

CLASSICAL MANY-PARTICLE DISTRIBUTION FUNCTIONS: SOME NEW APPLICATIONS

E.E.Tareyeva, V.N.Ryzhov

Vereschagin Institute for High Pressure Physics,
Russian Academy of Sciences, 142092 Troitzk, Russia

We present a new purely equilibrium microscopic approach to the description of liquid-glass transition in terms of space symmetry breaking of three- and four-particle distribution functions in the cases of two and three dimensions, respectively. The approach has some features of spin glass theories as well as of density-functional theories of freezing.

The main purpose of the report is to present a new purely equilibrium microscopic approach to the description of liquid-glass transition in terms of space symmetry breaking of three- and four-particle distribution functions in the cases of two and three dimensions, respectively. The approach has some features of the spin glass theories as well as of the density-functional theories (DFT) of freezing.

It is usually believed that there are two essential differences between spin glasses and real structural glasses: 1) in the Hamiltonian of spin glasses there is explicit randomness from the very beginning, while in the case of real glasses there is no such randomness. 2) In experiments with spin glasses there is always the range of the concentration of magnetic impurities where nothing else that a spin glass phase appears while in the case of space glass there exists a crystalline ground state. However, in real systems one can consider these differences simply as time scales differences for the freezing of corresponding degrees of freedom with respect to the time scale of the real or computer experiments. In fact, there are now some indications that two possible candidates for equilibrium glasses do exist: some polydisperse hard-sphere systems and some binary mixtures of hard spheres. Even if it is not so, it seems to us that one needs an «underlying» equilibrium theory of liquid-glass transition to understand what really glasses present as space symmetry breaking problem. We should mention that beautiful and fruitful time-dependent mode-coupling theory [1] which describes a number of subtle experimental facts does not consider the problem of space symmetry breaking. Some other arguments can be found in the recent papers by Parisi (see, e.g., [2] and references therein).

To describe different kinds of space symmetry breaking we use the formalism of classical many particle conditional distribution functions

$$F_{s+1}(\mathbf{r}_1|\mathbf{r}_1^0\dots\mathbf{r}_s^0) = \frac{F_{s+1}(\mathbf{r}_1, \mathbf{r}_1^0, \dots, \mathbf{r}_s^0)}{F_s(\mathbf{r}_1^0, \dots, \mathbf{r}_s^0)}.$$

Here $F_s(\mathbf{r}_1, \dots, \mathbf{r}_s)$ is the s -particle distribution function. The functions $F_{s+1}(\mathbf{r}_1|\mathbf{r}_1^0\dots\mathbf{r}_s^0)$ satisfy the equation [3]

$$\begin{aligned} \frac{\rho F_{s+1}(\mathbf{r}_1|\mathbf{r}_1^0\dots\mathbf{r}_s^0)}{z} &= \exp\left\{-\beta \sum_{k=1}^s \Phi(\mathbf{r}_1 - \mathbf{r}_k^0) + \sum_{k \geq 1} \frac{\rho^k}{k!} \int S_{k+1}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) \right. \\ &\quad \left. \times F_{s+1}(\mathbf{r}_2|\mathbf{r}_1^0\dots\mathbf{r}_s^0) \dots F_{s+1}(\mathbf{r}_{k+1}|\mathbf{r}_1^0\dots\mathbf{r}_s^0) d\mathbf{r}_2 \dots d\mathbf{r}_{k+1}\right\}. \end{aligned} \quad (1)$$

Here z is the activity, ρ is the mean number density, $S_{k+1}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1})$ is the irreducible cluster sum of Mayer functions connecting (at least doubly) $k+1$ particles, $\beta = 1/k_B T$ and T is the temperature.

If one takes the derivative of (1) relative to \mathbf{r}_1 , one obtains the equilibrium Bogoliubov hierarchy [4] along with the explicit expression for F_{s+2} as the functional on F_{s+1} which gives the formally exact closure. However it contains infinite series and integrals and one has to use some approximations to exploit it. The same can be said about the Eq.(1) itself.

