Vacancy theory of melting

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The features of alternative approach of non-equilibrium evolution thermodynamics are shown on the example of theory of vacancies by opposed to the classic prototype of Landau theory. On this foundation a strict theory of the melting of metals, based on development of Frenkel ideas about the vacancy mechanism of such phenomena, is considered. The phenomenon of melting is able to be described as a discontinuous phase transition, while the traditional Frenkel's solution in the region of low-concentration of vacancies can describe such transition only as continuous one. The problem of limiting transition of shear modulus to zero values in the liquid state, as well as the problem of the influence of extended state of vacancies on their mobility, is discussed.

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I. INTRODUCTION

The solids have a large number of variants of crystallographic structures and violations of these structures with such defects as vacancies, dislocations, grain boundaries etc. Under different severe external influences, such as radiation, severe plastic deformation and others they change the internal crystallographic and defect structures. To describe the changes the techniques of the theory of phase transitions is used, where the concept of order parameter or internal state variable is introduced.

The rudiments of the concept of internal state variable were offered yet Duhem in 1903 [1] (see also more detailed review in Ref. [2]). In 1928 the idea was reanimated by Herzfeld and Rice for the account of internal structure evolution of polyatomic gas when they studied the dispersion and attenuation of sound [3]. It got development in other numerous researches of that time [4—7]. Supplemented with elements of rational mechanics, the concept took a completed and closed form in the works by Coleman and Gurtin [8, 9]. In the modern science, the line is developed too [10—14]. In the works by Landau the concept was developed anew, through introducing the internal state variable in the form of the order parameter, the theory of phase transitions was built by him at a high-quality level [15, 16]. The Landau approach has resulted in further development in the theories of the phase fields [17—23]. In addition, the mesoscopic non-equilibrium thermodynamics approach was developing to fit the description of soft matter [24—29]. Studies of the problem gave birth to a plenty of variants of kinetic equations, describing the evolution of internal structure during non-equilibrium processes within the framework of different approaches (see [30] and review there).

Earlier, an alternative approach of non-equilibrium evolutionary thermodynamics (NEET) proposed to describe the processes in solids with structural defects [30—33]. In Ref. [30] the problem was subdivided into thermal and structural parts. In the first part, the molecular dynamics simulation was used to represent a thermo-motion as a superposition of equilibrium and non-equilibrium contributions. The non-equilibrium constituent was the acoustic emission, arising from dynamic transition phenomena at a moment of defect (dislocations) formation. The acoustic emission has not been considered such context before. There it was considered not only as an attenuating wave process as a consequence of both scatter on internal heterogeneities and nonlinear pumping to other frequency regions of the spectrum, but as a part of thermodynamic process of the internal energy transformation. The resulting were kinetic (evolution) equations for the production of non-equilibrium entropy and its sinking into an equilibrium thermal subsystem.

The structural part was demonstrated on the example of a solid with vacancies, and the evolution equations were deduced in terms of the internal energy. In Ref. [34] this part was justified with the attraction of the elements of statistical physics, namely, the probability distribution function (PDF). There are two levels of rigor in the description of non-equilibrium processes. At the first level the PDF, which does not change in time is taken. Maxima of this function determine the equilibrium (most probability) states and the system tends to one of them starting from an arbitrary non-equilibrium one. The second level takes into account the possibility of probability evolution in time (kinetic equations of Boltzmann, Fokker-Plank etc). But already at first level of rigor one can obtain new additional relationships.

There are few approaches to description of the melting of solids. The most simple is based on the Lindemann criterion, which determines a melting-point by the amplitude of thermal vibrations. That is, when the amplitude becomes of the order of 10 percent of interatomic distance, the crystal lattice loses stability and collapses (melts) [35—36]. This approach is not, however, universal type and for different crystals of BCC-, FCC- and HCP-type, the Lindemann constant is different. In addition, the Lindemann theory is one-phase, it does not determine the free energy for the liquid state [37]. The second
approach is based on the mechanical Born criterion of stability, a solid melts when the shear modulus becomes zero \[38, 39\]. However, the Born model is also one-phase theory which does not contain direct description of the liquid phase. The third approach, issuing from Frenkel and Eyring works, is based on order-disorder transitions with the participation of vacancies \[10, 42\]. Unlike the former approaches this theory is biphasic, however, up to now the discontinuous nature of transition between the solid and liquid state was not taken into account.

