Reprint of "Theoretical description of non-Debye relaxation, and boson peak in terms of gauge theory of glass transition" ☆

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ABSTRACT

The slow kinetics of relaxation processes in supercooled liquids is described in terms of the gauge theory of glass transition. It is shown that the theory allows us to explain the non-Debye relaxation and to derive its exponent, as well as to predict the appearance of the boson peak in the low frequency part of the spectrum of the dynamic structural factor. According to the theory, both phenomena have common nature and are caused by the cooperative motion of liquid's atoms, which is described by the correlation function of the gauge field.

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1. Introduction

One of the theoretical approaches to the vitrification description based on the concept of "frustration" [1–3] presence in supercooled liquids is considered in this paper. Over the past three decades this idea has been developed in the gauge theory of glass [2–6]. The combination of this theory with the methods of description of the quasi-nonergodic system dynamics [7,8] allows one to obtain a qualitatively correct description of glass transition, which was named gauge theory of glass transition (GTGT) in [9,10].

However, in the above papers not enough attention was paid to the description of the kinetic properties of glass-forming systems. Although the modern non-equilibrium dynamics technique, giving an advantage right in the kinetics description, is the basis of this theory. The kinetics contains the distinctive features and general properties of glass-forming liquids. Among the properties attracting the researchers' attention one can notice the non-Debye relaxation, the boson peak as well as the dynamic heterogeneity which especially intrigues theoreticians. This work is devoted to the theoretical description of these characteristic kinetic properties of the supercooled glass-forming liquid in terms of GTGT.

At the beginning the brief formulation of the gauge model of the glass-forming system as well as the basic facts on the theoretical description of its non-equilibrium dynamics close to the glass transition are presented. Then in the framework of the perturbation theory the

Kohlrausch and Cole–Cole equations that describe a non-Debye relaxation close to the temperature of glass transition are derived. In conclusion, the analytical expression of the frequency dependence of the dynamic structural factor is derived. It allows us to describe the boson peak in the low frequency part of the spectrum, and investigate the dependence of the position of this peak on temperature.

2. Gauge theory of glass transition

First of all, let us formulate the gauge model of the glass-formed condensed matter by writing its Hamiltonian.

This problem had been solved long ago, and was discussed in a number of works [2,3,6]. Below I present only the basic assumptions and results of above works. Firstly, as an order parameter the $\mathbf{Q} = Q_{ij}$ multipole, which has the symmetry of the favorite local molecular packing, is proposed. With this order parameter the systems Hamiltonian can be written as follows:

$$\mathcal{H} = \sum_{\vec{r}, \vec{r}'} \mathbf{L}_{\vec{r}, \vec{r}'} \mathbf{Q}(\vec{r}) \mathbf{Q}(\vec{r}') + O(\mathbf{Q}^3, \mathbf{Q}^4, \ldots), \tag{1}$$

where $\mathbf{L}_{\vec{r}, \vec{r}'}$ is the interaction energy of multipoles. It was shown that at some temperature T_c in this system the phenomenon similar to the second order phase transition appears, the correlation length rapidly grows and reaches the value of several coordination spheres. Besides, in the low temperature state the translation symmetry is absent. It allows us to conclude that at this temperature the system turns into glass. The important property of this Hamiltonian is its local rotation invariance corresponding to the order parameter symmetry. For example, it is Y in the case of a system with the spherical interaction potential [2]. In addition,

the described system is complicated by the presence of geometrical frustration appearing because of the impossibility of uniform paving of Euclidian space by the elements with Y symmetry. Therefore, the system action in continuous representation contains a gauge field, $\mathbf{A}$, and its sources, $\mathbf{J}$:

$$\mathcal{S} = \beta \int \left[\frac{1}{2} (\overline{D} \mathbf{Q})^2 - U(\mathbf{Q}) + \frac{1}{4} \mathbf{F}^2 + \mathbf{J}\mathbf{A} \right] d\mathbf{r}, \tag{2}$$

where

$$\begin{aligned} U(\mathbf{Q}) &= \frac{1}{2} \mu^2 \mathbf{Q}^2 + \frac{1}{4} v \mathbf{Q}^4, \\ D_i Q_{lk} &= \partial_i Q_{lk} + g \varepsilon_{iab} A_{la} Q_{kb}, \\ F_{a\mu\nu} &= \partial_\mu A_{a\nu} - \partial_\nu A_{a\mu} + g \varepsilon_{abc} A_{b\mu} A_{c\nu}, \end{aligned} \tag{3}$$

and we believe that $\mu^2 = a(T - T_c)$ [3,5,6].

