# 9. ELEMENTS OF LIQUID THEORY

## 9.1 Distribution Functions in Classical Fluids

### 9.1.1 $n$-particle density and $n$-particle distribution function in the canonical ensemble

The formalism of the ensembles provides a probabilistic description of the equilibrium structure of a material, if the potential energy is known as a function of the microscopic configuration. This structure is conveniently described by many-particle density and distribution functions, which we briefly introduce in this section. Our discussion here follows mainly Hansen and McDonald (1986).

Consider a monatomic substance of $N$ molecules in volume $V$ at temperature $T$. We will use the Cartesian coordinates $\mathbf{r}_i$ of molecular centers to describe the configuration of this system. From Eqs. (4.15), (4.16) and (4.31), the equilibrium probability density of this system in *configuration space* is

$$\rho(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \int\limits_{\substack{all\\ momentum\\ space}} \rho^{NVT}(\mathbf{r}_1,\mathbf{r}_2\ldots,\mathbf{r}_N,\,\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)\,d^3p_1\ldots d^3p_N =$$

$$\frac{\displaystyle\int\limits_{\substack{all\\ momentum\\ space}} e^{-\beta\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\;\mathbf{p}_1,\ldots,\mathbf{p}_N)}\,d^3p_1\,d^3p_2\,\ldots\,d^3p_N}{\displaystyle\int\limits_{\substack{all\\ phase\\ space}} e^{-\beta\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\;\mathbf{p}_1,\ldots,\mathbf{p}_N)}\,d^3r_1\,d^3r_2,\ldots\,d^3r_N\,d^3p_1\,d^3p_2\,\ldots\,d^3p_N} =$$

$$\frac{\left\{\prod_{i=1}^{N}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} exp\left[-\beta\,\frac{\mathbf{p}_i}{2m}\right] d^3p_i\right\} exp\left[\mathcal{V}(\mathbf{r}_1,\,\mathbf{r}_2,\,\ldots,\,\mathbf{r}_N)\right]}{\left\{\prod_{i=1}^{N}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} exp\left[-\beta\,\frac{\mathbf{p}_i}{2m}\right] d^3p_i\right\} \int_{\substack{all\\ config.\\ space}} exp\left[\mathcal{V}(\mathbf{r}_1,\,\mathbf{r}_2,\,\ldots,\,\mathbf{r}_N)\right] d^3r_1\, d^3r_2\,\ldots\, d^3r_N}$$

or

$$\rho(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\right]}{\int exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\right] d^3r_1\, d^3r_2\,\ldots\, d^3r_N} =$$

$$\frac{1}{Z(N,\,V,\,T)}\, exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\right] \tag{9.1}$$

By definition, the quantity $\rho(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\, d^3r_1\, d^3r_2\,\ldots\, d^3r_N$ equals the probability of finding molecule 1 at position $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, molecule 2 at position $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, ... , molecule $N$ at position $\mathbf{r}_N$ to $\mathbf{r}_N + d\mathbf{r}_N$.

We can define the $n$-particle configurational probability density, where $n \leq N$, by projecting $\rho(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ onto the $3n$-dimensional space spanned by all possible combinations of positions of particles $1,\ldots,n$:

$$\rho^{1\ldots n}(\mathbf{r}_1,\ldots,\mathbf{r}_n) \equiv \int \rho(\mathbf{r}_1,\ldots,\mathbf{r}_n,\mathbf{r}_{n+1},\ldots,\mathbf{r}_N)\, d^3r_{n+1}\, d^3r_{n+2}\,\ldots\, d^3r_N$$

The quantity $\rho^{1\ldots n}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\, d^3r_1\, d^3r_2\,\ldots\, d^3r_n$ equals the probability of finding molecule 1 at position $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, molecule 2 at position $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$, ... , molecule $n$ at position $\mathbf{r}_n$ to $\mathbf{r}_n + d\mathbf{r}_n$.

In practice, one is more interested in expressing the probability of finding *a molecule* at $\mathbf{r}_1$ to $\mathbf{r}_1{+}d\mathbf{r}_1$, *a molecule* at $\mathbf{r}_2$ to $\mathbf{r}_2{+}d\mathbf{r}_2$, ..., *a molecule* at $\mathbf{r}_n$ to $\mathbf{r}_n{+}d\mathbf{r}_n$, *irrespective of the identities* of these molecules. Since there are $N$ ways of choosing the molecule at

$\mathbf{r}_1$, $(N-1)$ ways of choosing the molecule at $\mathbf{r}_2$, … , $(N-n+1)$ ways of choosing the molecule at $\mathbf{r}_n$, this probability density is *proportional* to

$$N\,(N-1)\,\ldots\,(N-n+1)\;\rho^{1\ldots n}(\mathbf{r}_1,\ldots,\mathbf{r_n}) = \frac{N!}{(N-n)!}\;\rho^{1\ldots n}(\mathbf{r}_1,\ldots,\mathbf{r_n})$$

We call this quantity the *n-particle probability density* and symbolize it by

$$\rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{N!}{(N-n)!}\frac{\int exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]\,d^3r_{n+1}\ldots d^3r_N}{Z(N,V,T)} \tag{9.2}$$

It should be noted that $\rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ is a function of $n$ *positions in space*. The quantity $\rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\,d^3r_1\;\ldots,d^3r_n$, multiplied by an appropriate normalization factor, equals the probability of finding a configuration with a molecule located between $\mathbf{r}_1$ and $\mathbf{r}_1 + d\mathbf{r}_1$, a molecule located between $\mathbf{r}_2$ and $\mathbf{r}_2 + d\mathbf{r}_2$, … , a molecule between $\mathbf{r}_n$ and $\mathbf{r}_n + d\mathbf{r}_n$.

By definition, $\rho_N^{(n)}$ obeys the normalization condition

$$\int \rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\,d^3r_1\ldots d^3r_n = \frac{N!}{(N-n)!} \tag{9.3}$$

In the special case of an ideal gas, $\mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N) \;=\; 0$ for all configurations, and $Z(N,V,T) = V^N$. Then,

$$\rho_N^{ig(n)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n) = \frac{N!}{(N-n)!}\frac{1}{V^n} = \rho^n\frac{N!}{N!\,(N-n)!} = \rho^n\left[1+\mathcal{O}\left(\frac{n^2}{N}\right)\right]$$

We define the *n-particle distribution function* as

$$g_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) \equiv \frac{\rho_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)}{\rho^n} \tag{9.4}$$

$g_N^{(n)}$ measures the extent to which the structure of a fluid deviates from complete randomness (which would prevail in an ideal gas).

### 9.1.1 $n$-particle density and $n$-particle distribution function in the grand canonical ensemble

Somewhat different definitions of the $n$-particle density and distribution functions have to be used in the grand canonical ensemble, where the number of particles fluctuates under constant chemical potential $\mu$, or activity $z = exp(\beta\,\mu)$.

The *$n$-particle density* is defined by

$$\rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \int d^3r_{n+1}\,\ldots\,d^3r_N\, \frac{exp\left[-\beta\mathcal{V}_N(\mathbf{r}_1,\,\ldots,\,\mathbf{r}_N) + \beta\,\mu\,N\right]}{N!\,\Lambda^{3N}\,\Xi(\mu,V,T)}$$

The term $\Lambda^{3N}$ comes from integrating the phase-space probability density, Eq. (6.6), over all the momentum space of $N$ particles. We can write, equivalently:

$$\rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{1}{\Xi}\sum_{N=n}^{\infty} \frac{\zeta^N}{(N-n)!} \int exp\left[-\beta\mathcal{V}_N(\mathbf{r}_1,\,\ldots,\,\mathbf{r}_N)\right]\, d^3r_{n+1}\ldots d^3r_N \qquad (9.5)$$

with $\zeta = \dfrac{exp(\beta\mu)}{\Lambda^3}$.

$\rho^{(n)}$ follows the normalization

$$\int \rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\, d^3r_1\ldots d^3r_n = \left\langle \frac{N!}{(N-n)!} \right\rangle \qquad (9.6)$$

where the angular brackets indicate a grand canonical average.

In the special case of an ideal gas, taking into account Eq. (4.45),

$$\rho^{ig(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{\sum\limits_{N=n}^{\infty} \dfrac{\zeta^N}{(N-n)!} V^{N-n}}{\sum\limits_{N=0}^{\infty} \dfrac{\zeta^N}{N!} V^N} = \zeta^n = \left[\frac{\rho\,\Lambda^3}{\Lambda^3}\right]^n = \rho^n$$

We define the *n-particle distribution function* by

$$g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{\rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)}{\rho^n} \tag{9.7}$$

where $\rho = \frac{\langle N\rangle}{V}$ is the mean molecular density under the given conditions of $\mu, V$, and $T$.

