Freezing transition in three and two dimensions by the
generalized density functional theory

E. E. Tareyeva and V. N. Ryzhov

Verecshagin Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142092,
Moscow region, Russia

Freezing is one of the most universal phenomena in nature. The ability to crystallize is common to quite different systems: systems of simplest atoms as well as of large molecules of complicated shape, systems of neutral as well as of charged particles, artificial colloidal suspensions of polysterene spheres as well as ionic plasma in white dwarfs.

The freezing transition may be induced either by cooling or by compression, and the problem of measuring melting curves is a classic one, having long standing history. To–day, due to the diamond anvil technique some melting curves are known with great accuracy and up to Megabar pressures. Nevertheless, the detailed microscopic mechanisms even of the classical phenomenon of 3D melting are far from being understood.

There are new problems which gained much interest during last decades connected with the problem of non periodic intermediate or ground states. A system which under normal conditions freezes into a crystalline phase can be made to freeze into either a quasicrystalline or glassy state by a suitable change in the rate of cooling. Further, there are systems in nature which do not transform directly from isotropic liquid to crystalline solid but exhibit a number of intermediate phases. Among those are surely some 2D systems and liquid crystals.

It is interesting to notice that although the window glass is widely used for a very long time, a great number of experimental investigations on glasses has been realized just during last decade. Two discoveries seem me the most fascinating among them. First, the fact that the most part of water in the Universe occurs to be in the glass state, being condensed from the gaseous phase at very low temperatures. Second, it is just the transition to a glassy state and the slowing of diffusion processes that provide the possibility of alimentary
product conservation and the life continuation in the desert.

There is no general theoretical argument that thermodynamically stable solid states must have a periodic density distribution (see 2). Evidence for the linear stability of aperiodic packing to small few-particle displacements can be obtained from a self-consistent phonon theory. In the density– functional theory (DFT) by Singh et al. 4 to the glass transition a first-order transition at the negative pressure was obtained. In this connection the papers by Stishov 5, 6 on phase transitions in expanded matter should be mentioned. Interesting indications can be found also in the theory of spin systems.

The study of disordered spin systems has become a rich and productive science. It seemed some time ago that attention completely shifted to neural networks. However, quite recently a number of papers has appeared concerning the possibility of obtaining a kind of spin glass regime in initially non-random systems. Glasses, of course, have no disorder in their Hamiltonian – the randomness is formed in the transition. The deterministic spin models with self-induced quenched disorder represent a convenient candidate to describe real glasses. Great expectations can be connected with the using of the methods of spin glass theory in the theory of real glasses, particularly if combined with DFT of freezing.

There is another new aspect of the problem in question, which is connected with a new concept which appears in the physics of liquid–solid transition just before 1980: bond orientational ordering. If we consider crystallization as a broken symmetry transition we can see that two distinct broken symmetries distinguish crystalline solid from isotropic liquids: translational and rotational ones. These two symmetries are not independent, because rotating one patch of perfect crystal relative to another clearly disrupts not only orientational correlations, but translational correlations as well. A relative translation of the two patches, on the other hand, decorrelates translational order, but leaves orientational correlations intact. In such a way one can obtain an exotic fluid or glass state of matter with extended correlations in the orientations of locally-defined crystallographic axes, but with short-range translational order. This subtle type of order is called bond-orientational order (BOO) (a
"bond" joining near-neighbor atoms) Anisotropic fluids of this kind are a part of recent theories of 2D melting proposed by Halperin and Nelson and Young and based on the ideas of Kosterlitz and Thouless. This KTHNY theory predicts that the transition may be fundamentally different from that observed in ordinary three-dimensional systems. It was found that the transition between two-dimensional solid and isotropic liquid can occur via two continuous transitions corresponding, respectively, to dissociation of dislocations and disclinations. The intermediate phase with BOO was called the hexatic phase. The properties of the hexatic phase are similar to those of a nematic liquid crystal, but with a cluster of spherical atoms instead of extended molecules. This theory has strong support from experiments with electrons on helium, computer simulations of 2D electron systems, experiments with polystyrene spheres and others. However, a conventional first-order transition between the two-dimensional solid and isotropic liquid is also a possibility.

There are some indications that BOO can exist in three-dimensional fluids and glasses, too (Steinhardt, Nelson, Toner, Hess, Mitus and Patashinskii, Ryzhov). It should be emphasized, however, that there is a great difference between 2D and 3D cases. In two dimensions the symmetry of elementary clusters is crystallographic so that they can simply order in a crystal. In three dimensions the energetically preferable symmetry of clusters for standard potentials is usually icosahedral, incompatible with 3D crystal. In the frame of the fivefold symmetry one can pack only 96 (not infinite number) particles. This means that the cooling of three-dimensional analog of hexatic phase can not give the icosahedrons packing into regular three-dimensional crystal: the clusters must be destroyed before the crystallization takes place. It is easier to obtain such a crystal from usual (not supercooled) liquids, where there are crystallographic – hexagonal and cubic – clusters. As to supercooled anisotropic liquid with icosahedral clusters – it possibly freezes into a glass phase. We shall discuss the problem of BOO later in more details.

Now it is the time to make a remark about 2D crystals. Strictly speaking there is no 2D crystals in the thermodynamic limit: they are destroyed by fluctuations. In 1935 Peierls has shown that if the temperature is nonzero then the longwavelength phonons destroyed
long range order in 2D crystals: the meansquare deviations of atoms from their equilibrium positions increase logarithmically with the size of system and the Bragg diffraction peaks become smoothed. Later such absence of two-dimensional long-range order was proved by Mermin with the use of well known Bogoliubov inequalities (1/q² theorem) for correlators. Now it is clear that one can discuss the quasilongrange translational order in 2D systems. The appearance of such an order means that the long-range correlations change the character of decay from exponential to algebraic.

In this report we shall discuss some theoretical aspects of the phenomenon of freezing, mainly the density–functional theory of the freezing of 3D and 2D systems. The fascinating problem of glass formation remains beyond the scope of this report, although there are some indications on the applicability of DFT in this case, too. This report has no intention of completeness. The chosen list of results and references is influenced by the authors own experience in DFT of freezing and in two-dimensional melting as well as by fruitful discussions with high-pressure physicists.

A great deal of information on the phenomenon of freezing can be found in reviews (see, for example, the reviews Ref.16–18 and Les Houches sessions19,20 of 1988 and 1989 for 3D systems and21,22 for the 2D case).

I shall begin with some very simple facts which are not widely known because the crystallization problems are usually avoided in courses and in standard manuals and textbooks.

The crystallization transition is strongly first-order in three-dimensions and is marked by large discontinuities in entropy, density and order parameters. The correlation functions remain short-ranged near the transition. In spite of this the transition is known to have a kind of quasuniversal behaviour. One can mention the following "universalities".

1. The Lindemann criterion states that the crystal melts when the ratio of the root-mean-squared thermal vibration amplitude to the nearest-neighbour spacing attains a certain critical value (∼0.1). The Lindemann criterion has been found to be reasonably correct for a number of simple systems. From computer simulations and indirectly, from
experiments, the ratio is indeed seen to be about 0.09 for close packed fcc structures and about 0.12 for open bcc structures. This is rather close to the actual melting point and gives a quasi-universal criterion of melting.

2. A comparable one-phase criterion, known as the Hansen-Verlet criterion\textsuperscript{23}, exists on the fluid side of the coexistence curve. During a course of extensive computer simulations of simple fluids, Hansen and Verlet found that the amplitude of the main peak of the structure factor $S(k_m)$ is approximately constant along the crystallization line. There is direct experimental evidence that simple fluids as different as sodium and argon, in addition to model systems such as a hard-spheres fluid, the LJ fluid, one–component plasma (OCP) etc., all freeze when $S(k_m) \simeq 2.9 \pm 0.1$.