In this paper, within the framework of the developed NEET approach the vacancy theory of the melting of solids taking into account its discontinuous nature is considered. In part II, formulation of NEET is given for a solid with vacancies and interstitial atoms. For a homogeneous problem the PDF is obtained and a new form of kinetic equations symmetric in view of the use of free internal energy is deduced. In the same part the vacancy theory of the melting of metals is considered from positions of Frenkel’s concept. In part III, the discussion of the obtained results is given. The problem of the shear modulus tending to zero during transition to liquid media is discussed. Part V contains the summarizing conclusions.

II. SOLID WITH VACANCIES AND INTERSTITIAL ATOMS

A. Probability distribution function

The expressions for the thermodynamic probability \(W_V\) and the configurational entropy \(S_{cV}\) assuming the maximal degeneration of the microstates were obtained by Boltzmann for a solid with vacancies \[40\]

\[
W_V = \frac{(N + n_V)!}{N!n_V!}, \quad (1)
\]

where \(N\) is a total number of atoms in the crystal, \(n_V\) is a number of vacancies, \(k_B\) is the Boltzmann constant. Note that the configurational entropy \(S_{cV}\) is a one-valued function of the number of vacancies and it does not depend on their energy (and on temperature as well).

The expression for the thermodynamic probability \(W_i\) and the configurational entropy \(S_{ci}\) for interstitial atoms can be quite similarly written down for the maximal degeneration in microstates

\[
W_i = \frac{(N_i + n_i)!}{N_i!n_i!}, \quad (3)
\]

\[
S_{ci} = k_B \ln W_i, \quad (4)
\]

where \(N_i\) is a total number of equilibrium positions for interstitial atoms in a crystal (local minima of the potential energy), \(n_i\) is number of interstitial atoms. For different symmetries of crystals the number of such positions can be different and multiple to \(N\). Note that the configurational entropy \(S_{ci}\) is also a one-valued function of the number of interstitial atoms, which does not also depend on the energy of interstitial atoms and temperature. Provided that the microstates of vacancies and interstitial atoms are statistically independent, the total thermodynamic probability \(W\) of the microstates is

\[
W = W_V W_i \quad (5)
\]

and the total configurational entropy \(S_c\) equals to the sum of entropies of subsystems

\[
S_c = S_{cV} + S_{ci}. \quad (6)
\]

Total probability of the state containing \(n_V\) vacancies and \(n_i\) interstitial atoms will contain a limiting exponential multiplier, probability of Gibbs for this microscopic state \[43, 44\]

\[
f(n_V, n_i) = \frac{W}{Z} \exp(-\frac{U(n_V, n_i)}{k_BT}), \quad (7)
\]

where \(Z\) is the normalizing statistical sum, \(U(n_V, n_i)\) is the internal energy taking into account the existence of vacancies and interstitial atoms, \(T\) is the temperature. In conditions of the total degeneration the internal energy is a linear function of the defect number \[40\]

\[
U = U_0 + u v_0 n_V + u_0 n_i, \quad (8)
\]

where \(U_0\) is the internal energy with no contribution of defects taken into account, \(u v_0, u_0\) are average energies of a vacancy and an interstitial atom, which in this case are constant values for all possible configurations of atoms of the system.

The condition of total degeneration is practically exactly satisfied for the low numbers (concentrations) of vacancies and interstitial atoms, when the interaction between defects can be neglected. At the same time, this condition is not fulfilled for those configurations for which vacancies are close to each other or merge at all (bi-vacancies, triple vacancies, vacancy pores) and at a high vacancy concentration. The same refers to the interstitial atoms as well. In these cases it is necessary to take into account the removal of condition of total degeneracy due to the interaction of point defects. As known, the coupling interaction reduces the total energy of a system that reduces the effect of action of the limiting exponential multiplier in Eq. \[3\] and results in a possible appearance of long-living configurations, which, thus, can compete with more numerous configurations of higher energy.

The probability distribution function with total (internal) energy \(E_l\) is \[45\]

\[
f(E_l) = \frac{w(E_l)}{Z} \exp(-\frac{E_l}{k_BT}), \quad (9)
\]

where \(w(E_l)\) is the distribution of states in energy \(E_l\) or the number of microstates (configurations) with energy
$E_l$, $Z$ is the statsum over all energy states of the system
\[ Z = \sum_{l=1}^{All\ states} w(E_l) \exp\left(-\frac{E_l}{k_BT}\right). \] (10)

The states are numbered in the order of energy growth $E_{l+1} > E_l$. Distribution $w(E_l)$ depends on the number of vacancies and interstitial atoms, and on their ratio, as well as on symmetry of their location (ordering). On this account, it is impossible to fix one-to-one correspondence between internal energy and number or concentration of defects. Finding of function $w(E_l)$ is a hard combination problem, determination of power spectrum of $E_l$ as a set of acceptable energies for $l$ state, is also a stubborn problem. However, such one-to-one correspondence can be obtained for the average value of internal energy $\overline{U}$ over all of the states for the fixed number of vacancies $n_V$ and interstitial atoms $n_i$. Using expression for PDF (10), it is possible to write down
\[ U(n_V, n_i) = \frac{1}{Z} \sum_{l=1}^{V_i} E_l w(E_l) \exp\left(-\frac{E_l}{k_BT}\right). \] (11)

