Melting as a phase transition into a space with constant curvature

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It is shown that at sufficiently high temperature the crystal lattice is unstable with respect to transition into a space with constant negative curvature. The physical meaning of the transition is elucidated—the transition represents melting of the crystal. The curvature is proportional to the density of disclinations in real physical space. The melting temperature is found as a functional of the interatomic pair potential. To a good approximation it depends only on the second derivative of the potential at its minimum, that is, on the bulk elastic modulus. It is shown that the Lindemann criterion for melting is satisfied. The mean square atom displacement at the melting point is expressed in terms of the first zero of the interatomic potential. The disclination density and the size of the regions in which the short-range crystalline order in the melt is preserved are estimated.

I. INTRODUCTION

A space with constant curvature was used in Refs. 1–3 to describe structures of amorphous materials and melts. In short, the ideas of this approach are the following. According to Refs. 1–3 an amorphous material or a melt is a crystal in appropriately curved $3D$ space (the spaces considered are the Lobachevski space H_3 with constant negative curvature and the 3-sphere S_3). Crystallographic groups in H_3 and S_3 allow for local order, such as rings with five, seven, and more bonds, which is forbidden in the flat, physical space E_3. According to a number of investigations (see, for example, Refs. 4 and 5), precisely such structure elements are characteristic of the amorphous state (in contrast with crystals in E_3 where the translational symmetry is consistent only with the rotations by $2\pi/n, n = 2, 3, 4, 6$). Embedding of an H_3 or S_3 crystal into E_3 is impossible without deformations. It was shown in Ref. 2 that this mapping can be realized while preserving the distances and the relative angles along a line. However, this isometric embedding cannot be extended continuously beyond the line. Therefore, such embedding of an H_3 or S_3 crystal into E_3 must be accompanied by appearance of line defects—disclinations. They are associated with the defect rings of the type shown in Fig. 1. It can be shown[6] that there is a line which passes through such a ring and which does not end within the body, that is, it is either a closed line or it exits at the surface. This line is the disclination axis. The disclination density must be very large in amorphous materials because the distance between disclinations is of the order of several atomic distances. Disclinations break an amorphous material or a melt into regions within which the usual crystalline order is preserved to a large degree.

A space with constant curvature was recently used also to describe the blue phase of cholesteric liquid crystals.[7,8] It was discovered in Ref. 8 that the gradient term in the free energy for this phase is proportional to the square of the covariant derivative of the order parameter with a connectivity compatible with the S_3 metric. A similar expression but with a different order parameter was suggested in the same reference for the elastic energy of metallic glasses.

We show here that at sufficiently high temperature a crystal lattice is unstable to a transition into a space with constant negative curvature. In accordance with the ideas of Refs. 1–3, we interpret this transition as melting of the crystal. The disordering is due to the occurrence of a large number of disclinations. We find a connection between the curvature and the disclination density, thus, giving a clear physical meaning to the curvature. Furthermore, we calculate the free energy of the lattice as a function of temperature and curvature, and we express the melting temperature in terms of the interatomic pair potential. The curvature plays a role analogous to the role of the order parameter in the Landau theory of phase transitions. However, in our case the curvature is zero in the crystalline phase and nonzero in the disordered phase, and it could be called "disorder" parameter.

The present work has the following structure. Following the Introduction, we cite in Sec. 2 some necessary information regarding spaces with constant curvature and we also find a connection between the curvature on the one hand and the disclination tensor and the disclination density on the other. In Sec. 3 we obtain the Hamiltonian for a crystal-atom lattice in curved space. Starting from this Hamiltonian, we calculate in Sec. 4 the free energy of a solid and we show that a transition from the crystalline state to the melt takes place as temperature is increased. In Sec. 5 we find an expression for the melting temperature as a functional of the interatomic pair potential. We show in Sec. 6 that the Linde-

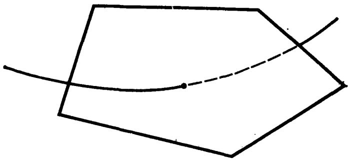

FIG. 1. A ring formed by five bonds and the corresponding disclination.

