Cluster model of glass transition in simple liquids

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(Dated: March 22, 2022)

On the basis of microscopic statistical mechanics of simple liquids the orientational interaction between clusters consisting of a particle and its nearest neighbors is estimated. It is shown that there are ranges of density and temperature where the interaction changes sign as a function of a radius of a cluster. The model of interacting cubic and icosahedral clusters is proposed and solved in mean-field replica symmetric approximation. It is shown that the glass order parameter grows smoothly upon cooling, the transition temperature being identified with the temperature of the replica symmetry breaking. It is shown that upon cooling a Lennard-Jones system, cubic clusters freeze first. The transition temperature for icosahedral clusters is about ten per cent lower. So the local structure of Lennard-Jones glass in the vicinity of glass transition should be most probably cubic.

PACS numbers: 75.50.Lk, 05.50.+q, 64.60.Cn

Despite the growing interest to physical properties of liquids and glasses (see, for example, for the recent reviews [1, 2, 3, 4, 5, 6]), nature of structural glass transition is still puzzling. While the experimental and phenomenological knowledge of non-ergodic amorphous phases has considerably improved in last time [1], progress in first-principle statistical mechanical studies of structural glasses is much more slow.

One of the promising ways to study the structural glasses is to explore the analogy between the phase transitions in spin glasses (which are well understood now [3, 4, 5, 6]) and the structural glass transition. In some extent this is motivated by the fact that the structure of the dynamical equations for the appropriate correlation functions of super-cooled liquids and p-spin spin glass model (p ≥ 3) are identical in the mean-field (MF) approximation [3, 4, 5, 6, 7], so this model may be used to describe, at least qualitatively, the properties of structural glasses. The main obstacle in this way is the absence in structural glasses of quenched disorder (in contrast to the spin glasses). Spin glasses are microscopically quite different from liquids and thus seem not suitable for their description. Furthermore, this approach does not include any information on the local structure of super-cooled liquids and glasses. In this paper we propose the scenario where the analog of quenched disorder in Lennard-Jones system appears in natural way allowing to apply the methods of spin glass theory to investigation of the structural glass transition.

The structure of supercooled liquids and glasses is incompletely understood even for simplest systems. Frenkel [4] has suggested a qualitative picture of local structure of a dense supercooled liquid: he supposed that in small volumes it has a crystal-like structure. On the other hand, as was argued by Frank [5], an icosahedral cluster of 13 particles has a significantly lower energy than more obvious arrangements having the symmetry of FCC or HCP crystals. It was inferred from the computer simulations of a dense supercooled Lennard-Jones liquid [3] that the local symmetry of simple liquids is determined by defective or fragmented icosahedral building blocks that exhibit a five-fold symmetry. However, as was shown later, in a supercooled Lennard-Jones liquid, small crystalline FCC clusters nucleate following the temperature quench [10]. It seems that the local structure of a supercooled Lennard-Jones liquid is a result of competition between FCC and icosahedral local symmetries [11].

The concept of interacting clusters was used in phenomenological theories of bond orientational order [12, 13] or "orientational melting" [14, 15]. The microscopic approach to description of the bond-orientational order (or hexatic phase in two dimensions) was developed in [11, 16, 17, 18]. In the present Letter we use this approach to analyze the intercluster interaction and to introduce the model of glass transition in a Lennard-Jones liquid which elucidates the structural properties of the corresponding glass.

Our starting point is the expression for the free energy of the system as a functional of a pair distribution function $g_2(r_1, r_0)$ which has the form [11, 16]:

$$ F/k_B T = \int d^d r_0 \rho g_2(r, r_0) \ln \left( (\lambda^3 \rho g_2(r, r_0)) - 1 \right) - $$

$$ - \sum_{n} \frac{\rho^{n+1}}{(n+1)!} \int S_{n+1}(r_1, \ldots r_{n+1}) g_2(r_1, r_0) \cdots$$

$$ \cdots \cdot g_2(r_{n+1}, r_0) d r_1 \cdots d r_{n+1} d r_0 -$$

$$ - \int \Phi(r - r_0) \rho g_2(r, r_0) d^d r.$$  (1)