Here, unlike the case of Eq. (8), the internal energy is not the linear function of $n_V$ and $n_i$, but is the function of general type. The increase of fraction of the symmetric low-energy states diminishes the average value of the internal energy. The transition to the states, where high-concentration vacancies and interstitial atoms can pass to higher-energy extended (and mobiler) states [46–48], results in internal energy growth. To reflect all the properties of the internal energy it is presented in the form of a polynomial with alternating signs
\[ U = U_0 + \sum_{m=V,i} \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k} u_m k-1 n_m^k - \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} (-1)^{k+l} u_k i n_k^l n_i^l. \] (12)

The first sum describes a contribution from every subsystem of point defects separately; the second one describes a contribution from the interaction between vacancies and interstitial atoms. Sign “minus” at the second sum is because the interaction between vacancies and interstitial atoms is, on the whole, of the attracting nature. Ignoring the degeneracy within one set of the states with the same number of vacancies $n_V$ and the number of interstitial atoms $n_i$, for such average internal energy we can write down the effective probability distribution function in the form of Eq. (7) with determinations (14), (15) and (16), in which the internal energy is set not by Eq. (15), but by a more general expression (12). Brining the variables independent of the number of defects $n_V$ and $n_i$ into the “inessential” constant $1/Z$ we can write expression (17) in the form
\[ f(n_V, n_i) = \frac{1}{Z} \prod_{i=1}^{N_V} (n_V + i) \prod_{j=1}^{N_i} (n_i + j) \exp\left(-\frac{U}{k_BT}\right). \] (13)

Note that the Boltzmann thermodynamic probability for vacancies and interstitial atoms is built within the concept of statistical independence of forming these subsystems (positions of interstitial atoms do not coincide with positions of lattice sites). At the same time, in the total distribution function these systems are not independent because of the mixed terms in the internal energy (see the last sum in (12)).

Values of $n_V$ and $n_i$, at which PDF has extreme values (equilibrium states), can be found from the following transcendental equations [24]
\[ \sum_{i=1}^{N+n_V} \frac{1}{i} - \sum_{i=1}^{n_V} 1 - \frac{u_V}{kT_B} = 0, \] (14)
\[ \sum_{j=1}^{N+n_i} \frac{1}{j} - \sum_{j=1}^{n_i} 1 - \frac{u_i}{kT_B} = 0. \] (15)

where
\[ u_V = \frac{\partial U}{\partial n_V} = \sum_{k=1}^{\infty} (-1)^{k-1} u_{V,k-1} n_V^{k-1} - \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} (-1)^{k+l} u_{kl} n_V^k n_i^l \] (16)
\[ u_i = \frac{\partial U}{\partial n_i} = \sum_{k=1}^{\infty} (-1)^{k-1} u_{i,k-1} n_i^{k-1} - \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} (-1)^{k+l} u_{kl} n_V^k n_i^l \] (17)

are energies or chemical potentials of a vacancy and an interstitial atom. Eqs. (16), (17) are the equations of state for a general non-equilibrium case. Eqs (14), (15) mesh due to the mixed terms in the expansion of the internal energy in (12), determining the interaction between the subsystems of vacancies and interstitial atoms.

The first two terms in Eqs. (14), (15) are sums $S$ of slowly divergent harmonic series. This part of the equations depends only on system size and doesn’t depend on material parameters. It is the fundamental part of Eqs. (14), (15), decreasing with the growing parameter $n_V$ or $n_i$, accordingly (curves 1 of Fig. 1, 2, 3). To calculate the fundamental curve $S$ we took $N = N_i = 2000$. The last terms in Eqs. (14), (15) depend on the parameters of material through the coefficients of $u_{kl}$, and they are material parts (M) of Eqs. (14), (15). As seen, the positions of Eqs. (14), (15) roots coincide with the maxima of PDF, calculated directly by formulas (12), (13).

In the case of low concentration of vacancies and interstitial atoms Eqs (14), (15) can be solved analytically and it gives the well-known Frenkel solution [40].

