

As it stands, this equation is applicable to any dense system. We now specialize this to the case of a fluid. Let $n = 2$ and introduce $g^{(2)}(r_{12})$ to get

$$-kT \ln g^{(2)}(1, 2, \xi) = \xi u(r_{12}) + \rho \int_0^\xi \int_V u(r_{13}) \left[\frac{g^{(3)}(1, 2, 3, \xi)}{g^{(2)}(1, 2, \xi)} - g^{(2)}(1, 3, \xi) \right] d\mathbf{r}_3 d\xi \quad (13-40)$$

Notice that this gives $g^{(2)}$ in terms of $g^{(3)}$ or, in general, gives $g^{(n)}$ in terms of $g^{(n+1)}$. Such a set of coupled equations is called a hierarchy. It is exact, but unfortunately not very usable as it stands. If we could derive some other relation for $g^{(3)}$ in terms of $g^{(2)}$ we could “uncouple” this hierarchy and have a “closed” equation for $g^{(2)}$. This apparently cannot be done exactly. A further examination of $g^{(n)}$, however, will suggest an approximation which can be used to uncouple these equations.

Define a quantity $w^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ by

$$g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv e^{-\beta w^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)} \quad (13-41)$$

Substitute this into the defining equation for $g^{(n)}$ [Eq. (13-9)], take the logarithm of both sides, and then take the gradient with respect to the position of one of the n molecules, $1, \dots, n$. This gives

$$-\nabla_j w^{(n)} = \frac{\int \int e^{-\beta U} (-\nabla_j U) d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N}{\int \cdots \int e^{-\beta U} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N} \quad j = 1, 2, \dots, n \quad (13-42)$$

Now $-\nabla_j U$ is the force acting on molecule j for any fixed configuration $\mathbf{r}_1, \dots, \mathbf{r}_N$, and so the right-hand side is the mean force $f_j^{(n)}$ acting on particle j , averaged over the configurations of all the $n + 1, \dots, N$ molecules not in the fixed set $1, \dots, n$. Thus

$$f_j^{(n)} = -\nabla_j w^{(n)} \quad (13-43)$$

This says that $w^{(n)}$ is the potential that gives the mean force acting on particle j , or, i.e., $w^{(n)}$ is the *potential of mean force*. In particular, $w^{(2)}(r_{12})$ is the interaction between two molecules held a fixed distance r apart when the remaining $N - 2$ molecules of the fluid are canonically averaged over all configurations. Figure 13-4 shows the typical behavior of $w^{(2)}(r) \equiv w(r)$ for a dense fluid. When the density becomes very small, the two molecules fixed a distance r apart are not affected by the remaining $N - 2$ molecules, and so $w^{(2)}(r) \rightarrow u(r)$ as $\rho \rightarrow 0$, in agreement with Eq. (13-26). Note that in a dense system, however, the energy term in a Boltzmann factor is the potential of mean force rather than just the intermolecular potential. In a sense, one enters the realm of rigorous statistical mechanics when this distinction is clearly appreciated.

We shall see that the radial distribution function of a fluid of hard spheres is quite similar to that of a more realistic system. This means that the curves shown in Fig. 13-4 are also fairly representative of a hard-sphere system. Thus we see that although the hard-sphere potential itself has no attractive region, the corresponding potential of mean force does. The explanation for this can be seen by considering two hard spheres separated by a small distance and immersed in a bath of other hard spheres. The collisions that the right-hand sphere suffers with the other $N - 2$ spheres making up the bath will occur mostly from the right since the left-hand sphere of the pair is in the way of the bath spheres. There will be a net force to the left on the right-hand sphere of the given pair. Similarly, the left-hand sphere will be collided mostly from the left and so will experience a net force to the right. Thus the two spheres will be

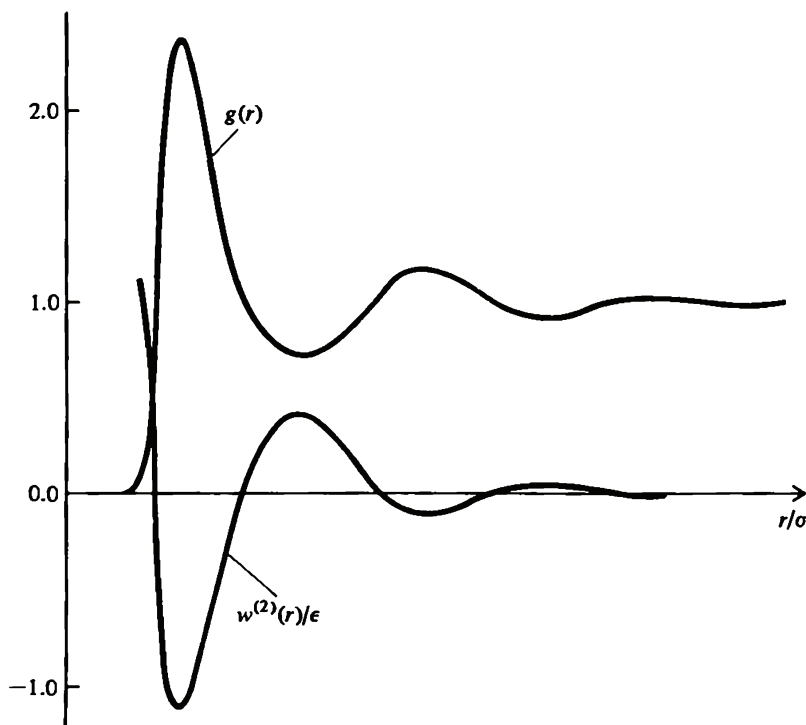


Figure 13-4. The radial distribution function $g(r)$ and the corresponding potential of mean force $w^{(2)}(r)$ for a dense fluid. Note that $w^{(2)}(r)$ has minima where $g(r)$ has maxima and vice versa.

driven toward each other due to the angular asymmetry of their collisions with the $N - 2$ bath spheres and so experience an effective attraction which manifests itself by the negative region in the potential of mean force.

