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Local structure and bond orientational order in a Lennard-Jones liquid

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Abstract. The long-range behaviour of the orientational fluctuations of a pair distribution function is studied. The existence of the instability of an isotropic liquid against formation of the state with bond orientational order is shown. The estimates for the instability points for a Lennard-Jones liquid are obtained, and a comparison with computer simulation is carried out.

1. Introduction

The structure of supercooled liquids and glasses is incompletely understood even for the simplest systems [1, 2]. Frenkel [3] has suggested a qualitative picture of local structure of condensed matter. The main assumption is that a dense liquid in small volumes represents a crystal-like structure. This concept was used in recent papers [4–9]. It was argued, however, that real metallic glasses and supercooled liquids are better described in terms of ordered but non-crystalline clusters. As pointed out by Frank [10], icosahedral clusters of 13 particles have a significantly lower energy than more obvious arrangements, corresponding to nuclei of FCC and HCP crystals. An icosahedron was used as the main structural unit of local order in [11–13].

It is natural to enquire whether the regions of local symmetry correlate with each other and create long-range orientational order: bond orientational order. Note that the 'bond' is the line joining an atom to its near neighbour. This type of order is well known in modern theories of two-dimensional melting (hexatic phase) [14, 15]. Three-dimensional cubic bond orientational order has been studied theoretically by Nelson and Toner [9]. Mitus and Patashinskii [6, 7] and Haymet [16] have studied the onset of this order on the basis of model Hamiltonians within the mean-field approximation and have found a first order phase transition. However, fluctuation effects can make the transition continuous [17]. Remler and Haymet [18] extended the study of model Hamiltonians to treat orientational ordering in systems with hexagonally close-packed symmetry.

Steinhardt *et al* [11] have studied bond orientational order in a computer simulation of supercooled Lennard-Jones liquids. On the basis of the calculated correlation in the orientation of 'bonds' joining near neighbours, they concluded that an increase in icosahedral ordering occurs as the liquid is supercooled about 10% below the equilibrium melting temperature. In this case, extended orientational correlations appear, with little

or no increase in the translational correlation length. The symmetry of the bond-oriented state is not perfectly icosahedral, however (see also [19, 20]). Haymet [16] has solved a simple lattice model of interacting icosahedra and found the first-order orientational phase transition within the mean-field approximation. The importance of the study of the icosahedral structure in bulk systems is illustrated by the recently discovered icosahedral phase [21].

In this paper we continue the study of orientational order in condensed phases on the basis of the non-linear equations for s -particle distribution functions. In section 2 we review the formalism, developed in our previous papers [22–24] for analysing the orientational correlations and give some modifications of main equations. In section 3 we present our results for the Lennard-Jones potential and make the comparison with computer simulation. In addition, we propose the phase diagram for the orientationally ordered state. A brief discussion of our results is given in section 4.

2. Main equations

As may be seen from section 1, our main problem is the investigation of the correlations between the directions of ‘bonds’. This is equivalent to the problem of the long-range behaviour of the orientational fluctuations of the pair distribution function in an isotropic liquid [22–24]. To solve this problem let us consider the four-particle distribution function $F_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ when one pair of particles described by \mathbf{r}_1 and \mathbf{r}_2 is removed from another pair described by \mathbf{r}_3 and \mathbf{r}_4 . The particles in pairs are the nearest neighbours of each other. This function gives us the information about the correlations between the bonds $\mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r}_3 - \mathbf{r}_4$.

We shall write $F_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ in the following form:

$$F_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = g(|\mathbf{r}_1 - \mathbf{r}_2|)g(|\mathbf{r}_3 - \mathbf{r}_4|)[1 + f_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)] \quad (1)$$

where $f_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \rightarrow 0$ as $R = |\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$ and $g(r)$ is the radial distribution function of the ordinary liquid.

For an isotropic liquid we have [25]

$$f_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = f_4(r, R, k, \vartheta_1, \vartheta_2, \varphi_1 - \varphi_2) \quad (2)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$, $k = |\mathbf{r}_3 - \mathbf{r}_4|$, $R = |\mathbf{r}_1 - \mathbf{r}_4|$, ϑ_1 and ϑ_2 are the angles of \mathbf{r} and \mathbf{k} , respectively, with \mathbf{R} , and $\varphi_1 - \varphi_2$ is the angle between planes (\mathbf{r}, \mathbf{R}) and (\mathbf{k}, \mathbf{R}) .