**B. Equilibrium states**

It is known that the interstitial atoms have higher mobility as compared to vacancies, therefore they come to
FIG. 1. Solution of Eq. (14) for a constant energy of vacancy. The fundamental curve $S(1)$, the material curve (2) (proportional to energy of vacancy $u_V$) and PDF (3): $u_V = 1(eV)$. Other parameters equal zero. $T = 2400; 3000; 4000 (K)$. The right-hand scale is for PDF. Hereafter the graphs are constructed as a function of vacancies concentration in percent $n = 100n/N$.

the equilibrium state first (adiabatic limit). For the times larger than the adiabatic limit the contribution of interstitial atoms can be ignored, as a result we get a pure vacancy problem [34]. Consider this problem in varying degree of approximation. In the linear with respect to the number of vacancies approach for the internal energy or for the constant vacancy energy there is only one solution of Eq. (14) that is the well-known Frenkel solution [40] (Fig. 1)

$$n_{Ve} = N \exp(-\frac{u_V}{k_B T}),$$

(18)

where $n_{Ve}$ is the equilibrium value of the number of vacancies.

At lowering the energy of vacancy or at the increase of temperature the solution is continuously displaced to region of higher number (or concentration) of vacancies. We can formally get any value of vacancy concentration, but, it is clear, that too high vacancy concentrations of about 100 percent lose physical sense and the theory becomes useless. However Frenkel proposed to consider not too high vacancy concentrations of about 10 percent as transition to the liquid state. At the same time, the solution proposed by him (in approximation of the independence of the vacancy energy of the vacancy concentration) can not explain or describe the process of melting of a solid as a jump-like first-order phase transition. Transition to the region of high concentration of vacancies is continuous during temperature growth.

In the quadratic with respect to the number of vacancies approximation for the internal energy or in the linear approximation for vacancy energy Eq. (14) has already two solutions in the region of high energy of vacancy or in the region of low temperatures (Fig. 2). One of them in the region of a lower concentration of vacancies, actually, coincides with the Frenkel solution, but it is somewhat shifted due to the interaction of vacancies. The second solution in the region of a higher concentration of vacancies describes the equilibrium or stationary solution of the problem as well; however, it corresponds to a minimum of PDF and is unsteady. Probability of this state is lower not only as compared to the stable stationary state but also to any non-equilibrium state. In addition, for the low energy of vacancy or for high temperatures we enter in a region in which the solutions of Eq. (14) are absent at all. The last circumstance testifies unsuitability of the approximation in this region, so a higher approximation is needed.

In the cubic with respect to the number of vacancies approximation for the internal energy or in the quadratic approximation for the energy of vacancy, Eq. (14) can already has one or three solutions (Fig. 3). In region of high values of the energy of vacancy or low temperatures Eq. (14) has one solution, which is a Frenkel solution modified due to the nonlinear contributions. At lowering the energy of vacancy or with temperature growth the equation has three solutions, one of which (the left-hand) is the modified Frenkel solution, the second one (intermediate) is unsteady, and the third one (the right-hand) in the region of high concentration of vacancies can be treated as one proper to the liquid state of the matter. In this case, we have an equilibrium coexistence of solid and liquid phases of the matter. For a still greater increase of temperature we pass to the region with only one solution, which corresponds to clear-melted matter. The transition from the solid state to liquid one is a jump-like first-order phase transition. In order to talk about the transition just to the liquid state (not for example to the amorphous state), we need not only the high concentra-
The free energy $F = U - TS$, where $S$ is the entropy, was introduced for solution of quasi-equilibrium thermal problems in the defect-free condensed matter, as one of types of thermodynamics potential, along with the internal energy, enthalpy and Gibbs energy. In certain external conditions it, as well as other thermodynamic potentials for other conditions, possessed extreme properties as opposed to internal non-equilibrium processes. For imperfect solids, in particular solids with vacancies, according to the hypothesis of Boltzmann, the free (configurational) energy was introduced by analogy

$$F_{cV} = U - TS_{cV},$$

where configurational entropy $S_{cV}$ is set by Eqs (11), (12). Properties of thermodynamics potential were also attributed to this (configurational) free energy, and it possesses the property of minimality as to a variation of concentration of structural defects. It is easy to see that this property issues from the fact that the free energy, in a logarithmic scale and with an opposite sign, coincides within a constant with PDF (17)

$$F_{cV} = -k_BT \ln (Z_f),$$

and as a consequence the minima of the free energy automatically coincide with the maxima of PDF (compare curves 1 and 2 of Fig. 4), which determine the most probable, that is, equilibrium states. In other words, the free energy $F_{cV}$ is a quantity reciprocal to PDF, expressed in energy units on a logarithmic scale.

