

Time in Crystal Growth Theory and the Correspondence Principle in Thermodynamics

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Received March 31, 2021; revised May 31, 2021; accepted June 8, 2021

Abstract—The crystal growth theories based on atomic phenomena are eventually oriented to the description of a macroscopic phenomenon. The adequacy of theoretical concepts can be justified using the Bohr’s correspondence principle. The time used in the equations of nonequilibrium thermodynamics is in complete correspondence with the Bohr’s principle. It is shown that the equation for a dynamic stationary form of a growing crystal, obtained within nonequilibrium thermodynamics at a decrease in the growth rates of the crystal faces, is transformed into the Wulff equation, which is used to describe the equilibrium crystal form. A continuous transition of the morphological spectrum of a dynamic stationary form of a growing crystal to the spectrum of an equilibrium crystal form within the Gibbs approximation of fluctuations is also demonstrated. However, the variable of time introduced into classical dislocation crystal-growth theories based on equilibrium statistical concepts hinders the application of the correspondence principle.

DOI: 10.1134/S1063774522020122

INTRODUCTION

In the beginning of the XX century, N. Bohr proposed the correspondence principle, which expressed the assurance of the great physicist that a continuous theoretical transition, predicting the same result but from different points of view, should be performed when a natural phenomenon is described at the boundaries of adjacent fields of natural science. The reason is the continuity of natural processes, whereas the natural science, being based on generalizations and abstractions is discrete [1]. It is well known how this principle (important for understanding the laws of nature) is implemented in quantum and classical physics and in gravity theories. It can also be applied to thermodynamics, which describes macroscopic phenomena.

Let us consider the correspondence of the limiting principles of equilibrium and nonequilibrium thermodynamics. According to the Prigogine’s principle [2], in the stationary mode of development of an open macrosystem, the entropy production due to the internal processes occurring in it tends to minimum:

$$\frac{d_i S}{dt} = \int \left(\sum_j^f F_j J_j \right) dV \rightarrow \min, \quad (1)$$

where F_j and J_j are, respectively, the thermodynamic forces and fluxes, fixed by external conditions in this open system, and f is the number of these processes. Integration is performed over the volume of the sys-

tem. In this case, the thermodynamic system is in the stationary state of order f . In the stationary state, the fluxes, conjugate with free (i.e., not fixed artificially) forces, turn to zero and, therefore, summation in expression (1) is performed only over the processes specified by the boundary conditions for an open system.

If no forces are observed ($f = 0$), the stationary state, according to (1), is characterized by zero entropy production. In this case, according to the Prigogine’s principle [2], all input and output fluxes of the system turn to zero with time, and the equilibrium state is achieved (one can reliably assume the macrosystem to be quasi-closed). Then, if the equality $d_i S/dt = 0$ is valid, the obtained result corresponds completely to the second law of thermodynamics: a quasi-closed system reaches the maximum entropy.

LIMITING FORMS OF CRYSTALS

According to the Wulff theorem [3], for a heterogeneous “crystal–medium” system in the equilibrium state (in the absence of external potential fields [4]), the ratio of the central distance to a face to its equilibrium surface-energy density is constant (C_{eq}) and identical for any crystal face j :

$$(h_j/\gamma_{ej})_{j=1,\dots,m} = C_{eq}, \quad (2)$$

where m is the number of crystal faces. The theorem is derived from the second law of thermodynamics, a particular case of which is the Gibbs–Curie principle

(it claims that the crystal surface energy should be minimized in the equilibrium state when the minimum free energy of the entire heterogeneous system is reached).

However, it was found that, at stationary development of an open nonequilibrium system, the ratios of the central distances to growing faces to their growth rates in the isotropic crystal environment are equal to the current process time [5]:

$$(H_j/v_j)_{j=1,\dots,m} = t. \quad (3)$$

This theorem can be derived based on the condition of minimum entropy production by the surface of a stationary growing crystal and the result of nonequilibrium thermodynamic analysis of the processes in the boundary layer of an inhomogeneous supersaturated solution at the surface of growing crystal face [5].

Let us show that stationary crystal form (3) corresponds in the limiting case to the equilibrium form (2).

