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Formation of the internal structure of solids under severe load

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An alternative form of kinetic equations, involving the internal and free energies symmetrically, has been derived in the framework of the theory of vacancies. Dynamical nature of irreversible phenomena during formation and motion of defects (dislocations) has been analyzed by a computer experiment. Results of this simulation are then extended into a thermodynamic identity, involving the law of conservation of energy at interaction with an environment (the first law of thermodynamics) and the law of energy transformation in the internal degrees of freedom (relaxation). This identity is compared to the analogous Jarzynski identity. The approach is illustrated by simulation of processes during severe plastic deformation; the Rybin kinetic equation for this case has been derived.

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I. INTRODUCTION

Thermodynamics of internal state variables has a long history. An important idea to account for internal microstructure changes in polyatomic gas by introducing an additional variable was proposed by Herzfeld and Rice in 1928 [1]. Later, the concept was used by Mandelshtam and Leontovich for solving a similar problem for liquids [2]. Supplemented with elements of rational mechanics, the concept took a completed and closed form in the works by Coleman and Gurtin [3]. The concept was given an alternative development in the works by Landau, who constructed a phenomenological theory of phase transitions based on the newly introduced internal state variable, the order parameter [4,5].

A large variety of kinetic equations has been proposed, describing changes in the internal structure under nonequilibrium conditions, within the conceptual framework of constitutional theories [6,7], continuum theories of defects [8–11], extended continuum theories [12,13], self-organization theories of dislocations [14–16], gradient [17,18] and nonlocal theories [19,20], mesoscopic theories [21,22], and so on. There is a special need to mention the works of Landau's school [4,5], which was developing one of the most physical lines of the theory of nonequilibrium phenomena. In the modern science, the line is presented by phase-field theories [23–29]. Unlike the Landau theory, the order parameter of phase-field theory is not well defined, but it does not hinder getting the results which are in a good accordance with the behavior of real systems.

The order parameter, introduced by Landau, is a type of an internal variable and, therefore, it should describe changes in real structural state of a system. This description, however, is not directly expressed in terms of structure itself but through an immediate indicator, connected with symmetry change. It may turn out that in some applications, it is more convenient to relate a system state directly to the change of a specific structural parameter, for example, the density of defects.

Internal phenomena in solids represent a complex pattern of mutual transformations of the energy between different forms. In most cases, the physical nature of these phenomena is not defined concretely [30]. It is assumed that they are of fluctuation origin [31,32]. At the same time, the generation and motion of structural defects in a solid under severe external action can also be regarded as some internal process, characterized by a set of internal variables [33]. These channels of energy dissipation still differ from traditional viscous channels due to the dynamic nature of relaxation, involving the defects. It does not run directly by means of transition of the organized energy to chaotic thermal one but goes through a series of intermediate levels and stages. During generation of defects, a part of organized (elastic) energy is spent directly on the formation of structural defects which, along with the thermal channel, make parallel channels of dissipation.

Transformation of the energy into thermal form is not immediate. Initially, it is radiated as low-frequency vibrations and waves (acoustic emission), which can be treated as a part of the general dissipation phenomenon [34–36]. Thereupon, this part of the energy replenishes the energy of the equilibrium thermal vibrations (waves). So, the energy stored in the nonequilibrium subsystem is usually small.

The present paper is devoted to the development of the Landau approach. In Sec. II on the example of the vacancy theory, an alternative form of kinetic equations symmetrical with respect to free and internal energy utilizations is proposed. In this section, invoking molecular-dynamics simulation, we separate equilibrium and nonequilibrium heat subsystems of a solid under severe load and introduce a notion of nonequilibrium temperature. In Sec. III, the results are extended in the form of a thermodynamic identity, combining the first and second laws of thermodynamics for the described processes. These results are discussed in Sec. IV. Section V is devoted to the application of kinetic equations to the description of grain refinement during severe plastic deformation. Our conclusions are presented in Sec. VI.

II. KINETIC EQUATIONS

To start with the analysis, it is convenient to maximally simplify the problem. Let us split it into two separately treated parts: the first, structural one, connected with genera-

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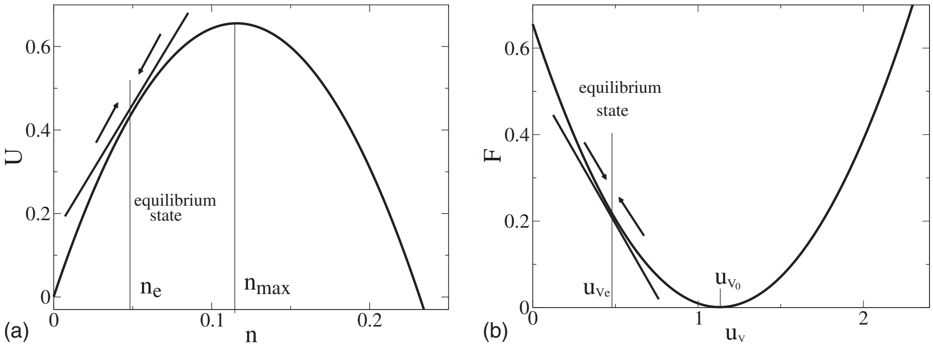

FIG. 1. Plots of the internal (a) and free (b) energies vs its eigenarguments. Tendency of the system to the equilibrium state is indicated by arrows.

tion of defects and the second, thermal part. Moreover, we consider the structural part of the problem basing on the simplest example of a solid with vacancies.