Energies $F$ and $F_{cV}$ to some extent similar have important principal distinctions. Namely, it is known that the internal and free energies, related by the Legendre transformations, depend on the arguments of its own $U = U(T,V)$, $F = F(S,V)$, we name them symbolically the eigen-arguments of these potentials. This property and the respective differential relationships, allow to interpret these energies as thermodynamics potentials. If we compare the energy of vacancy $u_V$ to the temperature $T$, then in this context, it is necessary to confront the number of vacancies $n_V$ with entropy $S$. It would seem the configurational free energy $F_{cV}$ must be a function of vacancy energy $u_V$, however, from relationships (11), (12) and (14) it is follows that it is a function of the number or concentration of vacancies $n_V$. It can be concluded that the free energy $F_{cV}$ is not a thermodynamics potential in strict sense.

To construct some thermodynamics potential of the free energy, note that in the case of vacancies according to (1) and (2), the configurational entropy $S_{cV}$ and the number of vacancies $n_V$ are in a mutual one-valued dependence with each other, that is, the number of vacancies $n_V$ can always be used as an independent argument instead of the configurational entropy $S_{cV}$. In this case, executing transformation of Legendre type with the pair of the conjugated thermodynamic variables $u_V$ and $n_V$, we get the alternative type of the free energy (curve 4 of Fig. 4)

$$\tilde{F}_{cV} = U - u_V n_V.$$  (21)

It is easy to show

$$n_V = \frac{\partial \tilde{F}_{cV}}{\partial u_V}.  \tag{22}$$

Relationships (16) and (22) are the joint pair of equations for the internal energy $U$ and the modified configuration free energy $\tilde{F}_{cV}$ on one side, and for the vacancy
approximation the modified configurational free energy $u$, or energy state. The stationary state corresponds to neither the maximum of the internal energy $u$ of the vacancy number, having a maximum at point $n_V = n_V_{\max}$, as is shown in the insert of Fig. 4. In that approximation the modified configurational free energy is a concave function with a minimum at point $n_V = 0$ (or $u_V = u_0$).

With relationships (16) and (22) it is easy to show that the stationary state corresponds to neither the maximum of the internal energy $U$ nor to the minimum of the free energy $F_{eV}$, as the stationary state is at point $n_V = n_{V,e}$, where $u_{V,e}$ and $n_{V,e}$ satisfy equations

$$u_{V,e} = \frac{\partial U}{\partial n_{V,e}} \neq 0, \quad n_{V,e} = -\frac{\partial F_{eV}}{\partial u_{V,e}} \neq 0. \quad (24)$$

It is known from thermodynamics that the product $TS_{cV}$ in (17), entered in determination of the canonical free energy $F_{cV}$, makes sense of the bound energy lost for the production of work. On the other side, the total energy of defects $u_V n_V$, in the main part, physically is the energy which is also lost for work production. Only a small part of it remains for work production. Then we can conclude that these two energies must be equal, at least, in the region of the equilibrium state (Fig. 5).

$$TS_{cV} \approx u_V n_V. \quad (25)$$

The energies are equivalent as we have deal, actually, with energy of the same origin, but written in different forms. The quantities, included in this relationship, are exactly enough defined, and energy $u_V n_V$, is to be understood as the total energy stocked in the defects. Temperature $T$ is the temperature of thermomotion, and it is directly unconnected with a defect subsystem. Approximate equality (23) reflects a dynamic thermal equilibrium between the thermal subsystem, as a dynamic motion of atoms, and the static subsystem of defects. The configurational entropy $S_{cV}$ is an interface between these subsystems. It is also interesting to note that both temperature $T$ and energy of vacancy $u_V$ are specific energetic characteristics of each subsystem. In addition, both the configurational entropy $S_{cV}$, and defect concentration $n_V$ possess property of additiveness, that along with their mutual one-valued accordance (1), (2) can be foundation for their interchangeability in general thermodynamic relationships.

Summarizing the above said, we can apply similar relationships and reasoning to interstitial atoms. The question of their application to other types of defects (dislocations, grain boundaries etc) remains open, as there are no simple and reliable statistical expressions for them, analogous to those presented in part II. At the same time, it is obvious that from the thermodynamics point of view all structural defects are characterized in identical way by surplus energy, spent for their formation, and they can be described by similar evolution equations, but written, for the present, at phenomenological level.
D. Kinetic (evolution) equations

If the system has deviated from the equilibrium (stationary) state it will tend to return back to that state at a speed the higher the larger the deviation. Evolutional equations for a solid with point defects, in this case, are

\[
\frac{\partial n_m}{\partial t} = \pm \gamma n_m \left( \frac{\partial U}{\partial n_m} - u_{me} \right),
\]

\[
\frac{\partial u_m}{\partial t} = \mp \gamma u_m \left( \frac{\partial \tilde{F}_{cm}}{\partial u_m} + n_{me} \right). \tag{26}
\]

Hereafter \( m = V, i \).

