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Thermodynamic Stability of Transition States in Nanosystems

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Abstract We present a theory which shows that, in a closed system of fixed volume capable of undergoing a phase transition, the transition state can be thermodynamically stable against the bulk phases if a certain material parameters criterion is fulfilled. In a small system below the critical size the transition state turns into a globally stable phase that can be observed experimentally. This effect is analogous to stabilization of icosahedral structures in clusters of certain sizes and energies. Stabilization of the transition state in small systems of limited resources allows us to conjecture that, in the case of a melting/freezing transition in pure substances, this state corresponds to an amorphous phase. Although unstable in open systems, this phase may be observed experimentally due to slow kinetics of its decomposition at low temperatures. The material-parameters criterion should help experimenters select the materials for the experimental verification of the phenomenon. In the present paper we consider thin films where the phase separation is permitted only parallel to the plane of the film. The calculations, however, hold true for 3D small systems: e.g., nanoparticles.

1 Introduction

Experimental progress in the area of nano-technology (-structure, -materials) challenges theorists to find new approaches to the study of transformations in small systems that is, materials composed of a significant (a billion or so) but still limited number of particles. Although researchers understand that mathematically, the significant differences between the phase behavior of bulk matter and nanomaterials can be attributed to the effect of large exponentials and physically, to the roles of fluctuations and surface-to-volume ratio of these systems, we need a reliable theoretical framework, which would allow us to study the properties of nanomaterials. Regular statistical mechanics methods may not be applicable to nanomaterials due to still insufficient number of particles for the thermodynamic limit.

Great progress has been made in the study of clusters—structural arrangements of $N = 10$–500 atoms or molecules [1, 2]. Clusters are usually described theoretically by the

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multiparticle potential energy function $\Phi(\mathbf{r}_i)$, which depends on the spatial locations of each of the particles of the system $\mathbf{r}_i$ [3, 4]. The minima of $\Phi(\mathbf{r}_i)$ correspond to mechanically stable arrangements of the $\mathcal{N}$ particles, and the saddle points of $\Phi(\mathbf{r}_i)$ correspond to the transition states that separate the "basins of attraction" of the minima. For a melting/freezing-type transition the lowest lying minima correspond to the crystalline phases, the liquid phase corresponds to a certain level of kinetic energy—that is, Lindemann-type criterion—and the amorphous phase corresponds to few shallow minima that separate the absolute-minimum basins of the crystalline phase. Over a certain range of temperature and pressure, clusters may exhibit effects that are not typical for bulk matter: dynamical coexistence—intermittent visitations of two or more different regions of the phase space $\{r_t, \dot{r}_t\}$ at equilibrium [5, 6];[1] existence of equilibrium phases which are completely unstable in the bulk, e.g. icosahedral [7, 8]. Distinction between first-order and second-order transitions in clusters is blurred [1, 2]. Researchers have found that a trajectory of a cluster through the phase space $\{r_t, \dot{r}_t\}$ has a high probability of absorbing entropy instead of producing it—fluctuation theorems [9, 10].

Nanomaterials differ from the clusters by the number of particles involved: for clusters $\mathcal{N} = 10$–500, for nanomaterials $\mathcal{N} = 10^3$–10^9. For nanomaterials, the mechanistic framework, despite its conceptual simplicity, remains largely qualitative due to the complexity of the "$\Phi(\mathbf{r}_i)$-scape topography." The number of geometrically distinct minima grows approximately exponentially with the number of particles $\mathcal{N}$ in the system [3, 4], which presents a significant obstacle for the quantitative analysis of the material systems larger than clusters of 30–50 atoms. *Ab initio* calculations and direct numerical simulations also are not feasible for such systems due to a large number of interacting particles.

The Landau paradigm of an order parameter is an important concept in the theory of phase transitions and cooperative phenomena overall. An order parameter is a low-dimensional characteristic of a particular transition in a multi-dimensional space of a system $\{r_t, \dot{r}_t\}$. It may be obtained from microscopic characteristics of a system through a so-called coarse-graining procedure, which removes irrelevant degrees of freedom and leaves only variables on the space-time scale relevant for the transition. From the thermodynamic point of view, an order parameter is a type of a 'hidden' variable, which, in addition to such thermodynamic variables as temperature T, pressure P, volume V, etc., characterizes different states of a system. Mathematically, the system is described by a free energy (generated by the multiparticle potential energy $\Phi(\mathbf{r}_i)$) expressed as a function of the thermodynamic and hidden variables. As a function of the order parameter, the free energy has at least two minima that correspond to the bulk phases separated by a maximum or a saddle point, called the transition state, which is usually considered to be unstable.