3. There is a kind of universality in the form of melting curves. Except some exotic curves with maxima in p-T coordinates they are monotonic and have no critical end points. There are three variants of tricritical points: Liquid-Gas-Solid; LiquidI-LiquidII-Solid; Liquid-SolidI-SolidII. The examples of calculations of such curves with tricritical points can be found in the recent papers by Baus and coworkers\textsuperscript{24–26} where the role of repulsive and attractive parts of pair potential in crystallization is analyzed in detail.

4. There is a kind of universality in the behaviour of thermodynamic functions along melting curves. It seems that the entropy change on melting is constant for a given material and that there is the following trend\textsuperscript{16,17}:

$$\frac{\Delta S}{R} \to \ln 2 \text{ when } \frac{\Delta V}{V_s} \to 0.$$ 

5. Closely connected with the previous "universality" is a kind of well known "scaling" observed in the course of detailed investigation of the freezing of soft spheres systems with inverse power potential:

$$u(r) = \varepsilon (\sigma / r)^n,$$

where $\varepsilon$ and $\sigma$ measure the strength and the characteristic length of the interaction. The reduced excess thermodynamic properties of the soft spheres depend on a single
variable which is defined as

\[ \gamma = (\rho \sigma^3) \left( \frac{\varepsilon}{k_B T} \right)^{3/n} = \rho^* T^{3/n}. \]

Freezing of soft-spheres fluids have been extensively studied by MC simulation for several values of the exponent \( n \), e.g., \( n = 12, 27, 9, 6, 4 \). The two extreme cases are: the HS system \( (n = \infty) \), and one component plasma (OCP) \( (n = 1) \). The computer simulations have revealed some symmetric trends in the melting properties of soft spheres when \( n \) decreases from \( \infty \) to OCP. The relative volume change on melting decreases rapidly with \( n \), while the entropy change per particle on melting is relatively insensitive to \( n \). Moreover, the more repulsive systems \( (n \geq 7) \) freeze into a close-packed fcc structure, while the soft repulsions \( (n \leq 7) \) lead to crystallization into a bcc phase. The Lindemann and the Hansen-Verlet criterion are exactly obeyed for any \( n \). There is also rather general result by Weeks who has shown for the case of arbitrary dimensions that for systems interacting by means of purely repulsive power-law potentials, \( \sim r^{-m} \), the change in specific volume \( \Delta v \) on melting approaches zero as \( m \to d \), where \( d \) is the dimensionality of the system.

All these facts are pointing towards the possibility of existing an underlying theory. But, in fact, there is no such theory so far. It should be emphasized that although the freezing is an example of phase transition but different theoretical methods employed for the study of other types of phase transitions cannot be employed in this case: 1) Many phase transition theories are based on lattice models: many magnetic transitions, gas-liquid transition. For the liquid-crystal transition lattice models have not proved very successful because the periodicity imposed by the lattice cannot be separated from the spontaneous order that ought to arise upon crystallization. 2) The renormalization group (RG) approach has not found much use for studying first-order transitions. 3) Computer simulations have given a great deal of information, but again have limitations. The system sizes that can be simulated are small, and the time scales are short. The question always remains whether the time scale of the simulation is sufficient to reach a true equilibrium between two phases. That
is why density functional theories (DFT) of freezing occur to be rather useful although they have their own limitations, too. DFT is ”good” particularly for hard core potentials and for high densities because it is a geometrical theory based on packing picture entering the theory through direct correlation function (DCF). However the conventional DFT occurs to fail in the case of long range potentials and can not describe the melting of some two–dimensional systems.

Now we shall briefly recall the main points of the conventional DFT of freezing, list some of the most interesting recent results in DFT and discuss our results on the amelioration of this theory. Particularly, we shall reformulate the basic equations of the DFT as to describe 2D melting in terms of distribution and correlation functions. The resulting integral equations theory can be considered as a variant of DFT theory appropriate to 2D melting and, possibly, glass transition.

The physical idea behind the DFT is the fact that at the freezing transition the correlation length is only a few atomic spacings. All phenomena at distances greater than the correlation length can be treated in a mean-field approximation. Implicit in this approach is an assumption according to which a system is either entirely in the liquid or entirely in the ordered phase, where no phase coexistence is permitted. Fluctuations are thought to be not of great importance in a completely entropy-driven first-order transition.

The DFT approach to crystallization is based on the theorem that the Helmholtz free energy $F[\rho(\mathbf{r})]$ of an inhomogeneous system is a unique functional of the one–particle density $\rho(\mathbf{r})$, which in a crystalline solid is extremely inhomogeneous. The mathematics of DFT is the bifurcation theory for the solutions of nonlinear integral equations for one–particle distribution function. This idea first appeared in the papers by Kirkwood and Monroe\textsuperscript{35}, Tyablikov\textsuperscript{36} and Vlasov\textsuperscript{37}.

The first papers on the DFT approach to crystallization problem appeared in 1979–1981\textsuperscript{38–41}.

To describe freezing in three (and two) dimensions we shall follow our papers\textsuperscript{39, 40, 43} and use a new formalism – that of classical many–particle conditional distribution functions.
These functions \( F(\mathbf{r}_1 | \Psi) \) give the probability of finding a particle at \( \mathbf{r}_1 \) in the external field \( \Psi(\mathbf{r}_1) \). The equations for these functions can be obtained from the non-linear integral equation for the singlet distribution function \( F(\mathbf{r}_1 | \Psi) \) in an external field \( \Psi(\mathbf{r}_1) \):

\[
\rho \frac{F(\mathbf{r}_1 | \Psi)}{z} = \exp \left\{ -\beta \Psi(\mathbf{r}_1) + \sum_{k \geq 1} \frac{\rho^k}{k!} \int S_{k+1}(\mathbf{r}_1, \ldots, \mathbf{r}_{k+1}) \right. \\
\left. \times F(\mathbf{r}_2 | \Psi) \cdots F(\mathbf{r}_{k+1} | \Psi) \, d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1} \right\},
\]

(1)

Here \( z \) is the activity, \( \rho \) is the mean number density, \( S_{k+1}(\mathbf{r}_1, \ldots, \mathbf{r}_{k+1}) \) 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.

This equation was derived for canonical ensemble by Arinstein on the base of Bogoliubov functional method and then rederived (for the case of small \( \rho \)) by Stillinger and Buff who have used the diagram technique. The simplest way to derive it in the case of grand canonical ensemble was given by Ryzhov.

If the external field has the form

\[
\Psi(\mathbf{r}_1) = \sum_{k+1}^s \Phi(\mathbf{r}_1 - \mathbf{r}_k^0)
\]

where \( \Phi(r) \) is the interparticle potential, then the function \( F(\mathbf{r}_1 | \Psi) \) is the probability of finding a particle at \( \mathbf{r}_1 \), if \( s \) particles are at the points \( \mathbf{r}_1^0, \ldots, \mathbf{r}_s^0 \)

\[
F(\mathbf{r}_1 | \Psi) = F_{s+1}(\mathbf{r}_1 | \mathbf{r}_1^0 \cdots \mathbf{r}_s^0) = \frac{F_{s+1}(\mathbf{r}_1, \mathbf{r}_1^0, \ldots, \mathbf{r}_s^0)}{F_s(\mathbf{r}_1^0, \ldots, \mathbf{r}_s^0)}.
\]

Here \( F_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \) is the \( s \)-particles distribution function.

