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Random First Order Transition from a Supercooled Liquid to an Ideal Glass (Review)

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Abstract

The random first order transition theory (RFOT) describing the transition from a supercooled liquid to an ideal glass has been actively developed over the last twenty years. This theory is formulated in a way that allows a description of the transition from the initial equilibrium state to the final metastable state without considering any kinetic processes. The RFOT and its applications for real molecular systems (multicomponent liquids with various intermolecular potentials, gel systems, etc.) are widely represented in English-language sources. However, these studies are practically not described in any Russian sources. This paper presents an overview of the studies carried out in this field.

Keywords: supercooled liquid, ideal glass, distribution functions, replicas, random first order transition.

Introduction

Equilibrium statistical physics views a macroscopic body as a system consisting of an infinite number of identical subsystems (replicas). Intermolecular interactions within each replica are identical, which ensures the microscopic homogeneity of the body. The probability distribution of each subsystem over various phases is described by means of the Gibbs measure. This is based on the ergodic hypothesis which states that macroscopic averages are equal to the averages of the Gibbs ensemble. Using the Gibbs distribution we can calculate the average of any observable either directly, employing the statistical integral, or using the particle size distribution functions of the positions of several particles in set points at the same time.

The ergodic hypothesis, however, is not applicable to metastable states. The random distribution of particles between fixed points results in local microscopic inhomogeneity. At the moment, there are two approaches used to describe the structure of the amorphous state: phenomenological approach and the method of particle size distribution functions employed in equilibrium statistical physics. The phenomenological approach [1] is based on intuitive ideas regarding the local structure of glass and its connection with the glass transition and melting temperatures. However, it does not describe the physics of the glass transition of melts [2]. [3] attempts to provide a microscopic explanation of the particle confinement time in melts.

According to the method of particle size distribution functions [4], the glass transition is performed following a specific increase in the density or a decrease in the temperature of the metastable system. Glass transition is determined

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substantially by the kinetic phenomena depending on the heat removal rate and the duration of the structural transformation. Therefore, there is still no single opinion regarding the way we can use the notions of thermodynamic equilibrium to describe metastable states.

[5,6,7] present heuristic considerations pertaining to the transition from a supercooled liquid to an ideal glass. A breakthrough was made by Mezard and Parisi [8] followed by further studies [3, 9–27] that formulated the replica theory of the "Random First Order Transition" (RFOT) based on the modernised method of particle size distribution functions. Replicas are identical copies of subsystems. Analogous to the systems in the state of thermodynamic equilibrium, the molecular interaction within the replicas is identical. It was determined, however, that the replicas themselves interact with each other. The parameters of the interaction are set so that the mean distance between the particles is smaller than that in a liquid. Basically, this is how we can differentiate between a supercooled liquid and an ideal glass. We can thus describe the transition from the initial equilibrium state to the final metastable state without considering any kinetics processes. The RFOT and its applications for real molecular systems (multicomponent liquids with various intermolecular potentials [28–31], viscous fluids and gel-like liquids [32–39], colloids [40–41], medicinal solutions [42–43], amorphous polymers [44], polydisperse crystals [45–48], etc.) are widely represented in English-language scientific literature. However, these studies are practically not mentioned in any Russian sources. The significance of the replica theory is similar to that of the Gibbs canonical distribution and the integral equations method used in the statistical theory of liquids in the state of thermodynamic equilibrium. It should be noted, however, that the RFOT does not in any way describe relaxation processes. The integral equations for particle size distribution functions only describe the structural characteristics of thermodynamic equilibrium and metastable states reached through infinitely large time intervals. Microscopic description of the kinetic processes occurring in dense gases and liquids is based on the Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy [49] for nonequlibrium

particle size distribution functions. This field of study is now actively being developed, but it is out of the scope of this paper. Listed below are just a few studies focusing on the issues closely related to the problem discussed in this paper. [50–51] focus on various implementations of the Bogoliubov and Boltzmann equations, particularly for granular media [52]. [53] develops a model for discrete velocity-jumps in a molecular system. [54] describes the asymptotic behaviour of the observables of a low-density fluid. [55] analyses the transport processes within a system of hard spheres.

There are also studies focusing on the thermodynamic [56–61], statistical [62-66], and kinetic [67–68] aspects when describing the transition of hard spheres and multidimensional hyperspheres from liquid to solid states [69–71].