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mann criterion follows from this expression and we calculate the Lindemann parameter. In Sec. 7 we consider the nature of the phase transition and we estimate the equilibrium curvature and the size of a microregion with crystalline ordering. In the Conclusion we summarized the results of this work.

2. SPACE WITH CONSTANT CURVATURE

We shall assume that a body in a disordered phase is homogeneous and isotropic. Corresponding properties must be also observed in the non-Euclidean space which we shall associate with this body. It is known that a homogeneous space that is isotropic in a neighborhood of some point is maximally symmetric.[9] Maximally symmetric spaces are uniquely defined by the scalar curvature k and by the signature of the metric. In our case the signature is the same as in the Euclidean case [that is, the signature is (1, 1, 1)] and, thus, only one parameter, the curvature k, enters the problem. The curvature tensor $R_{\mu\nu\alpha\beta}$ and its contractions can be expressed in terms of the metric tensor $g_{\mu\nu}$ and k in the following manner:

$$R_{\mu\nu\alpha\beta}=k(g_{\alpha\nu}g_{\mu\beta}-g_{\nu\beta}g_{\alpha\mu}), \tag{1}$$

$$R_{\mu\nu}=-2kg_{\mu\nu}, \tag{2}$$

$$R_\mu{}^\mu=-6k. \tag{3}$$

For the two-dimensional case k is the Gaussian curvature of the surface, $k = 1/R_1R_2$, where R_1 and R_2 are the principal curvature radii. If the centers of the corresponding circles are on the same side of the surface then $k > 0$, if they are on different sides $k < 0$. For a sphere $k = 1/R^2$.

It is easy to find a connection between the curvature and the disclination density n. Let us draw within the body a small closed contour bounding a surface S. The turning angle of a vector during the parallel transport along the curve is[10]

$$\Delta\varphi=\iint_S k\sqrt{g}\,dx^1\Lambda\,dx^2, \tag{4}$$

where $g = \det g_{\mu\nu}$ is the determinant of the metric tensor. For small k one finds to first order in k

$$\Delta\varphi=kS+O(k^2). \tag{5}$$

If the disclination density is n and each disclination has strength φ_0 ($\varphi_0 = 2\pi/6$ for an elementary disclination, see Fig. 2) then during the parallel transport of a vector along the contour the vector turns through an angle

$$\Delta\varphi=nS\varphi_0=(\pi/3)\,nS. \tag{6}$$

By parallel transport we mean here the transport of a vector along a bond without a change in the angle between the vector and the bond.

By comparing (5) and (6) we obtain

$$|k|=(\pi/3)\,n. \tag{7}$$

The mean distance ξ between disclinations is

$$\xi=n^{-1/2}=(3/\pi)^{1/2}R,\quad R=|k|^{-1/2}. \tag{8}$$

The disclination tensor φ_{pq}, defined in Ref. 11, is related to $\Delta\varphi$ by the equation[11]

$$(\Delta\varphi)_q=\iint_S \varphi_{pq}\,dS_p, \tag{9}$$

where dS_p is the vector perpendicular to the surface dS and whose magnitude equals to the area dS. By comparing with (5) and (6) we find

$$\varphi_{pq}=k\delta_{pq}. \tag{10}$$

We need the explicit form of the metric tensor $g_{\mu\nu}$. It can be easily found if we represent the three-dimensional curved space as surface of a sphere (for $k > 0$) or of a pseudosphere ($k < 0$) in four-dimensional Euclidean space. By using the definition of the metric tensor

$$dl^2=g_{\mu\nu}dx^\mu dx^\nu \tag{11}$$

where dl is the element of length, one can determine $g_{\mu\nu}$ as[12]

$$g_{\mu\nu}=\delta_{\mu\nu}+kR_\mu R_\nu/(1-kR^2). \tag{12}$$

The metric-tensor determinant g which enters the invariant volume $\sqrt{g}d^3R$, equals

$$g=(1-kR^2)^{-1}. \tag{13}$$

We shall also consider the conformally Euclidean metric in which the infinitesimal length is proportional to its Euclidean expression

