of microstates, W. (Use the appropriate counting formula, eqn. IIIA-7a,b, or c).

b. Calculate the macrostate probabilities, p_i.

c. Calculate the ensemble average pseudopressure, $\hat{\varepsilon}^{\frac{1}{2}}$.

d. Calculate the deviation between the ensemble average and more probable macrostate pseudo-pressures

$$\left[\left|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}_{mp}}\right| / \hat{\varepsilon}^{\frac{1}{2}}\right] \%$$

III. EQUILIBRIUM

A four particle example has been developed extensively (Tables IIIA-2, 3, and 4). Included in the tabulation of its properties are the deviations of the macrostate's pseudopressure from the ensemble average pseudopressure, $|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}}|/\hat{\varepsilon}^{\frac{1}{2}}$ (Table IIIA-4). When these deviations are compared for each of three statistics we find that the most probable macrostate's pseudopressure is a close approximation of the average, $\overline{\varepsilon^{\frac{1}{2}}_{mp}} \approx \hat{\varepsilon}^{\frac{1}{2}}$.[24] As this tiny system has only 5 macrostates and the most probable macrostate rather dominates its probability distribution, it is not unexpected that the most probable macrostate's properties would be close to the probability-weighted average properties. But our purpose in this section is to determine those characteristics of systems small enough to be studied in detail, that are maintained or enchanced as we extrapolate to realistically large systems.[25] We will find that as N increases I^* increases geometrically. As a result, the probability of individual macrostates, including the most probable, decreases. The most probable macrostate does not dominate the probability distribution of real systems. Yet, we will also find that the correspondence between the properties of the most probable macrostate and the ensemble average properties gets better and better as system size increases. The following section demonstrates how this trend is evidenced and explains why. With the help of this study we can recognize the meaning of equilibrium.

A. Extrapolation to Large Systems

In this section we extend the conclusions drawn from the 4 particle example, Table IIIA-4, by considering successively larger Boltzon systems with the same average energy per particle in the same 5 energy levels. For a six particle system, Table IIIA-5, we

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[24]In the case of the Boltzon systems, the next to least probable macrostate is even closer. In large systems it is not unusual for several macrostates to be closer to the average than the most probable. This has no particular significance. The emphasis is on the observation that the easily identified most probable is always a close approximation.

[25]Trial and error determination of macrostate distributions is inconceivable in real systems. There are 10^{19} molecules/cm^3 in air at STP. The 30-particle example, see Table IIIA-7 below, required a large fraction of an hour in execution time on a large computer to find its macrostate distributions.