A. Structural part of the problem

The classical theory of vacancies was developed by Frenkel [37], who presented the internal energy of a solid with vacancies in the form $U=U_0+u_V n$, where U_0 is the internal energy of the vacancy-free crystal, u_V is the average vacancy energy, and n is the number of vacancies. Next, the transformation to the configurational free energy $F_c=U-TS_c$, where T is the temperature and S_c is the configurational entropy, is performed. The product TS_c is the vacancy-bounded energy. The configurational entropy is uniquely determined by the number of vacancies $S_c=S_c(n)$ and, for example, at low vacancy density [38]

$$S_c = kn\left(1 + \ln\frac{N}{n}\right), \tag{1}$$

where k is the Boltzmann's constant and N is the total number of occupied lattice sites. The equilibrium value of the number of vacancies n_e is found from the free-energy minimum, assuming that the vacancy energy is independent of the number of vacancies, that is, $u_V=u_{V0}$, where u_{V0} is a constant value for a given matter. The free-energy minimization procedure results in the equation of state $n_e=N\exp[-(u_{V0}/kT)]$.

To account for the dependence of vacancy energy on the vacancy number, a quadratic correction to the internal energy is considered

$$U = U_0 + u_{V0}n - \frac{1}{2}u_{V1}n^2, \tag{2}$$

where u_{V1} is a constant. As the energy needed for the formation of a new vacancy in the presence of the others is smaller than in the vacancy-free crystal, the correction term has a negative sign. Note that expression (2) is true for both equilibrium and nonequilibrium states. In this approximation, the internal energy is a convex function of the defect number having the maximum at point $n=n_{\max}$, as shown in Fig. 1(a). For the transition to the free energy with the Legendre's transformation, the bound energy TS_c should be subtracted from the internal energy.

Many problems in statistical mechanics simplify greatly when treated in terms of chemical potential [39]. Regarding a vacancy as an effective particle, one can, equivalently, reformulate the approach in terms of the chemical potential. In this context, the product $u_V n$ is the vacancy-bound energy too, as this part of energy is lost for work. Consequently, one can write down the bound energy in two closed forms

$$TS_c \approx u_V n. \tag{3}$$

Following the Landau style, we present a generalized thermodynamic force for nonequilibrium state in the form

$$u_V = \frac{\partial U}{\partial n} = u_{V0} - u_{V1}n. \tag{4}$$

Relationship (4) can be treated as an equation of state, valid both for the equilibrium and nonequilibrium cases. Applying, though formally, the Legendre transformation with respect to the pair of conjugate variables u_V and n and with the relation (3) and the equation of state (4), one obtains for the main part of configurational free energy

$$\tilde{F}_c = U - u_V n = U_0 + \frac{1}{2u_{V1}}(u_{V0} - u_V)^2. \tag{5}$$

Note that an eigenargument of the internal energy is the vacancy number (density) and the eigenargument of the configurational free energy $\tilde{F}_c$ is the vacancy energy. In this approximation, the free energy is a concave function with the minimum at point $u_V=u_{V0}$, as it is shown in Fig. 1(b).

We define the equilibrium state from a macrocanonical distribution, taking it in the form

$$f(n) = C\frac{(N+n)!}{N!n!}\exp\left(-\frac{U(n)}{kT}\right). \tag{6}$$

The pre-exponential factor describes the combinational (that is, entropic) part of the distribution function, associated with degeneration of macrostates. The exponential factor describes the restrictive part of the distribution function, associated with the overcoming of potential barriers between the microstates. The most probable state determined from condition $\partial f(n)/\partial n=0$ gives the equation of state in the form

$$n_e = N\exp\left(-\frac{u_{Ve}}{kT}\right), \tag{7}$$

which is true only for an equilibrium case. Here, the additional subscript e denotes the equilibrium value of the variable. The equations of state (7) and (4) must be identical for the equilibrium case. Substituting Eq. (7) into Eq. (4), one gets a condition for determination of this state

$$kT\ln\frac{N}{n_e} = u_{V0} - u_{V1}n_e. \tag{8}$$

In accordance with relationship (8), it is easy to show that the equilibrium state corresponds neither to the maximum of the internal energy U nor to the minimum of the free energy $\tilde{F}_c$. The equilibrium state is at point $n=n_e$, where

$$u_{Ve} = \frac{\partial U}{\partial n_e}, \quad n_e = -\frac{\partial \tilde{F}_c}{\partial u_{Ve}}. \tag{9}$$