We present a theory which shows that, in a closed system of fixed volume capable of undergoing a phase transition, the transition state can be thermodynamically stable against the bulk phases if a certain material parameters condition is fulfilled. In a small system below the critical size, the transition state turns into a globally stable phase that can be observed experimentally. Although unstable in open systems, this phase can also be observed experimentally in these systems at low temperatures due to slow kinetics of its decomposition. In the case of melting/freezing, stabilization of the transition state in small systems of limited resources allows us to conjecture that this state corresponds to an amorphous phase of pure substances. In the present Paper we consider a case of a thin film where the phase separation is permitted only parallel to the plane of the film. The calculations, however, hold true for a 3D small system, e.g., a nanoparticle.

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[1]The term "static coexistence" in the literature refers to a heterogeneous system.

2 Homogeneous Systems

In the framework of Landau theory, a state of a system—in addition to such thermodynamic variables as temperature T and pressure P—is represented by a certain value of a 'hidden' variable η, called an order parameter (OP) [11, 12]. OP is a low-dimensional characteristic of a particular transformation in a multi-dimensional space.[2] The transformation is fully characterized by the coarse-grained free energy, which may be significantly simplified by taking into account all the symmetries of the system. Introduction of the OP allows one to define a *phase* as a locally stable homogeneous in the OP state of the system. The free energy function that describes melting/freezing transition must have at least two minima with respect to OP that correspond to the liquid, $\eta = \eta_l$, and solid, $\eta = \eta_s$, phases and the *transition state* (TS), $\eta = \eta_t$—that is, the barrier that separates the basins of stability of the liquid and solid phases (see Inset a to Fig. 1). In an open one-component system, the stable phases correspond to the minima of the molar Gibbs free energy, $G(T, P, \eta)$, and can be found among the roots of the following equation:

$$\left(\frac{\partial G}{\partial \eta} \right)_P = 0. \tag{1}$$

In this paper we consider effects of pressure and molar volume change on the transitions, e.g. melting/freezing, in a completely isothermal isochoric system

$$\mathcal{V} = const, \tag{2}$$

without mass exchange with the environment—that is, (*NVT*) ensemble or closed (not isolated) system. Hence, temperature T may be omitted from the equations here and below. The equilibrium pressure, P^E, is defined by the equation $G_l(P^E) = G_s(P^E)$ where $G_{l(s)}(P) = G(P, \eta_{l(s)})$ is the Gibbs free energy of the liquid (solid) phase. TS, a maximum with respect to OP, may also be found among the roots of (1) but, as opposed to the bulk phases, it is locally unstable under the conditions of constant pressure that is $G_t'' \equiv (\partial^2 G / \partial \eta^2)_P(\eta_t) < 0$.[3]

In a closed system instead of the Gibbs free energy, $G(P, \eta)$, as a function of pressure P it is more convenient to use the Helmholtz free energy, $F(V, \eta)$, as a function of the molar volume V. This function can be found from the Gibbs one through the Legendre transformation:

$$F(V, \eta) = G - P \left(\frac{\partial G}{\partial P} \right)_\eta; \quad V = \left(\frac{\partial G}{\partial P} \right)_\eta. \tag{3}$$

Differentiation of the Legendre transformation, (3), with respect to the proper thermodynamic variables, shows:

$$\left(\frac{\partial^2 F}{\partial V^2} \right)_\eta \left(\frac{\partial^2 G}{\partial P^2} \right)_\eta = -1, \tag{4}$$

that the free energy of a stable state is a convex function of its extensive variables, $F(V)$, but a concave function of its intensive variable, $G(P)$, c.f. Figs. 1 and 2 [14, 15].

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[2]For a more detailed discussion of the definition of an order parameter see [13].

