Energy-Temperature relation for the Einstein solid

(a) In Problem #4 of HW set # 5 we found the number of accessible states $\Omega(E)$ for an Einstein solid with $M$ phonons and $N$ atoms to be well-approximated as

$$\ln \Omega(E) = (M + 3N) \ln(M + 3N) - M \ln M - 3N \ln 3N, \quad (1)$$

where the energy dependence is contained in $M$

$$M = \frac{E}{\hbar \nu} - \frac{3N}{2}. \quad (2)$$

Each vibrational mode has the same fundamental frequency $\nu$. To find the relationship between $E$ and $T$, we resort to the fundamental statistical thermodynamic definition of absolute temperature

$$k \beta = \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_x \quad (3)$$

where the entropy $S$ is, of course, given by the famous postulate of Boltzmann,

$$S = k \ln \Omega(E). \quad (4)$$

From Eqs.(1) and (3), we find using the chain rule,

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial \ln \Omega}{\partial M} \frac{\partial M}{\partial E} = \frac{1}{h \nu} \frac{\partial \ln \Omega}{\partial M} = \frac{1}{h \nu} \ln \left( 1 + \frac{3N}{M} \right). \quad (5)$$

This is easily solved for $M$,

$$\frac{M}{3N} = \frac{1}{\exp(\beta h \nu) - 1}, \quad (6)$$

and with Eq.(2), we obtain

$$E = 3Nh\nu \left( \frac{1}{2} + \frac{1}{\exp(\beta h \nu) - 1} \right). \quad (7)$$

The constant term, $3Nh\nu/2$, is the zero-point energy of the solid. The other term represents the temperature dependent contribution of the $3N$ vibrational modes to the total energy.

(b) At high temperature, we have

$$\beta h \nu = \frac{h \nu}{kT} \ll 1, \quad (8)$$

so we can expand the exponential term to first order

$$\exp(\beta h \nu) = 1 + \beta h \nu, \quad (9)$$
and substitute this into Eq.(7) to find

\[ E = 3NkT \left( 1 + \frac{1}{2} \frac{\hbar \nu}{kT} \right) \rightarrow 3NkT. \]  

(10)

Thus the high temperature limit of the energy is the classical limit for \( 3N \) independent harmonic oscillators.

At low temperature, we have

\[ \beta \hbar \nu = \frac{\hbar \nu}{kT} \gg 1, \]  

(11)

and it is no longer justified to expand the exponential function. Instead, we recognize that \( \exp(-\beta \hbar \nu) \ll 1 \), so if we rewrite Eq.(7) as

\[ E = 3Nh\nu \left( \frac{1}{2} + \frac{\exp(-\beta \hbar \nu)}{1 - \exp(-\beta \hbar \nu)} \right), \]  

(12)

we can expand the this function in powers of the very small variable \( x \), where \( x = \exp(-\beta \hbar \nu) \). Upon doing so, we find

\[ E = 3Nh\nu \left( \frac{1}{2} + \exp(-\beta \hbar \nu) \left( 1 + \exp(-\beta \hbar \nu) + \cdots \right) \right), \]  

(13)

which yields, to lowest order in \( \exp(-\beta \hbar \nu) \), the result

\[ E = 3Nh\nu \left( \frac{1}{2} + \exp(-\beta \hbar \nu) \right). \]  

(14)

From this we see that at absolute zero, \( E \) equals just the zero point energy, \( 3Nh\nu/2 \). The additive exponential term describes the temperature dependence near absolute zero.