If a system has deviated from the equilibrium state, then it should tend back to that state with a speed, which is the higher, the larger the deviation

$$\frac{\partial n}{\partial t} = \gamma_n\left(\frac{\partial U}{\partial n} - u_{Ve}\right), \quad \frac{\partial u_V}{\partial t} = -\gamma_u\left(\frac{\partial \tilde{F}_c}{\partial u_V} + n_e\right). \tag{10}$$

Both variants of the kinetic equations are equivalent and their application is a matter of convenience. The form of kinetic equations (10) is symmetric with respect to the use of the internal and configurational free energies. In the right-hand parts of Eq. (10), the signs are chosen based on solution stability, so that the internal energy is a convex function and the free energy is a concave one. For the well-known Landau-Khalatnikov kinetic equation

$$\frac{\partial n}{\partial t} = -\gamma\frac{\partial F_c}{\partial n}, \tag{11}$$

the contradiction is typical. It is written in terms of the free energy, but the evolved variable is not its eigenargument. However, one could show that Eq. (11) can be derived from the second Eq. (10) in the limit of independence of the defect energy of the defect number $u_{V1} \to 0$.

Thus, the Landau-Khalatnikov equation can be conveniently extended to the types of defects, where the above condition is satisfied. In the general case, when the defect energy depends on the defect number and considerably changes in a studied process (for example, in the case of severe plastic deformation in metals with grain boundaries as defects), it is more convenient to use kinetic equations in the form (10). Peculiarities of the thermal part of the problem can be considered for a special case of dislocation generation during the indentation.

B. Thermal part of the problem

Time scans of the vibrationlike thermal motion of lattice atoms can be processed as time series using signal-processing methods. Every atom participates simultaneously in the equilibrium and nonequilibrium motions. Due to differences in frequency, they can be separated by means of an ordinary filtration.

At present, however, there are no experimental methods to register the motion of individual atoms. At the same time, molecular-dynamics simulation allows to calculate motions of all atoms of the lattice in detail. As an example, let us consider the simulation of indentation into a two-dimensional (2D) copper crystallite consisting of 80 ×70 atoms. The indenter (three atoms under arrow) moves at a constant velocity of 5 m/s (see Fig. 2). The lowest row of atoms is motionless. All lateral faces are free. The sample consists of copper atoms interacting through the Lennard-Jones potential. A detailed general formulation of the problem can be found in Ref. [40].

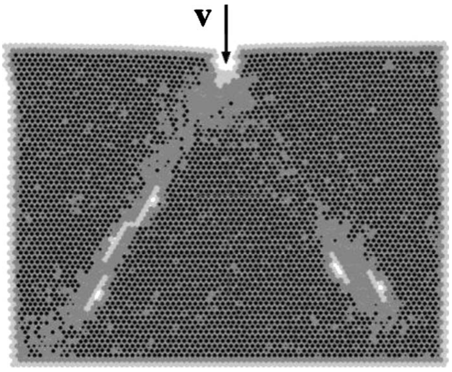

FIG. 2. Geometry of 2D computer experiment positions of atoms at the time 0.21 ns. Brighter hue corresponds to higher potential energy of particles near dislocation cores.

The applicability of centrosymmetric MD potentials, in particular, such as the Lennard-Jones Cu model used here to large-scale plastic deformation, frequently has poor matches for defect energies, such as dislocation cores. For the present problem, this is not a serious issue as we do not claim that we are modeling real copper. It is well known that the Lennard-Jones potential more suits the modeling of crystals of noble gases [41,42]. Nevertheless, it is often used for qualitative modeling of simple metals, copper, gold, and so on [43–46], including 2D systems [47,48].

At certain moments, during the indentation, dislocations emerge, as shown in Fig. 2. They correspond to bends of the curve 1 in Fig. 3, showing the time dependence of the total internal energy or to the jumps of total potential and kinetic energies (curves 2 and 3). The external work performed during the indentation increases total energies of all kinds. Further, for t=0.055, 0.14, 0.24, 0.39, and so on, the potential energy decreases sharply. Part of this energy transforms into defect energy and the remaining part must dissipate into heat.

Bottom subplots in Fig. 3 present the time dependences of the X and Y components of velocity for an arbitrarily chosen particle of the system (near the center of the model), which actually are records of its thermal motion (incurves 4 and 6). From a formal point of view, thermal motion can be treated as a high-frequency signal, close to a harmonic one for separate interatomic (bond) vibrations. The spectrum severely oscillates because of the interference of a large set of high-frequency phonons [see region 1 in Fig. 4(a)]. In the low-frequency region, a large peak 2 stands up sharply against the rest of the spectrum. One can assume that its presence is associated with the regular low-frequency vibrations in the system.

