$$Z_E = \left[\frac{e^{-\theta_E/2T}}{\left(1-e^{-\theta_E/T}\right)}\right]^3 \qquad \bar{u}_E = 3\bar{R}\theta_E\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_E/T}-1\right)}\right] \qquad \bar{c}_{v,E} = 3\bar{R}\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$$

$$\bar{s}_E = \frac{\bar{u}_E}{T} - \bar{R}\ln Z_E = \frac{3\bar{R}\,\frac{\theta_E}{T}}{\left(e^{\theta_E/T}-1\right)} - 3\bar{R}\ln\left(1-e^{-\theta_E/T}\right)$$

Application of these relationships to perfect gases was facilitated by the availability of spectroscopically measured values of $\theta_{v,p}$ (Table IIIC-2). These measurements are possible since intramolecular vibration within independent gaseous molecules occurs in the manner of the model, viz., at fixed frequencies. In comparison, the Einstein model bears very little resemblance to an actual vibrating lattice, see Fig. IIIC-2. Vibration of a lattice point along the axis of one of its bonds will obviously induce vibration in both of the other bond directions and the vibration of a single atom will immediately propagate to induce vibration in its nearest neighbors. The 3N oscillators of the lattice are not independent and their vibrations do not occur at a single frequency. Thus the concept of a single Einstein frequency is artificial and one cannot measure θ_E directly. It must be interpreted from property data. (Usually it is deduced from specific heat data.) This drawback is sufficient that in practice the Einstein model is used very little for the analysis of lattice vibrations.[11] However, once θ_E has been determined, the property predictions of the Einstein model are quite successful.[12,13] The only serious deficiency is its prediction of low temperature properties. For example, $\bar{c}_{v,E}(T \Rightarrow 0) \propto e^{-\theta_E/T}$; but measurements show that $\bar{c}_{v,phn}(T \Rightarrow 0) \alpha T^3$. The following section shows that both of these deficiencies are overcome by the *Debye Model*.

2. <u>The Debye Model</u> ignores the detailed behavior of individual vibrating lattice points. It deals with the acoustical waves produced by the vibrations. The characteristics of acoustical radiation, or phonons, closely parallel those of electromagnetic radiation, or photons. Photons are generated by electron motions and propagate at the speed of light. Phonons are generated by lattice motions and propagate at the speed of sound. Thus the phonon distribution is governed by eqn. IIID-3 and 4 with the modifications that the average sound speed, c_s, is

---

[11]The Einstein model remains accurate for interatomic vibrations in solids whose lattice points are occupied by multiatom molecules rather than atoms, e.g., in solid water (H_2O), carbon dioxide (CO_2), nitrogen (N_2), etc. (See below.)

[12]One frequently finds that transparently superficial microscopic models yield amazingly accurate macroscopic predictions. It seems that the technique of summation or integration to obtain total properties tends to smooth over the detailed inaccuracies of the model.

[13]It is very common for the Einstein model to be compared to data using the measurable characteristic temperature of the Debye model, see below, as the value of the Einstein temperature. This is an unjustified and erroneous assumption, $\theta_E \neq \theta_D$. Such reported comparisons are an unfair criticism of the Einstein model.