The form of kinetic equations (26) is symmetric with respect to the use of internal and configurational free energy. If the equilibrium state is closer to the maximum of internal energy, then, in view of solution stability, the upper sign is chosen (convex function). If it is near the minimum of internal energy, the lower sign is taken (concave function). Both variants of the kinetic equations are equivalent and their application is a matter of convenience.

At the same time, for a number of reasons, more preferable are evolution equations expressed in terms of the internal energy. First, concentration (or number) of defects is a more easily measurable variable, second, the internal energy is a base quantity in thermodynamics (the first law of thermodynamics), it is universal both for the equilibrium and non-equilibrium state and, finally, internal energy is the analogue of Hamiltonian. Setting the internal energy, as a function of state variables we specify the system and fully determine it from the thermodynamics point of view.

If we assume that the equilibrium energy of defect \( u_V = u_{V_e} \) (or \( u_i = u_{i_e} \)) and the number of defects \( n_V = n_{V_e} \) (or \( n_i = n_{i_e} \)) are slowly changing during an external load, then their product can be introduced under differentiation sign (26). It permits us to specify a new kind (shifted) of internal and free (effective) energies (see curves 5 and 6 in Fig. 4):

\[
\tilde{U} = U - u_{me} n_m, \quad \tilde{F}_{cm} = F_{cm} + u_{me} n_{me}. \tag{27}
\]

Then equations (26) are simplified a little

\[
\frac{\partial n_m}{\partial t} = \pm \gamma n_m \left( \frac{\partial \tilde{U}}{\partial n_m} \right), \quad \frac{\partial u_m}{\partial t} = \mp \gamma u_m \left( \frac{\partial \tilde{F}_{cm}}{\partial u_m} \right). \tag{28}
\]

The original potentials \( U \) and \( F_{cm} \) are connected by means of transformation of the Legendre type (21). The shifted potentials \( \tilde{U} \) and \( \tilde{F}_{cm} \) are connected by means of transformation

\[
\tilde{F}_{cm} = \tilde{U} - u_m n_m + u_{me} n_{me} + u_{me} n_{me}, \tag{29}
\]

which differs from the Legendre-type transformation by anticommutation bracket \([u_m n_m] = u_{me} n_m + u_{me} n_{me}\).

For the shifted potentials the stationary point coincides with maximum of \( \tilde{U} \) (curve 5 of Fig. 4) and with minimum of \( \tilde{F}_{cm} \) (curve 6 in Fig. 4) for the upper signs in Eq. (28). Thus, \( \tilde{U} \) is an effective thermodynamic potential, for which the tendency of the original part of the internal energy to a minimum is completely compensated by the entropic factor. Free energy \( \tilde{F}_{cm} \) tends to a minimum, but it tends to a minimum in the space of eigen-argument \( u_m \), while the free energy \( F_e \) tends to a minimum in the space of “non-eigen-argument” \( n_m \).

In the presence of only one equilibrium state \( n_{me}, u_{me} \), the effective internal energy is determined simply. In the presence of two such states transformation (27) can done for each one. In this case, we get two graphs of the effective internal energy (Fig. 6).

As the first state is in the region of convexity of the internal energy (curve 1), the graph of its respective effective internal energy has a maximum (curve 2), and in equations (26), (28) the upper signs are chosen. The second state is in region of concavity of the internal energy, and the graph corresponding to its effective internal energy has a minimum (curve 3), and in equations (26), (28) lower signs are chosen. Obviously, the evolution of the system from non-equilibrium states to the nearest equilibrium states till the inflection point on the graph of internal energy should be described by evolution equations (28), taken with upper signs, and past at that point, vice versa, with lower ones.

III. DISCUSSION AND PROSPECTS

Above it has been shown, that with the increase in the temperature of a solid some new state with high concentration of vacancies is formed, which in accordance with the hypothesis of Ya. I. Frenkel can be interpreted as the liquid state. At the same time, according to the Born hy-
pothesis a distinctive property of liquid is the absence of shear rigidity or equality to the zero of the shear modulus of material. Shear rigidity displays activation character, and it is in inverse dependence with mobility of point defects.