First, we divide the left- and right-hand sides of expression (3) by time t and select the time-independent invariant of the central distance $H'_j = H_j/t$. Following Wulff [3], we make a quite evident assumption that, at stationary growth under these physicochemical conditions, the rate of attachment of building particles to the face is proportional to the density of uncompensated chemical bonds of surface atoms. In terms of thermodynamics, when describing a macroscopic phenomenon, this statement is equivalent to the statement that the normal face growth rate in the first approximation is proportional to the surface-energy density of the crystal face in this nonequilibrium thermodynamic situation:

$$v_j = C_s \gamma_j. \quad (4)$$

In the first approximation, the kinetic coefficient C_s can be considered as constant for all surfaces of a crystal growing under these thermodynamic conditions in an isotropic environment, independent of the crystallographic indices and face fine structure (degree of roughness or the density of elementary steps on a smooth surface). Note that the face growth mechanism manifests itself in the value of dynamic nonequilibrium surface-energy density γ_j , the measurement of which during crystal growth is a separate difficult problem. Obviously, this energy density should differ from the easily measurable [6] equilibrium value γ_{ej} at zero supersaturation but at the same values of the main thermodynamic variables (temperature, pressure, average chemical medium composition). As a result, the following equation for the central-distance invariant can be derived from expression (3):

$$(H'_j/\gamma_j)_{j=1,\dots,m} = C_s, \quad (5)$$

which coincides in form with the Wulff equation (2).

However, there are several important differences. First, the central distances in expressions (2) and (5)

are counted from different points inside the crystal. In the former and latter cases, they are the center of the equilibrium form (the only point in crystal that satisfies the second law of thermodynamics) and the center of a stationary form (also the only point in a steadily growing crystal, according to the entropy-production minimum), respectively [5]. Second, as follows from Eq. (4), the constant C_s should be smaller at a lower supersaturation and a low rate of stationary growth of crystal face. Simultaneously, the surface-energy density of a nonequilibrium face, which depends on the growth mechanism (dislocation, normal) or the degree of face roughness, will tend to the equilibrium value.

It is also noteworthy that the Wulff theorem is valid only for small equilibrium crystals, when the gravitational factor in the fundamental Gibbs equation for a quasi-equilibrium system can be neglected [4]. In this case, all central distances to equilibrium crystal faces should satisfy the condition

$$h_j \ll \sqrt{\frac{\gamma_j}{2g\Delta\rho}}. \quad (6)$$

Here, g is the acceleration of gravity at the crystal location point and $\Delta\rho$ is the difference in the densities of the crystal and surrounding equilibrium solution.

According to the correspondence principle, the linear sizes of the described objects (equilibrium and nonequilibrium crystals) must be equal. Therefore, at any current instant, the central distances to the faces of stationary nonequilibrium form should be limited from above ($H_j < h_j$) to fulfill the equality $H_j = h_j$ in the limit $t \rightarrow \infty$. Taking into account the latter circumstance, we obtain the following condition from (2) and (5):

$$\gamma_j C_s t < \gamma_{ej} C_{eq}. \quad (7)$$

Based on (4), (7), and the ratio of crystal sizes, one can conclude that the correspondence principle can be implemented only at stationary growth rates of all crystal faces with time, approaching to zero. Then, in the limit $t \rightarrow \infty$, the following equalities will be performed simultaneously:

$$v_j = 0, \quad H_j = h_j, \quad \gamma_j = \gamma_{ej}, \quad C_s = 0,$$

the uncertainty of (7) is removed by the equality $C_s t = C_{eq}$, and the centers of equilibrium and stationary forms move closer and coincide. As a result, the Wulff equation (2) for a growing crystal is derived from the stationary form (3):

$$(H_j/\gamma_{ej})_{j=1,\dots,m} = C_{eq}.$$

Thus, the relevance of expression (4), which is independent of the atomic–molecular mechanism of crystal growth, follows from the correspondence principle.

The above considerations suggest implicitly that the habits of stationary and equilibrium crystal forms coincide at least at low growth rates. This axiom follows necessarily from the conditions of minimum entropy production of a stationary growing crystal and minimum free energy of an equilibrium crystal [7]. However, in the general case, the following statement is sufficient: at a quasi-step decrease in the growth rate of all faces and achievement of stationary mode at each individual stage, the habit of the stationary non-equilibrium crystal form approaches gradually the habit of the equilibrium form.

