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Abstract

Full Text

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RADIAL DISTRIBUTION OF ATOMS IN A LIQUID

(Presented by Academician N. N. Bogoliubov, 4 XII 1959)

In the theory of the liquid state, the radial distribution function is of great importance. As is known (^{1}), for small values of the density N/V, by the method of N. N. Bogoliubov' s correlation functions one can obtain the probability of configurations of two atoms

$$dw(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1, \mathbf{r}_2) \frac{d\mathbf{r}_1 d\mathbf{r}_2}{V^2}, \tag{1}$$

calculating $\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho(r)$ for an isotropic medium. For a liquid (at large densities N/V) the calculation of $\rho(r)$ is considerably more difficult.

In the present work it is proposed to replace the superposition approximation used for calculating $\rho(r)$ (^{2}) by the assumption that, for a liquid, one can establish a system of coordinates of the particles $\mathbf{r}_0 = \{\mathbf{r}_1^0, \mathbf{r}_2^0, \dots, \mathbf{r}_N^0\}$ such that $U(\mathbf{r}_1^0, \mathbf{r}_2^0, \dots, \mathbf{r}_N^0) = \min$.

Let us introduce the concept of the conditional probability of realization of the configuration of two particles in positions $\mathbf{r}_1, \mathbf{r}_2$, if their equilibrium centers are at the points $\mathbf{r}_1^0, \mathbf{r}_2^0$:

$$P(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_1^0, \mathbf{r}_2^0) = \frac{d\vec{\eta}_1 d\vec{\eta}_2 \int_{\omega_3} \cdots \int_{\omega_N} \exp(-U(r)/kT)\, d\vec{\eta}_3 \cdots d\vec{\eta}_N}{\int_{\omega_1} \int_{\omega_2} \cdots \int_{\omega_N} \exp(-U(r)/kT)\, d\vec{\eta}_1 \cdots d\vec{\eta}_N}, \tag{2}$$

where the integration over each of the coordinates is carried out within the limits of a cell, so that the prescribed configuration of cell centers is preserved. For this reason the conditional coordinates $\vec{\eta}_i = \mathbf{r}_i - \mathbf{r}_i^0$ have been introduced.

For an isotropic medium—a liquid—the conditional probability (2) can be averaged over directions and the probability obtained of finding two conditionally selected particles at a distance r from one another independently of direction (^{3}):

$$P(r/r^0) = k(r/r^0)\, dr = \int_{\omega_1} \int_{\omega_2} P(\vec{\eta}_1, \vec{\eta}_2)\, d\vec{\eta}_1\, d\vec{\eta}_2 \cdot \delta(|\mathbf{r}_{12}| - r), \tag{3}$$

Fig. 1

Figure 1: Fig. 1

$$r = |\mathbf{r}_1 - \mathbf{r}_2|, \qquad \mathbf{r}_{12} = \mathbf{r}_1^0 - \mathbf{r}_2^0 - \vec{\eta}_1 + \vec{\eta}_2,$$

δ is the Dirac function, and $k(r/r^0)$ is the conditional density of the probability distribution.

By the formula of total probability,

$$\frac{4\pi r^2}{V}\rho(r) = \frac{4\pi}{V}\int k(r/r^0)\, p(r^0)(r^0)^2\, dr^0 \tag{4}$$

we define $\dfrac{\rho(r)\, r^2 4\pi}{V}$—the density of the probability distribution of finding any two particles at a distance r from one another, if the density is given

of the probability distribution for the positions of the equilibrium centers. We may suppose that the distribution of particles in the liquid is either the same as, or differs very little from, the distribution of the equilibrium centers of these particles. Under this assumption, the problem of calculating the radial distribution function reduces to solving the integral equation (4).

The concrete calculation of $k(r/r^0)$ depends on the possibility of neglecting correlations between particles. In the limiting case, the condition

$$\partial^2 U/\partial\eta_i\partial\eta_j = 0$$

for every $i \neq j$ means independence of the motion of particles in the cells and corresponds to the so-called one-cell variant of the self-consistent-field method.

Then

$$k(r/r^0)\, dr = \frac{1}{\omega^2}\iint_{\omega\ \omega} \psi(\eta_1)\psi(\eta_2)\, d\vec{\eta}_1\, d\vec{\eta}_2\, \delta\left(|r_{12}| - r\right). \tag{5}$$

Fig. 1

In the first approximation, let us solve the problem for the hard-sphere model:

$$\Phi(r) = +\infty, \quad r \leq d_0; \qquad \Phi(r) = 0, \quad r > d_0;$$

d_0 is the diameter of a sphere.

