10.48)).

$$C_V = N \left( \frac{\partial \langle \epsilon \rangle}{\partial T} \right) = N \left( \frac{\partial \langle \epsilon \rangle}{\partial \beta} \right) \left( \frac{\partial \beta}{\partial T} \right) = -\frac{N}{kT^2} \left( \frac{\partial \langle \epsilon \rangle}{\partial \beta} \right), \quad (10.46)$$

where the right-hand expressions convert from  $T$  to  $\beta$  to make the next step of the differentiation simpler. Take a derivative of the form  $d(u/v) = (vu' - uv')/v^2$ , where  $u = \epsilon_0 e^{-\beta\epsilon_0}$  and  $v = 1 + e^{-\beta\epsilon_0}$ , to get

$$\begin{aligned} \left( \frac{\partial \langle \epsilon \rangle}{\partial \beta} \right) &= \frac{(1 + e^{-\beta\epsilon_0})(-\epsilon_0^2 e^{-\beta\epsilon_0}) - \epsilon_0 e^{-\beta\epsilon_0}(-\epsilon_0 e^{-\beta\epsilon_0})}{(1 + e^{-\beta\epsilon_0})^2} \\ &= \frac{-\epsilon_0^2 e^{-\beta\epsilon_0}}{(1 + e^{-\beta\epsilon_0})^2}. \end{aligned} \quad (10.47)$$

Substitute Equation (10.47) into the right-hand side of Equation (10.46) to find the heat capacity  $C_V$  in terms of the energy level spacing  $\epsilon_0$ :

$$C_V = \frac{N\epsilon_0^2}{kT^2} \frac{e^{-\beta\epsilon_0}}{(1 + e^{-\beta\epsilon_0})^2}. \quad (10.48)$$

The heat capacity is plotted in Figure 10.9(b), and is discussed in more detail in Chapter 12. Heat capacity peaks are characteristic of bond-breaking and melting processes. At low temperatures, the thermal energy  $kT$  from the bath is too small to excite the system to the higher energy level. At intermediate temperatures, the system can absorb heat from the bath and particles are excited into the higher energy state. At the highest temperatures, the system takes up no further energy from the bath because most particles already have their maximum energy.

To get the entropy, substitute Equation (10.43) for  $q$  and  $Q = q^N$  into Equations (10.39) and (10.38):

$$\frac{S}{N} = \frac{\epsilon_0 e^{-\beta\epsilon_0}}{T(1 + e^{-\beta\epsilon_0})} + k \ln(1 + e^{-\beta\epsilon_0}). \quad (10.49)$$

To get the free energy,  $F = U - TS$ , use  $U = N\langle \epsilon \rangle$  with Equation (10.45) and and  $S$  from Equation (10.49) to get

$$\frac{F}{NkT} = -\ln q = -\ln(1 + e^{-\beta\epsilon_0}). \quad (10.50)$$

As  $\epsilon_0 \rightarrow \infty$ , the excited state becomes inaccessible so  $S \rightarrow 0$ , and  $F \rightarrow 0$ . On the other hand, as  $\epsilon_0 \rightarrow 0$ , both states become accessible so  $S \rightarrow Nk \ln 2$ , and  $F \rightarrow NkT \ln 2$ .