In this case the equation (1) takes the form

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

(2)

The value of \( z \) in general case can be obtained from the normalization condition

\[
\frac{1}{V} \int F_{s+1}(\mathbf{r}_1 | \mathbf{r}_1^0 \cdots \mathbf{r}_s^0) \, d\mathbf{r}_1 = 1.
\]

(3)
If one takes the derivative of (2) relative to \( r_1 \), one obtains the equilibrium BBGKY hierarchy:

\[
k_B T \nabla_1 F_{s+1}(r_1, r_0^1, ..., r_s^0) + F_{s+1}(r_1, r_0^1, ..., r_s^0) \nabla_1 \sum_{k+1}^s \Phi(r_1 - r_k^0) + \\
\rho \int \nabla_1 \Phi(r_1 - r_s) F_{s+2}(r_1, r_2, r_0^1, ..., r_s^0) \, dr_2 = 0,
\]

along with the explicit expression for \( F_{s+2} \) as the functional on \( F_{s+1} \):

\[
F_{s+2}(r_1, r_2, r_0^1, ..., r_s^0) = F_s(r_0^1, ..., r_0^s) e^{-\beta \Phi(r_1 - r_2)} F_{s+1}(r_1 | r_0^1...r_s^0) F_{s+1}(r_2 | r_0^1...r_s^0)
\times \sum_{k \geq 1} \rho^{k-1} \frac{1}{(k-1)!} \int \cdots \int S_{k+1}(r_1, ..., r_{k+1}) \frac{\partial S_{k+1}}{\partial f(r_{12})} F_{s+1}(r_3 | r_0^1...r_s^0) \cdots \\
... F_{s+1}(r_{k+1} | r_0^1...r_s^0) \, dr_3 \cdots dr_{k+1},
\]

with

\[
f(r_{12}) = e^{-\beta \Phi(r_{12})} - 1
\]

This equation gives the 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.(2) itself. It is formally closed although the gain is not obvious: the price is the infiniteness of series.

The free energy functional (FEF) of such inhomogeneous system with the density \( \rho(r) = \rho_F(r) \) has the form:

\[
\mathcal{F}/k_B T = \int d\mathbf{r}_1 \rho(\mathbf{r}_1) [\ln(\lambda^d \rho(\mathbf{r}_1)) - 1] - \\
- \sum_{k \geq 1} \frac{1}{(k+1)!} \int \cdots \int \frac{\partial S_{k+1}}{\partial f(r_{12})} \rho(\mathbf{r}_1) \cdots \rho(\mathbf{r}_{k+1}) \, dr_1 \cdots dr_{k+1}.
\]

or

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

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

\[
c_n(\mathbf{r}_1...\mathbf{r}_n) = \frac{\delta^n \mathcal{F}_{ex}[\rho(\mathbf{r})]/k_B T}{\delta \rho(\mathbf{r}_1)\cdots \delta \rho(\mathbf{r}_n)}. \tag{7}\]
If the external field is the potential of atom held fixed at the origin then the functional to be extremized depends only on the one particle distribution function $\varrho(r)$ and we can write the Taylor expansion for the excess free energy around the liquid in the following form:

$$\beta \Delta F = \int d\varrho(r) \ln \frac{\varrho(r)}{\varrho_0} - \sum_{k \geq 2} \frac{1}{k!} \int c^{(n)}(r_1, ..., r_k) \Delta \varrho(r_1) ... \Delta \varrho(r_k) dr_1 ... dr_k,$$

where

$$\Delta \varrho(r) = \varrho(r) - \varrho_l$$

is the local density difference between solid and liquid phase.

Integral equation for $\Delta \varrho(r)$ which extremizes $\Delta F$ is formally closed and nonlinear. The bifurcation point of the trivial solution of this equation determines temperature and pressure when the nontrivial solution appears. This is the point of absolute instability of liquid phase against nonconstant density state formation. It can be obtained through exact linearisation of the Eq.(8). We can obtain

$$\nabla_1 \ln \varrho(r_1) = \int d\varrho_2 c_2(r_1, r_2) \nabla_2 \varrho(r_2).$$

or, for the Fourier–transforms:

$$\delta \varrho(k) = -\beta \rho S(k) \tilde{U}(k),$$

$$S(k) = 1 + \rho \int dke^{ikr}[g(r) - 1].$$

$S(k)$ has the following form in terms of DCF:

$$S(k) = \frac{1}{1 - \rho \tilde{c}_2(k)}$$

Now one can see that the poles of the structure factor $S(k)$ (the instability points) given by the Eq. (11) are the points of mechanical instability of the system.

In order to obtain the actual point of the phase transition one must use the conditions of equality of chemical potentials and pressures for liquid and solid phases and to compare the free energy values.

The full system of equations to be solved in the DFT contains the nonlinear integral equation for the function $\rho(r)$, obtained as the extremum condition for the excess free energy and the equilibrium conditions.
\[(T_1 = T_2); \quad P_1 = P_2; \quad \mu_1 = \mu_2; \quad (12)\]

with \(\mu_i\) - the chemical potential and \(P_i\) - the pressure of the \(i\)-th phase, written in terms of the same functions as in (8). Namely the chemical potential of the inhomogeneous phase is

\[\mu = \frac{1}{V} \int d\mathbf{r} \frac{\delta \mathcal{F}(\rho(\mathbf{r}))}{\delta \rho(\mathbf{r})} \quad (13)\]

The pressure in the solid phase is

\[P_s = P_l + \sum_{n=1}^{\infty} \frac{1}{n!} \left[ \frac{\delta^n P}{\delta \rho(\mathbf{r}_1) \cdots \delta \rho(\mathbf{r}_n)} \right]_{\rho(\mathbf{r})=\rho_l} \Delta \rho(\mathbf{r}_1) \cdots \Delta \rho(\mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n. \quad (14)\]

where \(P\) is the functional of \(\rho(\mathbf{r}) :\)

\[P = \frac{k_B T}{V} \left\{ \int d\mathbf{r} \rho(\mathbf{r}) (1 - c_1(\mathbf{r}; \{\rho(\mathbf{r})\}) + \beta \mathcal{F}_{ex}(\rho(\mathbf{r})) \right\}. \quad (15)\]

To proceed constructively in the frame of the DFT we must choose a concrete form of FEF – a kind of closure or truncating – and we must make an ansatz for the average density of the crystal. The importance of such 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. Now it is necessary to specify the crystal symmetry (e.g. lattice type) and to locate the freezing transition for that particular lattice type. Other lattice types can then be studied as well. There is always the possibility, though, that a more complex lattice that has not been examined will turn out to be more stable.

Let us demonstrate now how the DFT works in the simplest case of hard sphere system truncating the free energy functional in the hypernetted chain (HNC) approximation. The one particle distribution function \(\rho(\mathbf{r})\) in the crystalline phase has the form

\[\rho(\mathbf{r}) = \rho_l + \Delta \rho(\mathbf{r}), \quad \frac{1}{V} \int \rho(\mathbf{r}) d\mathbf{r} = \rho_s. \quad (16)\]

Here \(\rho_l\) and \(\rho_s\) - are the averaged density of liquid and solid phase, respectively, and the function \(\Delta \rho(\mathbf{r})\) contains the term having the crystal symmetry. Let us use the following actual form for the density change \(\Delta \rho(\mathbf{r}) :\)
\begin{equation}
\Delta \rho(r) = \rho_l \sum_k \varphi_k e^{ikr} = \rho_l \varphi_0 + \rho_l \varphi(r), \tag{17}
\end{equation}

\begin{equation}
\varphi_k = \frac{1}{\Delta} \int_{\Delta} \frac{\Delta \rho(r)}{\rho_l} e^{-ikr} dr.
\end{equation}

The sum is over reciprocal lattice vectors and the integral is taken over the elementary lattice cell \( \Delta \).

If \( J \) labels the sets of the points in reciprocal lattice with equal coefficients \( \varphi_k \) (from symmetry condition), then

\begin{equation}
\Delta \rho(r) = \rho_l \varphi_0 + \rho_l \sum_J \varphi_J \xi_J(r), \quad \xi_J(r) = \sum_{k \in J} e^{ikr}. \tag{18}
\end{equation}

and \( \varphi_J(r) \) are independent order parameters.

