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A description of Fischer cluster formation in supercooled liquids within the framework of the continuous theory of defects

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Abstract

Liquid is represented as a complicated system of disclinations according to a defect description of liquids and glasses. The expressions for the linear disclination field of arbitrary form and the energy of the inter-disclination interaction are derived in the framework of the gauge theory of defects. This allows us to describe liquid as a disordered system of topological moments and reduce this model to the Edwards–Anderson model with long-range interaction. Within the framework of this approach, vitrification is represented as a 'hierarchical' phase transition. The suggested model allows us to explain the process of Fischer cluster formation and the slow dynamics in supercooled liquids close to the liquid–glass transition point.

1. Introduction

Fischer clusters are long-range correlations of density fluctuations, which are observed in supercooled liquids (∼100 K above the glass transition temperature T_g) [1]. To date, these clusters have been discovered in polymeric fluids, glass-forming (vitreous) melts and single fluids. The typical size of these formations is ∼100–300 nm, whereas the correlation radius of usual short-range thermal density fluctuations is ∼1 nm. The fractal-like structure and long lifetime are important typical properties of the Fischer clusters [2]. There are theoretical works in which the formation of these clusters is supposed to be a process of condensation of atom groups with a common type of local atomic ordering [2, 3]. However, in the case of dense liquids (at low temperatures), these models encounter complications in the definition of the order parameter. Besides this, the approach does not allow us to explain the roots of the fractal-like structure of these formations. Therefore the nature of the Fischer clusters is not quite clear yet.

In the present work a theoretical model of the glass transition based on the known approaches of disordered systems physics is offered. Our model is based on the disclination model of amorphous structures suggested by Nelson. At the beginning we write down the

system Lagrangian and derive the expressions for the linear disclination field and energy of the inter-disclination elastic interaction (section 2). After that we define the topological moment of the disclination system and describe liquid as a disordered system of interacting topological moments. This allows us to represent the liquid–glass transition in terms of spin-glass systems physics, and use the spin-glass theory to estimate the size of the long-range correlations in supercooled liquids (section 3).

2. The disclination description of liquids

The disclination description of liquids suggested by Nelson is the basis of our model. The basic thesis of this is that a regular tetrahedron represents the closest and most profitable local atomic packing. Indeed, it has been demonstrated that the structure of atomic liquids and glasses has a significant polytetrahedral character [4], first due to the success of the close random packing of hard spheres [5] as a model for metallic glasses and later due to computer simulations [6]. In the framework of this polytetrahedral model the liquid structure is considered to be a tessellation of all space with tetrahedra with atoms at their vertices. However, it is known that Euclidean space cannot be paved only with regular tetrahedra. With mathematical rigour, it was demonstrated that this was possible only in the case of a four-hypersphere space [7]. Nelson demonstrated that in order to transform a hypersphere into a flat space, it was necessary to introduce linear defects (such as disclinations and dislocations) into the structure [8]. Thus, the system of linear defects is an integral element of the polytetrahedral structure, and, owing to the topological stability, disclinations can be considered as a basic structural element of the liquid structure. Hence, we can represent the liquid structure as a disclination system.

In order to describe the disclination system, we use the gauge theory of defects [9]. To write down the Lagrangian of the defect system, let us make use of the standard theory of elasticity. The simplest Lagrangian describing a system with elastic deformations has the form

$$L_0 = \tfrac{1}{2}\rho_0 \partial_4 \chi_i \partial_4 \chi_i - \tfrac{1}{8}\left[\lambda u_{\alpha\alpha} u_{\beta\beta} + 2\mu u_{\alpha\beta} u_{\alpha\beta}\right],$$

where $\chi_i(\bar{r}, t)$ is the elastic strain field, λ and μ are the Lamé constants, ρ_0 is the mass density (which is considered to be constant for simplicity), and u_{ij} are the relative deformation components:

$$u_{ab} = C_{ab} - \delta_{ab} = \partial_a \chi^i \partial_b \chi^i - \delta_{ab}$$

(Greek letters $\alpha, \beta, \ldots$ are used to denote the space component set $\{\alpha\} = \{1, 2, 3\}$ and Roman letters $a, b, \ldots$ are used to denote the full index set, including the time component $X^4\{a\} = \{1, 2, 3, 4\}$.)