TIME IN CRYSTAL GROWTH THEORY

It is rather difficult to verify the correspondence principle in crystal growth theories [8, 9]. The general pattern of crystal growth phenomenon (macroscopic in essence) is often described applying fanciful combinations of equilibrium and nonequilibrium concepts (which are sometimes incompatible). Let us consider the classical study by Burton, Cabrera, and Frank, where the crystal growth is described in terms of the dislocation mechanism [9]. In the first pages, the authors use the following classical thermodynamic equilibrium Boltzmann distribution over energies to describe the number of adsorbed molecules per face unit area:

$$n_{s0} = n_0 \exp(-W_s/kT). \quad (8)$$

Note that this law is based on the equilibrium Gibbs distribution [10], which implies the use of the concept of a phase (homogeneous part of a thermodynamic system, separated from another part by a phase boundary) [11]. In this case, the numerator and denominator of the exponential should be considered as the energies calculated for molar amounts of material, to which the phase concept can be applied. However, according to the remark by Gibbs [10], this fraction allows for transformations in correspondence with any scale factor and makes the reported distribution independent of the used units. Therefore, researchers often discuss molecules (building particles) at the atomic scale. Having separated the numerator and denominator by Avogadro's number, we obtain the ratio (8), where W_s is the evaporation energy of a particle located on the kink of elementary step and k is the Boltzmann constant. However, one must not ignore the fact that this scale transition can be performed only at thermodynamic equilibrium. At the same time, the variables present in this formula beyond the exponential are not actually thermodynamic ones. According to the Gibbs concepts [10], only the n_{s0}/n_0 ratio in (8), which reflects the statistical probability of equilibrium adsorption of building particles, may have a thermodynamic sense.

Furthermore, the path length of adsorbed molecules on the face was estimated using the known Einstein formula for diffusion, which describes an obvi-

ously nonequilibrium Wiener process, and a lifetime for adsorbed molecule was introduced. However, to substantiate the introduction of a new variable (unit time interval, without which one cannot deal in kinetic theory), the authors had to use the frequency of thermal atomic vibrations and write again an equilibrium exponential dependence of type (8). Note that the equilibrium thermodynamic description of a physical problem does not require time; therefore, the frequency factor cannot be considered as a good version for introduction of time variable into the theory of nonequilibrium crystal growth. Finally, the authors introduced supersaturation as a thermodynamic value denoting the deviation from equilibrium and passed to the field theory equations, describing fluxes in a nonequilibrium system at a higher scale level, without referring to molecules. The final mathematical expressions contain simultaneously the mean energies (which are characteristic of equilibrium conditions but assigned to one molecule); the equilibrium frequency factor; and supersaturation, which determines all nonequilibrium processes in the system. It is unclear, how validity of the Bohr's correspondence principle can be verified in this situation.

The authors of [9] and their followers are in essence right in the main thing: crystal growth is a macroscopic phenomenon and, therefore, should be described primarily in terms of a macroscopic theory. However, one must provide reasonable grounds for introducing a time variable into the process of nonequilibrium growth of a crystal face.

HIERARCHY OF NONEQUILIBRIUM CRYSTAL GROWTH PROCESSES

Along with the time variable, there is another (second in importance) problem of all crystal growth theories: the scaling problem. From an atom incorporated into the crystal structure to the macrocrystal form, there are no less than seven orders of magnitude of changes in the object linear size. The adsorption-fluctuation model of crystal-face growth, which describes the hierarchy of the phenomena implemented successively at four scale levels, was presented in [12].

The thermodynamic variables have no physical meaning at the lowest atomic and supramolecular levels, because they cannot be measured. Time events occur in the range from the period of thermal vibrations to the characteristic lifetimes of the transition states of molecular clusters. However, some chemical phenomena with a set of equilibrium statistical properties can be described using classical regularities, which also manifest themselves at the macroscopic level. An example is the phenomena of equilibrium Langmuir adsorption [13]. The classical Kossel theory [14, 15] and the theory of chains of strong bonds [16, 17] (including its modern interpretation [18–20]) are also known to be implemented on the atomic scale.