$$g_{\mu\nu}=\delta_{\mu\nu}(1+kR^2/4)^{-1}, \tag{14}$$

$$g=(1+kR^2/4)^{-6}. \tag{15}$$

We shall show that T_m is independent of the choice of metric. It is only necessary that it correspond to a space with constant negative curvature. The metric (12) is invariant to a six-parameter group: the three rotations around the origin and the three quasi translations[9] given by the transformations

$$R_\mu'=R_\mu+a_\mu[(1-kR^2)^{1/2}-bk\mathbf{Ra}], \tag{16}$$

where

$$b=1-[1-(ka^2)^2]^{1/2}(ka^2)^{-1}. \tag{17}$$

The vector $\mathbf{a}$ need satisfy only a single condition:

$$|ka^2|\leqslant 1. \tag{18}$$

The transformation (16) translates the origin into any point within a finite region. The form of this transformation is different for the metric (14) but the relationship (18) remains unchanged. The largest allowed $a = |k|^{-1/2} = R$ corresponds in our case to the size of clusters within which the

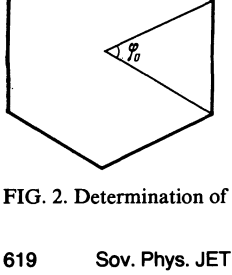

FIG. 2. Determination of the angle φ_0.

crystalline order is preserved.

3. THE EFFECTIVE HAMILTONIAN

Let us consider a crystal without specifying at present the type of its crystal lattice. We shall write the Hamiltonian of a given atom as

$$H=p^2/2m+\sum_i \varphi_0(R_i), \tag{19}$$

where **p** and m are the momentum and the mass of the atom, $\varphi_0(R)$ is the interatomic pair potential, and R_i is the distance from the nearest neighbors. It includes the fluctuation displacements,

$$\mathbf{R}_i=\mathbf{a}_i+\mathbf{r}_i, \tag{20}$$

where $\mathbf{a}_i = a\mathbf{n}_i$, a is the nearest-neighbor distance, $\mathbf{n}_i$ is the unit vector in the direction of the ith nearest neighbor, and $\mathbf{r}_i = \bar{\mathbf{r}}(0) - \mathbf{r}(\mathbf{a}_i)$ are the relative atomic displacements resulting from thermal motions. The index 0 indicates that $k = 0$.

In the harmonic approximation

$$\sum_i \varphi_0(R_i)=\sum_i \varphi_0(a)+\frac{1}{2}\sum_i \nabla_\alpha\nabla_\beta\varphi_0(R_i)\,r_{\alpha i}r_{\beta i}. \tag{21}$$

We shall be interested in fluctuations averaged over the angles. Therefore, we set

$$\langle r_{\alpha i}r_{\beta i}\rangle={}^2/_3 r^2(0)\,\delta_{\alpha\beta}, \tag{22}$$

where **r**(0) is the fluctuation displacement of one atom. By making this assumption we are neglecting correlations between fluctuations of different atoms. As a result, the Hamiltonian takes the form

$$H=\frac{p^2}{2m}+\Phi_0(a)+\frac{\alpha_0 r^2}{2}, \tag{23}$$

where we introduced the notation

$$\Phi_0(a)=\sum \varphi_0(a)=N\varphi_0(a), \tag{24}$$

α_0 is the force constant,

$$\frac{\alpha_0}{2}=\frac{1}{3}N\frac{d^2}{dR^2}\varphi_0(R)\,|_{R=a}=\frac{1}{3}\Phi_0''(R)\,|_{R=a} \tag{25}$$

and N is the number of nearest neighbors. In deriving (25) it was taken into account that $\varphi'_0(a) = 0$. Our basic assumption, consistent with the ideas of Refs. 1-3, is that the crystal starts to melt at the onset of the instability to the transition into a space with constant curvature. In order to investigate such an instability it is necessary to write the Hamiltonian (23) in the space with metric (12) or (14).