### 9.1.3 The pair distribution function

Of particular significance are the *pair distribution functions*, defined by Eqs. (9.4) and (9.7) for $n = 2$. This is because pair distribution functions are experimentally measurable, and at the same time appear in equations relating important thermodynamic properties to molecular-level interactions. In the case $n = 2$, the general definitions of $g_N^{(2)}$ and $g^{(2)}$ give

Canonical ensemble:

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{N\,(N-1)}{\rho^2} \frac{\int exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]\; d^3r_3\,\ldots\, d^3r_N}{Z(N,V,T)} \tag{9.8}$$

Grand canonical ensemble:

$$g^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^2} =$$

$$\frac{\sum\limits_{N=2}^{\infty} \frac{1}{(N-2)!}\frac{exp(N\beta\mu)}{\Lambda^{3N}} \int exp\left[-\beta\mathcal{V}_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right]\; d^3r_3\ldots d^3r_N}{\rho^2\,\Xi(\mu,V,T)} \tag{9.9}$$

The two functions obey the normalizations

$$\rho^2 \int g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, d^3r_1\, d^3r_2 = N\,(N-1) \tag{9.10}$$

$$\rho^2 \int g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d^3r_1\, d^3r_2 = \langle N(N-1)\rangle = \langle N^2\rangle - \langle N\rangle \tag{9.11}$$

In view of the definition, Eq. (9.8), and the normalization, Eq. (9.10), the quantity $\frac{\rho^2}{N(N-1)} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d^3r_1\, d^3r_2$ equals the probability of finding a molecule within volume element $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, and another molecule within volume element $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$ of three- dimensional space. An important corollary is that, if $\mathcal{A}(\mathbf{r}_i, \mathbf{r}_j)$ is any function of the positions of two molecules $i$ and $j$ in the system, the canonical ensemble average $\left\langle \sum_{i \neq j} \sum \mathcal{A}(\mathbf{r}_i, \mathbf{r}_j) \right\rangle$ can be calculated as

$$\left\langle \sum_{i \neq j} \sum \mathcal{A}(\mathbf{r}_i, \mathbf{r}_j) \right\rangle = \rho^2 \int d^3r_1 \int d^3r_2\, \mathcal{A}(\mathbf{r}_1, \mathbf{r}_2)\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \tag{9.12}$$

The same relation holds in the grand canonical ensemble.

In the limit $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$, we expect that structural correlations in the material will disappear. In this limit, structure will be indistinguishable from that in an ideal gas at the same density. Thus, we expect the limiting behavior

$$\lim_{|\mathbf{r}_1 - \mathbf{r}_2| \to \infty} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_N^{ig(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{\rho^2 \dfrac{N(N-1)}{N^2}}{\rho^2} = 1 - \frac{1}{N} \tag{9.13a}$$

$$\lim_{|\mathbf{r}_1 - \mathbf{r}_2| \to \infty} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{ig(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{\rho^2}{\rho^2} = 1 \tag{9.13b}$$

In the thermodynamic limit, the functions $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ become indistinguishable, and are symbolized simply as $g(\mathbf{r}_1, \mathbf{r}_2)$; the limiting value of both for large intermolecular separations is 1.

In a *homogeneous medium*, structure is the same around any point. This means that the functions $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ will depend only on the *relative* position vector $\mathbf{r}_2 - \mathbf{r}_1$:

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g_N^{(2)}(\mathbf{r}_2 - \mathbf{r}_1) \equiv g_N^{(2)}(\mathbf{r}_{12}) \tag{9.14}$$

and similarly for $g^{(2)}$.

In an *isotropic medium*, structure depends on the magnitude, but not on the direction of the intermolecular separation vector. Such is the case in liquids and amorphous solids. One can write

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g_N^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|) \equiv g(r_{12}) \tag{9.15}$$

The symbol $g(r)$ will be used to denote the pair, or *radial* distribution function in an isotropic medium, a function of intermolecular distance only.

A more transparent physical interpretation of $g_N^{(2)}$ can be arrived at as follows. By definition, the normalized quantity $\dfrac{\rho^2}{N\,(N-1)}\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d^3r_1\, d^3r_2$ equals the probability of finding a molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$, and another molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$. Since the fluid is isotropic, the probability of finding a molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$ is $\dfrac{d^3r_1}{\int d^3r_1} = \dfrac{d^3r_1}{V}$. Therefore, the probability of finding a molecule at $\mathbf{r}_2 + d\mathbf{r}_2$ *provided* another molecule has been placed at $\mathbf{r}_1 + d\mathbf{r}_1$ is $\dfrac{\rho^2}{N\,(N-1)}\, \dfrac{g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d^3r_1\, d^3r_2}{\frac{d^3r_1}{V}}$. Consequently, the expected *number* of molecules in the volume element $\mathbf{r}_2 + d\mathbf{r}_2$ provided a molecule has been placed at $\mathbf{r}_1 + d\mathbf{r}_1$ is $\dfrac{\rho^2\,(N-1)}{N\,(N-1)}\, \dfrac{g_N^{(2)}\, d^3r_1\, d^3r_2}{\frac{d^3r_1}{V}}$. Taking into account that $N/V = \rho$ and $d^3r_1\, d^3r_2 = d^3r_1\, d^3r_{12}$, we conclude that, in an isotropic material, the quantity

$\rho\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d^3 r_{12}$ equals the number of molecules we expect to find within a volume element $\mathbf{r}_{12}$ to $\mathbf{r}_{12} + d\mathbf{r}_{12}$ defined relative to position $\mathbf{r}_1$, provided there is a molecule at $\mathbf{r}_1$. Equivalently, we can say

$\rho\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \;=\; \rho\, g_N^{(2)}(r) \;=$ local *density* of molecules at a distance $r$ from a given molecule in the material, averaged over all configurations (see Fig. 9.1).

(9.16)

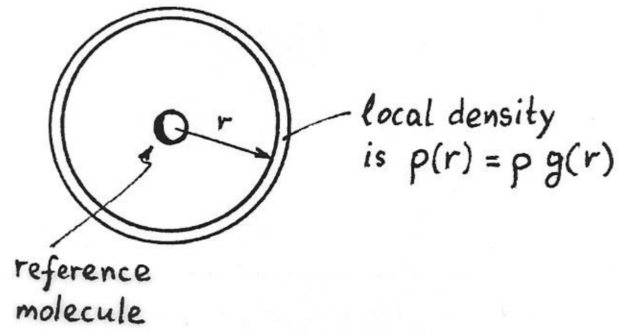


**Figure 9.1** Definition of the pair distribution function in an isotropic material

An alternative interpretation of $g(r)$ is arrived at as follows: By definition,

$$\frac{\rho^2}{N\,(N-1)}\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1\, d^3 r_2$$

is the probability of finding a molecule at $\mathbf{r}_1$ to $\mathbf{r}_1 + d\mathbf{r}_1$ and another molecule at $\mathbf{r}_2$ to $\mathbf{r}_2 + d\mathbf{r}_2$. Consequently,

$$\frac{\rho^2}{N\,(N-1)} \int d^3 r_1 \int_{r<|\mathbf{r}_{12}|<r+dr} d^3 r_{12}\; g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

is the probability of finding a pair of molecules at distance $r$ to $r + dr$ from each other. In an isotropic system,

$$\int d^3 r_1 \int_{r<|\mathbf{r}_{12}|<r+dr} d^3 r_{12}\, g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = V \int_{r<|\mathbf{r}_{12}|<r+dr} d^3 r_{12}\; g_N^{(2)}(\mathbf{r}_{12}) =$$

$$V \int_{r<r_{12}<r+dr} 4\pi\, r_{12}^2\, g(r_{12})\, dr_{12} = V\, 4\pi r^2\, g(r)\, dr = \frac{N^2}{\rho^2}\frac{1}{V} 4\pi r^2 g(r) dr$$

Hence,

$$\frac{N}{N-1}\frac{1}{V}\, g(r)\, 4\pi r^2\, dr = \text{Probability of finding a pair of molecules ar a distance } r \text{ to } r+dr$$

from each other.