Let us consider this system behavior in the fluctuation region close to the critical temperature T_c in the isotropic disordered phase $\langle \mathbf{Q} \rangle = 0$. In this state the liquid's molecules form the ordered structure with $bf Q \neq 0$ in arbitrary local space areas. These fluctuations spontaneously appear and disappear, randomly oriented and different in sizes. The mean radius of these fluctuations is $r_c \sim \mu^{-1}$. According to the fluctuation theory of phase transition close to T_c the order parameter can be presented as the sum of "slow", Φ, and "fast", Ψ, parts [11], $\mathbf{Q} = \Phi + \Psi$. Ψ is the sum of the harmonics with large wave vectors, and Φ encloses the rest ones. The "fast" part contains the information on the correlation functions in $L \ll r_c$ scales, the "slow" part — on the correlation functions in large scales. The mean square of the "fast" part of the order parameter in the fluctuating region $\langle \Psi^2 \rangle = \mu^2/v$, though $\langle \Psi \rangle = 0$.

According to the fluctuation theory of phase transition one should carry out the procedure of exception of the "fast" degrees of freedom by integrating the distribution function over Ψ. Then

$$\mathcal{S} = \beta \int \left[\frac{1}{2} (\overline{D}\Phi)^2 + \frac{g^2 \mu^2}{4v} \mathbf{A}^2 + \frac{1}{2} \mu^2 \Phi^2 + \frac{1}{4} v \Phi^4 + + \frac{1}{4} \mathbf{F}^2 + \mathbf{J}\mathbf{A} \right] d\mathbf{r}. \tag{4}$$

Note, that the described system is in the liquid state. In this case the gauge field is a dynamic one, and the geometric frustration leads to the appearance of the sources of this field, which are generally movable. It is supposed that in the disordered state, when $T > T_c$, the system of the sources is in thermal equilibrium [4]. Then one can perform averaging of the partition function, Z, over $J_{a\mu}$:

$$Z = \int \left[\int \exp \left(-\mathcal{S} - \frac{\beta}{2} \int I_0^{-1} \mathbf{J}^2 d\mathbf{r} \right) \mathfrak{D}\mathbf{J} \right] \mathfrak{D}\Phi \mathfrak{D}\mathbf{A}, \tag{5}$$

where $\int \dots \mathfrak{D}x$ means the path integration. This leads to the appearance of the additional contribution to the "mass" of the gauge field A_μ^a, which, in result, takes the form of

$$M^2 = \mu^2 g^2 / 2v - I_0. \tag{6}$$

As a result the action of the frustrated system has the following form:

$$\mathcal{S} = \frac{\beta}{2} \int \left[(\overline{D}\Phi)^2 + M^2 \mathbf{A}^2 + \mu^2 \Phi^2 + \frac{v}{2} \Phi^4 + \frac{1}{2} \mathbf{F}^2 \right] d\mathbf{r}. \tag{7}$$

The derived renormalization of the gauge field mass affects the system behavior. It shifts the $M^2 = 0$ singularity in the range of temperatures above the temperature of the virtual phase transition T_c, since according to Eq. (6) the correlation length of the gauge field diverges in $T_0 = T_c + 2I_0 v / a g^2$. In [9] it has been shown that this leads to the critical slowing-down of all the system in T_0, wherein the temperature dependence of the relaxation time satisfied the Vogel–Folcher–Tamman law.

3. Analysis of the theory in dynamic case

It is natural that the static theory cannot describe glass transition in full because the dynamic properties of the system are not taken into account in it. In order to overcome this deficiency one can investigate the non-equilibrium dynamics close to T_0 by using the functional methods [9,10]. In this case the analog of the partition function is the stochastic generating functional:

$$\mathcal{Z} = \int \exp(-\mathcal{S}^*) \mathfrak{D}\overrightarrow{\Phi} \mathfrak{D}\overrightarrow{\mathbf{A}}, \tag{8}$$