We obtain the kinetic energy by the covariant generalization

$$\frac{p^2}{2m}\to\frac{p^\mu p^\nu}{2m}g_{\mu\nu}. \tag{26}$$

In order to find the new potential energy $\Phi(R)$ it is necessary to solve the Poisson equation in the space with the metric $g_{\mu\nu}$,

$$\frac{1}{\sqrt{g}}\frac{\partial}{\partial R^\mu}\sqrt{g}\,g^{\mu\nu}D_\nu=4\pi\rho, \tag{27}$$

where $D_\nu = E_\nu/\sqrt{g_{00}} = E_\nu$, E_ν is the electric field strength

$$E_\nu=-\frac{\partial}{\partial R^\nu}\Phi(R), \tag{28}$$

and $g^{\mu\nu}$ is the tensor reciprocal to $g_{\mu\nu}$. For the metric (12)

$$g^{\mu\nu}=\delta^{\mu\nu}-kR^\mu R^\nu. \tag{29}$$

As for the charge density ρ we shall assume that it is the covariant generalization of the ideal-crystal charge density ρ_0

$$\rho=\rho_0/\sqrt{g}. \tag{30}$$

We then obtain from (27)-(30) the following equation for $\Phi(R)$:

$$\frac{\partial}{\partial R^\mu}\left(\frac{R_\mu}{R}\frac{\Phi'}{(1-kR^2)^{1/2}}\right)=4\pi\rho_0, \tag{31}$$

where the prime indicates the derivative with respect to R. By introducing the zero-curvature potential $\Phi_0(R)$ and expressing $\rho_0(R)$ in its terms [by setting $k = 0$ in (31)], we can write the equation for Φ in the following form:

$$\Phi''+\left(\frac{2}{R}-\frac{kR}{1-kR^2}\right)\Phi'-\frac{1}{(1-kR^2)^{1/2}}\left(\frac{2}{R}\Phi_0'+\Phi_0''\right)=0. \tag{32}$$

This equation can be solved by the substitution

$$\Phi=\Phi_0+f, \tag{33}$$

where f satisfies the condition

$$f'=y\Phi_0', \tag{34}$$

and y is a new unknown function. It can be easily determined from (32) with the boundary condition $\Phi(\infty) = 0$

$$y=(1-kR^2)^{-1/2}-1. \tag{35}$$

Consequently,

$$\Phi=\int_{R_0}^{R}\frac{\Phi_0'(R)}{(1-kR^2)^{1/2}}dR. \tag{36}$$

In (36) R_0 is the first zero of the potential (see Fig. 3)

$$\Phi_0(R_0)=0. \tag{37}$$

For the metric (14) the solution has the form

$$\Phi=\Phi_0+k\int_{R_0}^{R}\Phi_0'(R)R^2dR. \tag{38}$$

The new potential $\Phi(R)$ has the minimum at the same point as $\Phi_0(R)$. That is, if $\Phi'_0(a) = 0$ then

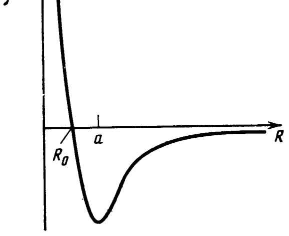

FIG. 3. Typical form of the interatomic pair potential $\varphi(R)$: a is the inter atomic distance and R_0 is the radius at which $\varphi(R)$ equals zero.

$$\Phi'(a)=(1-y(a))\Phi_0'(a)=0. \tag{39}$$

The new force constant $\alpha=(2/3)\Phi''(a)$ is different from the old force constant α_0 by the factor $[1+y(a)]$. Namely, since

$$\Phi''(R)=(1+y(R))\Phi_0''(R)+y'(R)\Phi_0'(R) \tag{40}$$

and since $\Phi_0'(a)=0$ at the minimum, we find

$$\Phi''(a)=(1+y(a))\Phi_0''(a), \tag{41}$$

$$\alpha=(1+y(a))\alpha_0. \tag{42}$$

It can be seen from (35) that the sign of $y(a)$ coincides with that of k. Therefore, a negative curvature corresponds to a frequency relaxation, while a positive curvature corresponds to a frequency increase. In the following we shall only consider the case of negative curvature because positive curvature corresponds to systems with finite volume,

$$V=\int\limits_0^{|k|^{-1/2}}\sqrt{g}\,d^3R=2\pi^2|k|^{-3/2}. \tag{43}$$

It is possible that the latter case has relevance to clusters.

