$$\rho_{j(i,\ell)} = \frac{g_{j(i,\ell)} e^{-\varepsilon_{j(i,\ell)}(\eta\bar{v})/kT}}{Z(T,\eta\bar{v})} = \frac{g_{ex,i} g_{in,\ell} e^{-[\varepsilon_{ex,i}(\eta\bar{v}) + \varepsilon_{in,\ell}]/kT}}{Z_{ex}(T,\eta\bar{v})\ Z_{in}(T)}$$

$$= \rho_{ex,i}(T,\eta\bar{v})\ \rho_{in,\ell}(T) \qquad \text{(IIIC-10)}$$

That is, the probability that a particle will be in the $j(i,\ell)^{th}$ level is the product of the probabilities that it will be in the ith external level and the ℓth internal level.[6] Notice that only the external mechanics of the particle is dependent on the system volume. (The volume enters the solution of the Schroedinger equation through the boundary conditions.) Therefore, *only the external energy levels and partition function are dependent on the system volume.*

Separation of the partition function into modes allows properties to be determined for each separate mode. Specifically since the partition function appears in property relationships as a logarithm (eqns. IIIC-3 to 7), its contributions are additive, $\ell n[Z(T,\eta\bar{v})] = \ell n[Z_{ex}(T,\eta\bar{v})] + \ell n[Z_{in}(T)]$. As applied in eqns. IIIC-3 to 7, we have

$$\bar{u} = \bar{u}_{ex} + \bar{u}_{in} \qquad \bar{c}_v = \bar{c}_{v,ex} + \bar{c}_{v,in}$$

$$p = p_{ex} + p_{in} \qquad \bar{h} = \bar{u}_{ex} + p_{ex}\cdot\bar{v} + \bar{u}_{in}$$

We can use the same approach with the entropy. The results are identical when applied to Boltzons, eqn. IIIC-2a.

$$\bar{s}^{MB} = \bar{s}^{MB}_{ex} + \bar{s}^{MB}_{in} = \left(\frac{\bar{u}_{ex}}{T} + \bar{R}\ell n Z_{ex}\right) + \left(\frac{\bar{u}_{in}}{T} + \bar{R}\ell n Z_{in}\right)$$

But when we apply this principle in the indistinguishable limit, the term that comes from N! (see Exmp. 1) must be included in the entropy; but only once. We therefore define the external and internal entropy components in the indistinguishable limit as

$$\bar{s}^{il} = \bar{s}^{il}_{ex} + \bar{s}^{il}_{in} \qquad \bar{s}^{il}_{ex} = \frac{\bar{u}_{ex}}{T} + \bar{R}\ell n\left(\frac{Z_{ex}}{\eta N_A}\right) + \bar{R} \qquad \bar{s}_{in} = \frac{\bar{u}_{in}}{T} + \bar{R}\ell n Z_{in} \qquad \text{(IIIC-11a,b,c)}$$

We have found that separate determination of $Z_{ex}(T,\eta\bar{v})$ and $Z_{in}(T)$ is sufficient to determine indistinguishable limit properties. In this case the energy levels and degeneracies of the *external* mode are those of the *particle in the box*, Unit IIIA. The physical mechanisms that contribute to the internal modes include:

1. Rotation of the particle about its center of gravity; 2. Vibration of the constituent atoms about their mean position in the molecule; 3. Excitation of bound electrons into higher electronic levels or, at higher energies, release of the intermolecular binding potential when atoms are dissociated from the particle, or, at still higher energies, release bound electrons from the particle, ionization; 4. Rotation of the nucleus about a nuclear spin axis.

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[6]The distribution function for the number of particles per level, n_j, cannot be written analogously. $n_{j(i,\ell)} \neq n_{ex,i} n_{in,\ell}$. Rather $n_{j(i,\ell)} = N\ \rho_{ex,i}\rho_{in,\ell}$.