The second (also quasi-equilibrium) local thermodynamic level is determined by the scale of thermodynamic fluctuations on which the thermodynamic variables (e.g., entropy, temperature, free and surface energies, chemical potential) acquire physical meaning and can be measured. The time range of the fluctuation-relaxation processes is limited from thermodynamic considerations (conditions for description of a quasi-closed local system, when the material or heat fluxes beyond its boundaries can be neglected). The phenomenological equilibrium two- and three-dimensional nucleation theories [8] are traditionally implemented at this scale level. It is known that the thermodynamic temperature fluctuation is a phenomenon of random momentum transfer to a specific local region near the crystal surface by high-energy molecules of the medium that are involved in Brownian motion. As a result of free-energy fluctuation, a sequence of relaxation processes develops in a quasi-closed system: desorption of impurity atoms from active centers on a rough crystal surface or from a dislocation elementary step, which increases the free surface energy in this local region, induces attachment of some building particles to the vacant centers or growth-step kinks, and finally reduces again the free surface energy due to the adsorption of new impurity particles [12]. The larger the fluctuation region, the larger the number of building particles attached to the crystal face in the presence of environmental supersaturation and the lower the probability of this fluctuation are. It is important that, according to the Gibbs fluctuation theory [10] (which is described by a canonical exponential distribution), the relaxation phenomena related to an individual fluctuation can be considered as time-independent.

Along with the nucleation theories, the local thermodynamic level allows for implementation of the phenomena of formation of supramolecular structures during aggregation of crystal-structure defects and the transition theory of crystal-surface roughness [21].

Several important circumstances should be noted. At the atomic level, laws of physics allow for time inversion (growth and dissolution cannot be distinguished, and events of particle attachment to the surface and detachment from it occur almost equiprobably). When passing to the local thermodynamic level, where the statistical equilibrium Boltzmann's concept about the entropy of a system as a logarithm of the number of equivalent microstates [22] is valid, there arises a time arrow in the form of the above-described strictly successive series of desorption-growth-adsorption processes, and the second law of thermodynamics comes into force. However, there is still no need in introducing the time scale into thermodynamic equations. At this level, equilibrium concepts can be used for an impurity, because it is not spent at a phase transition; however, the equilibrium approach is not applicable to the building material. Note that the process of relaxation of fluctuation changes should

not change the physical state of the face, and the nonequilibrium surface-energy density of the face area should not change as a result of fluctuation.

The following microscopic nonequilibrium level is selected to introduce the time scale of a nonequilibrium process as a critical thermodynamic variable [12]. For each physicochemical crystallization system, in which the limiting case of Langmuir adsorption (complete poisoning of the growing surface with impurity atoms and canonical distribution of independent free-energy fluctuations) is implemented, one can choose a characteristic elementary time range τ of stationary nonequilibrium process, starting with which the above-described series of fluctuation events on the face can be interpreted as a continuous nonequilibrium process in an open system. There is a transport theorem [23, 24] in the probability theory, which can be formulated as follows for the case of crystal-face growth: if a random number of fluctuations ν on some face area during time τ is described by the geometric distribution law

$$P(\nu) = (1 - q)q^{\nu-1}, \quad (9)$$

with a parameter q approaching unity, the material formed during this time interval is described by the exponential law

$$f(h, \lambda) = \lambda \exp(-\lambda h), \quad (10)$$

where λ is the scale parameter.

The average number of fluctuations in geometric law (9) for elementary time τ is $1/(1 - q)$, and the mean increment of material is $1/\lambda$. Therefore, the stationary growth rate is $\nu = 1/\lambda\tau$. At this scale level, of importance are not only elementary time τ , which makes it possible to pass to an open system, but also the minimum linear size of the face area on which the phenomena discussed are implemented. The fluctuation islands have some specific linear sizes, which can be found using autocorrelation analysis in atomic-force experiments with crystal growth [12]. At the microscopic scale level, the limiting principle of nonequilibrium thermodynamics (the minimum entropy production, implemented for the mean values of material increment during time interval τ) is applicable in full measure.

The last (macroscopic) level is determined quite naturally: the events occurring successively in all ranges of stationary elementary time up to the current instant are summed in this case. However, to describe a macrosystem including the macrocrystal form, one must additionally substantiate the condition for conservation of the main statements of the model in all parts of the macrosystem on extended areas of crystal surface.