(9.17)

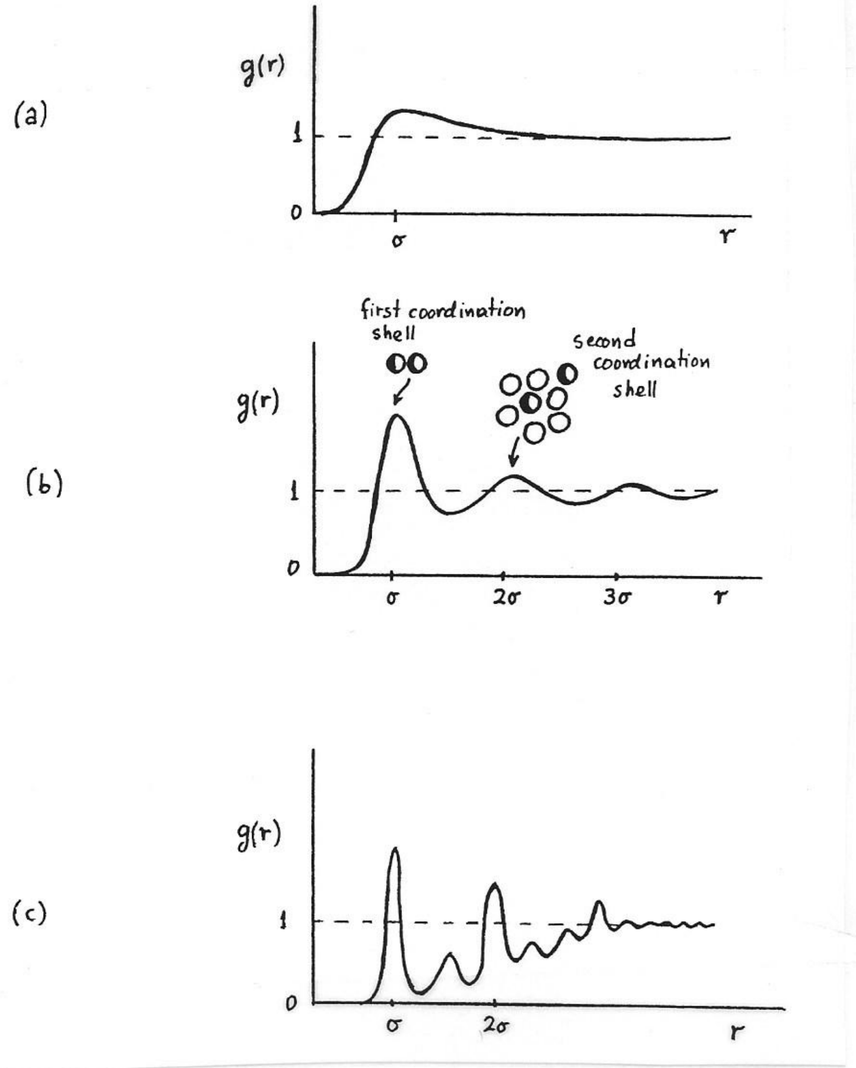


**Figure 9.2** Rough schematic of the orientationally averaged pair distribution function $g(r)$ for a Lennard-Jones gas $(a)$, liquid $(b)$, and solid $(c)$.

The typical behavior of the orientationally averaged pair distribution function $g(r) \equiv \frac{1}{4\pi r^2}\frac{d}{dr} \int\limits_{r<|\mathbf{r}_{12}|<r+dr} g_N^{(2)}(\mathbf{r}_{12})\, d^3 r_{12}$ in a pure component substance whose molecules interact though a pairwise additive Lennard-Jones potential,

$$\mathcal{V}_{pair}^{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

is given in Fig. 9.2. In the gas ($a$) there is very little structure. $g(r)$ is zero at intermolecular separations substantially smaller than the collision diameter $\sigma$ because of the excluded volume effect between the steeply repulsive cores of molecules. There is a maximum in $g(r)$ around the van der Waals diameter (location of attractive minimum of the potential), while $g(r)$ attains the asymptotic large separation value of 1 at large distances. In the liquid ($b$) there is some order at short distances. $g(r)$ exhibits a strong peak near the van der Waals diameter, corresponding to the first coordination shell of nearest neighbor molecules around a given molecule. $g(r)$ goes through a minimum and then rises to a second maximum, corresponding to the second coordination shell, *i.e.*, to molecules sharing a nearest- neighbor with the reference molecule. The oscillations in $g(r)$ die out with increasing distance; there is no long range order. In the solid ($c$) there is long-range order, imposed by the crystal lattice. The LJ substance crystallizes in the *fcc* lattice, giving rise to sharp peaks at 1, $2^{1/2}$,$3^{1/2}$, 2, $\frac{20^{1/2}}{2}$, $6^{1/2}$,... times the nearest-neighbor distance. As one moves out in radial distance, the spacing between peaks imposed by the structure of the lattice becomes smaller and smaller, until the peaks merge into an almost uniform background at $g(r) = 1$. Information about the long-range order of the lattice is preserved in the three- dimensional function $g_N^{(2)}(\mathbf{r}_{12})$, which is necessary in this case for a full description of the anisotropic structure of the solid.

In a molecular system containing $s$ types of atoms or interaction sites, one can define $\frac{s(s-1)}{2}$ pair distribution functions $g^{\alpha\beta}(r), \alpha < \beta = 1, 2, \ldots, s$, one for each species pair. If $\rho^{\alpha}$ is the number density of sites of type $\alpha$ in the system, then the local density of type $\alpha$ sites at distance $r$ from a type $\beta$ site is $\rho^{\alpha}\, g^{\alpha\beta}(r)$. For example, in a polyethylene melt, consisting of C and H atoms, we can speak of $g^{CC}$, $g^{CH}$, and $g^{HH}$. Each $g^{\alpha\beta}$ has both an *intermolecular* and an *intramolecular* component.

### 9.1.4 Experimental Measurement of $g(r)$ via X-ray or neutron Diffraction

Direct experimental information about the pair distribution function can be obtained through elastic scattering of electromagnetic radiation or of particle beams of wavelength commensurate to interatomic distances (X-ray, neutron, electron diffraction). A simple schematic of the diffraction experiment is shown in Fig. 9.3. The observable is the diffracted intensity $I(\theta)$ as a function of direction with respect to the incident radiation. If the scattering sample is isotropic, $I$ depends only on the angle $\theta$ between incident direction and direction of observation. Here we confine ourselves to *elastic* scattering, *i.e.*, to the case where the observed intensity has the same wavelength $\lambda$ as the incident intensity.

A relationship between the diffracted intensity $I(\theta)$ and the pair distribution function $g(r)$ can be arrived at through a simple classical analysis of the scattering process. Our discussion here follows the treatment of McQuarrie (1976). Let $\mathbf{u}_0$ be the unit vector in the direction of propagation of the incident wave, and $\mathbf{u}$ the unit vector in the direction of observation of the scattered radiation. The positions of the scatterers $j$ (atoms in the sample) is denoted by $\mathbf{r}_j$ relative to a fixed origin in space, $O$.

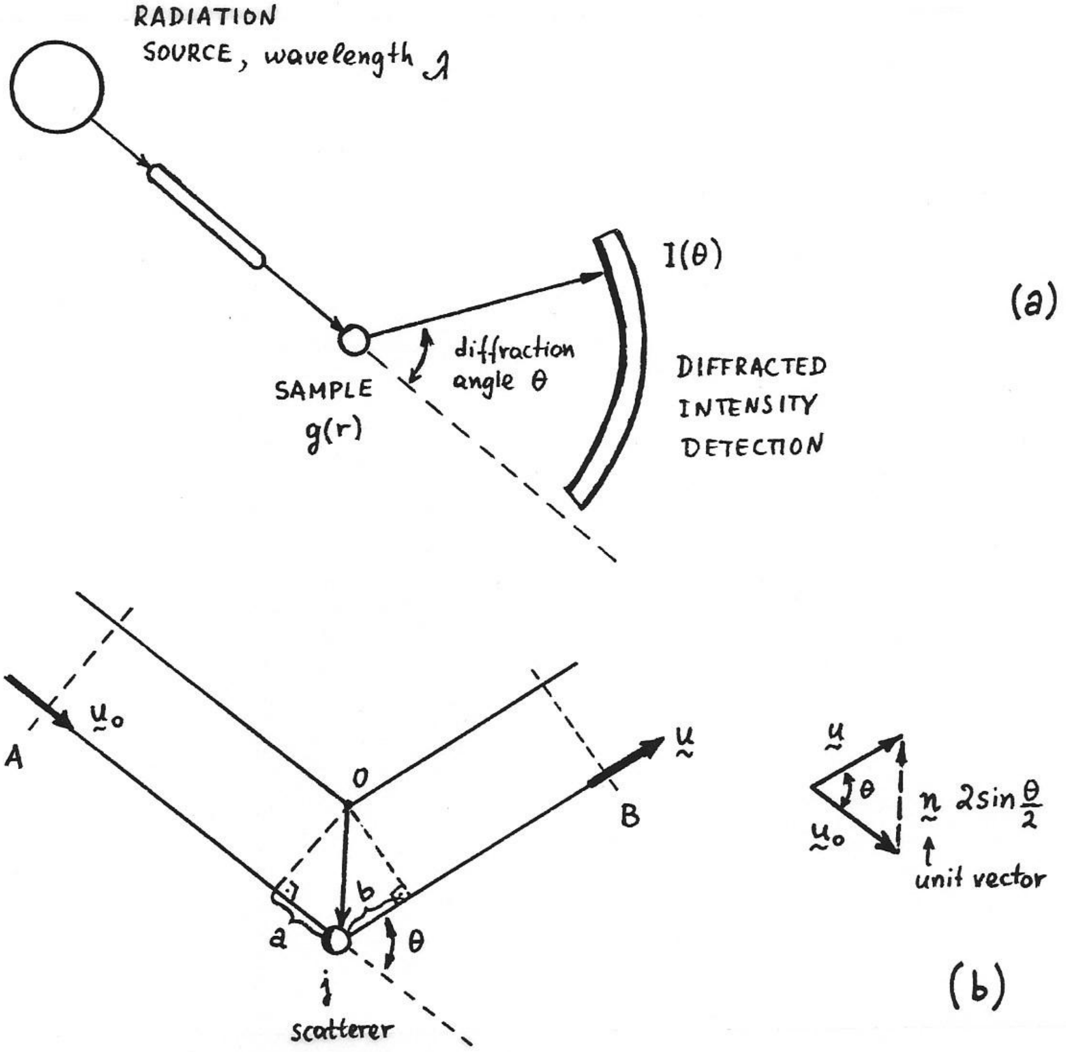


**Figure 9.3** (*a*) Simple schematic representation of a diffraction experiment. (*b*) Geometry of incident and diffracted beams.