In the HNC approximation \( c_n(r_1 \cdots r_n) = 0, \ n \geq 3 \), and we obtain from \( P_l = P_s \) the following equation for the density change \( \Delta \rho(r) \):

\begin{equation}
(1 - \rho_l \tilde{c}_2(0)) \int \Delta \rho(r) dr - \frac{1}{2} \int c_2(|r_1 - r_2|) \Delta \rho(r_1) \Delta \rho(r_2) dr_1 dr_2 = 0, \tag{19}
\end{equation}

or

\begin{equation}
(1 - \rho_l \tilde{c}_2(0)) \varphi_0 \rho_l - \frac{1}{2} \varphi_0^2 \rho_l^2 \tilde{c}_2(0) - \frac{1}{2} \rho_l^2 \sum_J m_J \tilde{c}_2(k_J) \varphi_J^2 = 0, \tag{20}
\end{equation}

where

\begin{equation}
m_J = \frac{1}{V} \int \xi_J^2(r) dr, \tag{21}
\end{equation}

\begin{equation}
\tilde{c}_2(k) = \int c_2(r) e^{-ikr} dr. \tag{22}
\end{equation}

The equality of chemical potentials gives the equation

\begin{equation}
(1 + \varphi_0) \exp(-\rho_l \varphi_0 \tilde{c}_2(0)) = \frac{1}{V} \int dr \exp \left\{ \rho_l \sum_J \tilde{c}_2(k_J) \varphi_J \xi_J(r) \right\}. \tag{23}
\end{equation}

Finally, using the equation

\begin{equation}
\frac{1}{V} \int \xi_J(r) \xi_{J'}(r) dr = m_J \delta_{JJ'},
\end{equation}

it is easy to obtain
\[ m_J \frac{\varphi_J}{1 + \varphi_0} = \frac{1}{V} \int \mathrm{d}r \exp \left\{ \rho l_\Sigma \tilde{c}_2(k_J) \varphi_J \xi_J(r) \right\} \exp \left\{ \rho l_\Sigma \tilde{c}_2(k_J) \varphi_J \xi_J(r) \right\}. \] \hspace{1cm} (24)

The equations (20), (23), (24) present the closed system of equations for the quantities \( \rho_l, \varphi_0, \varphi_J \) – the liquid density at the transition, the density change at the crystallization and the components of the one–particle distribution function, respectively.

One can also obtain the entropy change in the form

\[ \frac{\Delta s}{k_B} = - \left( (\varphi_0 - \varphi_0^2) \frac{P_l}{\rho_l k_B T} + \varphi_0^2 (1 - \rho_l \tilde{c}_2(0)) \right). \] \hspace{1cm} (25)

Even this simple approach gives rather good results. Here in the table we list the result of the calculation for HS system in the case of FCC lattice with two reciprocal lattice vector values: \( \varphi_1 \) and \( \varphi_2 \).

| Method              | \( \eta_l \) | \( \Delta \rho/\rho_l \) | \( P^* \) | \( \Delta s/k_B \) |
|---------------------|-------------|----------------|-----------|------------------|
| Simulations (MC)    | 0.494       | 0.103          | 11.7      | 1.16             |
| This approach       | 0.494       | 0.074          | 12.6      | 1.29             |
| GELA                | 0.495       | 0.101          | 11.9      | 1.15             |
| SCELA               | 0.508       | 0.105          | 13.3      | 1.27             |
| WDA                 | 0.480       | 0.141          | 10.4      | 1.41             |
| MWDA                | 0.476       | 0.139          | 10.1      | 1.35             |
| ELA                 | 0.520       | 0.090          | 16.1      | 1.36             |

It is worth to notice that the interparticle potential (as well as the temperature) does not enter the equations. This means, in particular, that they are valid for many–body forces, too. The liquid–phase properties enter the theory through the Fourier–transform of the DCF, connected with the liquid structure factor \( S(k) \) \( (S(k) = 1 + \rho \int \mathrm{d}re^{ikr} [g(r) - 1]) \) by

\[ S(k) = \frac{1}{1 - \rho \tilde{c}_2(k)} \] \hspace{1cm} (26)
The structure factor characterizes the relative position of particles in the liquid and so we can speak about the DFT approach as a geometrical one and of packing character.

Let us emphasize that we have truncated the Taylor expansion at second order. Although this is a rather crude approximation it is reasonably successful in studying the freezing of a number of systems.

In work done so far using this perturbation theory either \( c^{(3)}(r_1, r_2, r_3) \) has been ignored completely, or only its long-wavelength behaviour has been included, to account for the density dependence of the compressibility.

Although the truncated perturbation approach has significant limitations it has one advantage over all approaches proposed to date. This is the fact that it depends only on the structure factor of the liquid at a fixed density in the liquid phase region. This is experimentally measurable quantity, and this opens up the possibility of studying the freezing of rather complex liquids, for which the interaction potentials are not very well known, provided that the experimental data on the structure factor exists.

If the potential is well known for the given real system or if we are dealing with a system subject to computer simulations then the direct correlation function to input is usually taken from hypernetted chain (HNC) or Percus-Yevic (PY) approximation or from the interpolation closure relation of Rogers and Young,

\[
g(r) = \exp\left[-\beta u(r)\right](1 + \{\exp[p(r)f(r)] - 1\}/f(r)), \tag{27}
\]

where \( p(r) = h(r) - c(r) \), \( h(r) = g(r) - 1 \) and \( f(r) \) is a ”switching function” chosen to be of the form

\[
f(r) = 1 - \exp(-\kappa r) \tag{28}
\]

The parameter \( \kappa \) in \( f(r) \) is varied until consistency is achieved between the equations of state derived from virial and compressibility routes. Another scheme is the modified HNC (MHNC) scheme of Rosenfeld and Ashcroft based on the closure

\[
g(r) = \exp[-\beta u(r) + p(r) + B(r)], \tag{29}
\]
where the bridge function $B(r)$ is assumed to be a universal function equal to its hard sphere (HS) form $B(\eta, r)$ calculated for some effective $\eta$; $\eta$ is adjusted to yield thermodynamic consistency.

The major limitation of perturbation approaches is that including even third-order term is very difficult. The natural question is whether there exists a non-perturbative approach, which might include important contributions from the other terms.

The DFT views the emerging ordered phase as a grossly inhomogeneous liquid with a rapidly varying one-particle density $\rho(r)$, reflecting the lower symmetry of the emerging phase. Given such a scenario, it seems unlikely in spite of its success, that the structure of the ordered phase can be approximated by the low-order perturbation expansion with a uniform system taken as the zeroth or unperturbed system. Motivated by this fact a number of workers have attempted to develop approximate but nonperturbative free energy functional (FEF).

This is the idea behind the set of approaches which use an imagined, unreal liquid at an auxiliary density with some kind of variational properties.

A very popular variant of the nonperturbation approach uses a uniform liquid which has different density than $\rho_0$, so that chemical potential of the solid is no longer equal to that of the liquid. The simplest version of such an ”effective–liquid approximation” (ELA) was proposed by Baus and coworkers\textsuperscript{51} and chooses the reference liquid density in such a way that the first reciprocal lattice vector $\vec{k}_1$ of solids matches the first peak in the structure factor of the liquid. Such a reference liquid is more dense than the liquid in coexistence with crystal at the same temperature, and an extrapolation into the metastable liquid phase is required. This is done using HS perturbation theory to calculate the DCF and the structure factor over a large range of densities.

A second set of approaches to constructing an approximate FEF are referred to as ”weighted density approximations” (WDA). This approach was due to Tarazona\textsuperscript{52} and Ashcroft and coworkers\textsuperscript{53,55}.

The authors have constructed a FEF in such a way that the free-energy density of an
inhomogeneous system at a given point is interpreted as that of a homogeneous system, but taken at an auxiliary density which depends parametrically on the chosen point. The effective density is obtained approximately by weighting the physical density over a given point. The resultant weighted density approximation (WDA) thus accounts by construction for the short-ranged nonlocal effects present in a real, interacting inhomogeneous liquid at the given point.