If the total crystal growth time $t = n\tau$ is counted from the instant of formation of a given face (current form of stationary growth), one can show (using the method of characteristic functions [24]) that the sum

of grown layers of crystalline material, distributed according to the exponential law (10), is described by the following gamma probability density function of the increase in the layer thickness:

$$f(h, \lambda, n) = \frac{\lambda^n h^{n-1}}{(n-1)!} e^{-\lambda h}, \quad (11)$$

where h can be referred to as a cumulative thickness of an accumulated layer of crystalline material on the face during the entire growth time, which takes values in the range of $(0, \infty)$. At an integer n value, the distribution (11) is the Erlang equation; it is described by two numbers: scale parameter (λ) and form parameter (n), which have a meaning of time in τ units.

During a stationary process and with an increase in the number n of discrete elementary increments in the amount of crystalline material at a constant λ value, according to the central limit theorem of the probability theory [24], the distribution function (11) tends to the normal law:

$$f(h) \cong \frac{\lambda}{\sqrt{2\pi n}} \exp\left[-\frac{(\lambda h - n)^2}{2n}\right]. \quad (12)$$

Here, another quite remarkable phenomenon is noteworthy. At the coefficient of variation in central distances $k = n^{-1/2} < 0.1$ (when one can pass from the gamma distribution (11) to the normal law (12)), the probability of combinatorial kinds of polyhedra forming the stationary-form spectrum ceases to depend on the coefficient of variation [25]. Starting from this instant, the morphological spectrum of the stationary form is independent of time. This important circumstance is related to the property of the Markovian process of the stationary crystal form spectrum. In the course of time, under stationary conditions, the central distances of all symmetrically equivalent faces tend to the corresponding mean values, and the morphological spectrum includes only a class of full-face polyhedra [25]. The transition to expression (12) is implemented at this stage, and, despite the fact that the distribution functions (11) and (12) change with time (n), the probabilities of polyhedra remain constant.

MORPHOLOGICAL SPECTRUM OF AN EQUILIBRIUM CRYSTAL AND THE CORRESPONDENCE PRINCIPLE

Let us consider the equilibrium crystal form in the approximation of the Gibbs fluctuation theory. The probability density for the equilibrium negative entropy fluctuation ΔS can be written as [11]

$$f(\Delta S) = Z \exp\left(\frac{\Delta S}{k}\right), \quad (13)$$

where Z is the normalization coefficient, calculated for the thermodynamic conditions of the problem. Here, in contrast to the Gibbs's idea, the entropy fluctuation

in the equilibrium state is an independent event, and the probability is its characteristic.

Formula (13) can be derived using the concepts of rare events within the theory of random processes [26]. To this end, it is sufficient to use three evident statements: entropy fluctuations are rare and independent events, the fluctuation probability depends linearly on the entropy-jump magnitude (at small changes in the entropy), and the zero-fluctuation probability is maximum.

The entropy fluctuation near the surface of a crystal that is in equilibrium with the medium may be caused by different reasons: temperature jump, local change in volume (in the case of vapor environment rather than condensed matter), and a decrease or increase in the number of moles at a transition of some part of material from the crystal to the environment (and vice versa). All these processes are statistically equiprobable in entropic calculus and are partly inter-related: one event is conjugated with the others on the fluctuation relaxation time scale.

Let us consider an entropy jump in a heterogeneous system that is in equilibrium isochoric–isothermal state as a result of a fluctuation of the number of moles:

$$\begin{aligned} \Delta S &= \delta S + \frac{1}{2} \delta^2 S = \left(\frac{\partial S}{\partial N}\right)_{T,V} \delta N \\ &+ \frac{1}{2} \left(\frac{\partial^2 S}{\partial N^2}\right)_{T,V} (\delta N)^2 < 0. \end{aligned} \quad (14)$$

A change in the entropy at the equilibrium point can be only negative. Taking into account that $(\partial S/\partial N)_{T,V} = A/T$ (A is the chemical reaction affinity, which turns to zero in equilibrium) [11], we obtain

$$\Delta S = \frac{1}{2T} \frac{\partial A}{\partial N} (\delta N)^2 < 0.$$

According to the Wulff theorem [3], under conditions of thermodynamic equilibrium (with gravity disregarded), all symmetrically equivalent crystal faces should be located at equal distances from the equilibrium-form center and (ignoring the Gibbs fluctuation theory and gravity influence) the crystal formed by the faces of one closed simple form should be an ideal polyhedron. However, fluctuations change the crystal shape. Taking into account close values of areas of all symmetric faces on the equilibrium crystal form, the molar amount of material δN removed from the face surface or accumulated on a face as a result of equilibrium fluctuation can be assumed to be proportional to the change of the face position in space δh . Therefore (13), the probability density can be written as

