Configurational D.O.F

In class we saw how to treat systems of identical, distinguishable, non-interacting *ad-atoms* were the only degrees of freedom were configurational. In this case, we consider M total positions for N identical particles. For such systems, assuming (N, V, T) boundary conditions, the partition function obtained was:

$$Q = \sum_E \Omega(E) e^{-\beta E}$$

Since the energy of this ensemble was independent of the actual configuration of the system, there is effectively one energy level and we just have:

$$Q = \Omega(E) e^{-\beta E}$$

The degeneracy $\Omega(E)$ of this energy level can be calculated as the total number of ways in which we can arrange N particles in M sites:

$$Q = \frac{M!}{N!(M-N)!} e^{-\beta N \varepsilon}$$

Using the known formalism for this ensemble,

$$F = -kT \cdot \ln Q$$
$$S = k \cdot \ln \Omega$$

Note that the entropy of this system corresponds to the entropy of the micro-canonical ensemble. This is due to the fact that the total energy of each sub-system (particle) is the same ε.

Equivalence between Ensembles

In class we also saw that the behavior of the system is independent of the ensemble that we use to describe it. In the previous example, we considered two possibilities:

- The ad-atoms were subjected to boundary conditions consistent with fixed N, V and T. This corresponds to the canonical ensemble.

- The ad-atoms were set in equilibrium with a vapor, so the B.C. were μ, V and T. This is the grand canonical ensemble.

In the case of the Canonical ensemble, we found an expression for the chemical potential as a function of x where x is the occupation fraction, $\frac{N}{M}$:

$$\mu = \varepsilon + kT \cdot \ln\left(\frac{x}{1-x}\right) \tag{1}$$

Using the Grand Canonical ensemble, we found an expression for x as a function of the chemical potential:

$$x = -\frac{e^{-\beta(\varepsilon-\mu)}}{1 + e^{-\beta(\varepsilon-\mu)}} \tag{2}$$

If we solve for μ in the expression above, we obtain the same expression as Eq. 1. Therefore, the *calculated thermodynamic properties of the system are independent of the ensemble chosen to describe it.*

Vibrational Degrees of Freedom

In class, we consider a collection of N independent and distinguishable $3-D$ harmonic oscillators. For this system, considering the Canonical ensemble, the partition function obtained was:

$$Q = \left(\frac{e^{\theta/2T}}{e^{\theta/T} - 1} \right)^{3N}$$

where $\theta = \frac{\hbar\omega}{k}$ and $\omega = \sqrt{\frac{f}{m}}$. Note that f and m are material-dependent properties. This simple approximation is called the Einstein's model for a vibrating crystal.

Using the already well known expressions for the thermodynamic properties of the Canonical ensemble, we obtained:

$$E = \frac{3N\hbar\omega}{2} + 3NkT \cdot \left(\frac{\theta/T}{e^{\theta/T} - 1} \right)$$

$$C_V = 3Nk \left(\frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1 \right)^2}$$

The following limits were obtained:

$$E_{T\to 0} = \frac{3N\hbar\omega}{2} \quad E_{T\to high} = 3NkT$$
$$C_{V,T\to 0} = 0 \quad C_{V,T\to high} = 3Nk$$

The universal function for the C_V as a function of $\frac{T}{\theta}$ has the following shape:

Observe how fast the solid reaches the Dulong-Petite limit of $\frac{C_V}{Nk} \sim 3$. For the majority of solids, $\theta_E \sim 1000\,K$.

The entropy of an Einstein Solid can be calculated from

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$S = 3Nk \left[\frac{\theta/T}{e^{\theta/T} - 1} - \ln \left(1 - e^{-\theta/T} \right) \right]$$
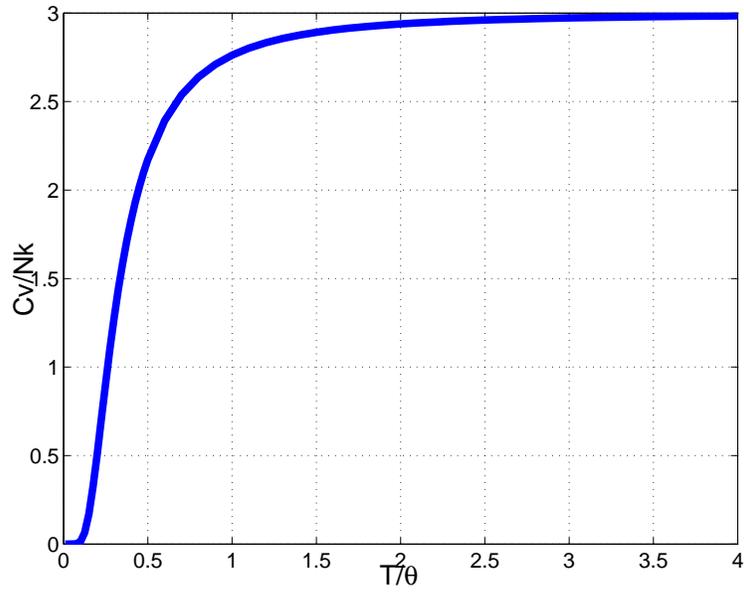
Figure 1: $\frac{Cv}{Nk}$ v.s. $\frac{T}{\theta}$

