

### Problem 3.36 The Chemical Potential of an Einstein Solid

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June 3, 2003

[xx grade = 2.5,if you want to revise you can xx] Thus far, we have studied thermal equilibrium, and mechanical equilibrium. These conditions occur when the temperatures or pressures of two systems are equal. Looking more closely, one might wonder about conditions for equilibrium of particles diffusing from one system to another. If two systems are in **diffusive equilibrium**, then particles diffuse from one system to the other and in the opposite direction at equal rates. Diffusive equilibrium is governed by a quantity called **chemical potential** ( $\mu$ ). It can be shown that

$$\mu \equiv -T \left( \frac{\partial S}{\partial N} \right)_{U,V}. \quad (1)$$

When system A is gaining and losing particles at an equal rate to system B,

$$\mu_A = \mu_B. \quad (2)$$

Otherwise, the one with the larger value of  $\partial S/\partial N$  will gain particles. This is because it will gain more entropy than the other loses (Schroeder, 136).

We can derive a formula for  $\mu$  by using Eq.(1). First, we will need an equation for  $S$ . This is given by

$$S = k \ln \Omega, \quad (3)$$

where [xx indicate for specific model, the Einstein model xx]

$$\ln \Omega = (q + N) \ln(q + N) - q \ln q - N \ln N \quad (4)$$

(Schroeder, 63). So, using Eq.(3),

$$\mu = Eq.(1) = -kT \frac{dS}{dN} \ln \Omega = -kT \ln \frac{N + q}{N}. \quad (5)$$

To gain insight into this formula, we will consider two cases. The first is when the number of oscillators is much greater than the number of available energy units, or  $N \gg q$ . Using Eq.(5), this means that  $\mu = 0$ . Suppose we add one more oscillator, increasing the value of  $N$  by one. The value inside the logarithm will change from

$$\frac{N + q}{N}, \quad (6)$$

to

$$\frac{(N + 1) + q}{N + 1}. \quad (7)$$

Since  $Eq.(6) < Eq.(7)$ , the entropy will increase slightly. However, in this case,  $\mu$  will not change. Intuitively, this means that when there are many more oscillators than energy units, energy [xx energy is held fixed in Eq. 1 xx] almost never crosses from one system to the next, and when  $N$  is changed, it still almost never diffuses due to the lack of available energy. We can also verify our formula by using the result

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}, \quad (8)$$

(Schroeder, 117). This clearly represents the fact that  $\mu$  is the amount the energy changes when one particle is added, and  $S$ , and  $V$  are held constant. In this case,  $\frac{\partial U}{\partial N}$  is zero, so  $\mu$  will be zero.

A second case is given by  $N \ll q$ . In this case, Eq.(5) reduces to

$$\mu = -kT \ln\left(\frac{q}{N}\right) = -kT(\ln q - \ln N). \quad (9)$$

Now,  $\mu$  is non-zero. In fact,  $\mu$  is very high, which means that a large number of particles are crossing from system A to system B.[xx there are not two systems, need to discuss effect of adding one particle to system xx] Using Eq.(9), we can see that since  $N$  is inside a logarithm, its value will not change by very much when the value of  $N$  is incremented by one. Again, looking at Eq.(8), we can see that for a large value of  $U$ , changing  $N$  by one will not have a large effect on  $\mu$ . Again,  $S$  will change by very little. Intuitively, this makes sense because with a very large number of particles diffusing from one system to the other, adding one more oscillator (energy slot) will not have a large effect on the number of particles moving from one system to the next. [xx the effect on entropy is different in the two limiting cases xx]

The elusive concept of chemical potential has been more clearly defined by the use of an Einstein Oscillator model with two carefully constructed examples. In either the high temperature limit ( $N \ll q$ ), or the low temperature limit ( $N \gg q$ ), increasing the number of oscillators did not have a large effect.