Carrying out the low-frequency filtration by a running average method over 200 time steps, one can separate the low-frequency vibration modes (bright curves 5 and 7 against main black signals). To make sure that these low-frequency

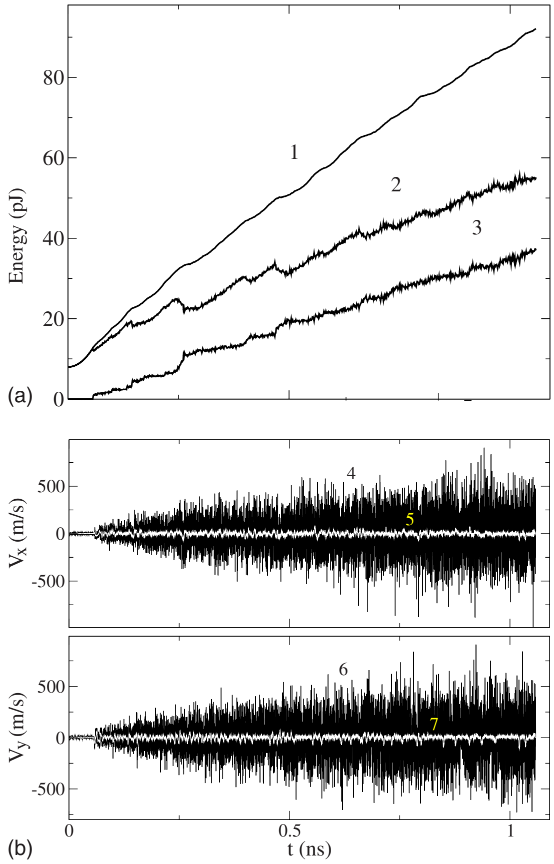

FIG. 3. (Color online) Time scanning: 1–3: total internal, potential, and kinetic energies, consequently, 4 and 5: *X* and *Y* components of velocity of an arbitrary particle in the center of the model (light lines are low-frequency records of particle velocity after filtration).

vibrations are associated, namely, with the peak 2 of the spectrum of Fig. 4(a), the filtrated record was subtracted from the total record and for this difference signal and the spectrum was calculated again [Fig. 4(b)]. As seen, the low-frequency peak vanishes from the spectrum of the difference record.

Comparing curves 2, 3, 5, and 7, one can immediately see that the initiation of the low-frequency vibrational excitations coincides in time with the generation of dislocations and they can be, in a sense, associated with strongly nonlinear acoustic emission. On the other hand, they can be treated as nonequilibrium phonons with amplitudes far exceeding the amplitudes of corresponding low-frequency range of the spectrum which would be realized in thermal equilibrium [compare spectra of Figs. 4(a) and 4(b)]. Thus, using the low-frequency filtration, it is possible to separate, in the pure state, the nonequilibrium subsystem (light curves 5 and 7) and the equilibrium subsystem (the difference signal) of a thermal motion. The acoustic waves scatter inelastically by the equilibrium high-frequency vibrations and, as a result, became damped. Decay of these waves is just a process of nonequilibrium state relaxation. As a result, the energy of the acoustic waves gradually transforms into the energy of the equilibrium thermal motion leading to slow increase of equilibrium temperature and entropy.

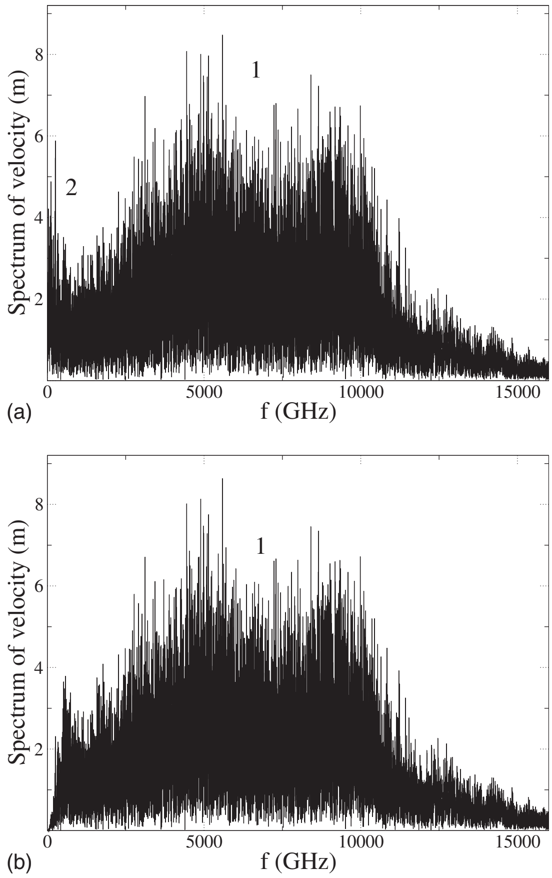

FIG. 4. Spectrum of complete record for velocity of a particle. 1: main high-frequency region; 2: low-frequency peak.