Here $S_{k+1}(r_1, \ldots r_{k+1})$ is the irreducible cluster sum of Mayer functions connecting (at least doubly) $k+1$ particles, $\rho$ is the mean number density, $\Phi(r - r_0)$ - interparticle potential, $\lambda = h/(2\pi m k_B T)^{1/2}$. 
In an isotropic liquid pair distribution function \( g_2(\mathbf{r}, \mathbf{r}_0) \) depends on \(|\mathbf{r} - \mathbf{r}_0|\) only: \( g_2(\mathbf{r}, \mathbf{r}_0) = g(|\mathbf{r} - \mathbf{r}_0|) \), where \( g(r) \) is the radial distribution function. In the state with bond orientational order rotational symmetry of the pair distribution function is broken:

\[
g_2(\mathbf{r}, \mathbf{r}_0) = g(|\mathbf{r} - \mathbf{r}_0|) + \delta g(\mathbf{r}, \mathbf{r}_0). \tag{2}
\]

\( \delta g(\mathbf{r}, \mathbf{r}_0) \) has the symmetry of the local environment of the particle at \( \mathbf{r}_0 \) and may be approximately written in the form

\[
\delta g(\mathbf{r}, \mathbf{r}_0) = f(\Omega)\delta g_s(|\mathbf{r} - \mathbf{r}_0|). \tag{3}
\]

Here \( \Omega \) determines the direction of the vector \( \mathbf{r} - \mathbf{r}_0 \), and \( r_s \) is the size of the cluster, which is approximately equal to the diameter of the first coordination shell. Function \( f(\Omega) \) gives the probability of cluster orientation and may be expanded in a series in spherical harmonics:

\[
f(\mathbf{r}, \Omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{lm}(\mathbf{r})Y_{lm}(\Omega). \tag{4}
\]

In expansion \( \delta g \) only the terms corresponding to the local cluster symmetry should be retained. Coefficients \( f_{lm} \) are the order parameters for the phase transition to the anisotropic phase.

To estimate the intercluster interaction, let us expand the free energy \( \delta g \) up to the second order in \( \delta g(\mathbf{r}, \mathbf{r}_0) \). Omitting the \( \Omega \)-independent terms, one has:

\[
\Delta F/k_B T = -\frac{1}{2} \int \Gamma(\mathbf{r}_1, \mathbf{r}_0, \mathbf{r}_2) \times
\]

\[
\times \delta g(\mathbf{r}_1, \mathbf{r}_0)\delta g(\mathbf{r}_2, \mathbf{r}_0)d\mathbf{r}_1d\mathbf{r}_2, \tag{5}
\]

where \( \delta g \) is given by:

\[
\Gamma(\mathbf{r}_1, \mathbf{r}_0^1, \mathbf{r}_2) = \sum_{k \geq 1} \frac{\rho^k}{(k-1)!} \int S_{k+1}(\mathbf{r}_1...\mathbf{r}_{k+1}) \times
\]

\[
\times g(|\mathbf{r}_3 - \mathbf{r}_0^1|)\cdots g(|\mathbf{r}_{k+1} - \mathbf{r}_0^1|) d\mathbf{r}_3 \cdots d\mathbf{r}_{k+1} =
\]

\[
= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \Gamma_l(r, r') \sum_{l=-m}^{l} \frac{Y_{lm}(\Omega_1)Y_{lm}^*(\Omega_2)}. \tag{6}
\]

The angles \( \Omega_1 \) and \( \Omega_2 \) determine the directions of the vectors \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_0 \) and \( \mathbf{r}' = \mathbf{r}_2 - \mathbf{r}_0 \).

After substituting \( \delta g \) and \( f(\Omega) \) in \( \Delta F \) we obtain:

\[
\Delta F(\mathbf{r}_s)/k_B T = -\frac{1}{2} \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \Gamma_l(r_s, r_s) \times
\]

\[
\times \int \sum_{l=-m}^{l} Y_{lm}(\Omega_1)Y_{lm}^*(\Omega_2)f(\Omega_1)f(\Omega_2)r_s^l d\Omega_1 d\Omega_2 =
\]

\[
= -\frac{1}{2} \sum_{l=0}^{\infty} J_l(r_s) \sum_{l=-m}^{l} |f_{lm}|^2. \tag{7}
\]

Here \( J_l(r_s) = \frac{4\pi}{2l+1} \Gamma_l(r_s, r_s) \).