[3]Here and below the prime means $(\partial / \partial \eta)_P$, the lower index defines a phase, the upper—thermodynamic state, and the subscript 't' means that the quantity must be calculated at $\eta = \eta_t$.
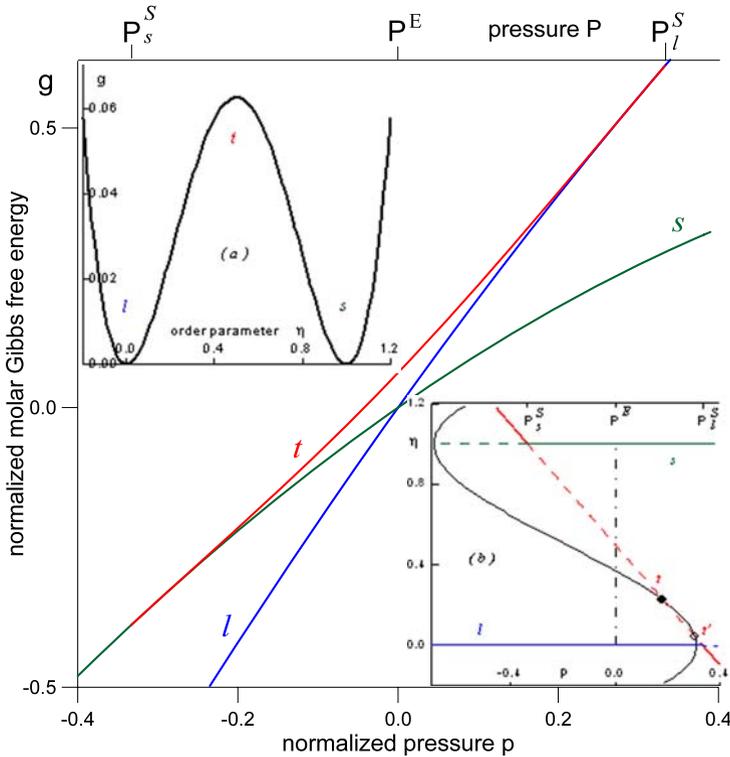
Fig. 1 (Color online) Normalized molar Gibbs free energy $g = \{G - G_l(P^E)\}/[V]P^E$ versus normalized pressure $p = (P - P^E)/P^E$ for the equilibrium states of an open system described by (17) with $[V] = ZP^E$ and $A = 2[V]P^E$ {s-solid (*green*), l-liquid (*blue*), t-transition state (*red*)}. *Inset* (**a**): g as a function of OP at $P = P^E$. *Inset* (**b**): Equilibrium state diagram (*dashed lines*—equilibrium states, *solid lines*—locally stable states, *double solid lines*—globally stable states, *curved line*—fixed volume trajectory with $V = V_l^G$)

Using the rules of differentiation of functions of multiple variables, $(\partial/\partial\eta)_V = (\partial/\partial\eta)_P + (\partial P/\partial\eta)_V(\partial/\partial P)_\eta$, one can see that

$$\left(\frac{\partial F}{\partial\eta}\right)_V = \left(\frac{\partial G}{\partial\eta}\right)_P. \tag{5}$$

This means that an equilibrium state of an open system ($P = const$) remains at equilibrium if the system is closed, (2). The local stability of the state, however, may change drastically as a result of the change of the boundary conditions (open to closed system). Indeed, using the same rule of differentiation we obtain:

$$\left(\frac{\partial^2 F}{\partial\eta^2}\right)_V = \left(\frac{\partial^2 G}{\partial\eta^2}\right)_P - \left(\frac{\partial^2 G}{\partial P\partial\eta}\right)^2 \bigg/ \left(\frac{\partial^2 G}{\partial P^2}\right)_\eta. \tag{6}$$