The electromagnetic field of the incident radiation has the same phase throughout a plane $A$ that is normal to $\mathbf{u}_0$. Consider a plane $B$ normal to the direction of observation $\mathbf{u}$. Beams scattered at different $\mathbf{r}_j$ arrive at $B$ having traversed different path lengths.

Consequently, the elastically scattered waves from different $\mathbf{r}_j$ are characterized by different phases; the interference pattern formed by all these waves contains information about the spatial distribution of the scatterers.

To quantify the relation between position $\mathbf{r}_j$ and phase of the scattered wave, it is convenient to consider a beam passing through the origin $O$ and scattered in the direction $\mathbf{u}$ as a reference. The path length difference between the bean through $\mathbf{r}_j$ and the reference beam (see Fig. 9.3 ($b$)) is

$$a + b = \mathbf{r}_j \cdot \mathbf{u}_0 - \mathbf{r}_j \cdot \mathbf{u} = \mathbf{r}_j \cdot (\mathbf{u}_0 - \mathbf{u}) = -2\,\mathbf{r}_j \cdot \mathbf{n}\, sin\frac{\theta}{2} \tag{9.18}$$

where $\mathbf{n}$ is the unit vector in the direction of $\mathbf{u} - \mathbf{u}_0$. The phase difference between the wave scattered by $j$ and the wave through the origin at $B$ is

$$\phi_j = 2\pi \frac{a+b}{\lambda} = -\mathbf{r}_j \cdot \frac{4\pi}{\lambda}\, sin\frac{\theta}{2} = -\mathbf{r}_j \cdot \mathbf{k} \tag{9.19}$$

where the *scattering vector* $\mathbf{k}$ is defined as

$$\mathbf{k} = \frac{4\pi}{\lambda}\, sin\frac{\theta}{2}\, \mathbf{n} = \frac{2\pi}{\lambda}\,(\mathbf{u} - \mathbf{u}_0) \tag{9.20}$$

Assuming that all scatterers are of the same kind (as would be the case in a simple liquid), the electric field at $B$ due to the wave scattered at $j$ is $\mathcal{E}_j = A\, cos\,[2\pi\nu t - \phi_j]$ where $\nu$ the frequency of the incident radiation. The total electric field at $B$ due to all scattered waves is

$$\mathcal{E} = \sum_{j=1}^{N} A\, cos\,[2\pi\nu t - \phi_j] \tag{9.21}$$

The *intensity* of the scattered radiation is proportional to $\mathcal{E}^2$, averaged over one period:

$$I(\theta) = K \frac{\int\limits_0^{1/\nu} dt\, \mathcal{E}^2}{\int\limits_0^{1/\nu} dt} = K\nu A^2 \int_0^{1/\nu} \left( \sum_{j=1}^{N} \mathit{cos}\,[2\pi\nu t - \phi_j] \right)^2 dt =$$

$$K\nu A^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \int\limits_0^{1/\nu} \mathit{cos}\,[2\pi\nu t - \phi_i]\; \mathit{cos}\,[2\pi\nu t - \phi_j]\; dt =$$

$$K\nu A^2 \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int\limits_0^{1/\nu} \{\mathit{cos}\,(4\pi\nu t - \phi_i - \phi_j) + \mathit{cos}\,(\phi_i - \phi_j)\}\; dt =$$

$$K \frac{A^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mathit{cos}\,(\phi_i - \phi_j) = K \frac{A^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mathit{cos}\,[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]$$

Now, as $\theta \to 0$, $I(\theta) \to K\frac{A^2}{2}N^2$. The ratio of $I(\theta)$ to $I(0)$ becomes

$$\frac{I(\theta)}{I(0)} = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mathit{cos}\,[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \tag{9.22}$$

The above analysis referred to a single configuration of the $N$ scatterers. Averaging over all configurations for an isotropic system at given temperature and density,

$$\frac{I(\theta)}{I(0)} = \frac{1}{N^2} \left\langle \sum_{i=1}^{N} \sum_{i=1}^{N} \mathit{cos}\,[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle = \frac{1}{N^2} \left\langle \sum_{i=1}^{N} 1 + \sum_{i\,\neq\, j}^{N} \sum^{N} \mathit{cos}\,[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle$$

Using Eq. (9.12) to substitute the canonical ensemble average of the double sum over different scatterers, we obtain

$$\frac{I(\theta)}{I(0)} = \frac{1}{N} + \frac{\rho^2}{N^2} \int g_N^{(2)}(\mathbf{r}_i, \mathbf{r}_j)\, \mathit{cos}\,[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]\; d^3r_i\, d^3r_j =$$

$$\frac{1}{N} + \frac{\rho^2}{N^2} V \int g(r_{ji})\, \mathit{cos}\,[\mathbf{k} \cdot \mathbf{r}_{ji}]\; d^3r_{ji} = \frac{1}{N} + \frac{\rho}{N} \int g(r_{ji})\, \mathit{cos}\,[\mathbf{k} \cdot \mathbf{r}]\; d^3r \tag{9.23}$$

To perform the integral in Eq. (9.23) it is convenient to introduce spherical polar coordinates $r, \alpha, \beta$ (see Fig. 9.4)

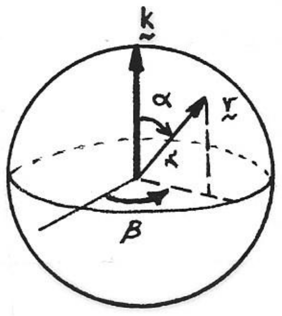


**Figure 9.4** Spherical polar coordinates used for the evaluation of the integral in Eq. (9.23)

The integral becomes

$$\int g(r)\, cos\,(\mathbf{k}\cdot\mathbf{r})\; d^3r = \int_0^\infty r^2\, dr \int_0^{2\pi} d\beta \int_0^\pi sin\alpha\; d\alpha\; g(r)\; cos(k\, r\, cos\alpha) =$$

$$-\int_0^\infty 2\pi r^2\, g(r)\, dr\, \frac{1}{k\, r} \int_0^\pi d(k\, r\, cos\alpha)\, cos(k\, r\, cos\alpha) =$$

$$\int_0^\infty 4\pi r^2\, \frac{sin(k\, r)}{k\, r} g(r)\, dr$$

Therefore, Eq. (9.23) gives

$$\text{“Scattering Function''} \equiv \frac{I(\theta)}{I(0)} = \frac{1}{N}\left[1 + \rho \int_0^\infty 4\pi r^2\, \frac{sin(k\, r)}{k\, r}\, g(r)\, dr\right] \tag{9.24}$$

Noting that

$$\int g(r)\, sin(\mathbf{k}\cdot\mathbf{r})\, d^3r = \int_0^\infty r^2\, dr \int_0^{2\pi} d\beta \int_0^\pi sin\alpha\; d\alpha\; g(r)\; sin(k\, r\, cos\alpha) = 0$$

we can also write Eq. (6.24) as

$$\frac{I(\theta)}{I(0)} = \frac{1}{N}\left[1 + \rho \int g(r)\, e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3r\right] \tag{9.25}$$

We define the *static structure factor* $S(\mathbf{k})$ by

$$S(\mathbf{k}) = 1 + \rho \int g(\mathbf{r})\, e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3r \tag{9.26}$$