The function $f_4(r, R, k, \vartheta_1, \vartheta_2, \varphi_1 - \varphi_2)$ may be expanded in a series in spherical harmonics:

$$f_4(r, R, k, \vartheta_1, \vartheta_2, \varphi_1 - \varphi_2) = \sum_{m=-\infty}^{\infty} \sum_{l, l'=|m|}^{\infty} B_{ll'}^m(r, R, k) Y_{lm}(\vartheta_1, \varphi_1) Y_{l', -m}(\vartheta_2, \varphi_2). \quad (3)$$

The angles $\Omega_1 = (\vartheta_1, \varphi_1)$ and $\Omega_2 = (\vartheta_2, \varphi_2)$ determine the directions of the bonds $\mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r}_3 - \mathbf{r}_4$, respectively. Therefore the long-range orientational correlations are determined by the behaviour of the functions $B_{ll'}^m(r, R, k)$ as $R \rightarrow \infty$. To obtain the equation for $B_{ll'}^m(r, R, k)$ we shall use the exact non-linear equation for many-particle distribution functions [22–24]:

$$\frac{\rho F_{s+1}(\mathbf{r}_1 | \mathbf{k}_1 \dots \mathbf{k}_s)}{z} = \exp \left(-\beta \sum_{i=1}^s \Phi(|\mathbf{r}_1 - \mathbf{k}_i|) + \sum_{k \geq 1} \frac{\rho^k}{k!} \int S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1}) \right. \\ \left. \times F_{s+1}(\mathbf{r}_2 | \mathbf{k}_1 \dots \mathbf{k}_s) \dots F_{s+1}(\mathbf{r}_{k+1} | \mathbf{k}_1 \dots \mathbf{k}_s) d\mathbf{r}_2 \dots d\mathbf{r}_{k+1} \right). \quad (4)$$

Here $F_{s+1}(\mathbf{r}_1|\mathbf{k}_1 \dots \mathbf{k}_s)$ determines the probability of finding a particle at \mathbf{r}_1 if s particles at points \mathbf{k}_i are fixed:

$$F_{s+1}(\mathbf{r}_1|\mathbf{k}_1 \dots \mathbf{k}_s) = F_{s+1}(\mathbf{r}_1, \mathbf{k}_1, \dots, \mathbf{k}_s)/F_s(\mathbf{k}_1, \dots, \mathbf{k}_s) \quad (5)$$

where $F_s(\mathbf{k}_1, \dots, \mathbf{k}_s)$ is the s -particle distribution function, z is the fugacity, $S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1})$ is the irreducible cluster sum of Mayer functions connecting (at least doubly) $k+1$ particles, ρ is the mean number density, $\beta = 1/k_B T$, T is the temperature and $\Phi(r)$ is the intermolecular potential.

Generally z can be obtained from the condition

$$\frac{1}{V} \int F_{s+1}(\mathbf{r}_1|\mathbf{k}_1 \dots \mathbf{k}_s) d\mathbf{r}_1 = 1.$$

For an isotropic liquid without external fields we can use the ordinary virial expansion

$$\frac{\rho}{z} = \exp \left(\sum_{k \geq 1} \frac{\rho^k}{k!} \int S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1}) d\mathbf{r}_2 \dots d\mathbf{r}_{k+1} \right). \quad (6)$$

Let us consider equation (4) with $s = 3$. We shall study correlations in the isotropic liquid, where $F_1(\mathbf{r}) \equiv 1$; so we do not regard the breaking of the singlet distribution function symmetry corresponding to the freezing transition (see, e.g., [26, 27]).

As was shown in [24, 28], we have, for $R = |\mathbf{k}_1 - \mathbf{k}_2| \gg 1$,

$$F_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = g(|\mathbf{k}_2 - \mathbf{k}_3|) + \rho^{-1} \{ (\partial/\partial\rho)[\rho^2 g(|\mathbf{k}_2 - \mathbf{k}_3|)] \} h(R) \quad (7)$$

where $h(R) = g(R) - 1$, $h(R) \rightarrow 0$ as $R \rightarrow \infty$.

For $R \gg 1$ the inequalities $h(R) \ll 1$ and $f_4(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \ll 1$ take place. In this case, using (1) and (7), we obtain

$$\begin{aligned} & F_4(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)/F_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ &= g(|\mathbf{r}_1 - \mathbf{k}_1|) [1 + f_4(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) - \Psi(|\mathbf{k}_2 - \mathbf{k}_3|)h(R)] \end{aligned} \quad (8)$$

where

$$\Psi(|\mathbf{k}_2 - \mathbf{k}_3|) = [\rho g(|\mathbf{k}_2 - \mathbf{k}_3|)]^{-1} (\partial/\partial\rho)[\rho^2 g(|\mathbf{k}_2 - \mathbf{k}_3|)].$$