2. Theoretical part

2.1. The method of distribution functions in the study of fluids

The statistical physics of fluids is based on the BBGKY (Bogoliubov–Born–Green–Kirkwood–Yvon) hierarchy for l-particle distribution functions $G_{l,...,i} = (\mathbf{r}_l,...,\mathbf{r}_i)$, equivalent to the Gibbs canonical distribution. The particles interact through the pair potential $\Phi_{ij}(r_{ij})$, where $r_{ij} = |\mathbf{r_i} - \mathbf{r_j}|$ is the distance between the centres of the particles i, j. By subsequently removing higher-order distribution functions from the equation chain, we can transform the BBGKY hierarchy into the Ornstein–Zernike (OZ) equation [72–73] describing single- and two-particle distribution functions

$$\omega_1 = n \int G_2 C_{12}^{(1)} d(2) + \mu,$$
$$h_{12} = C_{12}^{(2)} + n \int G_3 C_{13}^{(2)} h_{23} d(3), \tag{1}$$

The integration is performed over the coordinates of the ith particle, $d(i) = d\mathbf{r}_i$, n is the density. A single-particle distribution function can always be represented as $G_i = \exp(-\Phi_i / kT + \omega_i)$, where the first summand in the exponent describes the direct interaction of the particle with the external field Φ_i, while the second summand describes the indirect interaction via the environment. The chemical potential μ is determined using the conditions of the transition to a spatially homogeneous

system in the absence of external fields. The pair correlation function $h_{ij} = \exp(-\Phi_{ij}/kT + \omega_{ij}) - 1$ is presented as a direct interaction of two particles Φ_{ij} and their indirect interaction with the environment ω_{ij}. Direct correlation functions $C_{ij}^{(k)}$

$$C_{ij}^{(1)} = h_{ij} - \omega_{ij} - 1/2 h_{ij}\left(\omega_{ij} + M_{ij}^{(1)}\right);$$

$$C_{ij}^{(2)} = h_{ij} - \omega_{ij} + M_{ij}^{(2)} \tag{2}$$

are represented as infinite functional series $M_{ij}^{(1)}$, $M_{ij}^{(2)}$ of the required distribution functions. When using these series to solve particular problems, we use only those summands that can be summed, while leaving out the others. As a result, we obtain a connection (closure) between the direct and pair correlation function, which makes the OZ equation approximate to nonlinear integral equations that have numerical solutions. The most common are the hypernetted chain, Percus–Yevick, Rogers–Young, and Martynov–Sarkisov closures [72–75].

Of great importance are also spatially homogeneous isotropic media (isotropic fluids without external fields and far from boundary surfaces), where $G_1(\mathbf{r}) \equiv 1$, $\omega_1(\mathbf{r}) \equiv 0$, $C_{12}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = C_{12}^{(1)}(r_{12})$. As a result, the first equation in the system (1–2) is reduced to the definition of the excess chemical potential $\mu = \ln a = \mathrm{const}$. The second equation in the system determines the direct correlation function $C_{12}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = C_{12}^{(2)}(r_{12})$, which can be calculated using a number of well-established methods. We should note that the Percus–Yevick equation includes the direct correlation function $C_{12}^{(2)}(r_{12}) = h_{12} - (\exp(\omega_{12}) - 1)$. Consequently, the exponential nonlinearity for a hard sphere system is replaced by the quadratic nonlinearity, i.e. decreases significantly. Therefore, we can obtain an analytical solution for the function $C_{12}^{(2)}(r_{12})$ [74, 76].

For spatially inhomogeneous systems (a molecular system near hard surface), functions $G_1(\mathbf{r}_1)$, $G_{12}(\mathbf{r}_1, \mathbf{r}_2)$ help to determine the microstructure of the substance and calculate all thermodynamic parameters. We should note that for the multivariable functions, a substantial numerical calculations are required to solve the equations (1–2). To simplify the calculation process, we can replace the direct correlation function $C_{12}^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$ (the so-called singlet approximation) with its boundary value $C_{12}^{(1)}(r_{12})$. Then, depending on the closure used in the calculation, $M_{ij}^{(1)}$, we obtain a certain nonlinear integral equation for a single-particle distribution function depending on a single variable, namely the distance between the particle and the surface. This equation is also solved numerically, but is much less resource intensive. The existing approaches are described in [77–79].

