Dependent Particles. Continuing our consideration of the particle in a box, the energy states accessible to the single-point particle are those of translation. This model can provide a basis for the consideration of gaseous behavior. But when more than one molecule is present in the box, it is no longer field free. A potential field acts between the particles as a result of their dipole interactions (see Unit ICS). As a result, the potential, V, appearing in the Schroedinger equation is no longer zero. This potential is, in fact, dependent on the position of all of the molecules present in the box, $V = V(x_1, \ldots V(x_1, y_1, z_1, y_2, z_2, \ldots; x_N, y_N, z_N)$. In these instances the Schroedinger equation must be solved simultaneously for the N particles and the allowed energies will not be the same as those for the original single particle, $\varepsilon_j(\text{one}) \neq \varepsilon_j(\text{many})$.

One can imagine that the simultaneous solution of the Schroedinger equation for a system of particles is not a simple matter. The usual procedure is to account for the effect of the dependence of particles by successively treating cases of increasing numbers of particles and examining the changes in behavior as each more accurate model is solved. Physical situations for which the first-order (single-particle), solution for the energy states gives accurate representations of properties of actual systems are not uncommon.

Independent Particles. Whenever the energy states and levels accessible to the many particles of a real system are the same as those for a single particle under the same conditions, $\varepsilon_j(\text{one}) = \varepsilon_j(\text{many})$, that system is composed of independent particles. This requires that the potential acting on each particle is, at most, dependent on its position, $V(x,y,z)$. For example, the molecules of a gas can be treated as independent particles whenever the total translational kinetic energy of the collection dominates the total potential energy associated with the fields between the particles. These conditions prevail in gaseous systems when the pressure is low, so that the distance between particles is comparatively large, or when the temperature is high, so that the average molecular kinetic energy is high.[11] Lattice vibrations of atoms in a solid can also be modeled as independent (Unit IIID). This approximation is valid not because the potential energy between the atoms is negligible but because the potential can be written in terms of a constant "mean" position of the neighboring atoms. Thus the potential is independent of the motions of the neighbors.

The independent particle approximation accurately predicts the properties of many important physical systems. It will allow us to apply statistical principles to groups of particles and it will not impair our subsequent understanding of equilibrium or the second law of thermodynamics. We will continue this assumption throughout Units III.

As defined, the macrostates of a given isolated system constitute all possible solutions of eqns. IIIA-6. Thus to determine a macrostate one must specify the internal energy, U, the number of particles, N, and the energy levels for the system $(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_j, \ldots, \varepsilon_J)$. One of the great frustrations of the science of statistical thermodynamics is that no technique to determine the full set of macrostate distributions has been found except trial and error. Fortunately, through our development, we will find a characteristic

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[11]We will see in Unit IIIC that a gaseous system of independent particles is a perfect gas (see also Unit ID).