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5.62 Physical Chemistry II  
Spring 2008

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## THERMODYNAMICS OF SOLIDS: EINSTEIN AND DEBYE MODELS

Reading: Hill, pages 86-98

For the next few lectures we will discuss solids, in particular crystalline solids, in which the particles are arranged in a regular lattice.

- The lattice could consist of single atoms or atomic ions, such as Ar or  $\text{Na}^+\text{Cl}^-$  arranged in something like a face-centered-cubic (FCC) or body-centered-cubic (BCC) crystalline array.
- Or the lattice could be a crystal of more complex molecules in a lattice, such as CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , penicillin, hemoglobin, etc.

TOTAL # DEGREES OF FREEDOM =  $3N$  (where  $N$  = # of atoms in the crystal)

$$\left. \begin{array}{l} 3 \text{ correspond to overall translation} \\ 3 \text{ correspond to overall rotation} \end{array} \right\} \text{ of whole crystal}$$

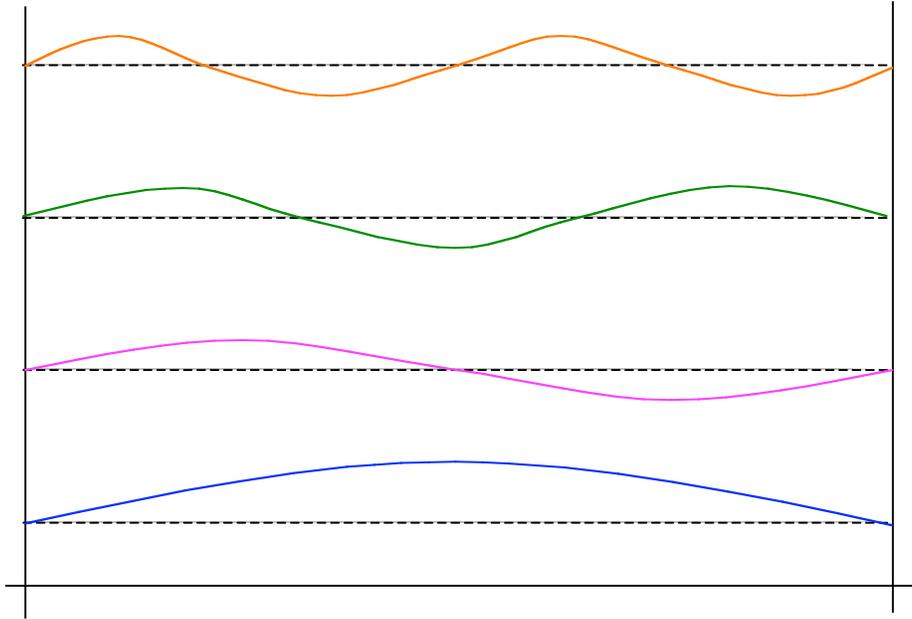
remaining  $3N-6$  correspond to internal vibrations within crystal

In this treatment the crystal is viewed as a giant polyatomic molecule undergoing simple harmonic motion in each of its  $3N-6$  vibrational normal modes.

The behavior of such a harmonic molecular crystal is described by the normal modes of vibration. There are  $3N-6$  harmonic oscillators that can be treated independently (a convenient idealization) to describe the motions and energies within the crystal.

There are many kinds of vibrations in a crystal. Viewed along a particular direction, there will be periodic distortions of alternating extension and compression, analogous to the stretching modes of a linear molecule. There will also be alternating displacements of atoms above and below the specified direction, analogous to the bending modes of a linear molecule. These *longitudinal* and *transverse* modes of a crystal can have wavelengths ranging from as short as a bond length (high frequency) and as long as the macroscopic crystal itself (low frequency). The distribution of frequencies, directions (relative to unit cell axes), and types of vibrations can be very complicated. The simplest models for crystalline solids are based on assumptions about the crystal vibrations that simplify calculation of  $Q_{vib}^*$  and the derivation of thermodynamic properties from  $Q_{vib}^*$ . These models also permit inferences about the nature of the vibrations in a crystal based on the small number (much smaller than  $3N-6$ ) of possible experimental observations of the macroscopic properties in the crystal.