Function \( \Delta F(\mathbf{r}_s) \) may be interpreted as the mean-field orientational interaction energy of the system of clusters having the size \( r_s \). To get the full energy of the system one should integrate \( \Gamma(\mathbf{r}_1, \mathbf{r}_0^1, \mathbf{r}_2) \) over the probability of finding the cluster with the size \( r_s \) which is given by the function \( r^2g(r) \) in the vicinity of the first maximum.

As was shown in \( \delta g \) there is a simple approximation for \( \Gamma(\mathbf{r}_1, \mathbf{r}_0, \mathbf{r}_2) \), which gives rather good results for the Lennard-Jones potential \( \Phi_{LJ}(\mathbf{r}) \):

\[
\Gamma(\mathbf{r}_1, \mathbf{r}_0, \mathbf{r}_2) = \rho \exp(-\Phi_{LJ}(|\mathbf{r}_1 - \mathbf{r}_2|)/k_B T) - 1. \tag{8}
\]

Using Eq. \( \delta g \) one can obtain the estimation for \( J_l(r_s) \) as a function of \( r_s \). Fig. 1 represents \( J_l(r_s) \) for \( l = 4 \) and \( 6 \) along with \( r^2g(r) \) in the vicinity of the first peak. It is seen that \( J_l(r_s) \) changes sign. From Eq. \( \delta g \) and Fig. 1 one can conclude that the frustration appears as a result of variations in the sizes of clusters due to local density fluctuations. Such kind of behaviour leads to frustration which is analogous to that in spin glasses.

![FIG. 1: \( J_l(r_s) \) for \( l = 4 \) and \( 6 \) along with \( r^2g(r) \) in the vicinity of the first peak as functions of \( r_s \) for dimensionless temperature \( T = 1.0 \) and density \( \rho = 1.2 \).](image-url)

To study the transition in the system of interacting clusters we introduce the simple lattice Hamiltonian:

\[
H = -\frac{1}{2} \sum_{\langle \mathbf{i}, \mathbf{j} \rangle} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} J_{ij}^l U_{lm}(\Omega_1)U_{lm}^*(\Omega_2). \tag{9}
\]

The functions \( U_{lm}(\Omega_1) \) the lattice harmonics for the space groups corresponding to the cluster symmetry. Taking into account that \( < U_{lm}(\Omega_1) >= J_{lm}^l \), one can see that in the MF approximation the energy calculated from Eq. \( \delta g \) coincides with the intercluster energy \( \Delta F \) under appropriate choice of \( J_{ij}^l \).
To simplify the problem we neglect in Hamiltonian (9) all the terms except for the ones corresponding to the unit representation of the space group. Furthermore, we consider only the cases \( l = 4 \) and \( l = 6 \) which represent the cases of cubic and icosahedral symmetries. This Ising-like model may be called a "minimal" model. The Hamiltonian of the minimal model has the form:

\[
H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \hat{U}_i \hat{U}_j. \tag{10}
\]

Functions \( \hat{U} \equiv U(\varphi, \theta) \) are the combinations of the spherical harmonics. We will consider separately symmetries of "simple" cube \((l = 4, m = 0, \pm 4)\), cube \((l = 6, m = 0, \pm 4)\) and icosahedron \((l = 6, m = 0, \pm 5)\) correspondingly \([13, 21]\). The trace in this case is defined as follows:

\[
\text{Tr}(\ldots) \equiv \int_{-\pi}^\pi d\varphi \int_{-\pi}^\pi d\cos(\theta)(\ldots). \tag{11}
\]

For example, for \( l = 4 \) one has:

\[
\hat{U} \equiv U(\varphi, \theta) = \sqrt{\frac{7}{12}} \{Y_{40}(\varphi, \theta) + \sqrt{\frac{5}{14}} (Y_{44}(\varphi, \theta) + Y_{44}(-\varphi, \theta)) \}. \tag{12}
\]

The order parameters are:

\[
J_{ij} = \frac{1}{\sqrt{2\pi J}} \exp \left[ -\frac{(J_{ij} - J_0)^2}{2J^2} \right]. \tag{13}
\]

with \( J = \tilde{J}/\sqrt{N} \), \( J_0 = \tilde{J}_0/N \).