A simple version of the WDA [known as modified WDA (MWDA)] emerges if one considers global free energy per particle instead of the local excess free energy per particle. In this case the effective density must be position independent.

Once a FEF has been specified and an ansatz has been made for the crystal density (usually it is the form \( \rho(r) = \sum_{i=1}^{N} \varphi(r - R_i) \)) or a sum over the direct lattice

\[
\rho(r) = \sum_{i=1}^{N} \varphi(r - R_i)
\]  

and assuming a spherically symmetric Gaussian form for \( \varphi \):

\[
\varphi(r - R_i) = \left( \frac{\alpha}{\pi} \right)^{3/2} e^{\alpha(r - R_i)^2},
\]

one has to calculate as in the simple example considered.

After 1979 hundreds of calculations were performed of the melting curves of different systems. There is a large number of results obtained by the use of DFT which are in excellent agreement with real or computer experiments. It should be noticed that according to geometrical nature of the theory higher is the pressure, better is the agreement. The progress in the DFT as describing the 3D classical melting is connected mainly with the papers by Baus, Hansen, Ashcroft and their coworkers. The details of slightly different approaches and the lists of results can be found in the reviews.

Technically, the calculations follow the same scheme, mentioned above. The following generalizations should be mentioned.

1. In the case of charged mixture DFT is formulated in terms of number density

\[
\rho^N(r) = \rho^+(r) + \rho^-(r),
\]
charge density

\[ \rho^Z(r) = \rho^+(r) - \rho^-(r), \]

number-number DCF

\[ c^{(2)}_{NN} = \frac{1}{2}[c^{(2)}_{++}(r) + c^{(2)}_{+-}(r)] \]

and charge-charge DCF

\[ c^{(2)}_{ZZ} = \frac{1}{2}[c^{(2)}_{++}(r) - c^{(2)}_{+-}(r)]. \]

Barrat\(^6\) has obtained the phase diagram (using the second-order DFT and the Gaussian parametrization for the solid density) for a mixture of charged HS of the same diameter \(\sigma\) and opposite charges known as the restricted primitive model (RPM) for ionic liquids.

2. Freezing of molecular fluids is described in DFT modified to include the angular dependence of potentials and DCF of the molecular liquid and to look for angle depending solutions for the density. The number of order parameters increases but using of symmetry conditions reduces this number. The number of order parameters is determined indirectly by the number of harmonics needed to get proper convergence, and this number increases with the anisotropy in the shape of molecules. The new phase transition is the orientational phase transition. If the anisotropic part of the potential is large enough and the shape of molecules differs strongly from the spherical, one has a set of liquid crystal phases. In the opposite case one has a small influence of the anisotropic part on the freezing transition and, possibly, an orientational phase transition in solid state which may affect or not the crystalline structure. All these problems, including a rich phase diagram of liquid and molecular crystal phases have been considered in the frame of DFT approach.

Again in the case of hard-core molecules (hard ellipsoids of revolution (HER), hard spherocylinders (HSC) and hard dumbbells (HD)) one obtains very good agreement of DFT with simulations. In this case the equivalent of HS potential is (hard body potential HB)

\[ u(r_{12}, \Omega_1, \Omega_2) = \begin{cases} \infty, & r_{12} < D(\hat{r}_{12}, \Omega_1, \Omega_2) \\ 0, & \text{otherwise}, \end{cases} \quad (32) \]
where $D(...)$ is the centre-to-centre distance between the pair of molecules in contact for
given orientation of the pair.

3. In order to distinguish between purely geometrical effects and bonding effects characteristic of real metals Igloi et al. have subtracted DCF of a HS fluid from the full DCF of the metal which they determined from a perturbation theory. We may note that for the HS system where the structure is determined solely by the geometrical necessities of a closed packing, the structural differences in the free energy (fcc and hcp) are extremely small. The observed differences in metals are due to $\Delta c(k)$ which measures the bonding effects.

4. As an example of the application of quantum DFT theory of freezing one can mention the paper by Rick et al. They have used this theory to calculate the phase diagram of $^3He$ and $^4He$ basing on second-order DFT and taking for the input the correlation functions found from the recently developed quantum MC technique.

All the investigations mentioned above bring to the conclusion that the DFT of freezing is a good enough theory in the case of short-range potentials or high pressures, when all potentials become more or less hard body potentials. In the case of long-range potentials the predictions of DFT theory differ essentially from real and computer experiments. This can be demonstrated using as the example the freezing of soft spheres, in which case the fcc or the bcc phase was found to be a stable structure independently of $n$ but depending on the approximation used.

Recently in the frame of DFT a number of interesting results were obtained for systems widely under investigation now both experimentally and by use of computer simulations. Two such systems are particularly "en vogue" now: colloidal suspensions of polydisperse spheres and extrême potential systems with isostructural transitions and the absence of liquid phase as in $C_{60}$.

The geometrical nature of the theory defines its success in the case of mixtures of hard core particles. Mixtures exhibit phase diagrams which are much richer than those of one component systems including crystals substitutionally ordered or disordered. The relative stability of these phases depends on the thermodynamic conditions, concentration ratios
and ratios of the sizes of atoms. The freezing transition in polydisperse HS system is a very interesting problem particularly because there exists now the experimental realization of this simple theoretical model – colloidal particles of different size (10-1000nm).

The DFT treatment of Barrat, Baus and Hansen was the first to show that, starting from monodisperse limit, the freezing transition of the fluid mixture into a constitutionally disordered solid changes from a spindle type (at $s=0.94$) to azeotropic type and (at $s=0.92$/later 0.875) to eutectic type ($s = \sigma_1/\sigma_2$). Later the DFT approach of was improved in and. The same results were obtained in simulations by Kranendonk and Frenkel.

The crystallization of the polydisperse hard sphere system with continuous distribution of particle size (given by gamma– or Gauss distribution) was investigated by use of DFT approach in a number of papers. As early as in 1986 in (see also) the critical value of polydispersity ($\approx 5–6\%$) was obtained giving the limit to the possibility of crystallization. Later the simulations and the real experiments confirm the existence of such critical dispersity (of a little greater value).

The other interesting experimental results on colloidal suspensions concern the phase diagram of ”big” spherical colloidal spheres in the liquid of very small polymers. This systems was modelled through additional attraction in the hard sphere potential. The range of the attraction reflects the polymer size. If the polymer size decreases the temperature of the liquid–gas transition decreases, too, and becomes lower than the triple point temperature. Consequently, the solid phase and only one fluid phase remain on the phase diagram. If the range of the attraction is decreasing more an isostructural polymorphic phase transition appears in solid phase (in the simulations and in the DFT approach). The main characteristics of phase transitions and the phase diagrams from the DFT calculations are in accordance with simulations. Analogous results were obtained for hard spheres with the Yukawa tail or for adhesive and sticky spheres.

This problem – the investigation of the attraction role for the crystallization – is a very interesting problem, considered as early as by van der Waals. The modern view on the problem can be found in.
To summarize the first part of the lecture, one can see that the DFT of freezing is simple theory which works well enough in the 3D case when one needs not to take into account the fluctuations.

The properties of 2D crystals are quite different from the 3D case. As we have mentioned above, in 30-th Peierls has shown that 2D harmonical lattice cannot exist in the thermodynamic limit: the meansquare displacement in harmonic crystals has logarithmic singularity. Later the absence of two-dimensional long-range translational order was proved by Mermin with the use of well known Bogoliubov inequalities (1/q^2 theorem) for the correlators. In fact, in the paper by Mermin mentioned above (where the absence of crystallographic 2D order was proved), it was shown that the true long range order – the orientational order of bonds – exists in 2D crystal. More precisely, it was shown that the direction of the vector between any two neighbouring atoms at finite temperature is the same as at T = 0.