The normal modes for a violin string correspond to one-dimensional particle-in-a-box solutions:



From Lectures 14 and 15 we recall that for a single harmonic oscillator (and excluding the zero-point energy)

$$q_{vib}^* = \sum_{v=0}^{\infty} e^{-vh\nu/kT} = \frac{1}{1 - e^{-h\nu/kT}} \quad \begin{array}{l} T \rightarrow 0, q^* \rightarrow 1 \\ T \rightarrow \infty, q^* \rightarrow \infty \end{array}$$

and for a set of independent (i.e. uncoupled), harmonic oscillators

$$Q_{vib}^* = q_{vib}^*(1)q_{vib}^*(2)q_{vib}^*(3)\dots q_{vib}^*(3N-6) = \prod_{i=1}^{3N-6} \frac{1}{1 - e^{-h\nu_i/kT}}$$

Energy

$$U_{vib} = kT^2 \left( \frac{\partial \ln Q_{vib}}{\partial T} \right)_{N,V} = E_0 + kT^2 \left( \frac{\partial \ln Q_{vib}^*}{\partial T} \right)_{N,V}$$

$$\begin{aligned}
 U_{\text{vib}} - E_0 &= kT^2 \left( \frac{\partial \ln Q_{\text{vib}}^*}{\partial T} \right)_{N,V} = kT^2 \frac{1}{Q_{\text{vib}}^*} \left( \frac{\partial Q_{\text{vib}}^*}{\partial T} \right)_{N,V} \\
 \left( \frac{\partial Q_{\text{vib}}^*}{\partial T} \right)_{N,V} &= \sum_j [1 - e^{-h\nu_j/kT}]^{-2} (-1) \left( -\frac{h\nu_j}{kT^2} \right) e^{-h\nu_j/kT} \prod_{i \neq j}^{3N-6} [1 - e^{-h\nu_i/kT}]^{-1} \\
 &= \sum_j [1 - e^{-h\nu_j/kT}]^{-1} \left( \frac{h\nu_j}{kT^2} \right) e^{-h\nu_j/kT} \underbrace{\prod_{i=1}^{3N-6} [1 - e^{-h\nu_i/kT}]^{-1}}_{Q_{\text{vib}}^*} \\
 kT^2 \frac{1}{Q_{\text{vib}}^*} \left( \frac{\partial Q_{\text{vib}}^*}{\partial T} \right)_{N,V} &= \sum_j h\nu_j e^{-h\nu_j/kT} [1 - e^{-h\nu_j/kT}]^{-1} \\
 &= \sum_{i=1}^{3N-6} \frac{h\nu_i e^{-h\nu_i/kT}}{1 - e^{-h\nu_i/kT}} = kT \sum_{i=1}^{3N-6} \frac{x_i}{e^{x_i} - 1} \quad \text{where } x_i = \frac{h\nu_i}{kT}
 \end{aligned}$$

Einstein Function

NB: This derivation treated all oscillators as harmonic and uncoupled.

### Heat Capacity

$$\begin{aligned}
 C_V^{\text{vib}} &= \left( \frac{\partial U_{\text{vib}}}{\partial T} \right)_{N,V} = \left[ \frac{\partial (U_{\text{vib}} - E_0)}{\partial T} \right]_{N,V} = \frac{\partial}{\partial T} \sum_{j=1}^{3N-6} h\nu_j [e^{h\nu_j/kT} - 1]^{-1} \\
 &= \sum_{j=1}^{3N-6} h\nu_j (-1) [e^{h\nu_j/kT} - 1]^{-2} (-1) \frac{h\nu_j}{kT^2} e^{h\nu_j/kT} \\
 &= \sum_{j=1}^{3N-6} k \left( \frac{h\nu_j}{kT} \right)^2 e^{h\nu_j/kT} [e^{h\nu_j/kT} - 1]^{-2} \\
 &= k \sum_{j=1}^{3N-6} x_j^2 e^{x_j} [e^{x_j} - 1]^{-2}
 \end{aligned}$$

### Free Energy (Helmholtz)

$$\begin{aligned}
 (A_{\text{vib}} - E_0) &= -kT \ln Q_{\text{vib}}^* = -kT \ln \left[ \prod_{i=1}^{3N-6} \frac{1}{1 - e^{-h\nu_i/kT}} \right] \\
 &= +kT \sum_{i=1}^{3N-6} \ln(1 - e^{-h\nu_i/kT}) = kT \sum_{i=1}^{3N-6} \ln(1 - e^{-x_i})
 \end{aligned}$$

Einstein Function

Entropy

$$S_{vib} = \frac{U_{vib} - A_{vib}}{T} = \frac{(U_{vib} - E_0)}{T} - \frac{(A_{vib} - E_0)}{T}$$

add and subtract the same quantity

$$= k \sum_{i=1}^{3N-6} \left[ \frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right]$$

So, we should be able to calculate “all” properties of solids, but it seems as though we need to know the frequencies of *all* of the normal modes.