Let us now substitute (8) in (4) with $s = 3$ and linearise the result with respect to $f_4(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) - \Psi(|\mathbf{k}_2 - \mathbf{k}_3|)h(R)$. Then, taking into account the fact that $g(r)$ is the solution of equation (4) for $s = 1$, we have the equation:

$$\begin{aligned} f_4(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) &= \int \Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2) g(|\mathbf{r}_2 - \mathbf{k}_1|) f_4(\mathbf{r}_2, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) d\mathbf{r}_2 \\ &+ \left[\Psi(|\mathbf{k}_2 - \mathbf{k}_3|)h(R) \left(1 - \int \Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2) g(|\mathbf{r}_2 - \mathbf{k}_1|) d\mathbf{r}_2 \right) \right. \\ &\left. - \beta\Phi(|\mathbf{r}_1 - \mathbf{k}_2|) - \beta\Phi(|\mathbf{r}_1 - \mathbf{k}_3|) \right]. \end{aligned} \quad (9)$$

The last term in equation (9) does not depend on the directions of the bonds $\mathbf{r}_1 - \mathbf{k}_1$ and $\mathbf{k}_2 - \mathbf{k}_3$ and may be omitted in what follows.

The function $\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{k}_2)$ has the form

$$\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2) = \sum_{k \geq 1} \frac{\rho^k}{(k-1)!} \times \int S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1}) g(|\mathbf{r}_3 - \mathbf{k}_1| \dots g(|\mathbf{r}_{k+1} - \mathbf{k}_1|) d\mathbf{r}_3 \dots d\mathbf{r}_{k+1}. \quad (10)$$

Owing to translational and rotational invariance, $\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2)$ depends on $r = |\mathbf{r}_1 - \mathbf{k}_1|$, $r' = |\mathbf{r}_2 - \mathbf{k}_1|$ and ϑ (the angle between \mathbf{r} and \mathbf{r}') only:

$$\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2) g(|\mathbf{r}_2 - \mathbf{k}_1|) = K(r, r', \vartheta). \quad (11)$$

The expansion for $K(r, r', \vartheta)$ takes the form

$$K(r, r', \vartheta) = g(r') \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \Gamma_l(r, r') \sum_{m=-l}^l Y_{lm}(\Omega_1) Y_{lm}^*(\Omega_2) \quad (12)$$

where Ω_1 and Ω_2 determine the directions of the vectors $\mathbf{r}_1 - \mathbf{k}_1$ and $\mathbf{r}_2 - \mathbf{k}_1$.

Substituting (2) and (12) into (9) (without the last term) and changing the variables ($\mathbf{r}_0 = \mathbf{r}_2 - \mathbf{k}_1$, $d\mathbf{r}_2 = d\mathbf{r}_0$), we find that

$$f_4(r, R, k, \vartheta_1, \vartheta_2, \varphi_1 - \varphi_2) = \int K(r, r_0, \vartheta) f_4(r_0, |\mathbf{R} + \mathbf{s}|, k, \vartheta'_1, \vartheta'_2, \varphi'_1 - \varphi'_2) d\mathbf{r}_0. \quad (13)$$

Here $\mathbf{s} = \mathbf{r}_2 - \mathbf{r}_1$; ϑ'_1 and ϑ'_2 are the angles of \mathbf{r}_0 and \mathbf{k} , respectively, with \mathbf{r}_2 , and $\varphi'_1 - \varphi'_2$ is the angle between the planes $(\mathbf{r}_0, \mathbf{r}_2)$ and $(\mathbf{k}, \mathbf{r}_2)$.

Inserting (3) and (12) into (13), we obtain the equations for $B_{ll}^m(r, R, k)$. The slowly varying solutions of these equations can be investigated by a gradient expansion technique [22–24]. In our case, $s \ll R$; therefore equation (13) can be well approximated by its Taylor expansion in powers of s . There are two small parameters, s/R and s/dR , in this expansion, and their relative sizes need not be specified. To obtain exponential asymptotic behaviour in R it is necessary to take into account the terms independent of $1/R$. The calculations are tedious but straightforward. In this case a set of equations for $B_{ll}^m(r, R, k)$ has been derived in our previous paper [24]. However, the symmetry of $F_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ relative to the rearrangement of particles (1, 2) and (3, 4) [25] has not been taken into account in [24]. To take into consideration this symmetry, we shall consider the coordinate system with the z axis along the vector \mathbf{R}_0 joining the middles of vectors \mathbf{k} and \mathbf{r} , respectively. ϑ_1^0 and ϑ_2^0 are the angles of \mathbf{k} and \mathbf{r} with \mathbf{R}_0 , and $\varphi_1^0 - \varphi_2^0$ is the angle between planes $(\mathbf{r}, \mathbf{R}_0)$ and $(\mathbf{k}, \mathbf{R}_0)$. In this coordinate system the expansion (3) may be written in the form

$$f_4(r, R_0, k, \vartheta_1^0, \vartheta_2^0, \varphi_1^0 - \varphi_2^0) = \sum_{m=-\infty}^{\infty} \sum_{l, l' = |m|}^{\infty} C_{2l, 2l'}^m(r, R_0, k) Y_{2l, m}(\vartheta_1^0, \varphi_1^0) Y_{2l', -m}(\vartheta_2^0, \varphi_2^0).$$