During the indentation, dislocations emerge repeatedly in time. That is why some number of the low-frequency nonequilibrium wave packets is always present as part of the integral thermal motion. On one hand, they are generated as a consequence of the mentioned processes of defect formation. On the other hand, they are constantly going to the equilibrium subsystem. By averaging the square of particle velocity (that is, the kinetic energy) for the difference record over time window containing 1000 time steps, we obtain an equilibrium temperaturelike variable T (curve 1, Fig. 5). Such averaging window contains nearly 20 periods of the high-frequency vibrations and it seems to be enough to smooth of random fluctuations of the thermal motion. As seen, the equilibrium temperature T increases as the energy of nonequilibrium low-frequency vibration transforms into the equilibrium high-frequency motion.

As the low-frequency acoustic wave differs from the high-frequency phonons only in the time scale, then applying the same averaging procedure but over a larger time window containing in the given example 10 000 time steps, it is possible to definite an analogous variable for the nonequilibrium subsystem (curve 2, Fig. 5). It can be given a sense of a nonequilibrium temperature $\widetilde{T}$ (or temperature of the nonequilibrium subsystem). Thus, the digital filtration allows us to separate equilibrium and nonequilibrium components in the initial data and to calculate their temperature parameters.

Now, equilibrium S and nonequilibrium $\widetilde{S}$ entropies can be defined as variables thermodynamically conjugate to the

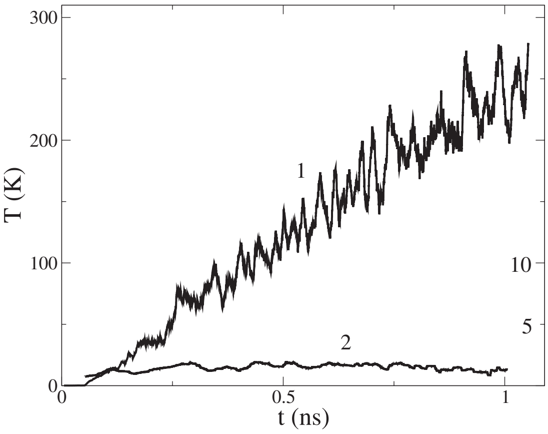

FIG. 5. Time scanning. 1: temperature of equilibrium subsystem; 2: temperature of nonequilibrium subsystem. For comparison, the scale of curve 2 (the right scale) is 10 times magnified.

two kinds of temperatures described above. The dependence of the internal energy U on the nonequilibrium entropy $\tilde{S}$ can be written in the form similar to Eq. (2)

$$U = U_0 + T_0\tilde{S} - \frac{1}{2}T_1\tilde{S}^2, \tag{12}$$

where U_0, T_0, and T_1 are some expansion coefficients. Then, the nonequilibrium temperature $\tilde{T}$ can be written down as

$$\tilde{T} = \frac{\partial U}{\partial \tilde{S}} = T_0 - T_1\tilde{S}. \tag{13}$$

Production of the nonequilibrium entropy can be described by a kinetic equation similar to Eq. (10)

$$\frac{\partial \tilde{S}}{\partial t} = \gamma_{\tilde{S}}\left(\frac{\partial U}{\partial \tilde{S}} - \tilde{T}_e\right) = \gamma_{\tilde{S}}(T_0 - T_1\tilde{S} - \tilde{T}_e). \tag{14}$$

Here, T_0 can be interpreted as some "temperature" of the internal entropy sources as a consequence of the dislocation generation such that $\gamma_{\tilde{S}}T_0$ is the power of entropy sources. This temperature characterizes the intensity of generation of the low-frequency vibrations during transient dynamical processes developing under genesis of dislocations (the acoustic emission). The second term $T_1\tilde{S}$ is a relaxation one. It describes transition of the entropy $\tilde{S}$ from the nonequilibrium subsystem to equilibrium one due to the absorption of the low-frequency vibrations as a consequence of their interaction with the equilibrium high-frequency ones. Coefficient T_1 characterizes the intensity of this relaxation process. $\tilde{T}_e$ is a stationary nonequilibrium temperature value the system tends to during its relaxation. Note finally that in the phenomenological definition (13), the temperature $\tilde{T}$ is somewhat different from the temperaturelike variable in the above computer experiment as, in the latter case, only the kinetic energy of a particle is taken in account.

III. THERMODYNAMIC IDENTITY

The results of the previous section and their interpretation allow us to make some useful generalizations. In thermodynamics and theory of self-organization, the subdivision of entropy change is well known [49]

$$\Delta S = \Delta_e S + \Delta_i S, \tag{15}$$

where $\Delta_e S$ is the entropy change owing to heat flux from external sources (thermostats). The heat flux is globally nonequilibrium but a locally equilibrium process. $\Delta_e S$ is positive at heating and negative at cooling. $\Delta_i S$ is the entropy production due to irreversible phenomena from internal sources. Namely, this part of the entropy specifies the second law of thermodynamics and is always nonnegative. It is of a dual nature: on one hand, this contribution to entropy is caused by nonequilibrium and irreversible nature of phenomena, on the other hand, this entropy part converts constantly to equilibrium form. Therefore, it is pertinent to present this part of the entropy as a sum