The bond orientation correlation function < \vartheta(r_1)\vartheta(r_2) > remains finite at r → ∞. Here \vartheta is the angle between local crystallographic axis and some axis of ideal lattice. In continuum approximation it has the form

\[ \vartheta(x, y) = \frac{1}{2}(\partial_x u_y - \partial_y u_x). \]  (33)

Anisotropic liquids with bond-orientational order are considered in the phenomenological theories of melting, developed by Halperin and Nelson and based on the ideas of Kosterlitz and Thouless. This KTHNY theory predicts that the transition may be fundamentally different from that observed in ordinary three-dimensional systems. It was found that the transition between two-dimensional solid and isotropic liquid can occur via two continuous transitions corresponding, respectively, to dissociation of dislocations and disclinations. The low-temperature solid phase is characterized by algebraic decay of translational order and true long-range bond-orientational order. Dislocations unbind at a temperature T_m into a phase with shot-range translational order, but with algebraic decay of bond-orientational order. This intermediate phase is called the hexatic phase. The properties of the hexatic phase are similar to those of a nematic liquid crystal, except that
triangular lattices melt into a phase with persistent sixfold, rather than twofold order. Paired disclinations in the hexatic phase ultimately unbind themselves, driving a second transition at a higher temperature $T_i$ into an isotropic liquid.

The base of the KTHNY theory is the mechanism of breaking of quasi–long–range order in 2D systems with continuous symmetry developed by Beresinskii\cite{94,95} and by Kosterlitz and Thouless\cite{11,96}. The well known example of such system is the classical $XY$ model with the Hamiltonian:

$$H = -\frac{J}{2} \sum_{i \neq j} S_i S_j \simeq \frac{J}{2} \int d^2 r (\nabla \varphi)^2.$$  \hspace{1cm} (34)

$\varphi$ is the angle between the vectors $S_i$ and $S_j$ ($i$, $j$ - the nearest neighbours).

At low temperature the quasi–long–range order exists characterized by an algebraic correlation decay $< S(r)S(0) > \propto r^{-\eta}$. At higher temperature the correlations decay exponentially $< S(r)S(0) > \propto \exp (-r/\xi)$. The symmetry breaking occurs through the appearance of free topological defects – vortices: $\oint (\nabla \varphi) \, dl = 2\pi q$.

The transition temperature can be obtained simply from energetic balance using the fact that the vortex energy is (from (34))

$$E_\nu = \frac{J}{2} \int_0^L \frac{2\pi}{r} \, dr = J\pi \ln (L/a),$$

where $a$ is the lattice constant and $L$ - the system size. The creation of a vortex changes the free energy: $\Delta F = E_\nu - TS$, where the vortex entropy $S = 2k_B \ln (L/a)$. At the temperature $T \geq T_0 = \pi J/k_B$ the value of $\Delta F = (J\pi - 2k_BT) \ln (L/a)$ becomes negative so that the vortex creation becomes energetically profitable. The Hamiltonian for vortex–vortex interaction is equivalent to that of 2D Coulomb gas:

$$H_c = -\pi J \sum_{|r-r'|>a} q(r)q(r') \ln \frac{|r-r'|}{a} + E_c \sum_r q^2(r).$$ \hspace{1cm} (35)

The physics of KT transition\cite{11} is the dissociation of vortex pairs in the presence of the screening. The KT theory presents a renormgroup approach to screening. The KT transition is a continuous transition from low temperature quasi–long–range ordered phase
to high temperature disordered phase. The $T_{KT}$ is just that obtained above from simple thermodynamical consideration.

Based on the KT theory the KTHNY theory describes the 2D melting as two continuous KT transitions. The first transition – the dislocation pairs unbinding, the second one – the unbinding of disclination pairs.

The description of the first transition in KTHNY theory is based on the elastic Hamiltonian for 2D triangle lattice:

$$H_E = \frac{1}{2} \int d^2r \left[ 2\mu u_{ij}^2 + \lambda u_{kk}^2 \right],$$  \hspace{1cm} (36)

where

$$u_{ij} = \frac{1}{2} \left[ \frac{\partial u_i(r)}{\partial r_j} + \frac{\partial u_j(r)}{\partial r_i} \right]$$  \hspace{1cm} (37)

and $\mu$ and $\lambda$ are the Lamé coefficients.

Free dislocations (analogs of the vortices in XY model) break the quasi-long-ranged periodic translational order and cause the shear modulus $\mu$ to vanish.

The dislocation Hamiltonian has the form:

$$H_{dis} = -\frac{a_0^2 K}{8\pi} \sum_{i\neq j}^M \left\{ b(r_i)b(r_j) \ln \frac{r_{ij}}{a} - \frac{(b(r_i)r_{ij})(b(r_i)r_{ij})}{r_{ij}^2} \right\} +$$

$$+ E_d \sum_{i=1}^M b^2(r_i),$$  \hspace{1cm} (38)

where $E_d$ is the core energy of dislocation.

$$K = \frac{4\mu(\mu + \lambda)}{2\mu + \lambda}. \hspace{1cm} (39)$$

The KT phase transition to the hexatic phase takes place at the temperature

$$\frac{a_0^2 K(T_m)}{k_B T_m} = 16\pi.$$  \hspace{1cm} (40)

Following Halperin and Nelson, the phenomenological orientational order parameter is

$$\psi(r) = e^{i\varphi(r)},$$  \hspace{1cm} (41)
where $\vartheta(r)$ is the bond orientation ($\mathbf{B3}$). The quasi-long-ranged orientational order at $T > T_m$ is described in terms of algebraic correlation decay:

$$<\psi^*(r)\psi(0)> \propto r^{-\eta_6(T)}.$$  \hspace{1cm} (42)

The Hamiltonian for the hexatic phase has the form\textsuperscript{9}:

$$H_A = \frac{1}{2}K_A(T) \int d^2r \left(\nabla \vartheta(r)\right)^2,$$  \hspace{1cm} (43)

The Frank constant $K_A(T)$ is connected to $\eta_6$ through the equation:

$$\eta_6(T) = \frac{18k_BT}{\pi K_A(T)}.$$  \hspace{1cm} (44)

In the solid phase the disclinations are tightly bound into pairs (the dislocations), however in the hexatic phase the interaction is screened by dislocations and so occurs to be logarithmic\textsuperscript{9,7}, and so for the disclination Hamiltonian in hexatic phase we obtain the 2D Coulomb gas like form again\textsuperscript{9,8}:

$$H_{\text{disc}} = -\frac{\pi K_A(T)}{36} \sum_{r \neq r'} s(r)s(r') \ln \frac{|r - r'|}{a} + E_{cd} \sum_r s^2(r),$$  \hspace{1cm} (45)

where $E_{cd}$ is the core energy of disclination, $s(r) = 1$ for the atom with 7 nearest neighbours, $s(r) = -1$ for 5 nearest neighbours.

The second KT transition – the disclination pairs unbinding – takes place at the temperature\textsuperscript{9,7} $T_i > T_m$:

$$T_i = \frac{\pi K_A(T_i)}{72k_BT_i}.$$  \hspace{1cm} (46)

The KTHNY picture is the following. At $T = 0$ there exist long-range translational and orientational orders, however, at $T > 0$ the long-range translational order is transformed into the quasi-long-range one due to smooth phase fluctuations, the orientational order remaining unchanged. At the melting temperature $T_m$, the quasi-long-range order is destroyed by the singular phase fluctuations (dislocations). The appearance of free dislocations means that the system ceases to offer any resistance to shear ($\mu = 0$), i.e., it becomes a liquid. It should
be emphasized that the amplitude of the order parameter $\rho_G$ does not become equal to zero at $T_m$, but it does at the some mean-field temperature $T_{MF}$, which can be determined by equating the free energies of the solid and liquid phases as the functionals of the local density. (It is important to note that it is this point $T_{MF}$ that has been considered by Ramakrishnan\cite{99} as the melting point.) The second transition into an isotropic liquid takes place at a higher temperature $T_i$.