In an *isotropic material*, $S(\mathbf{k})$ depends only on the magnitude of the scattering vector $\mathbf{k}$, and Eq. (9.26) can be written simply as

$$S(k) = 1 + \rho \int_0^\infty 4\pi r^2\, \frac{sin(k\,r)}{k\,r}\, g(r)\, dr$$

Noting that an ideal gas is characterized by $g(r) = 1$ for all $r$, and that $\int e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3r = \delta(\mathbf{k})$, and in view of Eq. (9.15), we can attribute the following physical significance to the structure factor for $\mathbf{k} \neq \mathbf{0}$:

$$S(\mathbf{k}) = \frac{\text{Diffracted intensity in direction } \mathbf{k}}{\begin{array}{c}\text{Diffracted intensity in same direction}\\ \text{if scatterers formed an ideal gas}\end{array}} \tag{9.27}$$

Note that $S(\mathbf{k})$ is the same as the measured scattered intensity $I(\theta)$, up to a multiplicative constant. The quantity $S(\mathbf{k}) - 1$ is the Fourier transform of $g(\mathbf{r})$. As a consequence, $g(\mathbf{r})$ can be obtained from the experimental observable $S(\mathbf{k})$ by an inverse Fourier transform:

$$\rho\, g(\mathbf{r}) = \frac{1}{(2\pi)^3} \int e^{i\,\mathbf{k}\cdot\mathbf{r}}\, [S(\mathbf{k}) - 1]\, d^3k \tag{9.28}$$

and for an isotropic medium:

$$\rho\, g(r) = \frac{1}{(2\pi)^3} \int 4\pi\, k^2\, \frac{sin(k\,r)}{k\,r}\, [S(k) - 1]\, dk$$

Note that Eq. (9.26) can also be written as

$$S(\mathbf{k}) - 1 = \rho\, \delta(\mathbf{k}) + \rho \int [g(\mathbf{r}) - 1]\, e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3r \tag{9.29}$$

from which it is obvious that the $S(\mathbf{k})$ approaches the limiting value 1 as $k \to \infty$. The delta function term on the right hand side is known as "forward scattering". It is often ignored, as scattered radiation is never measured exactly in the direction of the incident beam.

Being a Fourier transform of $g(r)$, the quantity $S(k) - 1$ brings out the characteristic wavelengths in the undulations of $g(r)$. In general, we expect $S(k)$ to exhibit a peak at a value of $k \simeq \frac{2\pi}{\Delta r}$, where $\Delta r$ the separation between successive peaks in $g(r)$. The small $k$ ("small angle") region of $S(k)$ contains information about structural features with large characteristic lengths; the large $k$ (wide angle) region of $S(k)$ contains information about short-range structure. "Wide angle" X-ray, neutron, or electron diffraction experiments are needed to get atomic-scale features of $g(r)$ in low-molecular weight liquids. "Small angle" diffraction experiments are used to get overall dimensions of polymer coils and structural correlations at the length scale of entire chains in polymer systems. The wide angle pattern of a crystalline solid is characterized by very sharp peaks "Bragg peaks") caused by the strict periodicity of the crystalline lattice. The pattern of a liquid or amorphous solid is much more diffuse, the predominant characteristic being a broad peak ("amorphous halo") at a $k$ commensurate with $2\pi$ over the nearest-neighbor separation of atomic centers. Examples of $S(k)$ for solid and liquid aluminum are given in Fig. 9.5.

A set of experimental structure factors for liquid Argon at $-125^o$C at a variety of densities is shown in Fig. 9.6. The state point $\rho = 0.280$ g cm$^{-3}$ is close to critical conditions. The pair distribution functions, obtained through inversion of the diffraction data, are also shown. These structural measurements have been used to fit a pairwise Lennard-Jones potential to liquid argon. The best potential parameters were $\sigma = 3.38 \pm 0.06$Å and $\epsilon/k_B = 134 \pm 10$K [Pings (1979)].

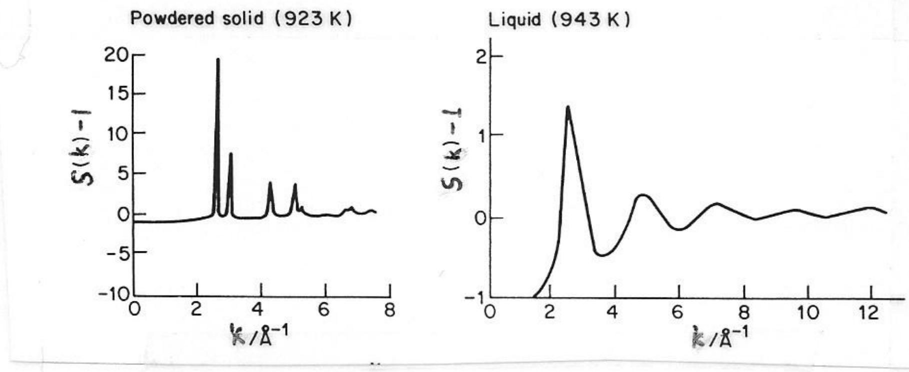


**Figure 9.5** Examples of experimentally determined structure factors for solid and liquid aluminum [after Murrell and Boucher (1982)].

The expressions Eq. (9.25) for the scattering function and (9.26) for the structure factor are restricted to systems where all scatterers are of the same kind. For a molecular system with several different atomic species ($\alpha = 1, 2, \ldots, s$) one can generalize the above analysis, arriving at the following expressions for $\mathbf{k} \neq \mathbf{0}$:

$$\frac{I(\theta)}{I(0)} = \frac{\sum_{\alpha} N_\alpha \left[f^\alpha(k)\right]^2 + \sum_{\alpha}\sum_{\beta} \rho_\alpha \rho_\beta V\, f^\alpha(k) f^\beta(k) \int \left[g^{\alpha\beta}(r) - 1\right] e^{-i\,\mathbf{k}\cdot\mathbf{r}} d^3r}{\left(\sum_{\alpha} N_\alpha\, f^\alpha(0)\right)^2} \tag{9.25a}$$

$$S(k) = 1 + \frac{\sum_{\alpha}\sum_{\beta} \rho_\alpha\, \rho_\beta V f^\alpha(k)\, f^\beta(k) \int \left[g^{\alpha\beta}(r) - 1\right] e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3r}{\sum_{\alpha} N_\alpha [f^\alpha(k)]^2} \tag{9.26a}$$

where $f^\alpha(k)$, the *atomic structure factor*, is a characteristic of atomic species $\alpha$, shaped by the physics of the scattering process (note that X-rays and electrons are scattered by the electronic clouds around atoms, neutrons by the nuclei). For the values of atomic structure factors or scattering cross-sections, see **Hukins (1981)** and **Page (1973)**.