According to the gauge theory of dislocations and disclinations, the plastic deformation of the matter structure can be considered as a breakdown of the homogeneity of the rotation and translation ($SO(3) \triangleright T(3)$) group action. In order to take into account these homogeneity breakdowns, the compensating fields are introduced into the Lagrangian (A_a^α and φ_b^i), and the transition from ordinary to covariant derivatives is effected:

$$\partial_a \chi^i \to B_a^i = \partial_a \chi^i + \gamma_{\alpha j}^i A_a^\alpha \chi^j + \varphi_a^i,$$

where $\gamma_{\alpha j}^i$ are three generating matrices of the semisimple group $SO(3)$. After that, the Lagrangian L_0 is replaced by the new Lagrangian

$$L = L_0 + s_1 L_1 + s_2 L_2,$$

where s_1 and s_2 are free parameters of the theory, and the first term describes elastic properties of matter:

$$L_0 = \tfrac{1}{2}\rho_0 B_4^i B_4^i - \tfrac{1}{8}\left[\lambda E_{\alpha\alpha} E_{\beta\beta} + 2\mu E_{\alpha\beta} E_{\alpha\beta}\right]$$

(where $E_{ab} = B_{ia}B_{ib} - \delta_{ab}$ is the strain tensor). The second term,

$$s_1 L_1 = -\tfrac{1}{2} s_1 D^i_{ab} k^{ac} k^{bd} D^i_{cd},$$

describes the dislocations; the following notation is used here:

$$D^i_{ab} = \partial_a \varphi^i_b - \partial_b \varphi^i_a + \gamma^i_{\alpha j}\left(A^\alpha_a \varphi^j_b - A^\alpha_b \varphi^j_a + F^\alpha_{ab}\chi^j\right)$$
$$\left(F^\alpha_{ab} = \partial_a A^\alpha_b - \partial_b A^\alpha_a + C^\alpha_{\beta\gamma} A^\beta_a A^\gamma_b\right);$$

in the general case $C^\alpha_{\beta\gamma}$ are constants of the structure of the semisimple group $SO(3)$ ($C^\alpha_{\beta\gamma} = \varepsilon^\alpha_{\beta\gamma}$). The third term,

$$s_2 L_2 = -\tfrac{1}{2} s_2 C_{\alpha\beta} F^\alpha_{ab} g^{ac} g^{bd} F^\beta_{cd} \qquad (g^{\alpha\beta} = -\delta^{\alpha\beta}, \quad g^{44} = 1/\zeta), \tag{1}$$

describes disclinations. The Yang–Mills fields, A^α_a, and φ^i_a describe disclinations and dislocations respectively.

Usually it is supposed that the disclinations are the most important structural elements in the description of amorphous matter, since they have the largest energy density $s_2 \gg s_1$, and govern two fundamental properties of glasses: the absence of long-range ordering and the resistance to crystallization. It is natural to suppose that disclinations are also fundamental structure elements in liquids; therefore hereinafter we will focus only on the case of breakdown of homogeneity of the rotation semi-group (monoid). In other words, we will neglect the φ^i_a field contribution to the action and restrict ourselves to the consideration of the theory with a purely disclination Lagrangian,

$$L = L_0 - s_2 L_2.$$

In the case of linear disclination, the difficulties concerning nonlinearity of the Yang–Mills fields can be avoided. The field of the disclination line element differs from the point disclination field, since in this case the rotational displacements corresponding to the gauge transforms can be performed only around the tangent to the defect line vector, directed along this element (wedge disclination), and, consequently, the gauge group reduces to $SO(2)$. Therefore, the theory becomes much simpler, since the rotation group $SO(2)$ is Abelian instead of being the non-Abelian group $SO(3)$ (in the work [10] this fact was used in the case of infinite rectilinear defects). In order to find the field of linear disclinations, let us introduce the tensorial fields G^α_k and P^α_k, which take the following forms:

$$G^\alpha_k \equiv F^\alpha_{k4} = \partial_k A^\alpha_4, \qquad P^\alpha_k \equiv \tfrac{1}{2}\varepsilon_{klm} F^\alpha_{lm} = \tfrac{1}{2}\varepsilon_{klm}\left[\partial_l A^\alpha_m - \partial_m A^\alpha_l\right];$$

then the energy functional of the 'free' disclination field (1) can take the form

$$L_2 = \tfrac{1}{4}\int (\mathrm{d}^3 x) F^\alpha_{ij} F^\alpha_{ij} = \tfrac{1}{2}\int (\mathrm{d}^3 x)\left[(P^\alpha_k - G^\alpha_k)(P^\alpha_k - G^\alpha_k)\right] + \int (\mathrm{d}^3 x) P^\alpha_k G^\alpha_k.$$

Minimizing this part of the Lagrangian we can get the quasi-stationary expression for the potential of the gauge field of the wedge disclination fragment $\mathrm{d}l_\alpha$:

$$A^\alpha_4 = x_\alpha\left(\frac{C}{r^3} + 2C_1\right)\mathrm{d}l_\alpha, \qquad A^\alpha_k = \varepsilon_{\alpha kj} x_j\left(\frac{C}{r^3} + C_1\right)\mathrm{d}l_\alpha,$$

where C and C_1 are arbitrary constants. It should be noted that in this expression there is no summing with respect to α and $C_1 = 0$ because $A^\alpha_k(\infty) = 0$.