This theory has strong support from experiments with electrons on helium\cite{100,101}, computer simulations of the 2D electron systems\cite{102,113}, elasticity simulations\cite{114}, experiments with polystyrene spheres\cite{103} (however, the topological defects in this case are complex and are not consistent with a simple KTHNY picture of melting).

A conventional first-order transition between the two-dimensional solid and isotropic liquid is also a possibility. Several theories predict a single first-order melting transition in 2D\cite{99,106,108,122,110}. The sum of the experimental evidence on adsorbed atoms is weighted against an interpretation in terms of KTHNY melting and seems to show a weak first-order transition\cite{111}. Most simulations studies of 2D melting indicate that the strictly two-dimensional hard-core potential systems melt via first-order transition (see, for example,\cite{8,112} and references therein), as do studies of systems interacting with intermediate strength potentials\cite{113,114}.

Therefore, we expect that the melting behavior may depend crucially on the interaction potential, and the first-order character of the transition is weakened as the potential is softened.

The simple physical picture may be painted in order to illustrate this possibility\cite{115,116}. As mentioned above, there is an analogy between the hexatic phase and a nematic liquid crystal, but the role of the rodlike molecules is played by the hexagon clusters consisting of an atom with its nearest neighbors. Ordering of these hexagons is possible only if the range of the interparticle interaction is large enough to provide the interaction between clusters. Therefore, the interparticle interaction should extend at least over several interparticle distances, and hexatic phase could exist for long-range potentials, but not for short-range ones.
However, only first-principles study could put these heuristic reasonings on firmer footing.

The microscopic theory of 2D melting can be obtained as a generalization of the DFT theory of freezing described above. We developed an approach appropriable to 2D melting\textsuperscript{115–121,123–125,115,116}. Our approach can predict, basing on the knowledge of interparticle potential, which scenario is to be realized: 1) $T_m < T_{MF}$, the system melts by means of two continuous transitions of KT type; 2) $T_{MF} < T_m$, the system melts by means of a first-order transition.

Our approach differs from the standard DFT theory of freezing in two main points:

First, we permit the Fourier coefficients $\rho_G(r)$ of the one-particle distribution function expanded in a Fourier series in reciprocal-lattice vectors $\{G\}$:

$$\rho(r) = \sum_G \rho_G(r)e^{iGr}$$

to fluctuate - to vary slowly over distances of order $G^{-1}$ and to have the amplitude and phase:

$$\rho_G(r) = \rho_G e^{iGu(r)}.$$  

Here $u(r)$ is the displacement field.

Second, we permit the liquid to be anisotropic: we consider as possible the existence of a phase with constant density but angular dependent two-particle distribution function $F_2(r_1 - r_0) \neq g(r_{10})$.

These two points of generalization define the two new order parameters: the fluctuating $\rho_G(r)$ and the Fourier coefficients characteristic for the broken symmetry of the function $F_2(r_1 - r_0)$. Our approach again is based on the Eq.(2) of previous section.

Let us describe in details the microscopic characteristics of a hexatic phase.

The relative spatial distribution of pairs of particles is characterized by the function $F_2(r_1 | r_0) = F_2(r_1 - r_0)$. The vector $r_1 - r_0$ defines the direction of the bond between the molecules at the points $r_1$ and $r_0$. 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 \( r'_0 \) is characterized by the bond directions \( r' = r_2 - r'_0 \). It occurs that if the point \( r'_0 \) is at sufficiently large distance from \( r_0 \) then there is no correlation between the directions \( r = r_1 - r_0 \) and \( r' = r_2 - r'_0 \). In this case after the averaging over the system as a whole the pair distribution function transforms into the RDF and the equation (2) for \( s = 1 \) has the solution \( F_2(r_1 - r_0) = g(|r_1 - r_0|) \), which corresponds to ordinary isotropic liquid.

When we approach the anisotropic liquid phase the long–ranged correlations between the bond directions \( r \) and \( r' \) do appear and the averaged two–particle distribution function depends on the bond direction now.

In the vicinity of the transition one can write

\[
F_2(r_1, r_0) = g(|r_1 - r_0|)(1 + f(r_1 - r_0))
\]

(47)

where \( f(r_1|r_0) \) has the symmetry of the local neighbourhood of the particle at \( r_0 \). In the two–dimensional case

\[
f(r_1|r_0) = f(a_0, r_0, \varphi).
\]

(48)

Here \( a_0 = |r_1 - r_0| \), \( a_0 \) is the radius of the first coordination sphere, and \( \varphi \) is the angle of the vector \( a_0 \). The function \( f \) may be expanded in a Fourier series

\[
f(a_0, r_0, \varphi) = \sum_{m=-\infty}^{\infty} f_m(a_0, r_0)e^{im\varphi}.
\]

(49)

The Fourier coefficients define the order parameters. These parameters become nonzero at the temperature \( M_F \leq T_h \) defined by the bifurcation condition, that is by the eigenvalue of the linearized (relative to \( f \)) eq. (2) with \( s = 1 \).

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 (2) for \( s = 3 \), if we write the long range part of the correlator using the principle of a weakening of correlations (25) as:
\[ F_4(r_1, \ldots, r_4) = g(|r_1 - r_2|)g(|r_3 - r_4|)(1 + f_4(r_1, \ldots, r_4)) \]  

\[ f_4(r_1, \ldots, r_4) = f_4(r, R, \varphi_1, \varphi_2). \]

Here \( \varphi_1 \) is the angle between the vector \( r = r_1 - r_2 \) and the axis \( R = r_2 - r_3 \), \( \varphi_2 \) is the angle between the vector \( \rho = r_3 - r_4 \) and the same axis. We have \( f_4(r, R, \varphi_1, \varphi_2) \to 0 \) when \( R \to \infty \).

The function \( f_4 \) can be presented as a Fourier series

\[ f_4(r, R, \rho, \varphi_1, \varphi_2) = \sum_{p,q} f_{pq}(r, R, \rho) \exp(ip\varphi_1 + iq\varphi_2). \]  

The asymptotics of the solution is of the form

\[ f_{pq} \propto e^{-R/\xi_{pq}}. \]

Here the correlation length \( \xi_{pq} \) is characterized by the properties of the isotropic liquid and diverges in the vicinity of the bifurcation line. The asymptotic behaviour of the correlation function \( f_{6,6} \), derived in our approach, (far away from the transition) can be compared with that of the phenomenological KT theory, thus giving the microscopic expression for Frank constant 123.

\[ K_A(T) = 648k_B T a_0^2 |f_6|^2 \left[ \Gamma_6(a_0, a_0) - 1/2(\Gamma_5(a_0, a_0) + \Gamma_7(a_0, a_0)) \right], \]  

\[ \Gamma_m(r_1, r_2) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \Gamma(r_1, r_2, \varphi) e^{-im\varphi} \]

where \( a_0^2 = 2/(\sqrt{3}p) \). The function \( \Gamma(r_1, r_2, \varphi) \) was introduced in our papers 117–120 on bond orientational order and has the form

\[ \Gamma(r_1, r_2, \varphi) = \sum_{k \geq 1} \frac{\rho^k}{(k - 1)!} \int S_{k+1}(r_1, \ldots, r_{k+1}) \]

\[ \times g(|r_3 - r_0|) \cdots g(|r_{k+1} - r_0|)d^2r_3 \cdots d^2r_{k+1}, \]  

where, as earlier, \( S_{k+1}(r_1, \ldots, r_{k+1}) \) is the irreducible cluster sum of Mayer functions connecting (at least doubly) \( k + 1 \) particles, \( r_1 = |r_1 - r_0|, r_2 = |r_2 - r_0|, \) and \( \varphi \) is the angle between the vectors \( r_1 \) and \( r_2 \).
In the spirit of DFT we expand the function (53) in a functional Taylor series in powers of \( h(r) = g(r) - 1 \):

\[
\Gamma(r_1, r_2, \varphi) = \rho \left( c^{(2)}(|r_1 - r_2|) + \sum_{n=1}^{\infty} \frac{\rho^n}{n!} \int c^{(n+2)}(r_1, \ldots, r_{n+2}) \right.
\times h(|r_3 - r_0|) \cdots h(|r_{n+2} - r_0|) d^2r_3 \cdots d^2r_{n+2}).
\]