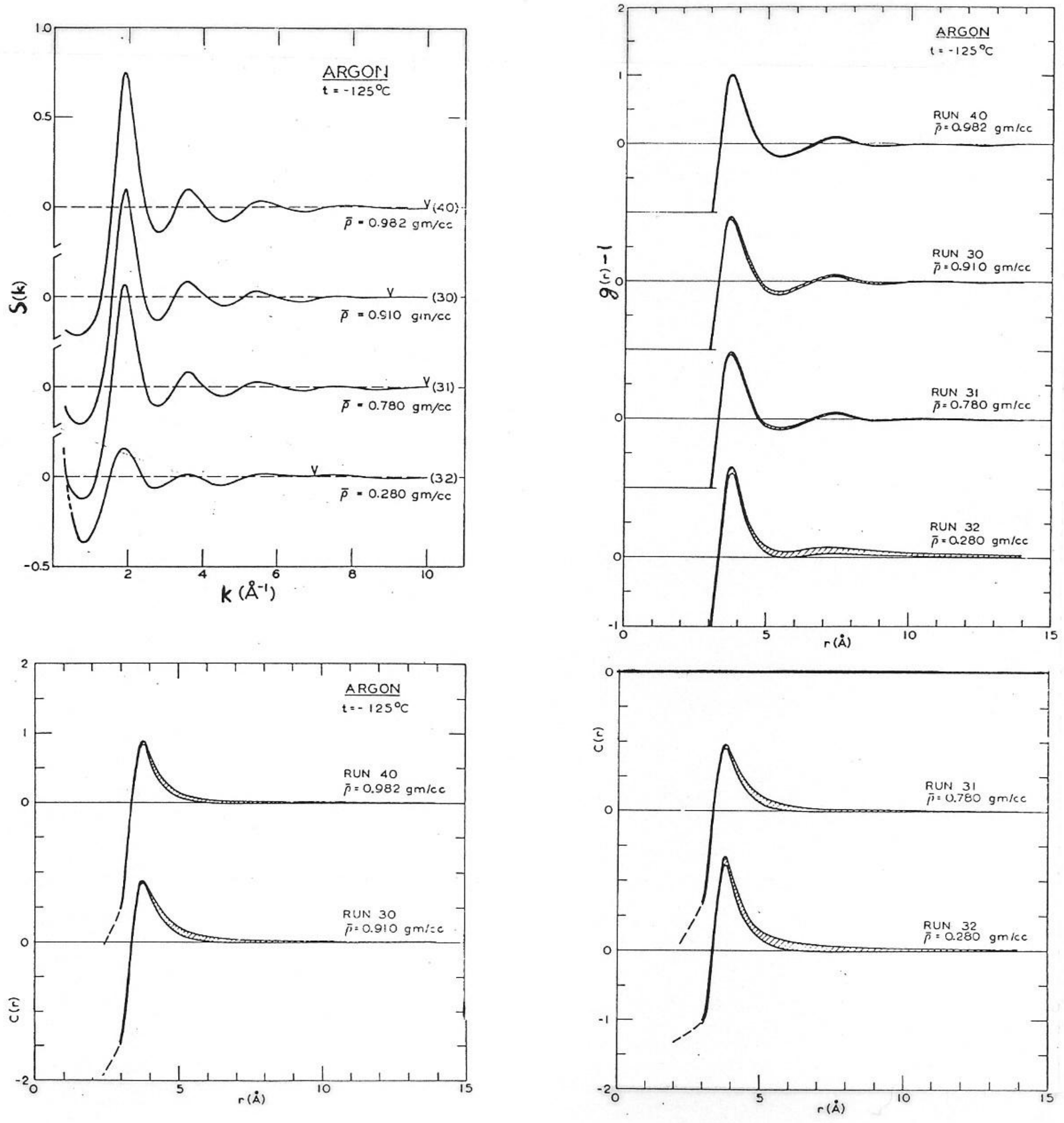


**Figure 9.6** Experimental structure factors for Argon at $-125^o$C and several densities, along with pair correlation functions $g(r)-1$ and direct correlation functions $c(r)$ obtained through Fourier inversion of the data.

### 9.1.5 Thermodynamic Properties from the Pair Distribution Function

As a consequence of the definition of the pair distribution function, many thermodynamic properties can be expressed as simple integrals over all intermolecular separations, involving that function. We present these important connections between structure and thermodynamic properties below.

#### Internal Energy

We define the *excess internal energy* as

$$U^{ex}(N,V,T) = U(N,V,T) - U^{ig}(N,V,T) \equiv \langle \mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle \tag{9.30}$$

Assuming *pairwise additivity* of interactions, with pair potential $\mathcal{V}_{pair}(\mathbf{r}_{12})$, and invoking Eq. (9.12) for a homogeneous material, we obtain

$$U^{ex}(N,V,T) = \frac{1}{2}\left\langle \sum_{i\neq}\sum_{j} \mathcal{V}_{pair}(\mathbf{r}_{ij})\right\rangle = \frac{1}{2}\rho^2 V \int g(\mathbf{r}_{12})\ \mathcal{V}(\mathbf{r}_{12})\ d^3r_{12}$$

For an *isotropic* material, this becomes

$$U^{ex}(N,V,T) \equiv U(N,V,T) - U^{ig}(N,V,T) = \frac{1}{2} N\rho \int 4\pi r^2\, g(r)\ \mathcal{V}(r)\ d^3r \tag{9.31}$$

Eq. (9.31) is known as the *energy equation.*

#### Pressure

A general relation between pressure as a configurational ensemble average has been derived in the form of the *virial theorem.* For a *pairwise additive* potential, Eq. (4.64) can readily be transcribed in distribution function notation. In the canonical ensemble,

$$P = \rho k_B T + \frac{1}{6V}\left\langle \sum_{i\neq}\sum_{j} (\mathbf{r}_i - \mathbf{r}_j)\cdot\mathbf{F}_{ij}\right\rangle \tag{9.32}$$

An isotropic pairwise additive potential generates central forces

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_{ji}} \mathcal{V}_{pair}(r_{ij}) = \left(\frac{\partial \mathcal{V}_{pair}}{\partial r}\right)_{r=r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}}$$

and consequently

$$(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} = -\mathbf{r}_{ij} \cdot \mathbf{F}_{ij} = -\left(\frac{\partial \mathcal{V}_{pair}}{\partial r}\right)_{r=r_{ij}} \frac{\mathbf{r}_{ij}^2}{r_{ij}} = -r_{ij}\left(\frac{\partial \mathcal{V}_{pair}}{\partial r}\right)_{r=r_{ij}} \tag{9.33}$$

The reader is reminded that $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$ and that $\mathbf{F}_{ij}$ symbolizes the force on $i$ due to $j$. Using Eqs. (9.12) and (9.33) in Eq. (9.32), one obtains

$$P = \rho k_B T + \frac{1}{6\,V}\rho^2\,V \int g(r_{12}) \left[-r_{ij}\left(\frac{\partial \mathcal{V}_{pair}}{\partial r}\right)_{r=r_{ij}}\right] d^3 r_{ij}\ , \quad \text{or}$$

$$P = \rho k_B T - \frac{\rho^2}{6}\int_0^\infty r\,\frac{\partial \mathcal{V}_{pair}}{\partial r}\,4\pi r^2\,g(r)\,dr \tag{9.34}$$

Eq. (9.34) is known as the *pressure equation.*

### Isothermal Compressibility

An interesting connection between the isothermal compressibility and the pair distribution function can be arrived at starting from the normalization condition, Eq. (9.11), in the grand canonical ensemble. For a homogeneous system, we have

$$\rho^2 V \int g^{(2)}(\mathbf{r}_{12})\,d^3 r_{12} = \langle N^2\rangle - \langle N\rangle \tag{9.11}$$

On the other hand, our analysis of fluctuations in the grand canonical ensemble has given

$$\left\langle (\delta N)^2 \right\rangle \equiv \langle N^2\rangle - \langle N\rangle^2 = k_B\,T\,\frac{\langle N\rangle^2}{V}\,\kappa_T \tag{6.20}$$

Combining Eqs. (9.11) and (6.20), we obtain

$$\rho^2 V \int g^{(2)}(\mathbf{r}_{12})\, d^3 r_{12} = k_B\, T\, \frac{\langle N\rangle^2}{V}\, \kappa_T + \langle N\rangle^2 - \langle N\rangle =$$

$$k_B\, T\, \rho^2\, V\, \kappa_T + \rho^2\, V^2 - \rho\, V\ , \quad \text{or}$$

$$\rho\, k_B\, T\, \kappa_T = \rho \int g^{(2)}(\mathbf{r})\, d^3 r - \rho\, V + 1 = 1 + \rho \int g^{(2)}(\mathbf{r})\, d^3 r - \rho \int d^3 r$$

or, in the thermodynamic limit,

$$\rho\, k_B\, T\, \kappa_T = 1 + \rho \int [g(\mathbf{r}) - 1]\ d^3 r = 1 + \rho \int_0^\infty 4\pi\, r^2\ [g(r) - 1]\ dr \qquad (9.35)$$

Eq. (9.35) is known as the *compressibility equation.* Remarkably, its validity *does not presuppose pairwise additivity.* In view of Eq. (9.29), a straightforward relation can be established between the isothermal compressibility and the zero-wavevector value of the static structure factor, *ignoring the forward-scattering contribution:*

$$S(\mathbf{0}) \equiv \lim_{\mathbf{k}\to\mathbf{0}} S(\mathbf{k}) = \rho\, k_B\, T\, \kappa_T = \frac{\kappa_T}{\kappa_T^{ig}} \qquad (9.36)$$

where $\kappa_T^{ig}$ is the isothermal compressibility the material would exhibit if it were an ideal gas at the same temperature and density. Eq. (9.36) is an important connection between experimentally obtainable structure and thermodynamic properties of equilibrium systems.

### 9.1.6 Potential of Mean Force and Pair Distribution Function

The pair distribution function can be used to define an interesting free energy quantity called the *potential of mean force*, whose physical meaning we briefly explore below. For an $N$-molecule system in volume $V$ at temperature $T$ (canonical ensemble) we define the potential of mean force $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ as a function of two positions in space, by

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv exp\left[-\beta w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\right] \tag{9.37}$$

Recalling the definition, Eq. (9.8),

$$w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) =$$

$$\frac{1}{\beta}\ln\left[\frac{N(N-1)}{N^2}\frac{V^2}{Z(N,V,T)}\right] - \frac{1}{\beta}\ln\int exp\left[-\beta\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right]\, d^3r_3\, d^3r_4\, \ldots\, d^3r_N \tag{9.38}$$

We now take the gradient of Eq. (9.38) with respect to $\mathbf{r}_1$:

$$\nabla_{\mathbf{r}_1} w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\int\left[\nabla_{\mathbf{r}_1}\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right]\exp\left[-\beta\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right]\, d^3r_3\, d^3r_4\, \ldots\, d^3r_N}{\int \exp\left[-\beta\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right]\, d^3r_3\, d^3r_4\, \ldots\, d^3r_N} =$$

$$- \left\langle \mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right\rangle_{\mathbf{r}_1, \mathbf{r}_2} \tag{9.39}$$

where $\mathbf{F}_1$ is the total force exerted on 1 from *all other molecules*, including 2, and the average is taken over all configurations of the fluid that have molecule 1 at position $\mathbf{r}_1$ and molecule 2 at position $\mathbf{r}_2$. All degrees of freedom other than $\mathbf{r}_1$ and $\mathbf{r}_2$ are averaged over, so the *mean force* on the right hand side of Eq. (9.39) is a function of only $\mathbf{r}_1$ and $\mathbf{r}_2$.