The analytical solution for a single-particle distribution function is only possible in individual cases, for instance, for one-dimensional and two-dimensional liquids [80]. An analytical solution of the singlet Percus–Yevick equation for a three-dimensional hard sphere system on the boundary with a hard surface was suggested in our earlier study [81]. The key idea is that all the summands left out in (2) are taken into account so that they could compensate for all the nonlinearities. Due to its axial symmetry, a single-particle distribution function depends only upon the coordinate z which denotes the distance between the particle and the hard surface. As a result, we obtain the following linear integral equation

$$e^{\omega_1(z_1)} - 1 = 2\pi n \int_0^\infty dz_2 (e^{\omega_1(z_2)} - 1) \int_{|z_{12}|}^\infty r_{12} dr_{12} C_{12}^{(1)}(r_{12}) -$$
$$-2\pi n \int_{z_1}^\infty dz_{12} \int_{|z_{12}|}^\infty r_{12} dr_{12} C_{12}^{(1)}(r_{12}), \tag{3}$$

which takes into account the fact that the liquid particles interact with the surface through the hard sphere potential $G_i = \exp(\omega_i)$. This equation is a linear Fredholm integral equation of second kind. It can be solved analytically, if the kernel and the right-hand side of the equation are solved analytically. Other closures first require a numerical solution of the corresponding integral equations. Then, standard application software packages can be used to solve the Fredholm integral equation numerically. This framework is significantly easier as compared to the solution of the equation system (1)–(2) for multivariable functions.

2.2. The main approaches to the description of the liquid–glass transition

When a liquid temperature falls rapidly below the crystallisation temperature T_f the liquid goes through a number of metastable

states before forming a stable amorphous phase. This phenomenon was well investigated by means of numerous calorimetric measurements, dielectric and spin relaxation, nuclear magnetic-resonance, and neutron scattering on various materials. However, despite the obvious progress reached in [12–15], the theory behind this phenomenon is still incomplete. Presented below is the commonly acknowledged approach to the description of the amorphisation of a supercooled liquid. At the temperature $T_c < T_f$ the kinetic transition to the equilibrium state is predicted by the phase connectivity theory. The chaos (ergodicity), however, is distorted by dynamic processes. Calorimetric measurements of supercooled liquids indicate rapid alterations in the molar volume or the enthalpy as the function of temperature. When the calorimetric glass transition temperature is $T_g < T_c$, the specific heat capacity C_p reaches its maximum. However, since T_g depends on the cooling rate, it is not a characteristic parameter of the material; T_g decreases at a lower cooling rate. Therefore, the "calorimetric glass transition" is not a true phase transition. In fact, the temperature T_g fixes the temperature at which the duration of structural relaxation becomes compatible with the experimental value (usually in minutes or hours). The temperature T_g is determined by comparing the Maxwell relaxation time $\tau_M = \eta / G_\infty$ (where τ is the shear viscosity and G_∞ is the instantaneous shear modulus) to the experimental value $\tau_{exp} = 10^3$ s. When the shear modulus is $G_\infty = 10^9 Nm^{-2}$, which is common for most materials, T_g is defined as the temperature at which the shear viscosity reaches $\tau = 10^{12} N \cdot m^{-2} \cdot s$ (or 10^{13} poise).

At a temperature of $T < T_g$ a supercooled liquid is always in a metastable state. At the same time, the calorimetric measurements predict the entropy crisis (Kauzmann temperature) at the temperature of $T = T_K$, when the configurational entropy S_{conf} of the supercooled liquid disappears (equals zero or becomes insignificant). The possible connection between the disappearance of S_{conf} and the change in the time of structural relaxation of an extremely supercooled liquid is determined by the phenomenological Vogel–Fulcher–Tamman equation for highly viscous liquids $\eta = \eta_0 \exp(-A / (T - T_0))$. It was then assumed that $T_0 = T_K$. A detailed analysis of the structural relaxation time for glasses is performed in [82]. The hierarchy of the characteristic length scales in liquid-glass transitions is considered in [83–85].

The key concept is that the Kauzmann temperature precedes the transition of a supercooled liquid into glass. The transition corresponds to a lower non-crystalline minimum of the dependence of the free energy on the temperature. An ideal glass is characterised by chaotic equilibrium position of the particles in the space $\{X_i\}$ $(1 \le i \le N)$. This kind of random first order transition is a formal analogue of the mean field theory of spin glasses [10–11, 86–88]. This concept was effectively employed by the replica model (random first order transition). The replicas, or copies (clones), of a multiparticle system are used to define the parameter (configurational overlap) that helps to differentiate between supercooled liquids and glasses. The two states have identical spatial symmetry and similar unordered microscopic structure, as opposed to the translational symmetry of the crystals. Various modifications of the RFOT theory are considered in [9, 22–25].