(54)

In the hypernetted chain approximation we can drop in the expansion (54) all terms with \( n \geq 3 \) and obtain

\[
\Gamma(r_1, r_2, \varphi) = \rho c^{(2)}(|r_1 - r_2|). \tag{55}
\]

In this approximation, Eq. (52) has the form

\[
K_A(T) = 648k_B a_0^2 |f_6|^2 [c_6(a_0, a_0) - 1/2(c_5(a_0, a_0) + c_7(a_0, a_0))],
\]

(56)

where

\[
c_m(a_0, a_0) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi c^{(2)}(\sqrt{2}a_0(1 - \cos \varphi)^{1/2}; \hat{\rho})e^{-im\varphi}.
\]

Now the equation for the absolute value of the order parameter is

\[
f_6 = \frac{\int_0^{2\pi} d\varphi \cos 6\varphi \exp[12c_6(a_0, a_0) \cos(6\varphi)f_6]}{\int_0^{2\pi} d\varphi \exp[12c_6(a_0, a_0) \cos(6\varphi)f_6]}.
\]

(57)

(We have made use of the Eq.(2) for the function \( F_2(r_1 | r_0) \)). As in the case of standard DFT this equation corresponds to the minimum of the free energy functional.

The phase transition from the hexatic phase to the 2D solid phase can be analyzed in a similar way. In this case the correlator which diverges is the density–density correlation function, the density Fourier components being the order parameters \( \langle \rho_G(r)\rho_G(0) \rangle \propto h_G(r); \)

\[
h_2(r) = \sum_G h_G(r)e^{iG r}, \quad \text{where } G \text{ are the reciprocal lattice vectors.}
\]

\[
\rho(r) = \rho_F(r) = \rho_0 + \Delta \rho(r) = \rho_0 + \sum_G \rho_G(r) e^{iG r}
\]

(58)

\[
\rho_G(r) = |\rho_G|e^{iu(r)}
\]
In both cases the solution with broken symmetry appears at the point where the correlation decay changes its character.

The microscopic expressions for the nonrenormalized Lamé coefficients were obtained in\(^\text{123}\) by comparing the long-range behaviour of our correlator with the asymptotic behavior of the order parameter correlator from the phenomenological elastic energy\(^\text{1}\). For short-range potentials, expressions were obtained in\(^\text{123}\) for the elastic moduli which correspond to fluctuations with wave vector equal to the smallest reciprocal lattice vector. Generalization to the case of an arbitrary number of inverse lattice vectors leads to the following expression for the Lamé coefficients:

\[
\mu = \frac{k_B T}{16 \rho} \sum_G \rho_G^2 m_G G^2 (\gamma_G + 2 \delta_G), \tag{59}
\]

\[
\lambda = \frac{k_B T}{16 \rho} \sum_G \rho_G^2 m_G G^2 (\gamma_G - 6 \delta_G), \tag{60}
\]

where

\[
\gamma_G = 2\pi \rho \int r^3 dr c^{(2)}(r; \hat{\rho}) J_0(Gr), \tag{61}
\]

\[
\delta_G = 2\pi \rho \int r^3 dr c^{(2)}(r; \hat{\rho}) J_1(Gr)/(Gr), \tag{62}
\]

\(J_0(x)\) and \(J_1(x)\) are the Bessel functions, and \(m_G\) is the number of reciprocal lattice vectors with the same length.

In the case of the long-range Coulomb interaction, an additional term arises in the elastic Hamiltonian\(^\text{126}\), which makes the effective modulus \(\lambda\) diverge, \(\lambda = \infty\), but the expression (59) for \(\mu\) remains to be valid. The modulus \(K\) takes the form:

\[
K = 4\mu a_0^2/k_B T. \tag{63}
\]

In\(^\text{115}\) the authors present the first-principles estimates for the stability limits of the solid and hexatic phases for the 2D electron system and the system of hard disks which are two opposite cases of the \(1/r^n\) potential. In\(^\text{116}\) 2D system of vortices in a superconducting film interacting via a potential which is even softer than in 2D electron system was considered. The transition temperatures \(T_m\) and \(T_i\) were obtained from the KT theory using microscopic
expressions for elastic and Frank moduli and were compared with the value of $T_{MF}$ from the standard DFT theory.

1. Beginning with the classic paper by Alder and Wainwright\textsuperscript{127} it has been assumed that a system of hard disks melts by means of the first order transition. However, only recently have convincing proofs of this fact been obtained\textsuperscript{112}. The standard DFT approach gives good qualitative and quantitative agreement with the results of computer simulations. In the simplest version we obtain $\rho_S = 0.933$ (to be compared with 0.921 from simulations\textsuperscript{128}). At the transition point we have $K/16\pi = 6.29$ which is much larger than the value $K/16\pi = 1$, at which the dissociation of dislocation pairs takes place.

However, an even more convincing argument in favor of the first order phase transition is provided by the analysis of the possible existence of hexatic phase. Using the equation (56) we obtain for the Frank constant for the system of hard disks $K_A(T) < 0$ at all density, so that the hexatic phase cannot exist.

2. In the case of 2D classical Wigner crystal we have obtained the two-stage scenario of melting. In terms of the dimensionless parameter $\Gamma = (\pi \rho)^{1/2} c^2/(k_B T)$ our results are: $\Gamma_{MF} = 21.58$, $\Gamma_{KT_m} = 80.15$ and $\Gamma_{KT_i} = 24.5$. However, the renormalization of parameters depends strongly on the unknown values of the core energies of disclinations and dislocations and this can change the result.

3. In thin superconducting film the interaction energy of two vortices located at the points $\mathbf{r}_i$ and $\mathbf{r}_j$ ($r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \gg \xi$) has the form\textsuperscript{129}

$$\Phi(r_{ij}) = \frac{\varphi_0^2}{8\pi \Lambda} \left[ H_0 \left( \frac{r_{ij}}{\Lambda} \right) - Y_0 \left( \frac{r_{ij}}{\Lambda} \right) \right]$$

$$\Phi(r_{ij}) \approx - \frac{\varphi_0^2}{4\pi \Lambda} \ln \left( \frac{r_{ij}}{\Lambda} \right) \quad r_{ij} \ll \Lambda$$

$$\Phi(r_{ij}) \approx \frac{\varphi_0^2}{4\pi^2 r_{ij}} \quad r_{ij} \gg \Lambda$$

where $\Lambda(T) = 2\lambda_B(T)/d$ is the effective penetration depth, $d$ is the film thickness, $\lambda_B$ is the bulk penetration depth, $\varphi_0 = hc/2e$ is the flux quantum, $H_0(x)$ - the Struve function and $Y_0(x)$ - the Neumann function. The potential (64) is long-ranged (it is even "softer" than the Coulomb potential $1/r$) and one might therefore expect that vortex lattice will
melt through two continuous transitions. As to real and computer experiments, not only the type of the transition, but even the very existence of vortex lattice melting, remains an open question. This system was investigated in details by the authors in [130–134].

On the basis of our approach we have made the calculations for the specific case of a niobium film of thickness 20Å, investigated experimentally in Ref. [135]. The region of the hexatic phase is very well pronounced on the H-T phase diagram. If the film thickness increases this region narrows (see figures in [116]).

The authors thank D. Yu. Irz, Yu. L. Klimontovich, N. M. Plakida and S. M. Stishov for helpful discussions and valuable comments and RFBR for financial support (grant N 96-02-16211).

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