**1** Classical Treatment — Equipartition Principle

Put  $\frac{1}{2} kT$  of energy into each “degree of energy storage”, where each normal mode of vibration has **TWO** degrees for storage of energy (one for kinetic energy and the second for potential energy).

$$U_{vib} = \bar{E}_{vib}^{class} = \sum_{i=1}^{3N-6} \left[ \left( \frac{1}{2} kT \right)_{P.E.} + \left( \frac{1}{2} kT \right)_{K.E.} \right] = (3N - 6)(kT) \cong 3NkT$$

$$\boxed{\bar{E}_{vib}^{class} = 3RT \text{ for a mole of ATOMS in crystal}}$$

$$C_v^{class} = \left( \frac{\partial U}{\partial T} \right)_{N,V} = 3R \text{ per mole}$$

This is correct at HIGH TEMPERATURE, and is known as the LAW OF DULONG AND PETIT (~1819)

- Heat capacity per mole is roughly the same for all substances
- Measure heat capacity per gram (different for all substances)
- The ratio is grams/mole = molecular mass!

The Classical Treatment, however, turns out to be incorrect at low temperature.

## 2 Einstein Treatment

Use quantum theory (as opposed to classical)

**Assume all  $\nu_i$  equal (all  $x_i$  equal)**

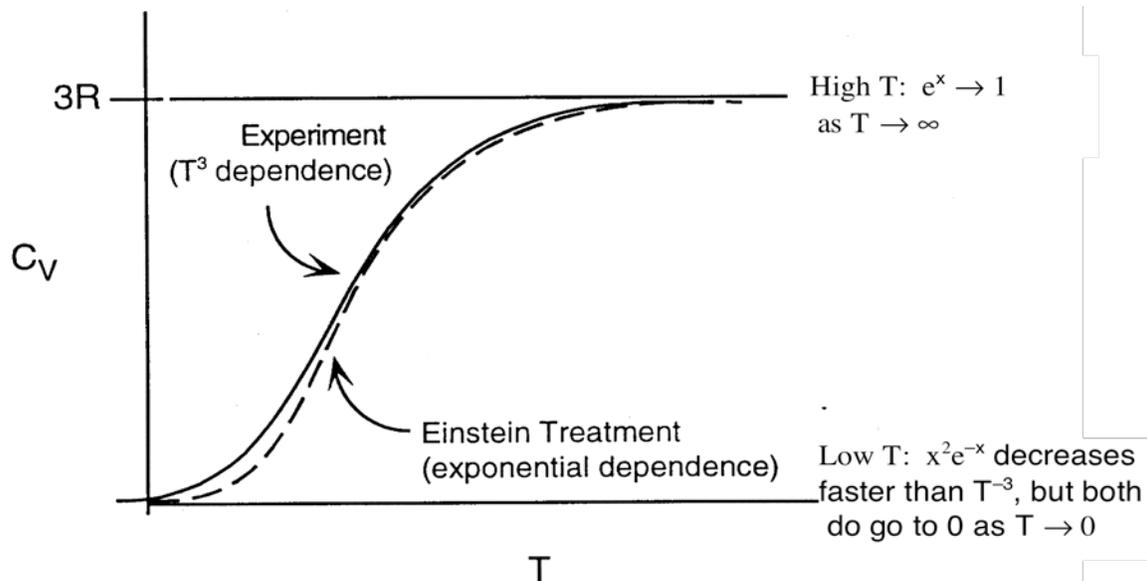
This makes it easy to evaluate the sum over vibrations.

$$C_V^{Einstein} = k \sum_{i=1}^{3N-6} \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} = k(3N-6) \frac{x^2 e^x}{(e^x - 1)^2} \cong 3R \frac{x^2 e^x}{(e^x - 1)^2} \quad \text{per mole } (N = N_a, kN_a = R)$$

$$\text{where } x = \frac{h\nu_E}{kT} = \frac{\theta_E}{T}$$

This approach provides a significant improvement over the classical (equipartition) result, because  $C_V \rightarrow 0$  for  $T \rightarrow 0$ .

$$\lim_{T \rightarrow 0} C_V^{Einstein} = \lim_{x \rightarrow \infty} C_V^{Einstein} = \lim_{x \rightarrow \infty} 3R x^2 \frac{e^{-x}}{(1 - e^{-x})^2} = 0$$



The success of the Einstein model gave important early support to quantum theory: it showed that quantization of vibrational energy could account for low-T heat capacity.