Therefore, in the harmonic approximation the Hamiltonian describing small oscillations in curved space has the form

$$H=\frac{p^\mu p^\nu}{2m}g_{\mu\nu}+\Phi_0(a)+f(a)+\frac{(1+y(a))\alpha_0r^2}{2}. \tag{44}$$

We note that the stiffness α_0 can be expressed through the bulk elastic modulus B which is by definition[13]

$$B=V\,dP/dV, \tag{45}$$

where P is pressure and V is volume. At $T=0$ we have $dU=-P\,dV$ so that

$$B=Vd^2\Phi(a)/dV^2. \tag{46}$$

For a face-centered cubic lattice with a lattice constant $b_0=a\sqrt{2}$, a being the nearest-neighbor distance, one finds

$$B=\frac{\sqrt{2}}{9a}\frac{d^2\Phi(a)}{dR^2}=\frac{\alpha_0\sqrt{2}}{9a}. \tag{47}$$

For a simple cubic lattice

$$B=\alpha_0/9a. \tag{48}$$

4. THE FREE ENERGY

Using the Hamiltonian (44) we shall now find the free energy of the crystal as a function of k. The free energy F is related to the partition function Z by

$$F=-T\ln Z, \tag{49}$$

where for a single atom in the lattice

$$Z=\int d^3r\,d^3p\,g\exp(-H/T) \tag{50}$$

(we set the Boltzmann constant equal to one). We introduced the factor g so that the integration is over an invariant volume. If g is carried into the exponential one sees that the effective single-atom Hamiltonian, H_{eff}, differs from H,

$$H_{\text{eff}}=H-T\ln g. \tag{51}$$

Integration over the momenta gives precisely the same result as in the flat space, independently from the form of the metric tensor,

$$Z_{\text{kin}}=\int d^3p\sqrt{g}\exp\left(-\frac{p^\mu p^\nu}{2m}g_{\mu\nu}\right)=(2\pi mT)^{3/2}. \tag{52}$$

The configurational part of the partition function is

$$Z_{\text{conf}}=\exp\left(-\frac{f(a)}{T}\right)\int d^3r\sqrt{g}\exp\left(-\frac{\alpha(k)r^2}{2T}\right). \tag{53}$$

If we denote $\varkappa=|k|$, we have for the metric (12)

$$f(a)=\int\limits_{R_0}^{a}((1+\varkappa R^2)^{-1/2}-1)\Phi_0'(R)\,dR, \tag{54}$$

$$\alpha(\varkappa)=\alpha_0(1+\varkappa R^2)^{-1/2}, \tag{55}$$

and for the metric (14)

$$f(a)=-\frac{1}{4}\varkappa\int\limits_{R_0}^{a}\Phi_0'(R)R^2\,dR, \tag{56}$$

$$\alpha(\varkappa)=(1-\varkappa a^2/4)\alpha_0. \tag{57}$$

The integration over r in the configurational integral (53) can be extended to ∞ because the amplitude of the atomic vibrations $(\overline{r}^2)^{1/2}\sim(T/\alpha)^{1/2}$ is of the order $0.1a$ even at the melting temperature. For the same reason we can neglect with good precision the $\varkappa$ dependence in g. With these approximations, the integral over r in (53) gives

$$Z_{\text{conf}}=\frac{3}{2}\exp\left(-\frac{f(a)}{T}\right)\ln\left(\frac{2\pi T}{\alpha}\right). \tag{58}$$