The quantities $R_0, \vartheta_1^0, \vartheta_2^0$ and $\varphi_1^0 - \varphi_2^0$ are the functions of $R, r, k, \vartheta_1, \vartheta_2$ and $\varphi_1 - \varphi_2$ and can be expanded in powers of d/dR and $1/R$. With necessary accuracy, we find that

$$\begin{aligned}
 B_{2l+1,2n}^m(r, R, k) &= -\frac{1}{2} \text{ir}\{[(2l+2)^2 - m^2]/(4l+3)(4l+5)\}^{1/2} \\
 &\quad \times \partial B_{2l+2,2n}^m(r, R, k)/\partial R + \frac{1}{2} \text{ir}\{[(2l+1)^2 - m^2]/(4l+1)(4l+3)\}^{1/2} \\
 &\quad \times \partial B_{2l,2n}^m(r, R, k)/\partial R \\
 B_{2l-1,2n}^m(r, R, k) &= -\frac{1}{2} \text{ir}\{(4l^2 - m^2)/(4l-1)(4l+1)\}^{1/2} \\
 &\quad \times \partial B_{2l,2n}^m(r, R, k)/\partial R + \frac{1}{2} \text{ir}\{[(2l-1)^2 - m^2]/(4l-3)(4l-1)\}^{1/2} \\
 &\quad \times \partial B_{2l-2,2n}^m(r, R, k)/\partial R.
 \end{aligned} \tag{14}$$

Inserting (14) into equation (18) of [24], we obtain the set of equations for $B_{2l,2l'}^m(r, R, k)$:

$$\begin{aligned}
 \int r_0^2 dr_0 g(r_0) &\left(a_{2l,m}(r, r_0) \frac{\partial B_{2l,2l'}^m(r_0, R, k)}{\partial R} \right. \\
 &+ b_{2l+2,m}(r, r_0) \frac{\partial B_{2l+2,2l'}^m(r_0, R, k)}{\partial R} \\
 &\left. - c_{2l-2,m}(r, r_0) \frac{\partial B_{2l-2,2l'}^m(r_0, R, k)}{\partial R} \right) - B_{2l,2l'}^m(r, R, k) \\
 &+ \frac{4\pi}{4l+1} \int r_0^2 dr_0 g(r_0) \Gamma_{2l}(r, r_0) B_{2l,2l'}^m(r_0, R, k) = 0
 \end{aligned} \tag{15}$$

where

$$\begin{aligned}
 a_{2l,m}(r, r_0) &= [4\pi/(4l+1)](\Gamma_{2l}(r, r_0)[\frac{1}{3}(r^2 + r_0^2) \\
 &\quad \times \{\frac{1}{2} - [3m^2 - 2l(2l+1)]/(4l-1)(4l+3)\} - \frac{1}{2}r_0^2 \\
 &\quad \times \{[(2l+1)^2 - m^2]/(4l+1)(4l+3) + (4l^2 - m^2)/(4l-1)(4l+1)\}] \\
 &\quad - \frac{1}{2}rr_0\{\Gamma_{2l-1}(r, r_0)(4l^2 - m^2)/(4l-1)^2 + \Gamma_{2l+1}(r, r_0) \\
 &\quad \times [(2l+1)^2 - m^2]/(4l+3)^2\}
 \end{aligned} \tag{16}$$

$$\begin{aligned}
 b_{2l+2,m}(r, r_0) &= [4\pi/(4l+3)] \\
 &\quad \times \{[(2l+1)^2 - m^2][(2l+2)^2 - m^2]/(4l+1)(4l+5)\}^{1/2} \\
 &\quad \times \frac{1}{2}r[\Gamma_{2l+1}(r, r_0)r_0/(2l+3) - \Gamma_{2l+2}(r, r_0)r/(4l+5)] \\
 c_{2l-2,m}(r, r_0) &= [4\pi/(4l-1)]\{[(2l-1)^2 - m^2](4l^2 - m^2)/(4l-3)(4l+1)\}^{1/2} \\
 &\quad \times \frac{1}{2}r[\Gamma_{2l-1}(r, r_0)r_0/(4l-1) - \Gamma_{2l-2}(r, r_0)r/(4l-3)].
 \end{aligned}$$

As has been shown in [22–24], the line determined with eigenvalues of the equation

$$B_{2l,2l'}^m(r, R, k) - \frac{4\pi}{4l+1} \int \Gamma_{2l}(r, r_0)g(r_0)B_{2l,2l'}^m(r_0, R, k)r_0^2 dr_0 = 0 \tag{17}$$

can be regarded as the instability criterion of the isotropic liquid against the formation of the phase with the bond orientational order.

