A microscopic picture of the “preparation” of a crystal to the transition to liquid state at the approach to melting temperature is proposed. Basing on simple crystallogeometric considerations and the analysis of the computational results for corresponding anharmonic characteristics an evaluation is given for the magnitude of atomic displacements leading to the appearance of close packed Bernal pseudonuclei in the crystal phase. A physical meaning of the classical Lindeman criterion and the mechanisms of the formation of free volume in the crystal phase are discussed.

Despite a great amount of collected experimental and theoretical information (see, e.g.,[1,2]) a classical question what is the melting is still unsolved. The melting temperature \(T_m\) itself is determined from thermodynamic considerations and, e.g., for alkali metals it can be calculated in the framework of microscopic theory in a good agreement with experimental data.[3] However, it does not elucidate the nature of the processes resulting in the reconstruction of the structure at the melting point. There are direct evidences of this reconstruction such as nonlinear in temperature \(T\) increase of the heat capacity and a significant softening of shear moduli at \(T \to T_m\) (for the most of metals the latter is as large as 50% decrease of one of the moduli but, e.g., for indium it is even 90%)[4]. To investigate the phenomena taking place in the crystal lattices near \(T_m\) a broad variety of techniques are used - from classical or quantum Monte-Carlo computer simulations to experiments with artificial “crystals” of charged drops.[5] Despite this we have no yet a complete and reliable picture of the melting of crystals. Here we try to suppose a qualitative scenario of the melting for a specific case of metals.

We are interested in the dynamic picture of the processes in a crystal near the melting point. According to the well-known Lindeman criterion of the melting one has \(\pi/d \simeq 0.1\) at \(T = T_m\) where \(\pi = \sqrt{\langle u^2 \rangle}\), \(\langle u^2 \rangle\) being average square of thermal atomic displacements, \(d\) is the minimal interatomic distance (see[6]). It is important that under such conditions, as a rule, phonons are well-defined collective excitations in all the Brillouin zone and anharmonic effects are relatively small up to \(T_m\). Microscopic calculations for metals with BCC and FCC structures[7-9] show that the value of relative phonon damping \(\Gamma_{q\xi}/\omega_{q\xi}\) (where \(q, \xi\) are the wavevector and phonon branch number, correspondingly) at \(T = T_m\) does not exceed 0.1-0.25 for the most of them. It is naturally to ask why so small anharmonic effects may lead, nevertheless, to the loss of stability of crystal lattices at the melting. To our opinion, the answer is connected with geometric properties of three-dimensional Euclidean space.

Microscopic calculations of structural and thermodynamic characteristics of liquid rare gases[10] and liquid metal[11-14] show that the accuracy of their description near \(T_m\) is dependent mainly on the simple geometric parameter of atomic packing \(\eta = \pi d^3 n/6\) where \(n\) is the atomic density, \(d\) is the diameter of non-overlapped spheres connected with each atom. It confirms qualitatively the adequacy of geometric approach to the description of structure of liquids proposed by Bernal[17], namely, the model of random packing of hard spheres. His conclusion that the value of relative phonon damping \(\Gamma_{q\xi}/\omega_{q\xi}\) is the most important for the scenario of the melting proposed here (they are called pseudonuclei because it is impossible to build regular structure from these formations). Locally they are characterized by the packing parameter \(\eta \simeq 0.78\) (at the average packing parameter \(\eta \simeq 0.64\) which is higher than the maximum possible packing in crystals, \(\eta \simeq 0.74\) (see[18]). To prevent misunderstanding note that we consider purely geometric definition of the packing parameter corresponding to the hard-sphere model with the interatomic potential

\[
\varphi_{HS}(r) = \begin{cases} \infty, & r < d \\ 0, & r > d \end{cases}
\]

Such definition does not take into account the effects of “softness” of interatomic interactions in metals, i.e. the role of the attractive part of the interactions, as well as nonpairwise forces (the dependence of the potential on mean electron density) which are important for metals. Because of this the effective packing parameter in liquid metals at \(T \simeq T_m\) can be estimated really as \(\eta_{met} \simeq 0.4\) [19]. Despite this molecular dynamics simulations give us evidences about qualitative adequacy of the Bernal model of the structure of liquids as a whole[20].

For metals as well as for liquid rare gases the closest packing is energetically favorable for small groups of atoms what is confirmed by the data about the structure of small metallic clusters. It is well known that in three-dimensional Euclidean space the closest packing is the tetrahedral one which, at the same time, cannot be reached in all the space. This is a drastic difference of three-dimensional space from the two-dimensional one. The latter can be filled completely by regular triangles, six of them being meet in each lattice site. In three-dimensional case only five regular tetrahedra can have
the common edge and the void appears in this case with the angle deficit \( \delta = 2\pi - 5\cos^{-1}(1/3) \approx 2\pi \delta \approx 0.02 \). This simple consideration is the base of an elegant approach to the description of structure of liquids and glasses. According to this approach the structure is defined not with the respect to usual Euclidean space but to Riemannian one. The latter can be, for a specific value of the curvature radius, filled completely by regular “tetrahedra”. The transition to the real physical space is carried out by introducing of corresponding “decurving” defects, namely, structural disclinations. Their appearance near \( T_m \) has been recently demonstrated in a simple model of a crystal by molecular dynamics simulations. Earlier a similar approach to the problem of melting basing on the consideration of statistics of linear defects has been developed phenomenologically by Patashinskii with collaborators. 