To study the issue let us consider a solid having only vacancies, by setting the internal energy in the form

\[ u(n_V) = u_0 + u_{V_1}n_V - \frac{1}{2}u_{V_1}n_V^2 + \frac{1}{3}u_{V_2}n_V^3, \]  

(30)

where \( u_0 \), \( u_{V_1} \) (\( l = 1, 2, 3 \)) are some coefficients dependent on temperature \( T \) and elastic deformation \( e_{ij}^e \), as on control parameters. For the sake of convenience and further standardization we have passed from the number of vacancies to their concentrations \( n_V \) (\( n_V = n_V/N \)), and in a similar way to specific internal energy \( u = U/N \). Then

\[ u_0 = \frac{1}{2}\lambda(e_{ii}^e)^2 + \mu(e_{ij}^e)^2, \]

\[ u_{V_0} = u_{V_0} + \frac{1}{2}\bar{\lambda}(e_{ii}^e)^2 + \bar{\mu}(e_{ij}^e)^2, \]  

(31)

where \( \lambda \) and \( \mu \) are Lame moduli for a vacancy-free solid, \( \lambda, \bar{\mu} \) are corrections to the elastic moduli due to existence of vacancies (defect of a modulus), \( e_{ij}^e \) is the first invariant of the tensor of deformations, \( (e_{ij}^e)^2 = e_{ij}^e e_{ji}^e \). It is assumed that contribution of invariants is the most substantial at the lower degrees of presentation \( \bar{\mu} \).

Expression for the effective shear modulus within the framework of this model is

\[ \mu_{ef} = \mu - \bar{\mu}V n_V. \]  

(32)

The sign “minus” is chosen provided, that the effective modulus in material with vacancies is less than in the vacancy-free one (see Fig. 2.3 in \[49\]). The first term \( \mu \) is shear modulus in a vacancy-free crystal. It can be interpreted as a local (microscopic) modulus of the lattice in regions far from vacancies. The effective (macroscopic) modulus \( \mu_{ef} \) is a quantity averaged over volume containing a lot of vacancies. It is remarkable, that at a phase transit point at melting, namely, the effective macroscopic modulus goes to zero exactly, while the microscopic modulus does not convert to zero \[39\].

A few types of the temperature dependence for the shear modulus are known. For example, there is a quadratic dependence \( \mu(T) = \mu_0(1 - T/T_0) \) \[39\]. More known semi-empirical relationship is \[51\], \[52\]

\[ \mu(T) = \mu_0 - \frac{D}{\exp \left( \frac{D}{T_0} \right) - 1}. \]  

(33)

where \( \mu_0 \) is the shear modulus for \( T = 0K \), and \( D, T_0 \) are material constants. The constant \( T_0 \) can be treated as an activation energy \( T_0 = E_a/k_B \), and the relationship \[33\] is presented as

\[ \mu(T) = \frac{\mu_0 - (\mu_0 + D) \exp \left( -\frac{E_a}{k_BT} \right)}{1 - \exp \left( -\frac{E_a}{k_BT} \right)}. \]  

(34)

According to Born principle, the temperature of melting can be defined on condition \( \mu(T_m) = 0 \)

\[ T_m = \frac{E_a}{k_B \ln \frac{\mu_0 + D}{\mu_0}}. \]  

(35)

A formal agreement between the theory presented in part II and relationship \[35\] can be obtained by taking the temperature of phase transition for the temperature of melting \( T_m \). At the same time, it is more logically to present the shear modulus as a two part one consisting of two terms, actually, shear modulus at zero temperature \( \mu_0 \) and an activation depressed term

\[ \mu(T) = \mu_0(1 - \exp \left( -\frac{E_a}{k_BT} \right)), \]  

(36)

However, in obedience to this expression, the shear modulus does not go to zero at limit temperature \( T_m \), but only at \( T = \infty \). It is known in the theory of amorphous materials, that activation energy is proportional to the shear modulus \( E_a \sim \mu \) \[53\]. It can be assumed that a similar supposition is just for crystalline solids too, at least, in the pre-melting state, for in this state its structure becomes amorphous-like. Then relationship \[36\] can be rewritten as

\[ \mu_{ef} = \mu_0(1 - \exp \left( -\frac{\alpha \mu_{ef}}{k_BT} \right)). \]  

(37)

It is taken into account that here we have the effective shear modulus.

It is remarkable that this equation has a trivial zero solution \( \mu_{ef} = 0 \). This solution is important as it can serve for description of non-activation motion of liquid phase to which all solids pass as a result of melting.

The graphs of temperature dependences of the shear modulus are shown in fig. 7. Curve 1 proper to semi-empirical theory \[34\], slowly changes at low temperatures and sharply diminishes to zero, passing to the region of negative unphysical values. Curve 2, built for the effective shear modulus by formula \[37\], changes already at low temperatures and is more declivous. It smoothly tends to zero, not passing to the region of negative values. In addition, zero values of the effective shear modulus identically satisfy equation \[37\], describing a liquid phase legalistically in the whole of temperature interval, however, this solution is realized only after the phase transition. Curve 3, which corresponds to the shear micro-modulus, does not go to zero at a “melting” point.

