C. Properties

The properties of a macroscopic system result from the microscopic behaviors of the particles of which it is composed. Specifically, the "instantaneous" properties of an isolated system are those of the macrostate in which it resides at that instant. The magnitudes of the energy levels, ε_j, and the distribution of particles among the levels, $n_{j,i}$, are sufficient information to determine properties. System properties are related to the energies of occupied levels by a functional relationship, say $\lambda(\varepsilon_j)$. For a specific macrostate an intensive property per particle is written

$$\bar{\lambda}_i = \frac{1}{N} \sum_{j=1}^{J} n_{j,i} \lambda(\varepsilon_j) \qquad \text{(IIIA-10a)}$$

An extensive property is written as

$$\bar{\Lambda}_i = N\bar{\lambda}_i = \sum_{j=1}^{J} n_{j,i} \lambda(\varepsilon_j) \qquad \text{(IIIA-10b)}$$

Example 9. The system of 4 particles restricted to 5 energy levels was found to have five macrostates as listed in Table IIIA-2. Calculate the intensive macrostate property that corresponds to the particle energy relation, $\lambda(\varepsilon_j) = \varepsilon_j^{\frac{1}{2}}$ for macrostate I.

Before we determine the value of this property, let us consider its significance. Our energy levels have been chosen consistently as those of the particle in a box. The particle in a box is a model for the translational kinetic energy of gaseous particles, $\varepsilon_j = (m^*\hat{V}_j^2/2)$. Thus our function is linearly proportional to particle velocity, $\lambda(\varepsilon_j) = \varepsilon_j^{\frac{1}{2}} \sim V$. Therefore, it is proportional to the gaseous particle momentum. The pressure in a gas is a measure of momentum exchange at an interface. The property to be determined is proportional to the pressure of the particle in a box. We will call this property the *pseudopressure*. The pseudopressure of macrostate I is determined by means of the substitution of its distribution ($n_{1,I} = 0$, $n_{2,I} = 1$, $n_{3,I} = 2$, $n_{4,I} = 0$, $n_{5,I} = 1$) into eqn. IIIA-10 a.

$$\overline{\varepsilon_I^{\frac{1}{2}}} = \frac{1}{N} \sum_{j=1}^{5} n_{j,I} \varepsilon_j^{\frac{1}{2}} = \frac{B_o^{\frac{1}{2}}}{4} (0 \cdot 3^{\frac{1}{2}} + 1 \cdot 6^{\frac{1}{2}} + 2 \cdot 9^{\frac{1}{2}} + 0 \cdot 11^{\frac{1}{2}} + 1 \cdot 12^{\frac{1}{2}}) = 2.97840\ B_o^{\frac{1}{2}}$$

Exercise 10. Use a calculator to determine the pseudopressure for macrostates II to V for the 4 particle example. Five place accuracy is needed below to emphasize differences. (The answers are listed in Table IIIA-4.)

The previous example and exercise have illustrated the manner in which macrostate properties are calculated. Our interest is in observed properties. Real systems shift from microstate to microstate with extreme rapidity under the action of particle collisions. These microstate shifts give rise to the appearance of a sequence of different macrostates. The system properties are those of the "then present" macrostate; thus the instantaneous properties vary in time. Though macrostate shifts do not necessarily occur with each collision (microstates of the same macrostate can occur in sequence), their frequency of change is sufficiently rapid that no observational technique can detect the