Let us now consider the symmetry breaking of the one-particle distribution function and formulate briefly DFT of freezing (see [6] and the reviews [7]). The equation (1) for $s=0$ is the extremum condition for the free energy functional of the inhomogeneous system with the density $\rho(\mathbf{r}) = \rho F_1(\mathbf{r})$ and has the form:

$$\begin{aligned} \mathcal{F}/k_B T &= \int d\mathbf{r}_1 \rho(\mathbf{r}_1) [\ln(\lambda^d \rho(\mathbf{r}_1)) - 1] - \\ &- \sum_{k \geq 1} \frac{1}{(k+1)!} \int \dots \int S_{k+1}(\mathbf{r}_1 \dots \mathbf{r}_{k+1}) \rho(\mathbf{r}_1) \dots \rho(\mathbf{r}_{k+1}) d\mathbf{r}_1 \dots d\mathbf{r}_{k+1} \end{aligned} \quad (2)$$

or

$$\mathcal{F}/k_B T = \int d\mathbf{r}_1 \rho(\mathbf{r}_1) [\ln(\lambda^d \rho(\mathbf{r}_1)) - 1] - \mathcal{F}_{ex}[\rho(\mathbf{r})]/k_B T. \quad (3)$$

The excess free energy $\mathcal{F}_{ex}[\rho(\mathbf{r})]/k_B T$ is just the generating functional for direct correlation functions

$$c_n(\mathbf{r}_1 \dots \mathbf{r}_n) = \frac{\delta^n \mathcal{F}_{ex}[\rho(\mathbf{r})]/k_B T}{\delta \rho(\mathbf{r}_1) \dots \delta \rho(\mathbf{r}_n)}, \quad (4)$$

so that Taylor expansion around the liquid can be written in the following form:

$$\beta \Delta F = \int d\mathbf{r} \varrho(\mathbf{r}) \ln \frac{\varrho(\mathbf{r})}{\varrho_0} - \sum_{k \geq 2} \frac{1}{k!} \int c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \Delta \varrho(\mathbf{r}_1) \dots \Delta \varrho(\mathbf{r}_k) d\mathbf{r}_1 \dots d\mathbf{r}_k, \quad (5)$$

where

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_l$$

is the local density difference between solid and liquid phases.

The full system of equations to be solved in DFT contains the nonlinear integral equation for the function $\rho(\mathbf{r})$, obtained as the extremum condition for the free energy and the equilibrium conditions for the chemical potential and the pressure written in terms of the same functions as in (5). To proceed constructively in the frame of DFT we must choose a concrete form of the free energy functional — a kind of closure or truncating — and we must make an ansatz for the average density of the crystal. The importance of such an ansatz follows from the fact that we are dealing with a theory which is equivalent to Gibbs distribution and one has to break symmetry following the Bogoliubov concept of quasiaverages [5]. Now it is necessary to specify the crystal symmetry (e.g., lattice type) and to locate the freezing transition for that particular lattice type

$$\begin{aligned}\Delta\rho(\mathbf{r}) &= \rho_l \sum_{\mathbf{k}} \varphi_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} = \rho_l \varphi_0 + \rho_l \varphi(\mathbf{r}), \\ \varphi_{\mathbf{k}} &= \frac{1}{\Delta} \int_{\Delta} \frac{\Delta\rho(\mathbf{r})}{\rho_l} e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}.\end{aligned}\quad (6)$$

The sum is over reciprocal lattice vectors and the integral is taken over the elementary lattice cell Δ . $\varphi_{\mathbf{k}}$ are the order parameters of the problem. The DFT approach occurs to be very fruitful and was used to calculate a lot of melting curves for different systems.

The 3D DFT scenario of freezing is valid for some 2D systems. However, there is a number of 2D systems which melts through two continuous phase transition including intermedeate (so-called hexatic) anisotropic liquid phase. The scenario for such a case of 2D melting is the well-known KTNHY [8] phenomenological scenario. We develop a microscopic approach to 2D melting [9, 10] in the spirit of 3D DFT. Our approach differs from the standard DFT theory of freezing in two main points: First, we allow the Fourier coefficients $\rho_{\mathbf{G}}(\mathbf{r})$ of the one-particle distribution function expanded in a Fourier series in reciprocal-lattice vectors $\{\mathbf{G}\}$: $\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}(\mathbf{r}) e^{i\mathbf{G}\mathbf{r}}$ to fluctuate and to have amplitude and phase. Second, we allow the liquid to be anisotropic: we consider as possible the existence of a phase with constant density but angular dependent two-particle distribution function $F_2(\mathbf{r}_1 - \mathbf{r}_0) \neq g(r_{10})$.