Then the free energy in the replica-symmetric approximation is equal to \([13, 21]\):

\[
F = -NkT \left\{ -\frac{\tilde{J}_0}{kT} \left[ \frac{m^2}{2} + \frac{q^2}{2} + t^2 \frac{p^2}{4} - t^2 \frac{p^2}{4} \right] + \right. \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} \exp \left[ -\frac{z^2}{2} \right] \ln \text{Tr} \left[ \exp \left( \tilde{U} \right) \right] \left. \right\}. \tag{14}
\]

where \( \langle \ldots \rangle = \frac{\text{Tr}(\ldots e^\tilde{U})}{\text{Tr} e^\tilde{U}} \) and \( \langle \ldots \rangle = \int_{-\infty}^{\infty} \frac{dz}{\sqrt{2\pi}} e^{-z^2/2} \ldots \). The temperature dependence of the order parameters is represented in Fig. 2. One can see that the glass phase grows smoothly upon cooling. The similar behavior takes place in a quadrupolar glass \([13, 21]\). It is not clear now whether the appearance of the nonzero bond-orientational order is an artifact of the model or an inherent property of the glass transition in the Lennard-Jones system.

We define the transition temperature as the replica symmetry breaking temperature. The replica symmetric solution is stable unless the replicon mode energy \( \lambda_{\text{repl}} \) is nonzero \([20, 22]\). For our model we have

\[
\lambda_{\text{repl}} = 1 - t^2\langle \langle \tilde{U} \rangle^2 \rangle, \tag{15}
\]

where \( \langle \langle \ldots \rangle \rangle \) denotes the irreducible correlator. The temperature \( T_{A-T} \) corresponding to \( \lambda_{\text{repl}} = 0 \) defines the
glass transition. In the Fig. 3 we plot the dependence $T_{A-T}$ on $J_0$ for $l = 6$. From Fig. 3 one can conclude that in the vicinity of the glass transition the cubic local symmetry appears first and, taking into account the contribution of the terms with $l = 4$, is preferable for the Lennard-Jones glass. This conclusion is in agreement with the result in Ref. [11], where it was shown that the correlation length of the cubic bond orientational order exceeds the icosahedral one.

From the condition of marginal stability [3, 6] we also evaluated numerically the so-called dynamical transition temperature $T_D$ at $J_0 = 0$ and found that within the accuracy of calculations $T_D$ and $T_{A-T}$ coincide. One can expect that in the minimal model [10] full replica symmetry breaking should occur (as in the Sherrington-Kirkpatrick model [1]) but further investigation is necessary to elucidate this question.

\[ F(T_{A-T}; J_0/\bar{J})/Nk_BT_{A-T} \]

FIG. 3: Evolution of the temperature $T_{A-T}$ with $J_0/\bar{J}$ is shown in the figure for the symmetries of cube and icosahedron for $l = 6$; below $T_{A-T}$ the replica symmetric MF solution becomes unstable. The free energy $F(T_{A-T}(J_0/\bar{J}))/Nk_BT_{A-T}$ is shown in the inset.

In summary, using the approach developed previously for study of a bond-orientational order in simple liquids [11], we estimated the orientational interaction between clusters consisting of a particle and its nearest neighbors. It is shown that there are ranges of density and temperature where the interaction changes sign as a function of a radius of a cluster, the probability of a radius being determined by the radial distribution function of a liquid in the vicinity of the first peak. The model of interacting cubic and icosahedral clusters was solved in mean-field replica symmetric approximation. Due to absence of reflection symmetry the glass order parameter grows smoothly upon cooling. The transition temperature is identified with the temperature replica symmetry breaking. It was shown that upon cooling a Lennard-Jones system cubic clusters freeze first. The transition temperature for icosahedral clusters is about ten per cent lower. So the local structure of Lennard-Jones glass in the vicinity of glass transition should be most probably cubic.

We thank V. V. Brazhkin for stimulating discussions. The work was supported by the Russian Foundation for Basic Research (Grant No 02-02-16622 (VNR, NMC, and TIS), Grant No 02-02-16621 (EET), and Grant No 03-02-16677 (NMC)).

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