where

$$\begin{aligned} \mathcal{S}^* = \frac{1}{2} \int &\left[\overrightarrow{\Phi}(t,\mathbf{r}) \hat{G}^{-1}\left(t - t', \mathbf{r} - \mathbf{r}'\right) \overrightarrow{\Phi}\left(t', \mathbf{r}'\right) \right. \\ &+ \overrightarrow{\mathbf{A}}(t,\mathbf{r}) \hat{\Delta}_{\mu\nu}^{-1}\left(t - t', \mathbf{r} - \mathbf{r}'\right) \overrightarrow{\mathbf{A}}\left(t', \mathbf{r}'\right)] d\mathbf{r} d\mathbf{r}' dt dt' \\ &+ \int \left[g\varepsilon_{abc} \left(\partial_\mu \overline{A}_{a\nu} \right) A_{b\mu} A_{c\nu} + g \varepsilon^{abc} \left(\partial_\mu A_{a\nu} \right) \overline{A}_{b\mu} A_{c\nu} + \right. \\ &+ g\varepsilon_{abc} \left(\partial_\mu A_{a\nu} \right) A_{b\mu} \overline{A}_{c\nu} + g^2 \varepsilon_{abc} \varepsilon_{aij} \overline{A}_{b\mu} A_{c\nu} A_{i\mu} A_{j\nu} \\ &\left. + g^2 \overline{\mathbf{A}} \mathbf{A} \Phi^2 + g^2 \mathbf{A}^2 \overline{\Phi} \Phi + v \overline{\Phi} \Phi^3] d\mathbf{r} dt, \right. \end{aligned} \tag{9}$$

and $\overrightarrow{\Phi} = \{\overline{\Phi}, \Phi\}$, $\overrightarrow{\mathbf{A}} = \{\overline{\mathbf{A}}, \mathbf{A}\}$ are vectors whose components are called "quantum" and "classical", respectively [12]. $G^{-1} \Delta_{\mu\nu}^{-1}$ are the matrixes, which are inverse to the appropriate matrixes of the initial correlation functions (the Green functions of the non-perturbated theory), according to [13] they have the following form:

$$\hat{G} = \begin{pmatrix} G_0^K & G_0^A \\ G_0^R & 0 \end{pmatrix}, \quad \hat{\Delta}_{\mu\nu} = \begin{pmatrix} \Delta_{\mu\nu}^K & \Delta_{\mu\nu}^A \\ \Delta_{\mu\nu}^R & 0 \end{pmatrix}, \tag{10}$$

$$G_0^A(k,t) = \theta(t) \frac{e^{-t\varepsilon_k(\mu)/\Gamma_\Phi}}{\Gamma_\Phi}, \quad G_0^K(k,t) = \frac{e^{-|t|\varepsilon_k(\mu)/\Gamma_\Phi}}{\varepsilon_k(\mu)}. \tag{11}$$

Γ_Φ is the kinetic coefficient of the order parameter field, and $\varepsilon_k(x) = k^2 + x^2$. In case if $M \to 0$

$$\Delta_{\mu\nu}^A(k,t) = \delta_{\mu\nu} \theta(t) \frac{e^{-t\varepsilon_k(M)/\Gamma_A}}{\Gamma_A}, \quad \Delta_{\mu\nu}^K(k,t) = \delta_{\mu\nu} \frac{e^{-|t|\varepsilon_k(M)/\Gamma_A}}{\varepsilon_k(M)}, \tag{12}$$

where Γ_A is the kinetic coefficient of the gauge field.

The critical dynamics of the considered system close to T_0 was investigated in [9,10]. It has been shown that the critical slowing-down of the relaxation processes occurs in the system at $T \to T_0^+$. As a result the system freezes in a disordered and nonergodic solid state. The reason of this is that the gauge interaction radius between the order parameter fluctuations grows much faster than the size of these fluctuations. This radius can be considered as the length of dynamic heterogeneity.

Prima facie it seems surprising that the frustration, which destroys the long-range order, leads to the growth of the correlation length of the gauge field at the freezing temperature. However, the physical meaning of this seems to be easy to understand: In the non-frustrated system the correlation radiuses of the gauge field and the order parameter field coincide (one can also interpret the correlation radius of the gauge field as the radius of elastic interaction). But in the frustrated system the parameter T_c is renormalized and shifts towards lower temperatures when the system approaches the glass transition point. Therefore, we have the grounds to believe that the size of the dynamic fluctuations, which corresponds to the correlation radius of the gauge field, diverges just as in a non-frustrated system, but the correlation radius of the order parameter lags, since the frustration prevents its growth.

In [9,10] it has also been shown that the temperature dependence of the relaxation time close to the T_0 is not a power function which is specific for second order phase transition, but it is described by the Vogel–Foulcher–Tamman dependence. However, the kinetics of the