isolated system volume is fixed. Only specific volume, or its reciprocal— density, could be observed to deviate. Deviations can only be measured in terms of specific volume, pressure, or temperature. These are intensive properties, they are defined, and must be measured, locally. Thus equilibrium, i.e., an absence of property deviations in an isolated system of identical particles, requires that the intensive properties be spatially uniform as well as temporally invariant.[28,29] As a consequence we recognize that each spatial subdivision of an isolated system of identical particles in equilibrium contains the same proportion of the constrained energy and number of particles. Moreover, the properties in that subdivision are the same as they would be if it were itself an isolated system.

B. Approach to Equilibrium

Our development has been premised on the hypothesis that macrostate sequences are governed by pure chance. Thus, over long times the probability of a sequence that passes through a series of nonequilibrium macrostates for a period long enough to exhibit property deviation is nil.[30,31] But it is unrealistic to limit our consideration to systems that have been isolated for long times. Indeed, our primary interest is energy exchange. Typically a system's energy is altered by heat or work occurring at a localized position on the boundary. Once the energy transport is concluded the system can be considered isolated. But when the transport has been rapid, the system is left with a surplus or deficit

---

[28]We are ignoring the effect of extrinsic fields imposed on the system, e.g., gravity. In the presence of an extrinsic field the equilibrium distribution might be nonuniform but it is still uniquely defined, e.g., hydrostatic pressure variation.

[29]A system of identical particles requires that each has the same accessible energy states. This eliminates multiphase systems from consideration. For example, particles in a solid have one set of accessible states while those in a surrounding vapor have another set. The more general procedures of a Grand Canonical Ensemble are required to extend our consideration to such cases.

[30]In the previously considered 30 particle system, if we assume 10^3 collisions/s the least probable macrostate would occur once every three years. Random probability would expect the system to exist in the less probable 80% of the macrostates 19 times per second. If we assume that a measurable deviation would require that the system exist in one of the less probable 80% of the macrostates 20% of the time for a period of 0.1 s, we could only expect such a sequence once every 6,767 years.

[31]Our development has concerned macrostates of the entire system, not the spatial distribution in subsystems. It is theoretically conceivable that a property might deviate locally while corresponding regions deviated in the opposite sense in such a manner that the ensemble average property over the whole system was constant. But one intuitively recognizes that this probability is even smaller than that of other events already found negligible.