These two points of generalization define two new order parameters: the fluctuating $\rho_{\mathbf{G}}(\mathbf{r})$ and the Fourier coefficients characteristic for the broken symmetry of the function $F_2(\mathbf{r}_1 - \mathbf{r}_0)$. Our approach again is based on the Eq.(1) but now, considering hexatic phase, we are dealing with the bifurcation of the solution for the two-particle distribution function. The relative spatial distribution of pairs of particles is characterized by the function $F_2(\mathbf{r}_1|\mathbf{r}_0) = F_2(\mathbf{r}_1 - \mathbf{r}_0)$. The vector $\mathbf{r}_1 - \mathbf{r}_0$ defines the direction of the bond between the molecules at the points \mathbf{r}_1 and \mathbf{r}_0 . In the ordinary isotropic liquid the nearest neighbouring of a given

molecule (the first coordination sphere) has a definite local symmetry, which can be characterized by the set of bond directions. The local structure of the liquid in the neighbourhood of a molecule at the point \mathbf{r}'_0 is characterized by the bond directions $\mathbf{r}' = \mathbf{r}_2 - \mathbf{r}'_0$. It occurs that if the point \mathbf{r}'_0 is at sufficiently large distance from \mathbf{r}_0 then there is no correlation between the directions $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_0$ and $\mathbf{r}' = \mathbf{r}_2 - \mathbf{r}'_0$. In this case after the averaging over the system as a whole the pair distribution function transforms into the RDF and the equation (1) for $s = 1$ has the solution $F_2(\mathbf{r}_1 - \mathbf{r}_0) = g(|\mathbf{r}_1 - \mathbf{r}_0|)$, which corresponds to ordinary isotropic liquid. When we approach the anisotropic liquid phase the long-ranged correlations between the bond directions \mathbf{r} and \mathbf{r}' do appear and the averaged two-particle distribution function depends on the bond direction now.

In the vicinity of the transition one can write

$$F_2(\mathbf{r}_1, \mathbf{r}_0) = g(|\mathbf{r}_1 - \mathbf{r}_0|)(1 + f(\mathbf{r}_1 - \mathbf{r}_0)), \quad (7)$$

where $f(\mathbf{r}_1 - \mathbf{r}_0)$ has the symmetry of the local neighbourhood of the particle at \mathbf{r}_0 . The bifurcation point is given by the linearized equation (1) for $s = 1$, namely,

$$f(\mathbf{r}_1 - \mathbf{r}_0) = \int \Gamma(\mathbf{r}_1, \mathbf{r}_0, \mathbf{r}_2) f(\mathbf{r}_2 - \mathbf{r}_0) g(|\mathbf{r}_2 - \mathbf{r}_0|) d\mathbf{r}_2, \quad (8)$$

where

$$\begin{aligned} \Gamma(\mathbf{r}_1, \mathbf{r}_0, \mathbf{r}_2) = & \sum_{k \geq 1} \frac{\rho^k}{(k-1)!} \int S_{k+1}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) \\ & \times g(|\mathbf{r}_3 - \mathbf{r}_0|) \dots g(|\mathbf{r}_{k+1} - \mathbf{r}_0|) d\mathbf{r}_3 \dots d\mathbf{r}_{k+1}. \end{aligned} \quad (9)$$

At the same time, when one approaches the line defined by the bifurcation condition, the correlation radius for the orientation fluctuations of the pair distribution function diverges. This fact can be shown with the use of the gradient expansion technique in the case of the equation (1) for $s = 3$, if we write the long range part of the correlator using the principle of vanishing correlations ([4]) as:

$$F_4(\mathbf{r}_1, \dots, \mathbf{r}_4) = g(|\mathbf{r}_1 - \mathbf{r}_2|)g(|\mathbf{r}_3 - \mathbf{r}_4|)(1 + f_4(\mathbf{r}_1, \dots, \mathbf{r}_4)) \quad (10)$$

$$f_4(\mathbf{r}_1, \dots, \mathbf{r}_4) = f_4(r, R, \rho, \varphi_1, \varphi_2).$$

Here φ_1 is the angle between the vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the axis $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_3$, φ_2 is the angle between the vector $\rho = \mathbf{r}_3 - \mathbf{r}_4$ and the same axis. We have $f_4(r, R, \rho, \varphi_1, \varphi_2) \rightarrow 0$ when $R \rightarrow \infty$.