The relative spatial distribution of pairs of particles is characterised by the function $F_2(\mathbf{r}_1|\mathbf{k}_1)$. We consider the system with unbroken translational symmetry. In this case, $F_1(\mathbf{k}_1) \equiv 1$ and $F_2(\mathbf{r}_1|\mathbf{k}_1) = F_2(\mathbf{r}_1 - \mathbf{k}_1)$.

For an anisotropic liquid the function $F_2(\mathbf{r}_1 - \mathbf{k}_1)$ can be written in the form

$$F_2(\mathbf{r}_1 - \mathbf{k}_1) = g(|\mathbf{r}_1 - \mathbf{k}_1|)[1 + f_2(\mathbf{r}_1 - \mathbf{k}_1)]$$

where the function $f_2(\mathbf{r}_1 - \mathbf{k}_1) = f_2(|\mathbf{r}_1 - \mathbf{k}_1|, \Omega)$ can be expanded in a series of spherical harmonics:

$$f_2(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{lm}(r) Y_{lm}(\Omega).$$

Here Ω determines the direction of the vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{k}_1$. The functions $f_{lm}(r)$ are the order parameters. In terms of the functions $f_{lm}(r)$ the instability criterion (17) has the form

$$f_{lm}(r) - \frac{4\pi}{2l+1} \int \Gamma_l(r, r_0) g(r_0) f_{lm}(r_0) r_0^2 dr_0 = 0. \quad (18)$$

3. Approximations and results

To investigate real systems we must propose some approximations for the quantities entering equations (15)–(17). The simplest possible approximation for the function $\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2)$ has been suggested in our previous papers [23, 24]. It has the form

$$\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2) = \rho \{ \exp[-\Phi(|\mathbf{r}_1 - \mathbf{r}_2|)] - 1 \}. \quad (19)$$

This approximation is exact in the low-density limit. As the density is increased, deviations from (19) occur. However, we believe that in the case of the short-range potentials with hard cores we can omit all terms in expansion (10) except for the first one. This is because $g(|\mathbf{r}_i - \mathbf{k}_1|)$ is equal to zero inside the hard core and $S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1})$ is the short-range function. Note that in [23] the leading term of an expansion in terms of the direct correlation function was proposed as a possible approximation for $\Gamma(\mathbf{r}_1, \mathbf{k}_1, \mathbf{r}_2)$ but, in our opinion, this approximation does not properly take into account the repulsion at short distances. The approximation based on the direct correlation function may be satisfactory in the case of the long-range interactions without hard cores. We hope that the crude but simple approximation (19) reflects the main features of the short-range potentials with hard cores (including the Lennard-Jones potential) and can be regarded as the basis for the consideration of the instability in a Lennard-Jones liquid. However, looking for more accurate approximations remains an important problem.

Using (19), we can calculate $\Gamma_l(r, r_0)$ entering (16)–(18). To simplify the set of equations (15), we introduce the following approximation for radial distribution function $g(r)$:

$$g(r) = \alpha \delta(r - r_s) \quad (20)$$

where r_s is the position of the first maximum of $g(r)$, and α may be obtained from

$$\alpha = \int_0^{r_{\min}} g(r) dr. \quad (21)$$

Here r_{\min} is the position of the first minimum of $g(r)$.

The substitution of (20) into (15) gives

$$A_{2l,m} d^2 B_{2l,2l'}^m(r_s, R, r_s)/dR^2 + B_{2l+2,m} d^2 B_{2l+2,2l'}^m(r_s, R, r_s)/dR^2 + C_{2l-2,m} d^2 B_{2l-2,2l'}^m(r_s, R, r_s)/dR^2 - \kappa_{2l}^2 B_{2l,2l'}^m(r_s, R, r_s) = 0 \tag{22}$$

where

$$\begin{aligned} \kappa_{2l}^2 &= [4\pi/(4l+1)]\alpha r_s^2 \Gamma_{2l}(r_s, r_s) & B_{2l,m} &= \alpha r_s^2 b_{2l,m}(r_s, r_s) \\ A_{2l,m} &= \alpha r_s^2 a_{2l,m}(r_s, r_s) & C_{2l,m} &= \alpha r_s^2 c_{2l,m}(r_s, r_s). \end{aligned}$$