From Eq. (9.39) it is obvious that $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv -k_B T \ln g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ can be viewed as an effective pair potential that generates the total force of interaction felt by molecule 1 for fixed positions of molecules 1 and 2, *averaged* over all configurations of the remaining $(N-2)$ molecules. Hence the name *potential of mean force* for $w_N^{(2)}(\mathbf{r}_{12})$. In homogeneous systems, one can write $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = w_N^{(2)}(\mathbf{r}_{12})$, and in homogeneous and isotropic systems one has $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = w_N^{(2)}(r_{12})$.

From Eq. (9.39) it is obvious that $w_N^{(2)}(\mathbf{r}_{12}) \equiv -k_B T \ln g_N^{(2)}(\mathbf{r}_{12})$ can be viewed as a potential that generates the force of interaction between two molecules at a fixed position $\mathbf{r}_{12}$ relative to each other in the fluid, *averaged* over all configurations of the remaining $(N-2)$ molecules. Hence the name *potential of mean force* for $w_N^{(2)}(\mathbf{r}_{12})$.

It is remarkable that $w_N^{(2)}(\mathbf{r}_{12})$ can be attractive over some separation ranges even in cases where the pair potential is purely repulsive. An example is shown in Fig. 9.7 for the hard sphere fluid. Two spheres at distance slightly larger than the collision diameter experiemce an effective attraction to each other because of the pounding action of spheres surrounding the pair.

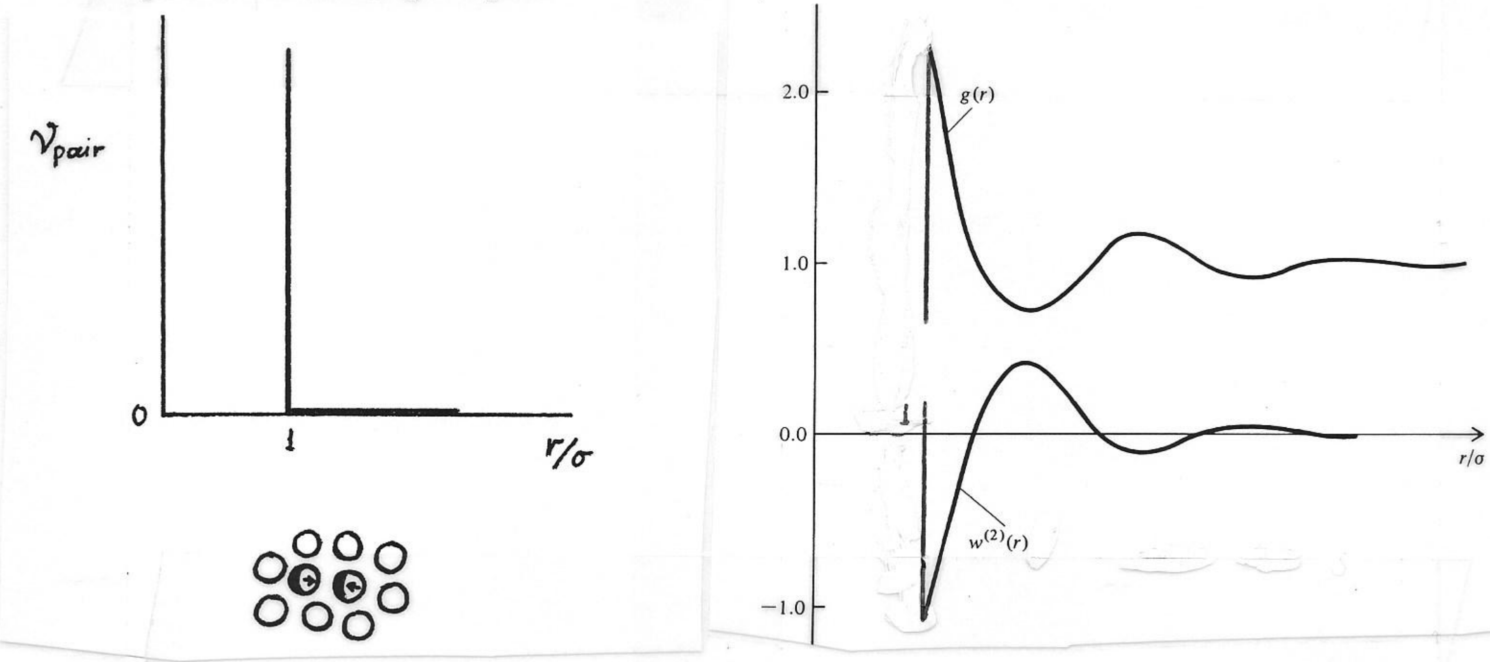


**Figure 9.7** Pair potential $\mathcal{V}_{pair}$, pair distribution function $g(r)$, and potential of mean force $w_N^{(2)}(r)$ for a hard sphere fluid at a liquid density

An interesting alternative expression for the $w_N^{(2)}$ can be arrived at as follows. From the definition of the pair distribution function, Eq. (9.8), one obtains:

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) =$$

$$\frac{\frac{1}{h^{3\,(N-2)}}\frac{1}{(N-2)!}\int exp\,[-\beta\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\,\mathbf{p}_1,\ldots,\mathbf{p}_N)]\;d^3r_3\;\ldots,\;d^3r_N\;d^3p_3\;\ldots\;d^3p_N}{\frac{1}{h^{3\,N}}\frac{1}{N!}\int exp\,[-\beta\mathcal{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\,\mathbf{p}_1,\ldots,\mathbf{p}_N)]\;d^3r_1\;\ldots\;d^3r_N\;d^3p_1\;\ldots\;d^3p_N}\times$$

$$\frac{1}{(\rho\,\Lambda^3)^2} =$$

$$\frac{Q(N-2,V,T;\mathbf{r}_1,\mathbf{r}_2)}{Q(N,V,T)}\frac{1}{(\rho\,\Lambda^3)^2} = \frac{Q(N-2,V,T;\mathbf{r}_1,\mathbf{r}_2)}{Q(N,V,T)}\,e^{-2\,\beta\,\mu^{ig}} \tag{9.40}$$

where $Q(N,V,T)$ is the canonical partition function for $N$ molecules in volume $V$ at temperature $T$; $Q(N-2,V,T;\mathbf{r}_1,\mathbf{r}_2)$ is the partition function for a system of $N-2$ molecules in volume $V$ and temperature $T$, interacting with each other and with two stationary molecules placed permanently at fixed positions $\mathbf{r}_1$ and $\mathbf{r}_2$; and $\mu^{ig}$ is the chemical potential of an ideal gas of molecules at temperature $T$ and density $\frac{N}{V}$. Taking the logarithm of both sides of Eq. (9.40), we obtain

$$w_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - 2\,\mu^{ig} = A_{N-2}(V,T;\,\mathbf{r}_1,\mathbf{r}_2) - A_N(V,T) \tag{9.41}$$

Eq. (9.41) makes it clear that the potential of mean force governing a subset of degrees of freedom of the system, which we choose to constrain (in this example $\mathbf{r}_1,\mathbf{r}_2$) is essentially a free energy obtained by integrating over all the remaining (unconstrained) degrees of freedom. This somewhat broader definition of the potential of mean force is useful in the study of a variety of complex material systems.