Generally, the studies using the RFOT theory consider m replicas. Every atom of each replica interacts with all the atoms of the other $m - 1$ replicas. The most basic option [89] is to consider ($m = 2$) two weakly coupled replicas and calculate the statistical correlations between them based on the numerical solution of the hypernetted-chain and Rogers–Young (RY) integral equations in a wide range of thermodynamic states. The study demonstrated that in the limit of vanishing inter-replica coupling, there are three branches of solutions for the pair distribution function. The main drawback of this study is the fact that the hypernetted-chain integral equation is thermodynamically inconsistent and too rough for high densities [74]. The equilibrium thermodynamics of glass is determined using the free-energy functional of Morita and Hiroike, which allows analytical calculation for any number of replicas m, followed by the limit transition $m \to 1$ [12–15]. This elegant approach was first applied to "soft spheres" and their mixtures and then extended to hard sphere models.

The calculations of the free energy and configurational overlap predict a random first order transition from a supercooled liquid to glass. The present-day situation in this field of study is described in [90].

3. The replica method as applied to the description of the liquid-glass transition

3.1 A two-replica model

Let us consider N particles of each replica (marked as a and b) interacting through the repulsive potential of "soft spheres"

$$v(r) = \varepsilon(\sigma / r)^n, \tag{4}$$

where ε and σ are the characteristic energy and the size of the particle, $\rho^* = N\sigma^3 / V$ is the dimensionless density (σ is the characteristic size of the particle, V is the volume), and $T^* = k_B T / \varepsilon$. Therefore, the distance can be measured in dimensionless units $x = r / \sigma$. The applicability of the potential (4) to real systems is supported by two assumptions. The first is that the dependence of thermodynamic properties on the temperature and density is determined by a single parameter $\Gamma = \rho^* / T^{*3/n}$, rather than by ρ^* and T^* separately. Therefore, the excess Helmholtz free energy for one particle is

$$\frac{F^{ex}(\rho,T)}{Nk_B T} = f_{ex}(\Gamma). \tag{5}$$

At the same time, the pair distribution function is invariant to the arbitrary scale parameter λ

$$g(x,\rho^*,T^*) = g(\lambda x, \rho^* / \lambda^3, T^* / \lambda^{12}). \tag{6}$$

The second assumption is proved by the results of the numerical experiment [91], which demonstrated that $n = 12$ is crystallised to a face-centred cubic lattice, if $\Gamma = \rho^* / T^{*1/4} = \Gamma_f = 1.15$ [7, 88–89].

We should take into account that the atoms of identical replicas interact through the pair potential $v_{aa}(r) \equiv v_{bb}(r) = v(r)$, while the pair potential $v_{ab}(r)$ of the atoms of different replicas is of attractive type

$$v_{\alpha\beta}(x) = -\varepsilon_{\alpha\beta} w(x) = -\varepsilon_{\alpha\beta}\left[\frac{c^2}{x^2 + c^2}\right]^6. \tag{7}$$

The constant C was chosen so that the size of the interaction area was smaller than the mean distance between the neighbouring atoms $d^* = d / \sigma \simeq \rho^{*-1/3}$, i.e. $A/d^* \ll 1$. Thus, due to strong repulsion between the atoms within one replica they interact with a larger number of atoms of the other replica. For the non-zero $\varepsilon_{\alpha\beta}$ the interaction (2) reduces the mean distance between the atoms of the other replica at lower temperatures. The exact value of the function $w(r)$ is irrelevant, since we focus on the limit $\varepsilon_{\alpha\beta} \to 0$. Full potential energy of the two replicas equals

$$V_{N,N}(\{x_i^1\},\{x_j^2\}) = \sum_i \sum_{j>i} v(|x_i^1 - x_j^1|) + \\ + \sum_i \sum_{j>i} v(|x_i^2 - x_j^2|) + \sum_i \sum_{j>i} v(|x_i^1 - x_j^2|), \tag{8}$$