The quantity $B_{2l,2l'}^m(r_s, R, r_s)$ determines correlations between orientations of bonds having the length r_s . We shall search for the solution of equations (22) in the form

$$B_{2l,2l'}^m(r_s, R, r_s) = C \exp(-R/\xi_{2l,m}).$$

Substituting this expression into (22), we obtain the equation for the correlation length $\xi_{2l,m}$. The smaller κ_{2l}^2 , the larger is $\xi_{2l,m}$. For $\kappa_{2l}^2 \ll 1$ we have

$$\xi_{2l,m}^2 = A_{2l,m}/\kappa_{2l}^2 \tag{23}$$

as $\kappa_{2l}^2 \rightarrow 0$, $\xi_{2l,m} \rightarrow \infty$. Equation (18) enables one to consider the condition $\kappa_{2l} = 0$ as the instability criterion of the isotropic liquid against the formation of the state with bond orientational order.

Let us consider now the behaviour of the correlation length of orientational fluctuations for the Lennard-Jones potential

$$\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

We shall consider the dimensionless quantities $T^* = k_B T/\varepsilon$ and $\rho^* = \sigma^3 \rho$. In this case the potential can be written in the form

$$\Phi_{LJ}(r) = 4(r^{-12} - r^{-6}). \tag{24}$$

The computer simulation of the system with the potential (24) has been studied by Steinhardt *et al* [11]. They have found that, if the temperature approaches $T^* = 0.626$ from above, the correlation length of the orientational fluctuations increases sharply.

The radial distribution function entering (21) for the potential (24) can be obtained with satisfactory accuracy from the approximation [29]

$$g(r) = \exp[-\beta\Phi_0(r)] y_{hs}(r/d, \eta) \tag{25}$$

where

$$\Phi_0(r) = \begin{cases} \Phi_{LJ}(r) + 1 & r \leq 2^{1/6} \\ 0 & r > 2^{1/6} \end{cases} \tag{26}$$

$$\eta = \pi\rho^* d^3/6$$

$$y_{hs}(r/d, \eta) = g_{WT}(r/d, \eta) - c_{WT}(r/d, \eta).$$

$g_{WT}(r/d, \eta)$ and $c_{WT}(r/d, \eta)$ are the radial distribution function and the direct correlation function for hard spheres, obtained by Wertheim [30] and Thiele [31] for the Percus–Yevick approximation. The effective hard-sphere diameter can be obtained using the methods developed in [29, 32].

To compare our results with those obtained by Steinhardt *et al* [11], we shall calculate $\xi_{2l,m}$ at $\rho^* = 0.973$. The correlation length $\xi_{2l,m}$ tends to infinity, as $\kappa_{2l}^2 \rightarrow 0$. We tried to

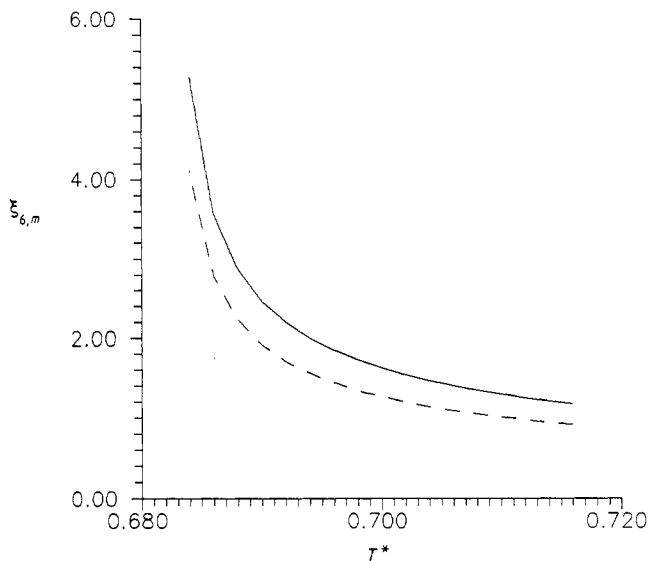


Figure 1. Orientational correlation length $\xi_{6,m}$, as a function of T^* , for m values of 4 (—) and 5 (---). The graphs are given for $\rho^* = 0.973$.

solve the equation $\kappa_{2l} = 0$ for $l = 4, 6, 8$ and 10. It turns out that there is no solution for $l = 4$ and 8. If $l = 6$, the instability occurs at $T^* = 0.683$; if $l = 10$, the instability takes place at $T^* = 0.402$.

Therefore the long-range correlations appear for the first time for $l = 6$. The long-range correlations with $l = 4$ are absent, and there is no cubic bond orientational order proposed by Nelson and Toner [9]. This conclusion coincides with the results of computer simulation [11]. The instability temperature $T^* = 0.683$ is in agreement with the result $T^* = 0.626$ obtained by Steinhardt *et al* [11].