Taking into account the elastic energy of the disclinations as well as the trends to the closest packing of atoms in “chemical” energy of interatomic interactions it may be shown that the formation of an inhomogeneous state can be in principle described by these considerations. This state is characterized by the existence of superdense packed regions and Bernal “voids” around them. The central regions have tetrahedral-like packing structure and are similar in this sense to Bernal pseudonuclei. Our main hypothesis is that such regions can be created by thermal fluctuations near the melting point.

To form the close packed region as a result of thermal motion of an atomic group it is necessary to “overcame” the angle deficit \( \delta \). It has to be done as a result of not just oscillations but of displacements of the centers of the oscillations, i.e. of long-lived component of atomic motion. The latter can be estimated from the following simple considerations. The irreversibility of atomic displacements results from the phonon damping. The weight of this irreversible component is of order of \( \Gamma/\bar{\sigma} \) where \( \Gamma, \bar{\sigma} \) are the average phonon damping and frequency, correspondingly. The close packed region will be long-lived enough after its formation by thermal fluctuations since it corresponds to a local minimum of free energy. Indeed, it is known that for a system of hard spheres with relatively weak attraction (which is a good approximation for the most of metals) the density of free energy of sufficiently small groups of atoms is minimal for the closest tetrahedral packing. As a result, the probability of formation of the close packed pseudonucleus can be not too small for atomic displacements satisfying the condition

\[
(\pi/d)(\Gamma/\bar{\sigma}) \approx \delta/2\pi \approx 0.02.
\]

We believe that this estimation is a realistic melting criterion. Empirically, it coincides approximately with the Lindeman criterion but, in contrast with the latter, it is directly connected with contemporary views about the structure of liquids and a scale of anharmonic effects, at least, for metals.

Provided that the average atomic density is fixed the formation of close packed region results inevitably in the appearance of Bernal voids around it. This changes essentially traditional views formulated by Frenkel about the leading role of the monovacancies in the formation of free volume near the melting point. According to the scenario proposed the latter appears first with the temperature increase as the voids around close packed regions. Molecular dynamics simulation shows that for systems with “soft” enough interatomic interactions (e.g., liquid metals) there are two kinds of Bernal voids: distorted tetrahedral and octahedral ones. Apparently these voids are the most energetically profitable “carriers” of the free volume in the solid phase also. Monovacancies should have higher free energy and appears only as a result of diffusion decay of the voids in the close vicinity of \( T_m \).

To check this assumption we have made the fitting of defect contributions to the heat capacity of sodium near \( T_m \) which can be obtained from the experimental data by substracting electronic, phonon and anharmonic contributions. Trying to fit this contribution \( C^d(T) \) by Arrhenius law in a broad temperature range \( (0.6T_m < T < T_m) \) we find that the decline of the curve has a jump at \( T \approx 0.8T_m \). The fitting for the narrower temperature range \( 0.8T_m < T < T_m \) gives the following results for the entropy \( S_{1v} \) and energy \( E_{1v} \) of the formation of monovacancies as well as their concentration at the melting point \( n_{1v} \): \( S_{1v} \approx 4.3, E_{1v} \approx 0.3 \text{ eV}, n_{1v} \approx 0.3 \text{%} \). For another temperature range \( 0.6T_m < T < 0.8T_m \) one has \( S_{1v} \approx 0.5, E_{1v} \approx 0.17 \text{ eV}, n_{1v} \approx 0.74 \text{%} \). The first set of the results is in much better agreement with the data obtained by differential dilatometry data \( S_{1v} \approx 5.2, E_{1v} \approx 0.35 \text{ eV}, n_{1v} \approx 0.3 \text{%} \) as well as the results of microscopic calculations of the energy of formation of monovacancy, \( E_{1v} \approx 0.3 \text{ eV} \).

This confirms that, in contrast with traditional views and in agreement with the scenario of the melting proposed here, the temperature increase leads first to the formation of clusters of vacancies (the voids) and the monovacancies appears only in the close vicinity of \( T_m \). Note also that the formation of monovacancies in a broad temperature range below \( T_m \) corresponding to Frenkel views about the nature of the melting was never observed in computer simulations by molecular dynamics and Monte-Carlo methods. At the same time, according to these simulations, pentagonal faces of Voronoi polyhedra are observed frequently for instant atomic configurations not only in liquids but also in crystals near the melting point. According to Bernal this is the main feature of the structure of liquids. It means that some structural elements which are characteristic for liquids arises by thermal fluctuations already in the crystal phase.

As a conclusion, consider a possible way to describe such fluctuations quantitatively. The formation of the closest tetrahedral packing near \( T_m \) has to lead to the appearance of icosahedral short-range order describing by the parameter

\[
\frac{2}{\pi} \delta \approx \frac{2}{\pi} \delta / 2\pi \approx 0.02.
\]
\[ Q_{6m}(\mathbf{r}) = Y_{6m}[\theta(\mathbf{r}), \varphi(\mathbf{r})] \]

where \( Y_{6m} \) are spherical functions, \( \theta(\mathbf{r}), \varphi(\mathbf{r}) \) are polar angles of the direction to the nearest neighbors of the atom at point \( \mathbf{r} \) and the corresponding correlation function.

\[ G(r) = \frac{4\pi}{13} \sum_m \langle Q_{6m}(\mathbf{r}) Q_{6m}^*(0) \rangle. \]

Its calculation in the crystal phase by molecular dynamics or Monte-Carlo methods could give an important information about the local structure of solids near the melting.

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