where $\{x_i^1\},\{x_j^2\}$ is a set of coordinates of the particles of each replica. The equilibrium structure of the two replicas is determined by two pair distribution functions, $g_{11}(x) \equiv g_{22}(x)$ and $g_{12}(x) \equiv g_{21}(x)$ respectively. The summands corresponding to the cross coupling in the equation (8) disturb the scaling invariance characteristic of the interaction between soft spheres (4). This means that the equilibrium properties of the two-replica system depend on two thermodynamic values as the function of the parameter Γ. The scaling invariance is restored for completely uncorrelated replicas ($\varepsilon_{12} = 0$) when the cross-correlation disappears, so $g_{12}(x) = 1$ for all the values of x. The spatial correlation between two replicas is

$$q_{1,2} = \frac{1}{N}\sum_{i=1}^{N} w(|x_i^1 - x_i^2|) \tag{9}$$

$g_{12}(x)$ allows us to calculate the order parameter Q for configurations $\{x_i^1\},\{x_j^2\}$ of the two replicas using the following formula

$$Q = \langle q_{1,2} \rangle = 4\pi\rho^* \int_0^\infty g_{12}(x) w(x) x^2 dx \tag{10}$$

If there is no correlation between two replicas ($g_{12}(x) = 1$), the direct calculation of the "random spatial correlation" performed using the formula (10) results in $Q_r = (7\pi^2 / 128)(c / d^*)^3 \ll 1$. In a supercooled liquid, Q tends to Q_r. However, we can expect it to be higher than in an ideal glass, since the coordinates $\{\vec{x}_i^1\},\{\vec{x}_j^2\}$ of the

atoms of the two replicas are fixed in random equilibrium points $\{X_i\}$. We assume that in the thermodynamic limit, the random first order transition is accompanied by a discrete change in the parameter Q.

3.2. Integral equations

$g_{11}(x)$ and $g_{12}(x)$ pair distribution functions of a symmetric two-replica system can be calculated using the Ornstein–Zernike (OZ) equation which connects the pair correlation function $h_{ij}(x) = g_{ij}(x) - 1$ and the direct correlation function $c_{ij}(x)$ $(1 \le i, j \le 2)$:

$$h_{11}(x) = c_{11}(x) + \rho^*[c_{11} \otimes h_{11}(x) + c_{12} \otimes h_{12}(x), \quad (11)$$

$$h_{12}(x) = c_{12}(x) + \rho^*[c_{11} \otimes h_{12}(x) + c_{12} \otimes h_{11}(x), \quad (12)$$

where $\otimes$ denotes the convolution, ρ^* is the density of each of the equivalent replicas. The OZ equation should be supplemented with the equation of closure between $h_{12}(x)$ and $c_{12}(x)$. A positive definite pair distribution function can always be represented as $g_{ij}(x) = \exp[-\beta v_{ij}(x) + \omega_{ij}(x)]$. We differentiate between a direct (vacuum) interaction $v_{ij}(x)$ an indirect (collective) interaction via environment $\omega_{ij}(x)$. The most common closures used in the study of fluids are the Percus–Yevick (PY), hypernetted chain (HPC), Martynov–Sarkisov (MS), and Rogers–Young (RY) closures. The latter can be used for the function $\gamma_{ij}(x) = h_{ij}(x) - c_{ij}(x)$, which for the first three looks like

$$\gamma_{ij}(x) = \exp(\omega_{ij}(x)) - 1, \; \gamma_{ij}(x) = \omega_{ij}(x),$$
$$\gamma_{ij}(x) = \omega_{ij}(x) + \omega_{ij}^2 / 2. \quad (13)$$

PY is more applicable for repulsive potentials and especially for the hard sphere potential than the HPC closure. However, at lower temperatures and with a moderate density, HPC produces better results than PY for more realistic pair potentials with attractive regions. At the same time, both closures are thermodynamically inconsistent: the characteristics calculated using the equation of state and compressibility result in an error margin of over 10 % [74]. The most thermodynamically consistent closure is the Martynov–Sarkisov closure: the error margin is below 2 % [72–73].

The ROFT theory most commonly employs either the HPC closure or the RY closure

$$g_{ij}(x) = \exp(-\beta v_{ij}(x) \times [1 + \frac{\exp(f_{ij}(x)\omega_{ij}(x)) - 1}{f_{ij}(x)}], (14)$$

where the function $f_{ij}(x) = 1 - \exp(-\alpha_{ij}x)$, depending on the adjusting parameters $\alpha_{11} = \alpha_{22}$ and α_{12}, makes the RY closure thermodynamically consistent. Within the limit $\alpha_{ij} \to \infty$ $(f_{ij}(x) = 1)$ we obtain the previous function definition g_{ij}.