### 9.1.7 Low-density Limit of the Pair Distribution Function. Application: Second Virial Coefficient from Pair Potential

When the density $\rho$ becomes very small, the interaction between two molecules fixed at a distance $r$ apart is not affected by the remaining $(N-2)$ molecules. Then, the potential of mean force $w_N^{(2)}$ becomes indistinguishable from the pair potential $\mathcal{V}_{pair}$, and

$$\lim_{\rho \to 0} g(r) = exp\left[-\beta \mathcal{V}_{pair}(r)\right] \tag{9.42}$$

Inserting this low-density limit of $g(r)$ into the pressure equation, Eq. (9.34), one obtains

$$\frac{\beta P}{\rho} \simeq 1 - \frac{2\pi\beta}{3}\rho \int_0^\infty exp\left[-\beta \mathcal{V}_{pair}(r)\right] r^3 \frac{d\mathcal{V}_{pair}}{dr}\, dr =$$

$$1 + \frac{2\pi}{3}\rho \int_0^\infty r^3\, d\left[exp\left\{-\beta \mathcal{V}_{pair}(r)\right\}\right] =$$

$$1 + \frac{2\pi}{3}\rho \left\{ \left[r^3\, exp\left\{-\beta \mathcal{V}_{pair}(r)\right\}\right]_0^\infty - \int_0^\infty exp\left[-\beta \mathcal{V}_{pair}(r)\right] 3r^2\, dr \right\} =$$

$$1 + \frac{2\pi}{3}\rho \lim_{R\to\infty} \left\{R^3 - 3exp\left[-\beta \mathcal{V}_{pair}(r)\right]\right\} r^2\, dr =$$

$$1 + \frac{2\pi}{3}\rho\, 3 \lim_{R\to\infty} \int_0^R \left[1 - exp\left\{-\beta \mathcal{V}_{pair}(r)\right\}\right] r^2\, dr \quad , \text{ or}$$

$$\frac{\beta P}{\rho} = 1 + B_2(T)\,\rho \tag{9.43}$$

where

$$B_2(T) = -2\pi \int_0^\infty \left[exp\left\{-\beta \mathcal{V}_{pair}(r)\right\} - 1\right] r^2\, dr \tag{9.44}$$

Eq. (9.43) is a virial equation of state, truncated at the second virial term. Eq. (9.44) is an expression for the second virial coefficient in terms of the pair potential.

### 9.1.8 Pair Correlation Function and Direct Correlation Function. Ornstein-Zernike equation

In addition to $g(r)$, two other functions describing positional correlations between pairs of molecules play a significant role in the theory of liquids. These are the pair correlation function $h(r)$ and the direct correlation function $c(r)$.

The pair correlation function is defined as

$$h(\mathbf{r}_1,\mathbf{r}_2) = g^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - 1 \tag{9.45}$$

In an isotropic fluid, one can write $h(r_{12}) = g(r_{12}) - 1$. $h(r_{12})$ is a measure of the total influence of molecule 1 on the position of molecule 2, lying a distance $r_{12}$ away from 1; it is often termed the *total* pair correlation function.

In 1914, Ornstein and Zernike introduced an important idea: They proposed a division of $h(r_{12})$ into two parts: a *direct* part, $c(r_{12})$, and an indirect part. A graphic representation of this idea is given in Fig. 9.8. Molecule 1 is correlated with molecule 2 because ($a$) it is directly correlated with 2; ($b$) it may be directly correlated to a third molecule, 3, which is correlated to 2 directly or indirectly through other molecules. The mathematical expression of this statement is the *Ornstein-Zernike equation*

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, h(r_{32})\, d^3 r_3 \tag{9.46}$$

Eq. (9.44) constitutes a definition of the direct correlation function $c(r)$.

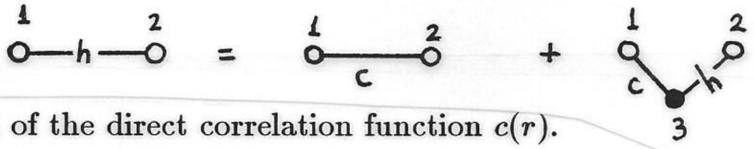
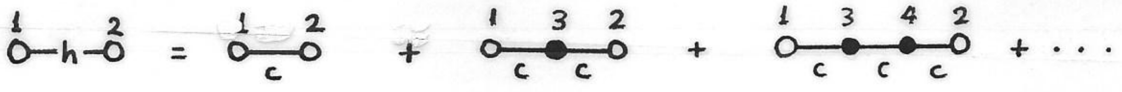


**Figure 9.8** For the definition of the direct correlation function $c(r)$.

Note thart recursive use of the Ornstein-Zernike equation leads to

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, c(r_{32})\, d^3 r_3 + \rho^2 \int\int c(r_{13})\, c(r_{34})\, c(r_{42})\, d^3 r_3\, d^3 r_4 + \ldots$$



The Ornstein-Zernike equation becomes particularly simple in Fourier-transformed space. Let $\hat{h}(k) = \int h(r)\, e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3 r$ and $\hat{c}(k) = \int c(r)\, e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d^3 r$. Taking the Fourier transform of Eq. (9.44) and invoking the convolution theorem, we obtain

$$\hat{h}(k) = \hat{c}(k) + \rho\, \hat{c}(k)\, \hat{h}(k) \quad ,\text{or}$$

$$\hat{h}(k) = \frac{\hat{c}(k)}{1 - \rho\, \hat{c}(k)} \tag{9.47}$$

Note that, from Eq. (9.29) for the structure factor, omitting the forward scattering contribution,

$$S(k) = 1 + \rho\, \hat{h}(k)$$

Hence, there is a simple relation between structure factor $S(k)$ and direct correlation function:

$$S(k) = \frac{1}{1 - \rho\, \hat{c}(k)} \tag{9.48}$$

The compressibility equation (9.36) gives

$$\rho \int c(r)\, d^3 r = \rho \hat{c}(0) = 1 - \frac{1}{\rho\, k_B\, T\, \kappa_T} = 1 - \frac{\kappa_T^{ig}}{\kappa_T} \tag{9.49}$$

Generally, the direct correlation function displays a simpler behavior than $h(r) = g(r) - 1$. The range of $c(r)$ is roughly the same as that of the pair potential $\mathcal{V}_{pair}$; *i.e.*, $c(r)$ is significantly different from zero over a distance roughly equal to the pair potential range. This means that, in non-ionic fluids, $c(r)$ will be significantly shorter-ranged than $h(r)$. This is seen characteristically in Fig. 9.9, which compares $h(r)$ and $c(r)$ for a Lennard-Jones liquid. Clearly, the undulations in $h(r)$ are an indirect correlation effect, and are not seen in $c(r)$. Plots of $c(r)$ for liquid argon at several densities, as extracted from experimental diffraction data, are given in Fig.9.6.

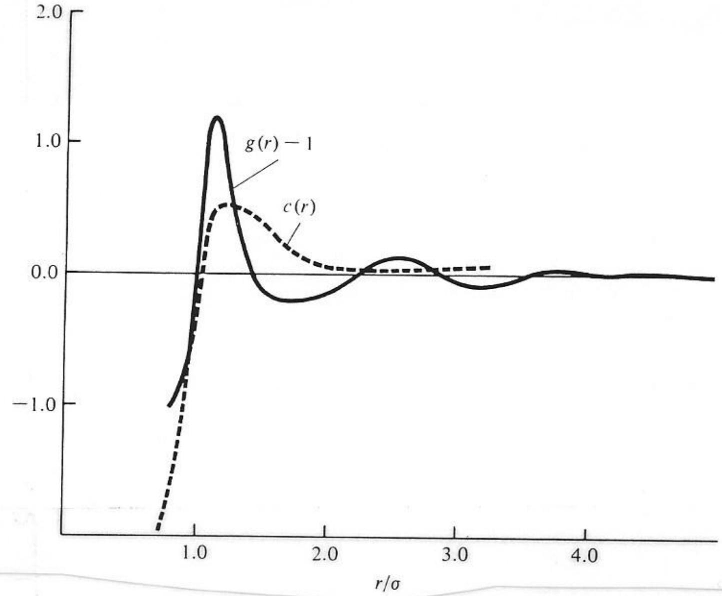


**Figure 9.9** Total correlation function $h(r) = g(r) - 1$ and direct correlation function $c(r)$ for a Lennard-Jones fluid [after Mc Quarrie (1976),p 270].

In molecular fluids, both *intramolecular* and *intermolecular* correlations between sites (atoms) must be considered. An extension of the Ornstein-Zernike equation to molecular fluids forms the basis for the powerful Reference Interaction Site Model

(RISM), an integral equation approach originally introduced by Chandler and Andersen (Chandler, 1982).

## 9.2 Elements of Integral Equation Theory for Simple Fluids

The Ornstein-Zernike equation, Eq. (9.46), is an integral equation in two unknown functions, $h(r)$ and $c(r)$. If one introduces a judicious approximation relating $h(r)$ and $c(r)$, one can convert the Ornstein- Zernike into an integral equation in one unknown function. By solving this integral equation, one can obtain the structure of the fluid ($h(r)$, therefore $g(r)$) at given density $\rho$ and temperature $T$, hence the fluid's thermodynamic properties.

Such an additional equation connecting $h(r)$ and $c(r)$ is said to provide *closure* to the Ornstein-Zernike equation. The system of the Ornstein- Zernike and the closure equation constitutes an *integral equation theory* for the fluid structure.

Closure equations can be arrived at by detailed analysis of the graphical expansions of $g(r)$ and $h(r)$, or through formulations that employ the theory of functionals. Here we will only present a heuristic justification of the *Percus-Yevick* closure, originally derived through a very different argument [Percus and Yevick (1958)]. Our brief discussion follows mainly McQuarrie [McQuarrie (1979), Chapter 13].