Let us consider the two basic examples:

(1) First we find the field of the infinite rectilinear disclination, directed along the axis i_α. For that we introduce the normal to the axis i_α vector R_j, which determines the point

location with respect to the disclination. Then the expression for the field of the rectilinear disclination, directed along the axis z, can be written in the form

$$A_i^z = C\varepsilon_{zij}\int_{-\infty}^{\infty}\frac{x_j}{r^3}\,\mathrm{d}l_z = C\varepsilon_{\alpha ij}\int_{-\infty}^{\infty}\frac{R_j}{\left(R^2+l_z{}^2\right)^{3/2}}\,\mathrm{d}l_z = 2C\varepsilon_{zij}\frac{R_j}{R^2}.$$

Due to the condition $\Omega = 2\pi\nu = \oint A_i^z\,\mathrm{d}l_i$, where Ω is the Frank vector, and ν is the Frank index, we get an expression which agrees with the result of [10].

(2) The field of the element of the round (with the radius equal to a) disclination loop has the form

$$A_i^\alpha = \frac{\nu}{2}\varepsilon_{\alpha ij}\frac{x_j}{r^3}\,\mathrm{d}l_\alpha = \frac{\nu a}{2}n_i\frac{1}{r^3}\,\mathrm{d}l_\alpha,$$

where n_i is the unit vector normal to the loop's plane.

If we consider only the low-angle disclinations, $\nu \sim 0.2$, which are typical for liquid-like structure, the stress field around the disclination line has the form

$$\sigma_{ai} = \mu E_{ai} = \mu\left(B_{aj}B_{ji} - \delta_{ai}\right) = \mu\left[\varepsilon_{\alpha al}x_l A_i^\alpha + \varepsilon_{\alpha il}x_l A_a^\alpha + \partial_i u_a + \partial_a u_i\right].$$

Hence, the volumetric density of the elastic interaction energy of disclinations, described by the fields A and A', has the form

$$F = \frac{1}{2}\sigma_{ai}E_{ai} \simeq \frac{\mu}{2}\varepsilon_{\alpha al}x_l A_i^\alpha \varepsilon_{\gamma aj}x'_j A_i'^\gamma + \mathrm{O}(a^4).$$

One can see that the form of this interaction is similar to the form of the electrodynamic interaction of currents. For example, the elastic interaction energy of two round loops Γ and Γ' with the radius a, remote from $\vec{r}$, has the form

$$F \simeq n_i n'_i\frac{\pi^2\mu a^2\nu\nu'}{4}\oint_\Gamma\oint_{\Gamma'}\frac{1}{r}\,\mathrm{d}l_j\,\mathrm{d}l'_j. \tag{2}$$

This expression agrees with the expression for the interaction energy of current loops on condition that $\vec{n} \parallel \vec{n}'$.

3. Description of the glass transition

The basic idea of our approach was first suggested by Rivier [11]. According to his theory the glass transition can be considered as a phase transition in the system of topological defects. In this theory there is no distinction in principle between the spin-and structure-disordered systems. In both the first and second cases the problem of description of the system is reduced to the description of the system of interacting disclinations. We would like to make use of this analogy and reduce this description to that of the disordered spin systems as much as possible, and apply the methods known from spin-glass physics to our system.

Computer simulation results testify that the disclination system is a tangled net of interacting disclinations. To describe this system, let us make use of an approach which is well known in classical electrodynamics [12]: we associate the system of linear disclinations, included in some small volume such that the numbers of positive and negative disclinations entering this volume are equal, with their general topological moment (the analogue of the magnetic moment of the electric currents system). Thus, the total elastic energy of interaction between all the elements of the disclination network can be represented as the interaction energy of the system of local topological moments. Since the disclination loop is the simplest structure element having a topological moment, to simplify the model let us imagine the disclination network as a system of randomly located and randomly directed disclination loops.