The solutions of the two integral equations (11)–(12) were first obtained in [89] for $\varepsilon_{12} = 0$ by gradually increasing Γ form the stable liquid state ($\Gamma < \Gamma_f$) to $\Gamma \approx 2$, corresponding to a supercooled liquid. The comparison of the values for $g(x)$, obtained via the HNC and RY closures demonstrates that the solution of RY is more structured than that of the HNC. A two-replica system ($\varepsilon_{12} > 0$) is used as an attempt to find a branch corresponding to an ideal glass in the state equation. For each $\Gamma > \Gamma_f$ the solutions of two integral equations are sought for the finite values ε_{12}. The accuracy of the obtained values $h_{12}(x)$ and Q is controlled by the correct limit transition ε_{12} which tends towards zero. It was determined [89] that there are two glass branches: glass G_1 and glass G_2. The first branch corresponds to the equilibrium transition from glass to a crystalline state. The second corresponds to the nonequlibrium transition to the metastable state of a supercooled liquid. Described below are the main assumptions that led to such results [89]. If the correlation of a two-replica system in the limit transition is $h_{12}(x) = 0$ and $Q = Q_r$, the supercooled state of the liquid is restored. Conversely, if the correlation between the configuration is too strong (i.e. if $h_{12}(x) \gg 0$ and $Q \gg Q_r$), the system remains in the state of an ideal glass. [89] describes three algorithms (a, b, c) used to reveal the expected random transition (RFOT) from a supercooled liquid to an ideal glass. In the algorithm a) the initial value ε_{12}^0 is preset and Γ is gradually increased. The central peak appears in $h_{12}(x)$ near $x = 0$, whose amplitude gradually increases with the growth of Γ, since the coupling between the atoms of the opposite replicas becomes stronger. Algorithms b) and c) are based on the gradual transition of a liquid from the "molecular" state to an ideal glass by gradually decreasing ε_{12}^0 from its initially high values corresponding to the strong coupling of the atoms of the opposite replicas. The difference

in the pair distribution function of a supercooled liquid and an ideal glass is demonstrated in Fig. 1.

We should note that the ROFT theory has been so far used to describe spatially homogeneous systems without external fields and far from the boundary surfaces. We suggest using the ROFT theory to describe the structure of a liquid on the boundary with the solid surface by means of equation (3). We first calculate the kernel and the right-hand side of the equation (3) using the RFOT, and then solve the integral equation using common approaches. As a result, we can describe the surface amorphisation of supercooled liquids using the methods of statistical physics.

3.3. Pair structure and thermodynamics

The thermodynamic properties of a supercooled liquid based on the HNC and RY closures for hard sphere liquids without replicas ($\varepsilon_{12} = 0$) for the parameter $\Gamma > \Gamma_f$: excess inner energy per one particle $u_{ex} = U_{ex} / Nk_BT$; the equation of state $\Pi_{ex}(\Gamma) = P / \rho k_BT - 1 = 4u_{ex}(\Gamma)$; and the compressibility $\chi(\Gamma) = \chi_T / \chi_T^{id} = (\partial\beta P / \partial\rho)_T^{-1}$ can be calculated from the pair distribution function $g(x)$ using standard methods [49].

For the HNC approximation, the excess chemical potential $\beta\mu_{ex}$ is also calculated from the function $h(x)$ and $c(x)$ according to (11–12).

The excess free energy per one particle is then calculated from the standard thermodynamic correlation $f_{ex}(\Gamma) = \beta\mu_{ex} - \Pi_{ex}$, while the excess entropy per one particle is described by the formula

$$s_{ex}(\Gamma) = S_{ex} / Nk_B = u_{ex}(\Gamma) - f_{ex}(\Gamma) =$$
$$= \frac{\Gamma}{4} f_{ex}'(\Gamma) - f_{ex}(\Gamma).$$

The RY approximation does not describe μ_{ex} (and therefore f_{ex}) through $h(x)$ and $c(x)$. f_{ex} It is, however, calculated by integrating the inner energy along Γ.

$$f_{ex}(\Gamma) = f_{ex}(\Gamma_0) + 4\int_{\Gamma_0}^{\Gamma} u_{ex}(\Gamma')\frac{d\Gamma'}{\Gamma'}.$$

The initial point Γ_0 can be quite small ($\Gamma_0 \simeq 0.5$), which allows accurate calculation of $\mu_{ex}(\Gamma_0)$ based on the HNC closure, and therefore, integration.

