5. Constant Volume Specific Heat, c_v is obtained by differentiating eqn. IIIC-3[3]

$$\bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T}\right)_{\bar{v}} = \left[\frac{\partial}{\partial T}\,\bar{R}T^2\left(\frac{\partial \ln Z}{\partial T}\right)_{\bar{v}}\right]_{\bar{v}} = 2\bar{R}T\left(\frac{\partial \ln Z}{\partial T}\right)_{\bar{v}} + \bar{R}T^2\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_{\bar{v}} \qquad \text{(IIIC-7)}$$

The above relationships demonstrate that if the partition function can be formulated analytically as a function of T and $\bar{v}$, the macroscopic properties are readily obtained. Therefore, microscopic determination of the properties of Boltzons, Bosons and Fermions in the indistinguishable limit reduces to finding $Z(T,\eta\bar{v})$.

II. EVALUATION OF THE PARTITION FUNCTION

The partition function is defined as the sum over the J levels, or equivalently P states, accessible to the particles composing the system.

$$Z(T,\eta\bar{v}) = \sum_{j=1}^{J} g_j e^{-\varepsilon_j(\eta\bar{v})/kT} = \sum_{p=1}^{P} e^{-\varepsilon_p(\eta\bar{v})/kT} \qquad \text{(IIIB-12)}$$

Example 2. Consider a system with a triply degenerate first level, $g_1 = 3$. Expand the first three terms of the sum over states and show that the result is equivalent to the first term of the sum over levels.

$$Z = \sum_{p=1}^{P} e^{-\varepsilon_p/kT} = e^{-\varepsilon_{p=1}/kT} + e^{-\varepsilon_{p=2}/kT} + e^{-\varepsilon_{p=3}/kT} + \sum_{p=4}^{P} e^{-\varepsilon_p/kT}$$

The first three states of this series are members of the same level, so $\varepsilon_{p=1} = \varepsilon_{p=2} = \varepsilon_{p=3} = \varepsilon_{j=1}$, $g_{j=1} = 3$. Thus the first terms can be written

$$Z = 3e^{-\varepsilon_{j=1}/kT} + \sum_{p=4}^{P} e^{-\varepsilon_p/kT}$$

The remainder of the series, beginning at $p = 4$, can be rewritten in terms of levels beginning at $j = 2$. States of equal value can be collapsed in an analogous manner with the degeneracy of each level. Thus

$$Z = 3e^{-\varepsilon_{j=1}/kT} + \sum_{j=2}^{J} g_j e^{-\varepsilon_j/kT} = \sum_{j=1}^{J} g_j e^{-\varepsilon_j/kT}$$

We thus see the equivalence of the two series formulations.

As written, the series of energy levels accounts for all contributions to the particle energy. In the evaluation of the partition function it is useful to subdivide particle energy into components.

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[3]The specific heat at constant pressure can be formulated in an analogous manner, using direct integration of eqn. IIIC-6, $\bar{c}_p = (\partial\bar{h}/\partial T)_p$. But the constant pressure condition is not easily applied. It is far easier to determine $\bar{c}_p$ from $\bar{c}_v$ using eqn. ID-6, $\bar{c}_p - \bar{c}_v = T\bar{v}\beta^2/\kappa$. For a perfect gas, $\bar{c}_p^* = \bar{c}_v^* + \bar{R}$.