$$\Delta_i S = \Delta_i^e S + \Delta_i^n S, \tag{16}$$

where $\Delta_i^e S$ is the part of produced entropy, succeeded in transforming to the equilibrium form during external action, and $\Delta_i^n S$ is the part of produced entropy, which remains in the nonequilibrium form and should relax later. The former part $\Delta_i^e S$ became indistinguishable from the other part of the equilibrium entropy (thermal degeneration) which had already been existing in the system before the action. Thus, it makes sense to integrate them denoting

$$\Delta_{eq} S = \Delta_e S + \Delta_i^e S, \tag{17}$$

so that the total entropy change is

$$\Delta S = \Delta_{eq} S + \Delta_i^n S. \tag{18}$$

Such representation of the entropy production is one of the original results of this paper. Usually, one neglects the nonequilibrium part of the entropy $\Delta_i^n S$. Entropy production is accompanied by heat production which, in the first approximation, can be presented as a linear combination of entropy changes of the both kinds

$$\Delta Q = T\Delta_{eq} S + \tilde{T}\Delta_i^n S, \tag{19}$$

where T and $\tilde{T}$ are some coefficients of proportionality with a dimension of temperature. Coefficient T has the physical meaning of the equilibrium temperature. Coefficient $\tilde{T}$ can be assigned a meaning of nonequilibrium temperature or of a temperature of nonequilibrium subsystem.

The total change of the internal energy under the external actions, due to the change of internal structure in relaxation processes, can be written as a linear combination of changes of all independent variables

$$dU = V\sigma_{ij} d\varepsilon_{ij}^e + TdS + \tilde{T}\Delta\tilde{S} + \sum_{l=1}^{N} \varphi_l \Delta H_l, \tag{20}$$

where more compact notations $dS = \Delta_{eq} S$ and $\Delta\tilde{S} = \Delta_i^n S$ are used. The first term is the change of the internal energy, coinciding with the change of the elastic energy, σ_{ij} is the stress tensor, and ε_{ij}^{e} is the elastic deformation tensor [3]. The last term stands for the change of the internal energy owing to defect subsystems, H_l is the number of l-type defects, and φ_l is the factor having the meaning of a defect energy. Here it is taken into account that the internal energy, the elastic deformation, and the equilibrium entropy are functions of state (therefore, their decrements are perfect differentials).

If, following Landau's idea, one treats the nonequilibrium variables $\tilde{T}$ and φ_l as generalized thermodynamic forces, for which relationships of the type (4)

$$\tilde{T} = \frac{\partial U}{\partial \tilde{S}}, \qquad \varphi_l = \frac{\partial U}{\partial H_l} \tag{21}$$

hold, then, in expression (20), the increments of the independent variables $\Delta\tilde{S}$ and ΔH_l can be replaced by their exact differentials

$$dU = V\sigma_{ij}d\varepsilon_{ij}^{e} + TdS + \tilde{T}d\tilde{S} + \sum_{l=1}^{N}\varphi_l dH_l. \tag{22}$$

Thus, the increment of the internal energy can be expressed in a perfect differential form and, consequently, we can introduce an extended nonequilibrium state, specified by a set of independent variables ε_{ij}^{e}, S, $\tilde{S}$, and H_l. Some of these variables ε_{ij}^{e} and S are equilibrated; the others, $\tilde{S}$ and H_l, are nonequilibrated. The internal energy is a function of these variables

$$U = U(\varepsilon_{ij}^{e}, S, \tilde{S}, H_l). \tag{23}$$

To describe the isothermal phenomena, it is convenient to convert to the free energy $F=U-TS$ of the differential form

$$dF = V\sigma_{ij}d\varepsilon_{ij}^{e} - SdT + \tilde{T}d\tilde{S} + \sum_{l=1}^{N}\varphi_l dH_l. \tag{24}$$

IV. DISCUSSION

One can treat relationship (22) as a combination of the first and second laws of thermodynamics, written in the form of identity. Previous attempts to formulate such an identity are known [50,51]. For example, in the Van's work, the Gibbs relationship in the context of extended thermodynamics with internal-state variables is presented in the form

$$du = Tds + \hat{t}\cdot\cdot\, d\hat{\varepsilon} - \vec{A}\cdot d\vec{\alpha}, \tag{25}$$

where u and s are densities of internal energy and entropy, T is the absolute temperature, $\hat{\varepsilon}$ and $\hat{t}$ are tensors of deformation (total) and stress, and $\vec{A}$ is a vector thermodynamically conjugate to the vector of internal parameters $\vec{\alpha}$. The first two terms are useful attributes of the combined first and second laws of thermodynamics; the last term $\vec{A}\cdot d\vec{\alpha}\geq 0$ quenches an excess energy. If one drops it, a common expression for the law in the form of inequality $du \leq Tds + \hat{t}\cdot\cdot\, d\hat{\varepsilon}$ results. In the case of the structureless body, this inequality arises as a common part of the internal energy that has been taken in account twice: first, in the form of irreversible work $\Delta A_n = \Delta A - \hat{t}\cdot\cdot\,\widehat{d\varepsilon^{e}}$ and, second, in the form of internal heat released $T\Delta_i^{e}S + \tilde{T}\Delta_i^{n}S$. This redundant energy is subtracted in the right-hand side of Eq. (25).