The microscopic expressions for the elastic moduli and Frank constant [10] enable us to understand on the microscopic level whether the 2D melting for any given potential is 3D like or whether it follows the KTHNY scenario.

Let us consider now a possible description of the liquid-glass transition in terms of space symmetry breaking for three- (four) particle distribution function in 2D (3D) systems. At high temperature the nearest neighbours of a molecule can take different relative positions and there is no short-range order (SRO). At lower temperature a SRO appears which can be of different kinds at different densities (for phase transitions in liquids see [11]). The rotation and the translation of the clusters of preferred symmetry give rise to the fact that one-particle and two-particle distribution functions remain isotropic. If a kind of bond orientational order (BOO) appears the clusters are oriented in similar way and the two-particle distribution function becomes to be anisotropic (as in 2D hexatic phase). However, we can imagine another situation — freezing of the symmetry axes of the clusters in different position. The isotropic phase can be considered as analogous to the paramagnetic phase (of cluster symmetry axes), the BOO phase — to the ferromagnetic phase, and the mentioned freezed phase — to a spin glass phase.

Let us consider for simplicity a 2D system. In the vicinity of the transition one can write (in the superposition approximation for the liquid)

$$F_3(\mathbf{r}_1|\mathbf{r}_1^0, \mathbf{r}_2^0) = g(|\mathbf{r}_1 - \mathbf{r}_1^0|)g(|\mathbf{r}_1 - \mathbf{r}_2^0|)(1 + f_3(\mathbf{r}_1|\mathbf{r}_1^0, \mathbf{r}_2^0)). \quad (11)$$

In 2D case $f_3(\mathbf{r}_1|\mathbf{r}_1^0, \mathbf{r}_2^0)$ depends in fact on two distances and two angles

$$f_3(\mathbf{r}_1|\mathbf{r}_1^0, \mathbf{r}_2^0) = f_3(R_0, \phi_0; R_1, \Theta_1), \quad (12)$$

where $\mathbf{R}_0 = \mathbf{r}_2^0 - \mathbf{r}_1^0$, $\mathbf{R}_1 = \mathbf{r}_1 - \mathbf{r}_1^0$, $\mathbf{R}_2 = \mathbf{r}_2 - \mathbf{r}_1^0$ and ϕ_0 is the angle of the vector \mathbf{R}_0 with the z axis, Θ_1 — the angle between \mathbf{R}_1 and \mathbf{R}_0 and Θ_2 — the angle between \mathbf{R}_2 and \mathbf{R}_0 .

The linearization of (1) for $s = 2$ gives:

$$\begin{aligned} & f_3(R_0, \phi_0; R_1, \Theta_1) = \\ & = \int \Gamma'(R_0, \phi_0; \mathbf{r}_2; R_1, \Theta_1) f_3(R_0, \phi_0; R_2, \Theta_2) g(|\mathbf{R}_2 - \mathbf{R}_0|) g(R_2) d\mathbf{r}_2, \end{aligned} \quad (13)$$

where

$$\begin{aligned} \Gamma'(R_0, \phi_0; \mathbf{r}_2; R_1, \Theta_1) = & \sum_{k \geq 1} \frac{\rho^k}{(k-1)!} \int S_{k+1}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) g(|\mathbf{r}_3 - \mathbf{r}_1^0|) \\ & \times g(|\mathbf{r}_3 - \mathbf{r}_2^0|) \dots g(|\mathbf{r}_{k+1} - \mathbf{r}_1^0|) g(|\mathbf{r}_{k+1} - \mathbf{r}_2^0|) d\mathbf{r}_3 \dots d\mathbf{r}_{k+1}. \end{aligned} \quad (14)$$