Consequently, the correction to the free energy, $\Delta F=F(\varkappa)-F(0)$, connected with the curvature $\varkappa$ is

$$\Delta F=f(a)+{}^3/_2T\ln(\alpha/\alpha_0). \tag{59}$$

By substituting $f(a)$ and α as given in (56) and (57) we obtain for the metric (14)

$$\Delta F=-\frac{\varkappa}{4}\int\limits_{R_0}^{a}\Phi_0'(R)R^2\,dR+\frac{3}{2}T\ln\left(1-\frac{\varkappa a^2}{4}\right). \tag{60}$$

Similarly, for the metric (12) we obtain

$$\Delta F=\int\limits_{R_0}^{a}((1+\varkappa R^2)^{-1/2}-1)\Phi_0'(R)\,dR-\frac{3}{4}T\ln(1+\varkappa a^2). \tag{61}$$

5. THE MELTING TEMPERATURE

As can be seen from Fig. 3, $\Phi_0'(R)<0$ in the interval from R_0 to a. Consequently, the first terms in the right-hand sides of (60) and (61) are always positive. The second terms are always negative but smaller than the first terms at sufficiently low temperature. In order to draw a clearer picture we expand ΔF in a series in powers of $\varkappa a^2$, which we assume small. From (6) we obtain

$$\Delta F=\frac{\varkappa a^2}{4}\left(-\int\limits_{R_0}^{a}\Phi_0'(R)\frac{R^2}{a^2}\,dR-\frac{3}{2}T\right)+O(\varkappa^2). \tag{62}$$

For small $\varkappa a^2$ the first term is the leading one. It becomes negative for $T>T_m$, where

$$T_m=-\frac{2}{3a^2}\int\limits_{R_0}^{a}\Phi_0'(R)R^2\,dR. \tag{63}$$

Therefore, for $T \geqslant T_m$ the crystal is unstable to a transition into a space with constant negative curvature. In the Introduction we explained a possible physical meaning of this instability—in the flat physical space its appearance leads to crystal melting with T_m its melting temperature, while $\varkappa a^2$ plays the role of the disorder parameter. Similarly, we obtain from (61)

$$\Delta F = \frac{\varkappa a^2}{2}\left(-\int_{R_0}^{a} \Phi_0'(R)\frac{R^2}{a^2}dR - \frac{3}{2}T\right) + O(\varkappa^2). \tag{64}$$

The first term in this expansion becomes negative at exactly the same temperature (63).

The integral in (63) can be expressed with good accuracy in terms of experimental data. For this reason we note that

$$a - R_0 \approx 0.1a \ll a. \tag{65}$$

Therefore, there exists the small parameter $\gamma = (a - R_0)/a \sim 0.1$. For example, for the Lennard-Jones potential

$$\Phi_0(R) = A/R^{12} - B/R^6, \tag{66}$$

the minimum is at $R = (2A/B)^{1/6}$ while the first zero of the potential $[\Phi(R_0) = 0]$ is at $R = (A/B)^{1/6}$. Consequently

$$\gamma = 1 - 2^{-1/6} \approx 0.11. \tag{67}$$

Similarly, for the Morse potential

$$\Phi_0(R) = D\left(e^{-2\beta(R-R_0)} - 2e^{-\beta(R-R_0)}\right), \tag{68}$$

whose parameters D, β and R_0 have been determined for inert gases,[14]

$$\gamma = \ln 2(\beta R_0)^{-1} \approx 0.12. \tag{69}$$

If the potential $\Phi_0(R)$ is expanded into a series about $R = a$,

$$\Phi_0(R) = \Phi_0(a) + \frac{1}{2}\Phi_0''(a)(R-a)^2 + O((R-a)^3), \tag{70}$$

then as a result of integration in (53) a rapidly converging series in γ is obtained. Let us make in (60), (61), and (63) the following substitution for the derivative of Φ_0:

$$\Phi_0'(R) = \Phi_0''(a)(R-a). \tag{71}$$

Then, the expression (60) equals

$$\Delta F = \varkappa a^2 \frac{\alpha_0 a^2 \gamma^2}{8} + \frac{3}{2}T\ln\left(1 - \frac{\varkappa a^2}{4}\right), \tag{72}$$