This relation shows that an equilibrium state unstable under the conditions of constant pressure, $G'' < 0$, may be stable under the conditions of constant volume, $(\partial^2 F/\partial\eta^2)_V > 0$. For this to happen, first, the second derivative $(\partial^2 G/\partial P^2)_\eta$ must be negative (i.e., the isothermal compression of the state is positive: $\beta_\eta \equiv -(\partial V/\partial P)_\eta/V > 0$; second, the absolute value
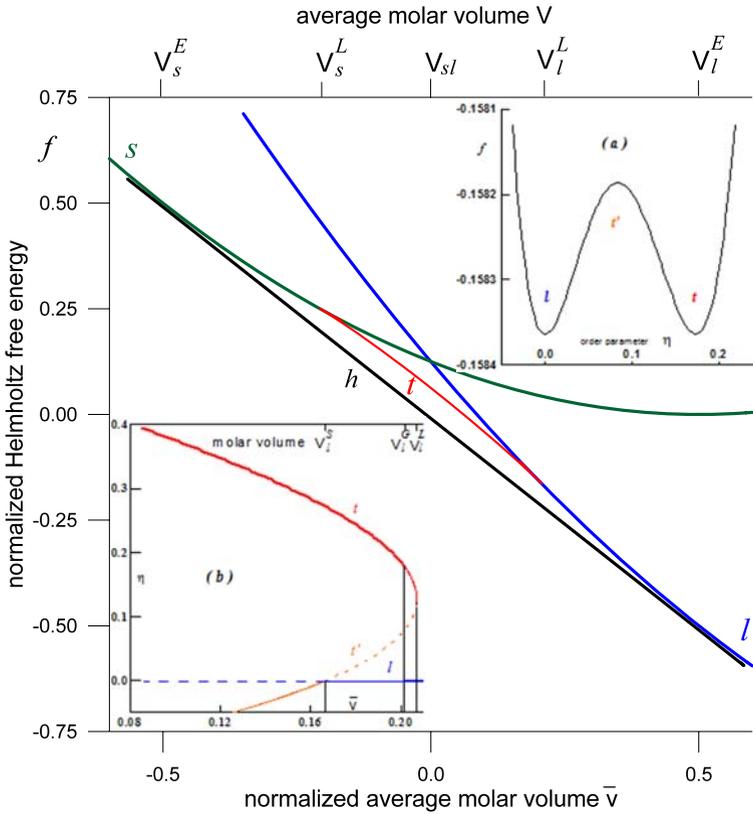
Fig. 2 (Color online) Normalized Helmholtz free energy $f = \{F/X - \frac{1}{2}(ZP^E + [V])P^E\}/P^E[V]$ of the homogeneous equilibrium states {s-solid (*green*), l-liquid (*blue*), t-transition state (*red*)} and heterogeneous mixture of the solid and liquid states (h) versus the normalized average molar volume $\bar{v} = (\bar{V} - V_{sl})/[V]$ in a closed system described in the caption of Fig. 1. *Inset* (**a**): f as a function of OP at $V = V_l^G$. *Inset* (**b**): Equilibrium state diagram of the closed system with the molar volumes close to V_l^L

of the mixed partial $(\partial^2 G/\partial P \partial \eta)$ must be large enough. For the TS ($G_t'' < 0$) these two conditions may be expressed through of the interaction modulus M as follows:

$$M(P, G) = \frac{(\frac{\partial^2 G}{\partial P \partial \eta})_t^2}{G_t''(\frac{\partial^2 G}{\partial P^2})_t} > 1. \tag{7}$$

Using (5) and the rules of chain differentiation for the mixed partials, one can show that the interaction modulus Legendre-transforms as $[M(V, F) - 1][M(P, G) - 1] = 1$. Differentiating volume with respect to the pressure along the equilibrium line $\eta = \eta_t(P)$ we obtain an expression for the isothermal compression of TS:

$$\beta_{TS}(P) = \beta_t\{1 - M(P, G)\}, \tag{8}$$

which shows that if the TS is stable under the constant volume conditions, see (7), its equilibrium isothermal compression β_{TS} must be negative. The physical implications of this fact will be discussed below.

A *phase diagram* is a convenient, geometric way to show the most stable states that occur in the system under equilibrium conditions. Analysis of the local stability of equilibrium states, (6), (7), does not exhaust the analysis of a phase diagram of a closed one-component substance because of two reasons. First, even being locally stable, the equilibrium states may have different amounts of the free energy and only the ones with the least amount appear on the phase diagram—the *global stability* criterion. Second, the states considered so far were assumed to be spatially homogeneous, which is not necessarily true in a real system. In fact, the constraint of closure, (2), may force the system to break down into domains of different phase content—a *heterogeneous state* (HS), which may also appear on the phase diagram.

3 Heterogeneous Systems

In the continuum field-theoretic framework of the Landau theory the structural inhomo-geneities are described by the gradients of the order parameter so that the molar Gibbs free energy of the substance is expressed as follows: $\hat{G} = G(P, \eta) + 1/2\kappa(\nabla\eta)^2$ [16–18], where $\kappa = const(P)$ is the pressure-independent gradient energy coefficient.[4] Then the *total* Gibbs free energy of the system is $\mathcal{G}\{\mathcal{N}, P, \eta(\mathbf{r})\} \equiv \int_{\mathcal{V}} \rho\hat{G}d^3x$ where $\rho \equiv (\partial G/\partial P)_\eta^{-1}$ is the molar density. Taking into account the constraint of fixed number of moles in the system $\mathcal{N} \equiv \int_{\mathcal{V}} \rho d^3x = const(P)$ we obtain that the open-system variational problem ($G \to min$, $V \neq const$) yields the following boundary-value problem [19]:

$$\frac{\partial\rho(G - \mu)}{\partial\eta} - \nabla\left(\rho\frac{\partial\hat{G}}{\partial\nabla\eta}\right) = 0 \quad \text{in } \mathcal{V}; \tag{9a}$$

$$\mathbf{n} \cdot \nabla\eta = 0 \quad \text{on } \hat{\mathcal{V}}; \tag{9b}$$

$$\rho[G - \mu - \kappa/2(\nabla\eta)^2] = 0 \quad \text{on } \hat{\mathcal{V}}. \tag{9c}$$

Here μ is the chemical potential of the system which depends on P and $\mathcal{V}$, $\hat{\mathcal{V}}$ is the boundary of V, and $\mathbf{n}$ is the unit vector on $\hat{\mathcal{V}}$. The free-boundary condition, (9c), appears because the volume of an open system is not specified.

Consider a thin film of fixed thickness X, volume $\mathcal{V}$, and the phase-separating interface parallel to the plane of the film. In this (1D) case the Euler equation, (9a), can be integrated once. Taking into account the free-boundary condition, (9c) and the fact that $\rho \neq 0$, we find that the 1D open-system equilibrium-state equation takes the form:

$$G(P, \eta) - \frac{\kappa}{2}\left(\frac{d\eta}{dx}\right)^2 = \mu \quad \text{for } 0 < x < X, \tag{10a}$$

$$\frac{d\eta}{dx} = 0 \quad \text{for } x = 0, X. \tag{10b}$$

In the closed system ($\mathcal{F}\{\mathcal{V}, \bar{V}, \eta(\mathbf{r})\} \equiv \int_{\mathcal{V}} \rho\hat{F}d^3x \to min$, $\mathcal{V} = const$) the free-boundary condition, (9c), is absent, and the 1D boundary-value problem, instead of (10a), yields: $\rho\{F(V, \eta) - \mu - \frac{\kappa}{2}(\frac{d\eta}{dx})^2\} = const(x)$. Applying this equation at $\hat{\mathcal{V}}$, the constant of integra-tion can be identified as the negative pressure. Then using the Legendre transformation, (3),

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[4]We define $q \equiv const(u)$ as a quantity that does not depend on u but may depend on other variables of the problem.

we find that the 1D closed-system equilibrium-state problem is the same, (10), as that in the open one. This means that the closed system has the same equilibrium HS's as the open one for the same volume $\mathcal{V}$ and internal pressure P.

The global stability problem in a 1D closed system can be formulated as follows: for a given size of the system, X, and the average molar volume, $\bar{V}$, which state $\{\eta(\mathbf{r})\}$ has the smallest amount of the total Helmholtz free energy $\mathcal{F}$? As known [20], if X is large enough, the boundary-value problem, (10), admits a small-amplitude harmonic solution $\eta_h(x) = \eta_t + \Delta\eta(x)$. Applying this solution to (10) and expanding the function $G(P, \eta)$ up to $O(\Delta\eta^2)$, one can find that

$$\Delta\eta = -H\cos\frac{\pi x}{L},$$

$$\text{for } 0 < x < X = nL, \quad n = 1, 2, 3\dots, \tag{11}$$

$$H = \sqrt{\frac{2(G_t - \mu)}{-G_t''}}; \quad L = \pi\sqrt{\frac{\kappa}{-G_t''}}.$$

Obviously the higher harmonics of (11), $n > 1$, have more free energy for the same X and $\bar{V}$ than the fundamental one, $n = 1$, and may be disregarded in the global stability analysis. The implicit functions $\mathcal{F}_{\eta(\mathbf{r})}(X, \bar{V})$ (per unit area of the film) for the TS and HS respectively have the following expressions:

$$\mathcal{F}_t = X\left\{\frac{G_t(P)}{\bar{V}} - P\right\}, \quad \bar{V} = \left(\frac{\partial G}{\partial P}\right)_t; \tag{12}$$

$$\mathcal{F}_h = X\left(\frac{\mu}{\bar{V}} - P\right) + \frac{\pi\sqrt{-\kappa G_t''}}{2V_t}H^2\left(1 + \frac{1}{8}\rho_t'' V_t H^2\right), \tag{13a}$$

$$\frac{X}{\bar{V}} = \frac{L}{V_t}\left(1 + \frac{1}{4}\rho_t'' V_t H^2\right); \tag{13b}$$

where P and μ are the internal, adjustable parameters. Notice that, in general, TS and HS have different internal pressures, P_t and P_h. Equating $\mathcal{F}_t$, (12), and $\mathcal{F}_h$, (13), for the same X and $\bar{V}$ (and, obviously, P, μ) one can find an expression for the *bifurcation line*:

$$X = \tilde{X}(\bar{V}) : \left\{\tilde{X} = L(P), \bar{V} = \left(\frac{\partial G}{\partial P}\right)_t\right\}. \tag{14}$$