At $l = 6$, in the correct coordinate system, cubic clusters have non-zero components with $m = +0, \pm 4$, icosahedral clusters, with $m = 0, \pm 5$, and hexagonal clusters, with $m = 0, \pm 6$. It is not difficult to show that $\xi_{6,m} < \xi_{6,m+1}$. Figure 1 shows the behaviour of $\xi_{6,m}$ for $m = 4$ and $m = 5$ ($\rho^* = 0.973$). Note that the correlation function $G_l(r)$, discussed in [11], is averaged over m and does not contain the information about the fluctuations with definite symmetry. Our correlation function does contain such information. The behaviour of $\xi_{6,m}$ suggests that the orientationally ordered phase has elements of cubic, icosahedral and hexagonal symmetry. In our opinion, the instability with $l = 10$ should intensify the icosahedral symmetry. Therefore the mixed symmetry of ordered phase is an inherent property of the Lennard-Jones system and cannot be exclusively regarded as the result of the influence of the boundary conditions in carrying out the computer simulation [11].

The expansion (3) shows that there exist correlations with different l but equal m . In our view, it is these correlations that result in the existence of the elements of symmetry with $l = 4$ and $l = 8$ in the ordered phase (see figure 4 in [11]).

We have attempted to solve the equation $\kappa_l = 0$ for the hard-sphere system. We have not found any solution, but the tendency of increasing correlation length was observed for $l = 6$. In [23, 24] we applied the other approximation for the function $f_2(\mathbf{r})$: $f_2(\mathbf{r}) = \delta(r - r_s)f(\Omega)$.

In this case the instability in the hard-sphere system does exist at very high densities. However, the approximations used in this paper seem to be more accurate.

Finally, let us consider the other possible approximation for the function (10). Changing the variables $\mathbf{R}_i = \mathbf{r}_i - \mathbf{k}_1$, we obtain

$$\Gamma(\mathbf{R}_1, \mathbf{R}_2) = \sum_{k \geq 1} \frac{\rho^k}{(k-1)!} \int S_{k+1}(\mathbf{R}_1 \dots \mathbf{R}_{k+1}) g(\mathbf{R}_3) \dots g(\mathbf{R}_{k+1}) d\mathbf{R}_3 \dots d\mathbf{R}_{k+1}. \quad (27)$$

To estimate this quantity, let us divide the potential into two parts, corresponding to the attraction and the repulsion [29, 32]:

$$\Phi(r, \gamma) = \Phi_0(r) + \gamma \Delta\Phi(r) \quad \Phi(r, \gamma=1) = \Phi_{LJ}(r)$$

where $\Phi_0(r)$ is determined by equation (26) and

$$\Delta\Phi(r) = \begin{cases} -1 & r \leq 2^{1/6} \\ \Phi_{LJ}(r) & r > 2^{1/6}. \end{cases}$$

We regard $\Delta\Phi(r)$ as a perturbation and calculate $\Gamma(\mathbf{R}_1, \mathbf{R}_2)$ to lowest order in $\Delta\Phi(r)$:

$$\Gamma(\mathbf{R}_1, \mathbf{R}_2) = \Gamma_0(\mathbf{R}_1, \mathbf{R}_2) + \{\partial\Gamma_\Phi(\mathbf{R}_1, \mathbf{R}_2)\partial\gamma\}_{\gamma=0}. \quad (28)$$

Here $\Gamma_\Phi(\mathbf{R}_1, \mathbf{R}_2)$ is the function (27) calculated with the potential $\Phi(r, \gamma)$. In the second term of equation (28) we retain only the part that is proportional to $\Delta\Phi(|\mathbf{r}_1 - \mathbf{r}_2|)$. The resulting approximation is similar to the ordinary mean spherical approximation. To estimate the first and the second terms of equation (28), further approximations are necessary. Firstly we replace $\Phi_0(r)$ with the hard-sphere potential with the effective diameter depending on the temperature and density [29, 30]. Secondly, we replace $\rho g(r)$ with some mean quantity ρ_0 . It is not difficult to show that in this case (28) can be rewritten in the form

$$\Gamma(\mathbf{R}_1, \mathbf{R}_2) = \rho c_{\text{hs}}(|\mathbf{R}_1 - \mathbf{R}_2|, \rho_0) + \rho g_{\text{hs}}(|\mathbf{R}_1 - \mathbf{R}_2|, \rho_0) [-\beta \Delta\Phi(|\mathbf{R}_1 - \mathbf{R}_2|)] \quad (29)$$

where $c_{\text{hs}}(|\mathbf{R}_1 - \mathbf{R}_2|, \rho_0)$ and $g_{\text{hs}}(|\mathbf{R}_1 - \mathbf{R}_2|, \rho_0)$ are the direct correlation function and radial distribution function for the hard-sphere system with density ρ_0 .