while (61) takes the form

$$\Delta F = \frac{\alpha_0 a^2\gamma^2}{2} + \frac{\alpha_0}{\varkappa}\left[(1+\varkappa a^2)^{1/2} - (1+(1-\gamma)^2\varkappa a^2)^{1/2}\right]$$
$$-\frac{\alpha_0 a}{\varkappa^{1/2}}\ln\left[\frac{(\varkappa a^2)^{1/2} + (1+\varkappa a^2)^{1/2}}{(1-\gamma)(\varkappa a^2)^{1/2} + (1+(1-\gamma)^2\varkappa a^2)^{1/2}}\right] \tag{73}$$
$$-\frac{3}{4}T\ln(1+\varkappa a^2).$$

From (63) and (71) we obtain for the melting temperature

$$T_m = \frac{1}{3}\Phi_0''(a)a^2\gamma^2 + O(\gamma^3). \tag{74}$$

Therefore, with good accuracy, the melting temperature is determined by three parameters: $\Phi_0''(a)$ [that is, according to (47) and (48), by the bulk elastic modulus at $T = 0$], the nearest-neighbor distance, and the radius at which the potential vanishes.

6. THE LINDEMANN CRITERION

The ratio of the root-mean-square atomic displacement and the interatomic distance is in many cases equal to a single number δ:

$$\overline{r^2}/a^2 = \delta^2. \tag{75}$$

The Lindemann criterion for the melting temperature[15] postulates that a crystal starts to melt when $\overline{r^2}$ reaches a value $\delta^2 a^2$ with δ^2 a universal constant. The most precise numerical molecular dynamics calculations[16] lead to the result $\delta \sim 0.15$–0.17.

The expression (74) for the melting temperature satisfies the Lindemann criterion with good accuracy. Indeed, in the harmonic approximation the mean-square radius of thermal atomic vibrations is

$$\overline{r^2} = \int_0^\infty \exp\left(-\frac{\alpha_0 r^2}{2T}\right) r^4\,dr\left\{\int_0^\infty \exp\left(-\frac{\alpha_0 r^2}{2T}\right) r^2\,dr\right\}^{-1} = 3\frac{T}{\alpha_0}. \tag{76}$$

It follows from here that

$$\delta^2 = 3T_m/\alpha_0 a^2. \tag{77}$$

On the other hand, by neglecting in (74) the terms of order γ^3 relative to γ^2 (note that by definition $\alpha_0 = (2/3)\cdot\Phi_0''(a)$) we obtain

$$3T_m/\alpha_0 a^2 = {}^3/_2\gamma^2. \tag{78}$$

Consequently,

$$\delta = \sqrt{{}^3/_2}\,\gamma. \tag{79}$$

For the Lennard-Jones potential, $\gamma = 0.11$ and $\delta = 0.135$. For the Morse potential, $\gamma = 0.12$ and correspondingly $\delta = 0.15$.

Effective pair potentials for a number of metallic glasses ($Ca_{0.33}Mg_{0.67}$, $CaZn_2$, $CaZn_5$, etc.) are given in graphic form in Ref. 17. For them, $\gamma \approx 0.11$–0.14 and δ, determined by the formula (77), equals 0.14–0.17.

7. THE NATURE OF THE PHASE TRANSITION

A crystal with free energy (72) or (73) becomes unstable at $T > T_m$ and goes into a state with the maximum value of $\varkappa a^2$. Since it is clear that $R = \varkappa^{-1/2} \gtrsim a$, this value is $\varkappa a^2 = 1$. The free energy jump is $\Delta F = F(0) - F(1/a^2) = 0.2T_m$. Therefore, for a system with free energy (72) or (73) a first-order phase transition occurs at $T = T_m$.