However, because the total deformation $\hat{\varepsilon}$ is irreversible, the elastic stresses $\hat{t}$ cannot be calculated as a derivative $\hat{t} = \partial u/\partial\hat{\varepsilon}$. Only the reversible (elastic) part of the deformation can suit the case $\hat{t} = \partial u/\partial\widehat{\varepsilon^{e}}$ [3]. Therefore, the structure of relationship (22) more correctly reflects the physical nature of the mutual energy transformations in internal processes. In relationship (22), two aspects of the law of conservation of energy are taken into account simultaneously. It is the law of conservation for a given reference volume interacting with the environment (the 1st law of thermodynamics) and the law of conservation or the law of transformation of energy in internal degrees of freedom $\Delta A_n = T\Delta_i^{e}S + \tilde{T}\Delta_i^{n}$. Moreover, in relationship (22), both the structural aspect $\varphi_l dH_l$ and the dynamic one $\tilde{T}d\tilde{S}$ are taken into account.

The presentation of the combined first and second laws of thermodynamics for a specific case of unstructured solids and for isothermal processes in form of Jarzynski's identity [52,53]

$$\exp\left(-\frac{\Delta F}{kT}\right) = \left\langle \exp\left(-\frac{W}{kT}\right)\right\rangle \tag{26}$$

is also known. Here, the angular brackets denote averaging over all states of the system, ΔF is the free-energy increment in an isothermal process, and W is the work performed for the system. If the increment ΔF and the work W are small, then, expanding the exponents in a series and restricting ourselves to the first terms of the series, we obtain

$$dF = \langle W\rangle - \frac{\langle W^2\rangle}{2kT} = V\sigma_{ij}d\varepsilon_{ij} - \frac{\langle W^2\rangle}{2kT} = V\sigma_{ij}d\varepsilon_{ij}^{e}. \tag{27}$$

The first term $\langle W\rangle$ represents the total work performed for the system; the second term $\langle W^2\rangle/2kT$ stands for the energy dissipated as a result of irreversible internal processes. Their difference is the reversible elastic energy. For an isothermal process $dT=0$, neglecting both transitional thermal processes $d\tilde{S}=0$ and contribution from structure of a solid $dH_l=0$, we obtain from Eq. (24) $dF = V\sigma_{ij}d\varepsilon_{ij}^{e}$ that coincides with the Jarzynski's identity in the limit (27).

V. OUTLINE FOR APPLICATION TO SEVERE PLASTIC DEFORMATION

It is of interest to consider how the above general relationships can be applied to solving practical problems. One of such problems are changes in the internal structure of metals, processed by severe plastic deformation (SPD) [54–56]. During SPD, the grain boundaries are intensively produced, resulting in refinement and fragmentation of the grains. The refinement of grains, at the expense of multiplication of their boundaries, is the main process of SPD and the grain boundaries are the main structural defects [56]. At the same time, the building materials for the grain boundaries are dislocations and dislocation pile-ups. That is why, for the description of SPD, these two kinds of defects or the two levels of defectiveness need to be taken in account as a minimum. Up to quadratic terms in the expansion of the internal energy

$$U = U_0 + \varphi_0 H - \frac{1}{2}\varphi_1 H^2 + \widetilde{\varphi_0}\tilde{H} - \frac{1}{2}\tilde{\varphi}_1 \tilde{H}^2 + \phi H \tilde{H}. \tag{28}$$

The corresponding kinetic equations (10) are

$$\tau_H \frac{\partial H}{\partial t} = \varphi_0 - \varphi_1 H + \phi \tilde{H},$$

$$\tau_{\tilde{H}} \frac{\partial \tilde{H}}{\partial t} = \tilde{\varphi}_0 - \tilde{\varphi}_1 \tilde{H} + \phi H. \tag{29}$$

Here, the dislocation-related variables are marked by tilde. The last terms describe the mutual influence of different levels. In an adiabatic limit $\tau_{\tilde{H}} \ll \tau_H$, the equilibrium value of dislocation number (or density) is derived from stationary condition for the second Eq. (14)

$$\tilde{H} = \frac{1}{\tilde{\varphi}_1}(\tilde{\varphi}_0 - \phi H). \tag{30}$$

This stationary value can be used to exclude the dislocation number from the first Eq. (29)

$$\tau_H \frac{\partial H}{\partial t} = \varphi_0 - \varphi_1 H + \frac{\phi}{\tilde{\varphi}_1}(\tilde{\varphi}_0 - \phi H) = \varphi_0^{ef} - \varphi_1^{ef} H. \tag{31}$$