For the supercooled region ($\Gamma > \Gamma_f$) the atomic configurations $\{x_i\}$ remain at the local minimum of the free energy for a long time oscillating near the equilibrium positions $\{X_i\}$. This enables us to differentiate between the "configurational" and entropy contributions to the free energy and entropy
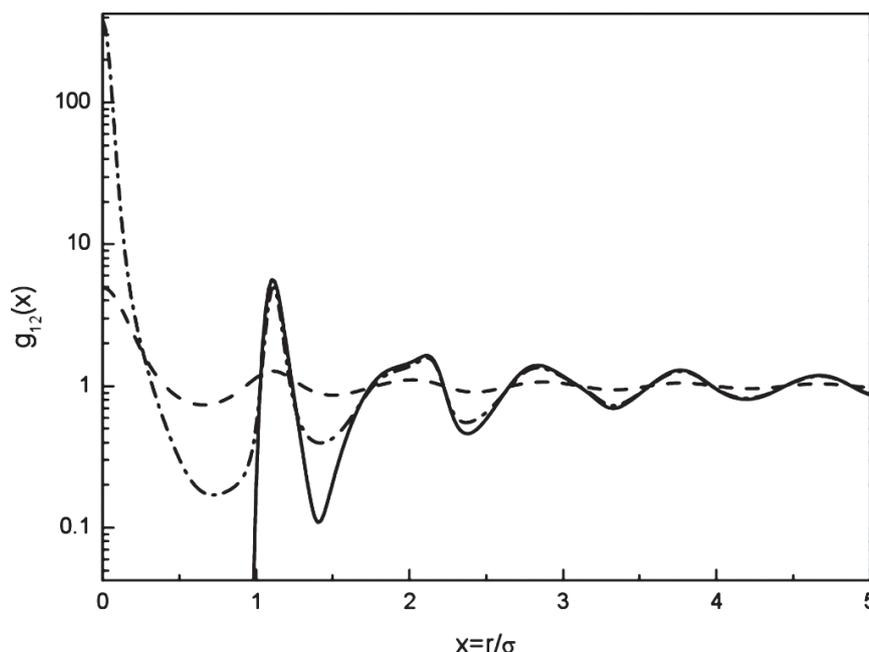

Fig. 1. RY results for the pair distribution function $g_{12}(x)$. $\Gamma = 1.8$. Dotted line denotes branch G_1; dash-and-dot line denotes branch G_2; the solid curve $g(x)$ is given for comparison and denotes the pair distribution function of the supercooled liquid. All pair distribution functions are plotted on a logarithmic scale

$$f = f_{id} + f_{ex} = f_c + f_v \,,$$

$$s = s_{id} + s_{ex} = s_c + s_v \,,$$

where s_c determines the exponentially large number of metastable states in the supercooled liquid $N_m \approx \exp(N s_c)$.

A detailed analysis of the calculation methods of statistical and thermodynamic values by means of numerical modelling is performed in [92–98].

4. Discussion

Let us name the development stages of the theory of classical molecular media.

The statistical theory of thermodynamically equilibrium classical molecular systems is based on the canonical Gibbs distribution. For imperfect gases of low density the statistical integral is calculated as an expansion in powers of density. This expansion is practically inapplicable to dense liquids when calculating the terms with higher exponents.

The problem is somewhat eliminated by the method of integral equations for the particle size distribution functions. There are integral equations describing the structural and thermodynamic properties of liquids with high accuracy (for real molecular systems). However, some basic problems remain unsolved. In particular, we still cannot describe the transitions from a thermodynamic equilibrium state to a metastable state.

A new stage of the statistical theory of classical molecular media is connected with the development of the random first order transition theory, based largely on the extension of the Gibbs distribution to metastable states. However, the random first order transition theory only describes the connection between the structure of a supercooled liquid and an ideal glass, while it does not consider the kinetic process. Nevertheless, a large number of English-language sources focus on the calculation of the structural and thermodynamic properties of real molecular systems. We hope that this overview will compensate for the lack of such studies published in Russian.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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