$$f(\delta h) = Z \exp\left[-\frac{(\delta h)^2}{2D}\right].$$

The dispersion in the denominator is determined by the expression

$$D = \frac{M^2 kT}{\rho^2 \Pi^2 (-\partial A / \partial N)},$$

where M is the molar mass; ρ is the crystal density; Π is the face area; and, according to (14), the derivative $\partial A / \partial N$, calculated for a crystal existing in a heterogeneous equilibrium system, should always be negative. Taking into account the mean central distance to the octahedron faces, h_0 , the distribution (13) after normalization is transformed into the Gauss law:

$$f(h) = \frac{1}{\sqrt{2\pi D}} \exp\left[-\frac{(h - h_0)^2}{2D}\right]. \quad (15)$$

Thus, under conditions of thermodynamic equilibrium, due to the Gibbs fluctuations, the central distances to the symmetrically equivalent faces of crystal cannot be equal. Therefore, according to combinatorics, the equilibrium crystal form should be represented (in most cases) by a set of polyhedra with different ideal symmetries rather than by one polyhedron. For example, there are five kinds of full-face polyhedra of octahedron, which are described within four point symmetry groups; six morphotypes of rhombododecahedron (five symmetry groups); seven morphotypes of tetragonal bipyramid (six groups); eight morphotypes of pentagontrioctahedron (five groups); nine morphotypes of tetragonal scalenohedron (three symmetry groups); etc. [27]. According to the Markovian process of transformation of combinatorial types of polyhedra, the equilibrium morphological spectrum should be described by a full-face class at small dispersion, and, by definition, the probability of equilibrium-form morphotypes is independent of time.

Thus, in the limiting case at $t \rightarrow \infty$ ($n \rightarrow \infty$), the laws of the central-distance distribution for symmetrically equivalent faces of stationary nonequilibrium (12) and equilibrium (15) forms coincide. This fact leads to identical morphological spectra (a unified set of combinatorial kinds of polyhedra and their probabilities), calculated according to the normal law. These conditions are characteristic of the process of natural nonequilibrium mineral formation [25].

However, there are a number of circumstances related to the size effect. In contrast to the stationary form, there exists a limit of single-crystal height for the equilibrium form under gravity [4]. With an increase in the crystal size, the equilibrium morphological spectrum exhibits the dissymmetry effect, related to the gravitational field according to its Curie limiting group (∞m). In addition, according to Eq. (15), the coefficient of the equilibrium-form variation \sqrt{D}/h_0 is always much smaller than the coefficient of variation of the real stationary form ($n^{-1/2}$), calculated from Eq. (11), which should manifest itself in practice. Finally, the stationary-form dissymmetry in both

growth and dissolution processes may be due to the factors that are not limited by only the aforementioned cone symmetry group [28].

CONCLUSIONS

It is well known how the Bohr correspondence principle, which provides uniformity and continuity of natural science, is implemented at the level of limiting laws of thermodynamics. In this study it was shown how it is performed at the transition from stationary to equilibrium form with a decrease in the crystal growth rate and an increase in the nonequilibrium-process time. It was demonstrated that the time introduced into the adsorption-fluctuation growth model [12] (in contrast to the time as a derivative of the frequency factor in the classical Burton–Cabrera–Frank theory [8]) completely obeys the correspondence principle and yields precise coincidence of the morphological spectra of the dynamic stationary and equilibrium fluctuation forms of macrocrystals at an infinite increase in the stationary-process time. The correspondence principle is likely implemented because, as a physical variable, time should be introduced into the crystal growth theory only at the thermodynamic scale level. Thus, when developing a kinetic theory, the molecular statistical regularities of nonequilibrium processes of attachment of atoms or molecular complexes to the growing-crystal surface cannot be directly translated to the macrocrystal scale (in contrast to the theory of equilibrium face state, in which time is of no importance). The equilibrium concept can be applied successfully, both at macroscopic and atomic levels, by performing a transition that was described by Gibbs [10] and implemented, e.g., in the theory of crystal-surface roughening [21].

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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Translated by Yu. Sin'kov