The graphs of Fig. 7 correspond a continuous change with the temperature of the shear modulus in the solid phase. However, at the real melting-point because of the first-order phase transition the change can be sharper (see the arrow). Similar transitions are observed in the real materials (see, for example, Fig. 1 in Ref. \[54\]).

At low temperatures, a basic contribution to shear deformation is from dislocations in view of their greater spatial size and higher mobility. In obedience to the Cottrell
theory, mobility of dislocations is the higher, the wider their dislocation cores \[55\]. Mobility of vacancies at low temperatures is negligibly small.

At more high temperatures the situation, however, changes cardinaly. Vacancies due to the thermomotion become delocalized in space, forming the so-called extended defects of higher mobility \[46–48\]. The total energy barrier of a vacancy splits on a great number of barriers of lower height, which are considerably easy overcome due to thermal fluctuations. The number of variants of overcoming these barriers increases thus, here the vacancies have certain advantage over dislocations. The extended vacancy is a three-dimensional defect and the number of variants for “lateral” passing by potential barriers grows quadratically, while dislocation is a two-dimensional object and the number of variants in plane the perpendicular to line of dislocation increases only linearly. Thus, in transition to the liquid state at point higher than the temperature of melting, a vacancy mechanism becomes so perfect, that a solid loses resistance to the change of form fully. And the vacancy emptiness is uniformly distributed (dissolves) in the bulk of material so, that a single vacancy can not be practically identified and its presence is talked about only legalistically.

For a more deep accordance it is necessary to take into account the fact of temperature dependence of the shear modulus in expansion of the internal energy \[30\], \[51\]. If we substitute relationships \[30\], \[32\] to PDF \[11\], we get a more complicated dependence of PDF on temperature in the presence of double exponents there. However, this does not at all affect the calculations of equilibrium values of point defects concentration in solids being in the free state, because in this state \(\epsilon_i^e = 0\). Due to it, it becomes possible to examine the phase transition and the change of elastic properties (shear modulus) during such transition separately. In the presence of external stresses and the resulting elastic deformations, the influence of defect mobility must already be taken into account, as well as to take into account the influence of other types of defects on the process.

Earlier in a phenomenological variant, the approach was applied for the description of processes of defect formation and work hardening in metals treated by severe plastic deformation \[31\], \[33\], auto-vibration transitions between the amorphous and nanocrystalline states in amorphous alloys \[58\], processes of slipping and stick-slip in the super-thin lubricants \[57\], \[58\]. In particular, within the indicated models, to describe the stick-slip effects the processes of transitions between solid and liquid states, that is, processes of melting and solidification, are examined. In prospect, the method can be applied for the description of kinetic processes of defect formation and forming the properties in different physical systems, including soft-matter \[59\], \[60\], complex protein compounds \[61\], etc.

IV. SHORT CONCLUSION

In the article, within the framework of ideas of non-equilibrium evolutional thermodynamics, the vacancy theory of melting of solids is considered. With the account of removal of degeneration of vacancy energies due to their interaction and approximation of this interaction by polynomial presentation of the internal energy it was possible to generalize Frenkel concepts and to describe the process of melting as jump-like 1st-order phase transition. It is evident that the influence of interstitial atoms on the process of melting is not of principle, as the corresponding material curves lie higher than the same curves for vacancies and do not cross the fundamental curve in this temperature region. They can only a bit shift the proper stationary (equilibrium) solutions for vacancies. Influence of dislocations on the behavior of the system can play a role at relatively low temperatures. At temperatures close to the melting point, because of the size effect of increasing vacancy mobility, they become decisive in shear deformation of the material. The shear modulus here tends to zero. It is shown that apart from the tendency to the zero of the shear modulus of the solid phase, the system has another state with the shear modulus identically equal to zero, which is realized exceptionally for the liquid state. The transition to this state can be realized earlier, than the shear modulus reaches zero, that is, the real melting point will lie somewhat to the left from the point at which the shear modulus becomes zero.

In addition, in the article on the example of solid with vacancies, a more general theory of non-equilibrium evolutional thermodynamics has been illustrated. It is shown that kinetic equations can be written not only in terms of the free energy, but also in terms of internal and modified free energy. The whole system of interconnected non-equilibrium thermodynamic potentials is obtained, including, effective internal and modified free energy.
energy. Intercommunication between classical and modified free energy through the component of bound energy in the both forms is analyzed (fig. 5).

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