To determine ρ_0 we suggest that $\rho g(r)$ is averaged over the region of volume $(4\pi/3)a^3$:

$$\rho_0 = \left(\rho \int_0^a g(r) r^2 dr \right) / (2a^3/3)$$

where $g(r)$ can be obtained from equation (25). Unfortunately, we have no efficient method of calculating quantity a . We take a equal to 1.565. This value comes from a fit of the computer simulation result for the temperature of the transition at $\rho^* = 0.973$ [11]. Using $c_{\text{hs}}(r, \rho_0)$ and $g_{\text{hs}}(r, \rho_0)$ in the Percus–Yevick approximation [30, 31], we can solve the equation $\kappa_l = 0$ by determining the instability line. At $l = 6$ and $\rho^* = 0.973$ we have $T^* = 0.63$. This value is equal to the value obtained in the computer simulation [11]. Figure 2 shows the phase diagram for the orientationally ordered state in the $\rho^* - T^*$ plane. The diagram is calculated using the approximation (29) with the adjustable parameter a and shows the border of the instability region for different densities. The maximum in the phase diagram corresponds to $T^* = 1.08, \rho^* = 1.43$. Destruction of the orientational order can be explained in the following way. Instability is absent in the hard-sphere system, and it is the last term in equation (29) that is responsible for the

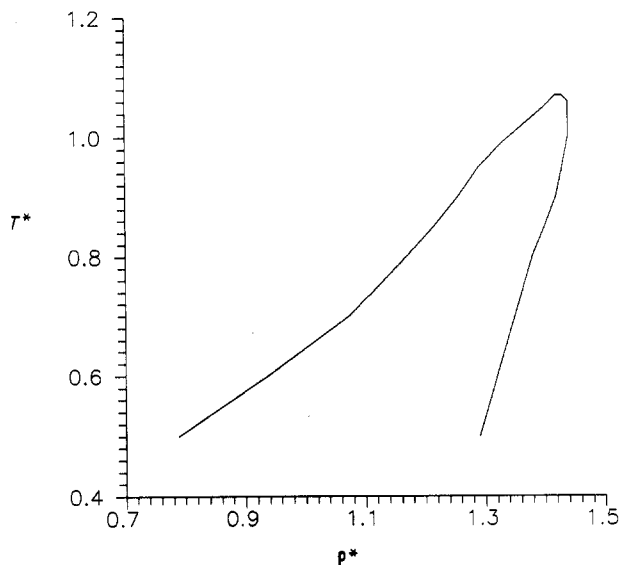


Figure 2. Phase diagram in the T^* - ρ^* plane for the orientationally ordered phase as obtained from the approximation (29).

instability in the Lennard-Jones system. When the density increases, the significance of attraction is decreased, and the ordered state becomes destroyed.

4. Conclusion

In this paper the behaviour of the orientational fluctuations of pair distribution function has been studied under the condition $F_1(\mathbf{r}) = 1$. This condition suggests the absence of crystallisation and gives us the possibility of considering supercooled liquids. It was shown that with decreasing temperature the correlation length of orientational fluctuations increases until the phase transition into the state with long-range bond orientational order takes place. It was suggested that the ordered state contains elements of cubic, icosahedral and hexagonal symmetry. Unfortunately, the linearised equations studied in this paper do not allow us to obtain full information concerning the symmetry of the ordered state. For this purpose it is necessary to find the approximate solution of the non-linear equation (4) with $s = 1$. The values of the instability points obtained in this paper for the Lennard-Jones potential are in satisfactory agreement with the results of computer simulation [11]. It would be interesting to verify the phase diagram shown in figure 2 by computer simulation.

The thermodynamically consistent description of the first-order phase transition from the isotropic to anisotropic state can in principle be developed by analogy with the density functional theories of freezing [26, 27]. Using equation (4), one can obtain the thermodynamic quantities (pressure, free energy and chemical potential) as the functionals of the functions $F_2(\mathbf{r}_1|\mathbf{r}_2)$ (compare [26]). Unfortunately we have no reliable approximation that would give us the possibility of deriving the closed set of equations

for the transition parameters. The search for such approximations is the subject of further investigations.

It is necessary to note that the anisotropic phase is similar to the icosahedral glass [21], but in our approach we cannot consider the dynamic aspects; therefore it is impossible to conclude whether the anisotropic phase is a liquid (probably supercooled) or a glass.

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