The two improbable macrostate distributions, in contrast, are bunched more tightly among the levels.[26] They are more "ordered." As the distributions of the probable macrostates are similar, so are their properties. Since the system spends time disproportionately in the probable macrostates, the ensemble average is determined predominantly by the properties of these macrostates. Correspondingly the pseudopressure deviations of the probable macrostates listed are small. Indeed this is true for each member of Group 1. Its RMS deviation is 0.298%. And the RMS deviation of each successively less probable group is increased. With this illustration we see how and why the most probable macrostate's properties can converge toward the ensemble average properties as the system size increases. The most probable macrostate is simply one member of the group of probable macrostates. The last column of Table IIIA-6 shows a continuous decrease in pseudopressure deviation as system size increases. It is not difficult to project that in real systems, $\overline{\varepsilon^{\frac{1}{2}}_{mp}} \rightarrow \varepsilon^{\frac{1}{2}}$. This conclusion eliminates the necessity for determining the macrostate distributions by trial and error. *We only need the distribution of the most probable macrostate*, $n_{j,mp}$. We will be able to determine this distribution analytically, Unit IIIB. We follow this procedure to determine properties in the remainder of Units III.

We have considered the relationship between macrostate probability and properties in successively larger isolated systems in order to achieve an understanding of the behavior of real systems. We conclude this extrapolation with a summary.

> Equilibrium. The macrostate probability in a real system is dominated by a tiny proportion of the macrostates, those with high relative probability. These macrostates constitute the *equilibrium group*. Individually, none of these macrostates is particularly probable, but collectively their probability is overwhelming. The macrostates of the equilibrium group are similar to one another; they are characterized by their disorder and they have essentially the same properties. As a result the long-time or ensemble average properties of the system are indistinguishable from those of the equilibrium group macrostates. A system is in equilibrium when its observed properties are the same as the long time average.
>
> Nonequilibrium. An isolated system is out of equilibrium when its properties are *observed* to deviate from the long time, ensemble average. Such an observation requires that the system traverse a sequence of macrostates that includes a large proportion of improbable nonequilibrium macrostates. The sequence must be of sufficient duration that observation of the property deviation is possible.

The test of equilibrium is the absence of property deviations. This implies property measurement. Our illustrative energy states are those of a simple compressible media.[27] Its measurable properties are pressure, temperature, and volume. But in an

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[26]The lowest and highest levels are nondegenerate; therefore they are less occupied.

[27]The levels of the particle in a box are governed by its volume, $\varepsilon_j = \varepsilon_j(V)$. The energy levels of other types of single media would be dependent on their displacement variable, $\varepsilon_j = \varepsilon_j(\bar{X})$, or variables in complex media, $\varepsilon_j = \varepsilon_j(\bar{X}_k)$.