For the sub-bifurcational sizes ($X < \tilde{X}$), the HS is not possible, which leaves the TS globally stable. To reveal the nature of the TS/HS transition at this line we subtract $\mathcal{F}_t$ from $\mathcal{F}_h$ and exclude H from the difference using (13b):

$$\mathcal{F}_h - \mathcal{F}_t = -\frac{\pi^2\kappa\bar{V}}{2(V_t')^2 - \bar{V}V_t''}\frac{(X - \tilde{X})^2}{\tilde{X}^3}. \tag{15}$$

(13b), (14), (15) show that for the super-bifurcational sizes ($X > \tilde{X}$) HS is globally stable.[5]

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[5]One can notice analogy with the second-order transition: the amplitude H plays the role of an OP, $(-X)$—the temperature, and $(-\tilde{X})$—the critical temperature.

4 Fluctuations in Nanosystems

As established in the Introduction, fluctuations are very important for small systems. As known [21–24] the validity of the Landau method depends on the magnitude of the fluctuations in the system whose probability, according to the Boltzmann's principle, is proportional to $\exp(-\mathcal{F}_\eta\{\mathcal{V}, \bar{V}\}/k_B T)$. In the present paper we propose a test according to which the method is applicable to the considered problem if the root-mean-square fluctuations of the OP near the TS in the film of the thickness equal to the bifurcation length are small compared with the characteristic OP difference $(\eta_s - \eta_l)$. The Helmholtz free energy of a state near TS in the closed system can be approximated as $F_\eta\{X, \bar{V}\} = F_t\{X, \bar{V}\} + \frac{1}{2}XG_t''(1-M)(\eta-\eta_t)^2/\bar{V}$ (Gaussian approximation for the fluctuations). Notice that $G_t''(1-M)$ is analogous to the inverse susceptibility in the theory of critical phenomena [25, 26]. Then using (11), (14) and the properties of a Gaussian distribution we find:

$$\langle (\eta - \eta_t)^2 \rangle = \frac{k_B T \bar{V}}{\pi^2 \kappa (M-1) \tilde{X}}. \tag{16}$$

Not surprisingly the fluctuations increase with the decrease of the bifurcation size $\tilde{X}(\bar{V})$ and diverge at $M = 1$ due to the flattening of the free energy at this point.

5 Model System

In order to elucidate the closed-system phase-stability analysis presented above, we will consider a particular model system capable of undergoing a melting/freezing transition. The molar Gibbs-Landau free energy of such system can be expressed as following:

$$
\begin{aligned}
G(P, \eta) &= G_l(P) + \frac{1}{2}A\omega^2(\eta) + \Delta G(P)v(\eta) \\
\omega(\eta) &\equiv \eta(1 - \eta), \qquad v(\eta) \equiv \eta^2(3 - 2\eta), \\
G_l(P) &= ZP\left(P^E - \frac{1}{2}P\right) + V_l^E P, \\
\Delta G &\equiv G_s(P) - G_l(P) = [V](P^E - P), \\
[V] &= V_l^E - V_s^E, \qquad V_{sl} = \frac{1}{2}(V_l^E + V_s^E).
\end{aligned}
\tag{17}
$$

Here $A = const(P)$ determines the height of the barrier that separates the phases, $Z = const(P)$ relates to the isothermal compression: $\beta^E \equiv \beta_{l(s)}^E = Z/V_{sl}$, V_l^E and V_s^E are the equilibrium molar volumes of the corresponding phases at $P = P^E$.[6] In Fig. 1 are depicted the molar Gibbs free energies versus pressure of the equilibrium states in the open system described by (17). The equilibrium state diagram (Inset b to Fig. 1) consists of the liquid state ($\eta_l = 0$), solid state ($\eta_s = 1$), and TS ($\eta_t = \frac{1}{2} + 3\Delta G/A$). The solid (liquid) spinodal

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[6]Material parameters, A, Z, P^E, and $V_{l(s)}^E$ may depend on temperature, which would result in the (P, T) phase diagram of the system.

pressure, $P_{l(s)}^S = P^E \pm A/6[V]$, is the pressure that terminates the local stability of the corresponding phase. Beyond these pressures ($P > P_l^S$ or $P < P_s^S$) TS becomes stable (transcritical bifurcation of exchange of stability);[7] between the spinodal pressures, $P_s^S < P < P_l^S$, the TS is absolutely unstable in the open system.