Let us determine the topology moment vector $\bar{S}_i$ in our system as the magnetic moment is determined in electrodynamics. In this case the Hamiltonian that describes the disclination loop system can be represented in the form of a Heisenberg model Hamiltonian:

$$H = \tfrac{1}{2}\sum_{i,j} J_{ij}\vec{S}_i\vec{S}_j,$$

with the inter-spin coupling (from (2))

$$J_{ij}^{lk} \approx \mu\pi^4 a^6 \nu_i \nu_j \frac{\cos(\angle \vec{S}_i\vec{S}_j)}{2|\vec{r}_{ij}|^3}\left(\delta^{lk} - 3\frac{r_{ij}^l r_{ij}^k}{r_{ij}^2}\right),$$

where l and k are the indices of the space coordinates of the vector $\bar{r}_{ij}$. The modulus and sign of the disclination loop coupling both depend on their situation and their mutual orientation. This system is frustrated. Indeed, from the last expression one can see that the moment coupling is an alternating quantity; hence, with equal probability these moments can interact in either a ferromagnetic-like or an antiferromagnetic-like manner ($\langle J_{ij}\rangle = 0$). This character of coupling is typical for spin glasses [13]. Therefore, we attempt to describe the system considered using the modification of the Edwards–Anderson model with large but finite-range interaction which was analysed in [13, 14]. According to this analysis, the glass transition in such systems is a so-called 'hierarchical' phase transition, which is a hierarchy of successive transitions that closes at the glass transition point T_g. Using the results of [14] and the expression for the defect coupling energy obtained above, one can estimate the transition points T_i for every ith step of this series, as well as the correlation lengths corresponding to these points: T_i can be estimated from

$$\ln\left[\frac{T_i - T_g}{T_g}\right] \approx \left[-\frac{p}{q-1}(q^{1+i} - 1)\right]\ln Z_0, \tag{3}$$

where $q = 32/15$, $p = 4/15$ [14]; the coordination number, Z_0, can be evaluated from the coupling radius R:

$$Z_0 = \tfrac{4}{3}c\pi R^3,$$

where c is disclination density, and R can by determined from the inter-disclination interaction energy and the thermal fluctuation energy parity condition:

$$E(A) = \frac{\mu a^6\pi^4\nu^2}{2R^3} \approx \frac{3kT}{2}, \tag{4}$$

where a is a typical interatomic distance. If we express R using (4) and substitute this expression in (3) we find that the freezing process begins at a temperature which can be estimated from solving the equation

$$T_0 \approx T_g\left[1 + Z_0^{-4/15}\right] = T_g\left[1 + \left[\frac{4\mu c\pi^5 a^6\nu^2}{9kT_0}\right]^{-4/15}\right]. \tag{5}$$

Subsequent cooling results in the formation of clusters which finally have shape at the temperature

$$T_1 \approx T_g\left[1 + Z_0^{-0.84}\right].$$

The correlation length characterizing the average size of these clusters as well as their average lifetime can be determined from

$$\xi \approx \left(\frac{Z_0^{2q}}{4c}\right)^{1/3}, \qquad \tau \approx \tau_0 Z_0^{14/5}. \tag{6}$$

For quantitative estimation of these parameters let us assume typical values: $a = 1 \times 10^{-9}$ m; $k = 1.38 \times 10^{-23}$ J K^{-1}, $T_g = 200$ K; $\tau_0 \approx 10^{-10}$ s; the estimation of the disclination density follows from the analysis of the experimental data (the typical inter-disclination distance is $\sim 5a$): $c = 1.4 \times 10^{24}$ m^{-3}; and the shear modulus of liquids is $\mu \approx 10^{10}$ N m^{-2}, according to [15]. As a result, after substitution of these parameters in (5) and (6), we get the following estimates: $T_0 - T_g \approx 100$ K; $T_1 - T_g \approx 20$ K; $\xi \approx 300$ nm; $\tau \sim 0.4 \times 10^{-6}$ s. Of course, these estimates are rather approximate as yet. But we hope that they can be improved in the future.

4. Conclusions

The structure frustrations and complicated cooperative character of atoms moving in liquids lead to the necessity of using state-of-the-art methods of statistical physics to understand the nature of the properties. In this paper we have tried to combine the gauge field theory and Anderson localization theory to describe the structure formation processes in supercooled liquids.

The above estimates allow us to conclude that the process of freezing of the degree of freedom begins at temperatures that are significantly above the glass transition temperature, T_g, and that correlations with size $\sim$100 nm form in the temperature range $(T - T_g) \sim 100$ K in the structure of the liquid. The disclination model allows us to explain the density beating in a natural way, since the atom density is larger close to a negative ($\nu > 0$) disclination core and smaller close to a positive ($\nu < 0$) one. Therefore, we think that these correlations conform with the long-range density correlations (Fischer clusters) which are observed in the experiments.

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