As a rule, the natural frequencies of a crystal relax during melting. As we already remarked, correlations between fluctuations of the atomic displacements are not included in the present work. Consequently, the force constant α_0 is connected with a single frequency ω_E,

$$\alpha = m\omega_E^2, \tag{80}$$

where ω_E is the Einstein frequency. Correspondingly, the frequency shift is determined by the change in α,

$$\Delta\omega_E/\omega_E = {}^1/_2\Delta\alpha/\alpha. \tag{81}$$

For the metric (12) we obtain from (55)

$$\Delta\alpha/\alpha = -{}^1/_2\varkappa a^2 \tag{82}$$

and, correspondingly,

$$\Delta\omega_E/\omega_E = -{}^1/_4\varkappa a^2. \tag{83}$$

One can try to connect the curvature $\varkappa$ and ΔV with the help of the Grüneisen formula

$$\Delta\omega/\omega = -G\Delta V/V, \tag{84}$$

where G is the Grüneisen constant and $\Delta V/V$ is the relative volume change. From (83) and (84) we find

$$\varkappa a^2 = -4G\Delta V/V. \tag{85}$$

The curvature radius $R = \varkappa^{-1/2}$ equals

$$R = a(4G|\Delta V/V|)^{-1/2}. \tag{86}$$

For $G \sim 1$ and $\Delta V/V \sim 1\%$, $R \approx 5a$. The physical meaning of this radius is in that it equals the dimension of a cluster which is produced in an amorphous body or in a melt and in which short-range crystalline order is preserved. Theoretical considerations[2,18] as well as experimental facts[19] attest to the existence of such clusters.

Clearly, the value of $\varkappa a^2$ given by the formula (85) does not correspond to the values $\varkappa a^2 = 1$ to which a system with the free energy (72) or (73) tends at $T \gg T_m$. An agreement between the result (85) and the expression for the free energy can obviously be obtained by adding to ΔF the elastic energy connected with the volume discontinuity,

$$E_{\text{el}} = {}^1/_2 B(\Delta V/V)^2, \tag{87}$$

where B is the bulk elastic modulus [see Eqs. (47) and (48)] and $(\Delta V/V) \sim \varkappa^2$ according to (85). Note that E_{el} is quadratic in $\varkappa$ so that its inclusion in ΔF is not reflected in the expressions for the melting temperature and for the Lindemann parameter which are linear in $\varkappa$ as shown in Secs. 5 and 6. A precise calculation of E_{el} will be made in another work.

We note that the values of T_m in (74) are two to four times larger than the experimental values for metals (this does not affect the accuracy of the calculated δ). The reason is that correlations between thermal atomic displacements are not taken into account here. As can be shown,[20] a rough account of these correlations decreases α_0 (meaning also T_m) by approximately a factor of 2.

8. CONCLUSION

It was shown in the present work that at sufficiently high temperature a crystal lattice is unstable to a transition to a space with constant negative curvature k. The physical meanings of the curvature parameter and of the metric tensor were clarified. A connection was found between the curvature and the density of disclinations in an amorphous body or in a melt. The lattice free energy was calculated as a function of temperature and curvature. The latter plays a role analogous to the role of the order parameter in the Landau theory of phase transitions. However, in the present case $k = 0$ for the crystal and is nonzero in a disordered phase. Consequently, k is a disorder parameter. The phase-transition temperature T_m is a functional of the interatomic potential Φ (63). To a good approximation T_m depends only on the force constant $\Phi''(a)$ (i.e., on the bulk elastic modulus), on the nearest-neighbor distance, and on the radius at which the interatomic potential becomes zero [see (74)]. The Lindemann criterion for melting is satisfied in the same approximation. The value (79) was obtained for the Lindemann parameter $\delta = (\overline{r}^2/a^2)^{1/2}$ is in very good agreement with the experimental values as well as with the numerical calculations. The Einstein frequency is decreased as a consequence of the melting. The frequency shift was found as a function of k and, using the Grüneisen formula, the parameter k was connected with the volume change ΔV on melting. Equilibrium values of the curvature k and of the density of disclinations near the melting point were estimated by using experimental values for the volume discontinuity ΔV. Radius of the curvature $|k|^{-1/2}$ gives the dimension of the microdomains (clusters) within which the crystalline order is preserved. In accordance with the estimate (86) the size of such a cluster equals 3 to 6 interatomic distances, depending on the Grüneisen constant and on the volume discontinuity at the transition.

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