As we pointed out above, the stability of the TS in open and closed systems may be drastically different. Application of the local stability criterion, (7), to the system described by (17) yields that if $A < 4.5[V]^2/Z$ there exists an interval of molar volumes (V_s^L, V_l^L) where TS is locally stable that is, a phase, although the internal pressure of the state is between the spinodal pressures, $P_s^S < P < P_l^S$. To find the criterion for the global stability of the homogeneous TS in a closed system we will compare its molar Helmholtz free energy with that of the liquid and solid phases at the molar volume V_{sl}. Applying the Legendre transformation, (3), to (17) we obtain:

$$F_l(V_{sl}) = F_s(V_{sl}) = \frac{1}{2}\left(ZP^E + [V]\right)P^E + \frac{[V]^2}{8Z}, \qquad (18a)$$

$$F_t(V_{sl}) = \frac{1}{2}(ZP^E + [V])P^E + \frac{A}{32}. \qquad (18b)$$

Comparison of (18a) and (18b) shows that the TS is globally stable against the solid and liquid phases if

$$A < A_{cr} \equiv 4\frac{[V]^2}{Z}. \qquad (19)$$

Notice that the condition of global stability is more restrictive than the condition of local stability mentioned above and it is independent of the sign of the transition volume change, $[V]$, but depends on the compression properties of the phases, Z.

In order to determine the kind of the transition near $V = V_{l(s)}^L$ one needs to compare the Helmholtz free energies of different states at different values of the molar volumes. The analysis shows that inside the interval (V_s^L, V_l^L), there is an interval $(V_s^G, V_l^G) : \{F_s(V_s^G) = F_t(V_s^G), \ F_l(V_l^G) = F_t(V_l^G)\}$ where the TS is globally stable against the solid and liquid phases—i.e., it has the least amount of free energy out of all the homogeneous states (see insets a and b to Fig. 2). Presence of the barrier separating TS from the liquid at $V = V_l^G$ (or solid at V_s^G) and the pressure difference between the states proves that the liquid/TS (or solid/TS) transition is of the first kind. Small magnitudes of the change of pressure and OP ($|\eta_t - \eta_{l(s)}| \ll \eta_s - \eta_l$) at the transition point allow us to classify the transition as weak first-order. Notice that near the transition point $V = V_{l(s)}^G$ the TS may be called liquid-like (solid-like) because $\eta_t \to 0(1)$.

As has been stated above, the closed system may break up into a combination of domains occupied by the stable, solid and liquid, phases. In the thermodynamic limit, the total Helmholtz free energy of the combination of two domains is represented by a common tangent line on the free-energy versus average-molar-volume plot, Fig. 2. At the average molar volume of $\bar{V} = V_{sl}$ it is equal to $\mathcal{F}_h(X, V_{sl}) = \frac{X}{2}(ZP^E + [V])P^E$. Comparison of this expression with (18b) shows that $\mathcal{F}_h(X, V_{sl}) < XF_t(V_{sl})$ for all values of A, which indicates that in the thermodynamic limit the HS is the most stable state. In a system of finite size the free energy of a *phase-separating interface, σ,* changes the energy balance, which makes

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[7]In molecular dynamics simulations this may be perceived as a secondary, e.g. liquid/liquid, phase transition. In experiments, however, the spinodal pressures are usually not attainable.

the phase separation impossible in the systems below the bifurcation size $\tilde{X}(\bar{V})$, (14). This leaves the homogeneous TS as the global minimizer of the free energy if:

$$X < \tilde{X}(\bar{V}); \quad V_s^G < \bar{V} < V_l^G,$$

$$X_{cr} \equiv \min_{V_s^G < \bar{V} < V_l^G} \tilde{X}(\bar{V}). \tag{20}$$

In the system described by (17) $X_{cr} = \pi(2\kappa/A)^{\frac{1}{2}}$ is reached at $\bar{V}_{cr} = V_{sl}$.