Thus, the account of dislocations in the adiabatic approach has brought only the renormalization of constants. Let us now consider the next level of approximation, assuming, namely, that the right-hand part of the second Eq. (29) is not strictly zero, but equals a small constant, depending on H parametrically (quasiadiabatic approximation)

$$\tilde{\varphi}_0 - \tilde{\varphi}_1 \tilde{H} + \phi H = \varepsilon. \tag{32}$$

Integrating the second Eq. (29), we obtain

$$\tilde{H} = \frac{1}{\tau_{\tilde{H}}}\varepsilon t + \frac{1}{\tilde{\varphi}_1}(\tilde{\varphi}_0 + \phi H). \tag{33}$$

Substituting this relationship into the first Eq. (29) and taking $\varepsilon = \varepsilon_0 + \varepsilon_1 H$, we find

$$\tau_H \frac{\partial H}{\partial t} = \varphi_0^{ef} - \varphi_1^{ef} H + \frac{\phi}{\tau_{\tilde{H}}}\varepsilon_0 t - \frac{\phi}{\tau_{\tilde{H}}}\varepsilon_1 H t. \tag{34}$$

Taking formally $H = \nu / k$ and $t = e / V$, and also $\varphi_0^{ef} = \kappa \tau_H e_0 V / k$, $\varphi_1^{ef} = \kappa \tau_H e_0 V$, $\varepsilon_0 = \kappa \tau_H \tau_{\tilde{H}} V^2 / k\phi$, and $\varepsilon_1 = \kappa \tau_H \tau_{\tilde{H}} V^2 / \phi$, we get an equation close to the Rybin's kinetic equation [57]

$$\frac{1}{\kappa}\frac{d\nu}{de} = - e_0 + e_0 \nu + e - \nu e. \tag{35}$$

Note that the first two terms in Eqs. (34) and (35) have opposite signs. The first term in Eq. (35) can be treated as annihilation of grain boundaries, developing by itself at a constant speed. The second term describes generation of boundaries, with a speed being the higher the more boundaries (or fragments) are present in a solid. For $e_0 \approx 0.2$ [57], it can be argued that the contribution of the first two terms to kinetics of fragmentation is small. Within this accuracy, Eqs. (34) and (35) coincide.

Thus, in the framework of the approach, the well-known and well-approbated kinetic equation for the description of the grain fragmentation during SPD has been derived. At the same time, the approach has more general context that permits to take the influence of thermal processes into account and to develop two-mode approximations with the expansion of thermodynamic potentials into a higher power series in terms of defectiveness of solids [58].

VI. CONCLUDING REMARKS

In the paper, a phenomenological approach, based on extension of Landau's technique to cases of quick-passing nonequilibrium phenomena, such as severe plastic deformation, is considered. For fast processes, thermal fluctuations have no time to exert essential influence and the problem can be considered in the mean-field approximation. The approach is based not on an abstract order parameter but on a physical parameters of structural defects—their quantity (density) and the average energy. Analysis from these positions, in the framework of a version of the theory of vacancies, shows that the known Landau-Khalatnikov kinetic equation is convenient only if the dependence of the vacancy energy on their density is neglected. In the case of an arbitrary dependence of vacancy energy on their density, it is convenient to use a more general form of kinetic equations, symmetric with respect to using the internal energy U and main part of free energy $\tilde{F}_c$. In this case, the density of defects and defect energy are related by a symmetric differential dependence of types (9) and (10). Because the defect energy in the steady state is not equal to zero, the extremal principle of equality to zero of the derivative of free energy with respect to order parameter (in this case the defect energy) breaks down. This principle need be substituted with principle of the tendency to a steady state. Steady-state characteristics cannot be determined in the framework of phenomenological approach; here statistical and microscopic approaches are required.

The present form of kinetic equations can be extended to all types of regularly or randomly distributed defects and to all types of nonequilibrium parameters, including thermal variables. On the basis of computer experiment, it has been shown that in the case of fast processes, the irreversibility is not so much connected to fluctuation phenomena, as to dynamical process of acoustic emission during the formation and motion of defects. In this case, the acoustic emission over all structural levels is a part of the relaxation process [34–36] that permits to describe the entropy generation (14) in the same form as generation of defects (10).

The results are extended in the form of thermodynamic identity, properly combining the first and second laws of thermodynamics in a finite-difference form. The finite-difference version coincides with the known Jarzynski thermodynamic identity for isothermal processes, expressed in terms of free energy.

To illustrate the applicability of the approach, the problem of description of nonequilibrium phenomena during severe plastic deformation is considered. In the framework of phenomenological one-mode (quadratic with respect to energy) model, taking into account two levels of defect structure, i.e., dislocations and grain boundaries, the approach results in the known Rybin kinetic equation [57]. But it also permits to consider more complex dependences of thermodynamic potentials on model parameters. For example, in the framework of two-mode approximation using the polynomials of the fourth power for presentation of thermodynamic potentials, the severe plastic deformation can be represented as a structural phase transition of the first kind [58].

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