In this case:

$$\psi(\eta) = 1, \quad \eta < \varepsilon; \qquad \psi(\eta) = 0, \quad \eta \geq \varepsilon;$$

ε is the radius of the free volume assigned to each particle. All this is valid only for $r > d_0$.

Formula (5) is written in the following form:

$$k(r - r^0) = \frac{1}{\omega^2} \int S_2(t, h_1)\, S_1(h_1)\, dh_1, \tag{6}$$

where $S_1(h_1)\, dh_1$ is the volume element of the first cell, and $S_2(t, h_1)\, dr$ is the volume element of the second cell under the condition of a given $t = r - r^0$.

Figure 1 gives an illustration of the scheme for calculating $k(t)$ for $r < r^0$ and $r > r^0$:

$$k(t) = \frac{\pi}{\omega^2} \int_{\varepsilon - t}^{\varepsilon} \{\varepsilon^2 - (h_1 - t)^2\}\{\varepsilon^2 - h_1^2\}\, dh_1, \qquad t > 0;$$

$$k(t) = \frac{\pi}{\omega^2} \int_{-\varepsilon - t}^{\varepsilon} \{\varepsilon^2 - (t + h)^2\}\{\varepsilon^2 - h_1^2\}\, dh_1, \qquad t < 0. \tag{7}$$

Putting $t/\varepsilon = l$, we obtain

$$k(l) = \frac{1}{\varepsilon} \left\{ \frac{3}{5} - \frac{3}{4}|l|^2 + \frac{3}{8}|l|^3 - \frac{3}{160}|l|^5 \right\}, \qquad -2 \leq l \leq 2. \tag{8}$$

Taking (5) into account, we obtain

$$\rho(x) x^2 = \varepsilon \int_{x-2}^{x+2} k(x - s) \rho(s) s^2\, ds \tag{9}$$

for $x > a = d_0/\varepsilon$, where $x = r/\varepsilon,\ s = r^0/\varepsilon$.

By direct substitution we verify that

$$x^2 = \varepsilon \int_{x-2}^{x+2} k(x - s)(s^2 - \alpha)\, ds,$$

where α is a very small quantity in comparison with s for $x > a$.

We can now write

$$x^2 \{\rho(x) - 1\} = \varepsilon \int_{x-2}^{x+2} k(x - s) \frac{(s^2 - \alpha)}{s^2} \{\Phi(s) - 1\} s^2\, ds. \tag{10}$$

Fig. 2

Figure 2: Fig. 2

By the normalization condition

$$\frac{1}{V}\int_0^\infty \{\rho(x)-1\}x^2\,dx = 0.$$

We find that $\Phi(s) \to 1$ as $s \to \infty$.

Apparently, $\Phi(s)$ has the same properties as $\rho(x)$, not only at infinity, but also for $a < x < \infty$.

Neglecting the small quantity α, we obtain the integral equation

$$\varphi(x) = \varepsilon \int_{x-2}^{x+2} k(x-s)\varphi(s)\,ds, \qquad x > a. \tag{11}$$

Fig. 2

For $x \leq a$, $\varphi(x) = -x^2$; by this we take into account the impenetrability of the particles. Consequently,

$$\varphi(x) = f(x) + \varepsilon \int_{-\infty}^{+\infty} k(|x-s|)\varphi(s)\,ds, \tag{12}$$

where $f(x) = -x^2,\ |x| \leq a; \quad f(x) = 0,\ |x| > a$, and $k(l) = 0$ for $|l| \geq 2$.

Solving equation (12) by the Fourier or Laplace transform method (^{4}), we obtain

$$\varphi(x) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{M(z)}{1-K(z)} e^{zx}\,dz, \tag{13}$$

where

$$K(z) = \varepsilon \int_{-2}^{+2} k(|l|)e^{-zl}\,dl, \qquad M(z) = -\int_{-a}^{+a} x^2 e^{-zx}\,dx.$$

The final solution is obtained in the form

$$\varphi(x) = x^2\{\rho(x)-1\} = \sum_n A_n e^{\alpha_n x}\cos(\beta_n x + \delta_n), \tag{14}$$

where $\alpha_n \pm i\beta_n = z_n$ is the n-th pole of the integrand in (13).

The first pair of roots of the equation $1 - K(z) = 0$ for our case is

$$z_1 = -0.35 + i \cdot 0.80, \qquad z_2 = -0.35 - i \cdot 0.80.$$

Figure 2 gives the function $\rho(r)$, calculated in the particular cases $d_0 = 3\,\text{Å}$, $\varepsilon_1 = 0.20\,\text{Å}$ (curve 1) and $\varepsilon_2 = 0.15\,\text{Å}$ (curve 2). The obtained function $\rho(r)$ in its general form reflects the properties of the experimental radial distribution function.

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Note: Figure translations are in progress. See original paper for figures.

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