Note that, as $T \to 0$, $S \to 0$. This means that, as $T \to 0$, the system sinks to its lowest energy state. Each atom is in its vibrational ground state (does not vibrate).

Problem 1

A system consists of N non-interacting atoms. Each atom may be in two states, a low energy state with energy, $E = 0$ and an 'excited' state, with energy E.

a) How many atoms are in the excited state?

b) What is the total energy U of this system as a function of N, E, k (the Boltzmann constant) and T?

Solution 1

(a) A system of N non-interacting particles with two possible states either 0 or ε. A good rule is too assume "particles" (e.g. atoms, electrons, etc) are indistinguishable unless they are localized in a crystal or on a surface. The number of atoms in the excited state can be determined using Boltzmann statistics under the assumption that we are working at high temperature and/or low density.

Consider a system on non-interacting indistinguishable particles, for which

$$Q(N, V, T) = \frac{q^N}{N!}$$

with

$$q(V,T) = \sum_j e^{\frac{\varepsilon_j}{kT}}$$

Remember that this holds when $\Phi\left(\varepsilon\right) >> N$.

For this system, the total energy is given by:

$$E = N \cdot \bar{\varepsilon} = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/kT}}{q}$$

Note that, according to the expression above,

$$\bar{\varepsilon} = \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/kT}}{q}$$

The probability that a molecule is in the jth state is

$$\pi_j = \frac{e^{-\varepsilon_j/kT}}{q} = \frac{e^{-\varepsilon_j/kT}}{\sum_j e^{-\varepsilon_j/kT}}$$

In this problem, the two available states are 0 and ε, and the total number of particles in the ε state are

$$N_\varepsilon = N\pi_\varepsilon$$

where π_ε is the probability an atom will be in state ε This probability is determined using the single particle partition function and can be written as

$$\pi_\varepsilon = \frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{\sum_i \exp\left[\frac{-\varepsilon_i}{kT}\right]} \tag{3}$$

But our system can be in only two states, so the sum in the denominator can be found explicitly:

$$\pi_\varepsilon = \frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{\exp\left[0\right] + \exp\left[\frac{-\varepsilon}{kT}\right]}$$

So N_ε can be written as

$$N_\varepsilon = N\pi_\varepsilon = N\frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{1 + \exp\left[\frac{-\varepsilon}{kT}\right]} = \frac{N}{1 + \exp\left[\frac{\varepsilon}{kT}\right]}$$

$$\boxed{N_\varepsilon = \frac{N}{1 + \exp\left[\frac{\varepsilon}{kT}\right]}}$$

(b) The total energy is simply $U = N\bar{\varepsilon} = N \sum_i \pi_i \varepsilon_i$ (McQuarrie 4-12 and 4-13)

$$U = N \sum_i \pi_i \varepsilon_i = N \left(\pi_1 \varepsilon_1 + \pi_2 \varepsilon_2 \right) = N \left[(1 - \pi_2) \cdot 0 + \pi_2 \cdot \varepsilon \right]$$

$$U = N \left(\pi_2 \varepsilon \right) = N \left(\frac{\exp\left[\frac{-\varepsilon}{kT} \right]}{1 + \exp\left[\frac{-\varepsilon}{kT} \right]} \right) \varepsilon$$

$$\boxed{U = \frac{N\varepsilon}{1 + \exp\left[\frac{\varepsilon}{kT} \right]}}$$

Note: Since many particles will occupy the same state (either 0 or ε) these particles must be Bosons. At lower temperatures we would have to use Bose-Einstein statistics (McQuarrie 4-26) which would lead to a much more complicated problem since we would have to determine the chemical potential μ.