Suppose now that we *assume* that the potential of mean force for a triplet of molecules is pair-wise additive, i.e., we *assume* that

$$w^{(3)}(1, 2, 3) \approx w^{(2)}(1, 2) + w^{(2)}(1, 3) + w^{(2)}(2, 3) \quad (13-44)$$

Then this gives us that

$$g^{(3)}(1, 2, 3) \approx g^{(2)}(1, 2)g^{(2)}(1, 3)g^{(2)}(2, 3) \quad (13-45)$$

Equation (13-45) has a probabilistic interpretation as well as a potential of mean force interpretation. If we assume that particles 1, 2, and 3 are completely independent of one another, then $g^{(3)}(1, 2, 3)$ would equal $g^{(1)}(1)g^{(1)}(2)g^{(1)}(3)$, essentially the product of the separate "probabilities." We see that Eq. (13-45) then assumes that the triplet correlation can be written as a product of pair-wise independent "probabilities." Substituting this approximation, called the *superposition approximation*, for $g^{(3)}$ into Eq. (13-40) gives finally the *Kirkwood equation* for $g(r)$, namely,

$$-kT \ln g(r_{12}, \xi) = \xi u(r_{12}) + \rho \int_0^\xi \int_V u(r_{13})g(r_{13}; \xi') [g(r_{23}) - 1] dr_3 d\xi' \quad (13-46)$$

Since the function to be determined in this equation occurs under an integral sign, an equation like Eq. (13-46) is called an integral equation. Thus Eq. (13-46) is an integral equation for $g(r_{12})$ and a nonlinear integral equation, in particular. The numerical solutions of this equation are difficult to obtain, but can be done on modern computers. We shall look at some of these solutions after we have derived a few other equations, but we can say here that the $g(r_{12})$ obtained from the Kirkwood and all

the other equations, in fact, are qualitatively satisfactory. Note that Eq. (13-46) gives that $g(r_{12}) = \exp[-\xi u(r_{12})/kT]$ as $\rho \rightarrow 0$.

There is another integral equation for $g(r)$ that is derived somewhat similarly to the Kirkwood equation. Instead of differentiating with respect to a coupling parameter, we differentiate with respect to the coordinates of some particular molecule. This gives a coupled hierarchy similar to the Kirkwood equations and must also be uncoupled by means of the superposition approximation. We shall not go through the details, but the result is called the Born-Green-Yvon equation, which has the form*

$$\begin{aligned} -\frac{\partial}{\partial r} [kT \ln g(r, \xi) + \xi u(r)] \\ = \pi \xi \rho \int_0^\infty u'(s) g(s, \xi) ds \int_{|r-s|}^{r+s} \frac{(s^2 + r^2 - R^2)}{r^2} R g(R) dR \quad (13-47) \end{aligned}$$

The derivation of this equation is given through Problem 13-13. If one wishes to accept that the next few sections derive two alternative integral equations for $g(r)$, the hypernetted-chain equation [Eq. (13-84)] and the Percus-Yevick equation [Eq. (13-81)], then he can go directly to Section 13-9 for a comparison with experimental data.

13-5 THE DIRECT CORRELATION FUNCTION

In the late 1950s a new class of integral equations was derived by methods quite different from those used to derive the Kirkwood and BGY equations. These new equations came not out of a hierarchy, but rather through consideration of another type of correlation function, the direct correlation function, which we introduce and discuss in this section.

The distribution functions that we considered before were defined in a closed system. Since we are about to generalize these ideas to open systems, let us label these as $\rho_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$. Then the probability of observing n molecules in $d\mathbf{r}_1 \cdots d\mathbf{r}_n$ at $(\mathbf{r}_1, \dots, \mathbf{r}_n)$, irrespective of N , is

$$\rho^{(n)} = \sum_{N \geq n} \rho_N^{(n)} P_N \quad (13-48)$$

where P_N is the probability that an open system contains N molecules, namely,

$$P_N = \frac{e^{\beta N \mu} Q(N, V, T)}{\Xi(\mu, V, T)} = \frac{z^N Z_N}{N! \Xi}$$

Substituting Eqs. (13-5) and (13-6) into (13-48) gives then

$$\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{1}{\Xi} \left\{ z^n e^{-\beta U_n} + \sum_{N=n+1}^{\infty} \frac{z^N}{(N-n)!} \int \cdots \int e^{-\beta U_N} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \right\} \quad (13-49)$$

where U_j denotes the total intermolecular potential of a system of j particles. Note that

$$\begin{aligned} \int \cdots \int \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n &= \frac{1}{\Xi} \sum_{N \geq n} \frac{z^N Z_N}{(N-n)!} = \sum_{N \geq n} P_N \cdot \frac{N!}{(N-n)!} \\ &= \left\langle \frac{N!}{(N-n)!} \right\rangle \quad (13-50) \end{aligned}$$

* T. L. Hill, *Statistical Mechanics* (New York: McGraw-Hill, 1956), Chapter 6.