There are two kinds of angles entering the equations and two kinds of order parameters, consequently. One angle (ϕ_0) fixes the position of one pair of particles of the cluster, and the other (Θ_i) — the position of the third particle in the coordinate frame defined by ϕ_0 . The order parameter connected with Θ_i is the generalization of intracluster hexatic parameter for the case of different coordinate

frames. The order parameter connected with ϕ_0 is an analogue of magnetic moment and in glass-like phase one can consider an Edwards-Anderson parameter $\langle \cos \phi_0(t) \cos \phi_0(0) \rangle$. In such a way we come to the concept of a «conditional» long range order: if we consider two pairs of particles at infinite distance from one another then there exists a preferable possibility for the relative position of the third particle near each pair. The directions of the bonds in the pairs of particles themselves are subjects to spin-glass-like order. In 3D case the rotation of clusters is given by matrices $D_{lm}^{l'm'}(\vec{\omega}_{0i})$ so that we obtain a kind of orientational multipole glass for the clusters.

This work was partially supported by Russian Foundation for Basic Researches, grant No. 98-02-16805.

REFERENCES

1. For review see, **Götze W.** — Liquid, freezing and glass transition. Les Houches, 1989, J.P.Hansen, D.Levesque, J.Zinn-Justin editors, North Holland.
2. **Coluzzi B., Parisi G., Verrocchio P.** — Lennard-Jones Binary Mixtures: a Thermodynamic Approach to Glass Transition, cond-mat/9904124.
3. The first derivation of the eq. (1) by use of Bogoliubov functional method [4] was given by **Arinshtain E.A.** — Dokl. Akad. Nauk (USSR), 1957, v.112, p.615. See also **Stillinger F.H., Buff F.P.** — J. Chem. Phys., 1962, v.37, p.1; **Ryzhov V.N.** — Thesis, JINR, Dubna, Russia, 1981.
4. **Bogoliubov N.N.** — Problems of Dynamical Theory in Statistical Physics. M.: Gostekhizdat, 1946.
5. **Bogoliubov N.N.** — JINR Preprint R-1451, Dubna, 1963; Phys. Abh. S.U., 1962, v.6, 1, p.113, 229.
6. **Ramakrishnan T.V., Youssoff M.** — Phys. Rev., 1979, v.B19, p.2775; **Ryzhov V.N., Tareyeva E.E.** — Phys. Lett., 1979, v.A75, p.88; Theor. Math. Phys. (Moscow), 1981, v.48, p.416; **Haymet A.D.J., Oxtoby D.W.** — J. Chem. Phys., 1981, v.74, p.2559.
7. **Singh Y.** — Phys. Rep., 1991, v.207, p.351; **Baus M.** — J. Phys.: Condens. Matter, 1989, v.1, p.3131; **Löwen H.** — Phys. Rep., 1994, v.237, p.249.
8. **Kosterlitz M., Thouless D.J.** — J. Phys., 1973, v.C6, p.1181; **Halperin B.I., Nelson D.R.** — Phys. Rev. Lett., 1978, v.41, p.121; **Nelson D.R., Halperin B.I.** — Phys. Rev., 1979, v.B19, p.2457; **Young A.P.** — Phys. Rev., 1979, v.B19, p.1855.
9. **Ryzhov V.N., Tareyeva E.E.** — Theor. Math. Phys. (Moscow), 1987, v.73, p.463; J. Phys., 1988, v.C21, p.819; Phys. Lett., 1991, v.A158, p.321. **Ryzhov V.N.** — Theor. Math. Phys. (Moscow), 1989, v.80, p.107; J. Phys.: Condens. Matter, 1990, v.2, p.5855; Zh. Eksp. Teor. Fiz., 1991, v.100, p.1627 [Sov. Phys. JETP, 1991, v.73, p.899].
10. **Ryzhov V.N., Tareyeva E.E.** — Theor. Math. Phys. (Moscow), 1992, v.92, p.331; Theor. Math. Phys. (Moscow), 1993, v.96, p.425; Phys. Rev., 1995, v.B51, No.14, p.8789-8794; JETP (Moscow), 1995, v.108, p.2044.
11. See, e.g., **Debenetti P.G.** — Metastable Liquids. Princeton Univ. Press, Princeton, 1997; **Angell C.A.** — Science, 1995, v.267, p.1924; **Roberts C.J., Debenetti P.G.** — J. Chem. Phys., 1996, v.105, p.658.