In most cases these internal mechanisms are independent, exceptions are noted below. When this is the case, the internal mode can be further subdivided into separate contributions and by analogy with eqn. IIIC-8, we have

$$Z_{in}(T) = Z_r(T)\ Z_v(T)\ Z_{el}(T)\ Z_n(T)$$

As before when the partition function is a product we can write the properties as a sum over the separate modes ($p_{in} = 0$).

$$\bar{u}_{in} = \bar{u}_r + \bar{u}_v + \bar{u}_{el} + \bar{u}_n \qquad \bar{c}_{v,in} = \bar{c}_{v,r} + \bar{c}_{v,v} + \bar{c}_{v,el} + \bar{c}_{v,n}$$

$$\bar{s}_{in} = \bar{s}_r + \bar{s}_v + \bar{s}_{el} + \bar{s}_n$$

This places even more stress on the determination of the partition functions.

B. The Characteristic Temperature of a Mode

The solution of the Schroedinger equation for each independent mode yields its energy levels, viz., for the pth mode, $\varepsilon_{p,\ell}$, and degeneracy, $g_{p,\ell}$. When these input data are available the mode partition function is determined in principle.

$$Z_p = \sum_{\ell=1}^{L} g_{p,\ell}\ e^{-\varepsilon_{p,\ell}/kT} \qquad \text{(IIIB-11)}$$

In most physical systems, including all of the modes we will investigate, $L = \infty$. Hence, eqn. IIIB-11 is an infinite series. The practicality of using direct summation to evaluate such series is governed by its rate of convergence. Moreover, the partition function has little value in itself. Its value is its relationship to properties. These require that one take its logarithm and derivative. It is, therefore, *highly advantageous that the partition function be expressed as an analytical function.* Circumstances for which the partition function can be so expressed are:

1. Exact Series: In at least one important case, the vibrational mode, the series representation reduces exactly to a transcendental function. In such cases general analytical expressions for the property contribution of that mode can be obtained.

2. Low-Temperature Limit: The sum over levels is arranged in the order of increasing energy, $\varepsilon_{p,1} < \varepsilon_{p,2} < \varepsilon_{p,3}$, etc. If the temperature satisfies the condition $(\varepsilon_{p,2} - \varepsilon_{p,1})/kT >> 1$ the series converges rapidly and is adequately represented by a few, often one or two terms.

$$Z_p(T) \simeq g_{p,1}\ e^{-\varepsilon_{p,1}/kT} + g_{p,2}\ e^{-\varepsilon_{p,2}/kT}$$

3. High-Temperature Limit: If the spacing between the adjacent energy levels is small, $(\varepsilon_{p,\ell+1} - \varepsilon_{p,\ell})/kT << 1$, then the rate of convergence of the series is slow and it can be represented by an integral.

$$Z_p = \sum_{\ell=1}^{L} g_{p,\ell}\ e^{-\varepsilon_{p,\ell}/kT} \simeq \int_{\ell=1}^{L} g_p(\ell) e^{-\varepsilon_p(\ell)/kT}\, d\ell \quad \text{or} \quad \int_{\varepsilon_{p,min}}^{\varepsilon_{p,max}} g_p(\varepsilon_p) e^{-\varepsilon_p/kT}\, d\varepsilon_p$$