A. External and Internal Energy Modes

We begin the division into components by separating the energy which is dependent on the internal structure of the particle, *internal modes,* from that which is not, the *external mode.* The energy of the external mode includes the kinetic energy contribution of center of gravity translation and the potential energy contribution due to interparticle forces. This unit is restricted to consideration of systems of *identical nonlocalized particles,* liquids or gases; that is, to systems of indistinguishable Bosons or Fermions and these only in the Boltzmann limit.[4] In addition, all of Units III are limited to independent particles (see Unit IIIA, Sect. IIA). To be considered independent nonlocalized particles must have negligible interparticle forces. Thus, the only external mode contribution to be considered is that of translation. The only phase to be considered is the gas phase.[5]

The principal advantage of separating energy into modes is that the energy levels and degeneracies (ε_j and g_j) of complex particles can be evaluated one mode at a time. Separation into modes allows the external mechanics of translation to be uncoupled from the internal particle mechanics. That is, the solution of the Schroedinger equation for independent particle translation—the particle in a box (Unit IIIA)—can be used in combination with separately obtained Schroedinger equation solutions for the internal modes. The total wave function can then be determined from $\psi = \psi_{ex}\psi_{in}$. The degeneracy is simply the number of distinct wave functions, that is, states that have the same energy. Thus, the degeneracy follows the same product rule as the wave function. The separate mode energy levels are additive.

$$g_{j(i,\ell)} = g_{ex,i}g_{in,\ell} \qquad \varepsilon_{j(i,\ell)}(n\bar{v}) = \varepsilon_{ex,i}(n\bar{v}) + \varepsilon_{in,\ell} \qquad \text{(IIIC-8a,b)}$$

The level designation, j, refers to the total mechanics of the particle. The separate modes have been ordered into levels in an analogous manner. Their index designations are i and ℓ. Therefore, the net level sequence is dependent on each subsequence, $j(i,\ell)$. Using eqns. IIIC-8a,b the total partition function becomes

$$Z(T,\bar{v}) = \sum_{j=1}^{J} g_{j(i,\ell)} e^{-\varepsilon_{j(i,\ell)}(n\bar{v})/kT} = \sum_{i=1}^{I}\sum_{\ell=1}^{L} g_{ex,i}g_{in,\ell} e^{-[\varepsilon_{ex,i}(n\bar{v}) + \varepsilon_{in,\ell}]/kT}$$

$$= \sum_{i=1}^{I} g_{ex,i} e^{-\varepsilon_{ex,i}(n\bar{v})/kT} \cdot \sum_{\ell=1}^{L} g_{in,\ell} e^{-\varepsilon_{in,\ell}/kT} = Z_{ex}(T,n\bar{v})Z_{in}(T) \qquad \text{(IIIC-9)}$$

Similarly, the probability distribution can be formulated as

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[4]Boltzons are also identical particles. Identical particles become distinguishable when they are tied to specific positions in a lattice.

[5]The translating particles in a liquid interact with one another. They are dependent.