As the parameters of the model, A and κ, are not standard, tabulated properties of materials, one would like to express the criteria of TS stability, (19), (20), through experimentally measurable quantities. This can be done with the help of two quantities, the free energy σ and thickness l of the solid/liquid interface. Using (10), (17) one can find the expressions for these quantities in an unlimited ($X \to \infty$) open system:[8]

$$\sigma \equiv \int_{-\infty}^{+\infty} \rho(\hat{G}^E - \mu)dx = \sqrt{2\kappa} \int_{\eta_l}^{\eta_s} \frac{\rho d\eta}{\sqrt{G^E - \mu}} = \frac{1}{6}\sqrt{\kappa A}\frac{\ln V_l^E/V_s^E}{[V]}, \tag{21}$$

$$l \equiv \frac{[\eta]}{\max(d\eta/dx)} = [\eta]\sqrt{\frac{\kappa/2}{G^E - \mu}} = 4\sqrt{\frac{\kappa}{A}}. \tag{22}$$

Then $X_{cr} = (\pi/2\sqrt{2})l$ and the condition of the global stability of the TS, (19), can be expressed as follows:

$$\varepsilon \equiv \frac{\sigma}{l} < \varepsilon_{cr} \equiv \frac{[V]\ln V_l^E/V_s^E}{6V_{sl}\beta^E}. \tag{23}$$

Here ε is the interfacial energy density that can be estimated from the experiments on nucleation or MD simulations while its critical value, ε_{cr}, which depends on the equilibrium properties of the solid and liquid phases only, can be calculated using the phase diagram data of the system. The condition of the global stability of the TS, (23), can also be expressed as a restriction on the interface thickness: $l > l_{cr} \equiv \sigma/\varepsilon_{cr}$. This criterion favors hard materials (small β^E) with large transformation strain, $[V]/V_{sl}$. Notice that $\varepsilon_{cr} \sim ([V]/V_{sl})^2$. Equation (23) does not contain parameters of the continuum method and, hence, can be verified experimentally for a material system of interest.

Using the model system described by (17), (21), (22) one can calculate the mean-square of the OP fluctuations, (16), at $\bar{V} = V_{sl}$:

$$\langle(\eta - \eta_t)^2\rangle = \frac{4\sqrt{2}k_B T\bar{V}}{3\pi^3\sigma l^2\delta}; \quad \delta \equiv \frac{3l[V]^2}{16\sigma\beta^E V_{sl}^2} - 1. \tag{24}$$

If the condition, (23), is satisfied then $\delta > 0$; if, in addition, δ is large then the criterion for applicability of the Landau method can be expressed as follows:

$$l > l_{fl} \equiv \frac{4(18)^{1/6}}{3\pi}\left(\frac{V_{sl}}{[V]}\right)^{2/3}(k_B T\beta^E)^{1/3}, \tag{25}$$

where l_{fl} is the characteristic fluctuation length of the system.

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[8]Notice the effect of compression on the interfacial energy, (21), while the interfacial thickness, (22), is unaffected by the volume change.

Another restriction on the interfacial thickness l comes from the fact that the continuum method is based on the coarse-graining procedure [25, 26] with a coarse-graining radius that must be greater than the interatomic distance but smaller than the interfacial thickness l. Thus the validity of the method and the conclusion of the global stability of TS are expressed in the form of the constraints on the thickness of the solid/liquid interface l.

6 Phase Diagram of a Closed System

As has been noted out in Ref. [1, 2], "one cannot represent phase equilibrium of (nanostructures) with conventional, two-dimensional phase diagrams. One needs another dimension." In Ref. [1, 2] a fraction of dynamically coexisting phases was added as the additional coordinate; in the present research we find that system size serves better as the additional coordinate of a phase diagram. Summarizing the calculations presented above, we can construct a size-volume phase diagram of a closed system capable of undergoing a solid/liquid phase transition and stabilizing the TS, see Fig. 3. Inside the two-phase interval of molar volumes (V_s^E, V_l^E) there is a smaller interval of the local stability (V_s^L, V_l^L) and still smaller interval of the global stability (V_s^G, V_l^G) where TS is the most stable homogeneous state. The regions of the stability of the homogeneous states are separated from that for HS by the bifurcation curve $X = \tilde{X}(\bar{V})$, (14), (20). In the large-system-size limit $(X \to \infty)$ this
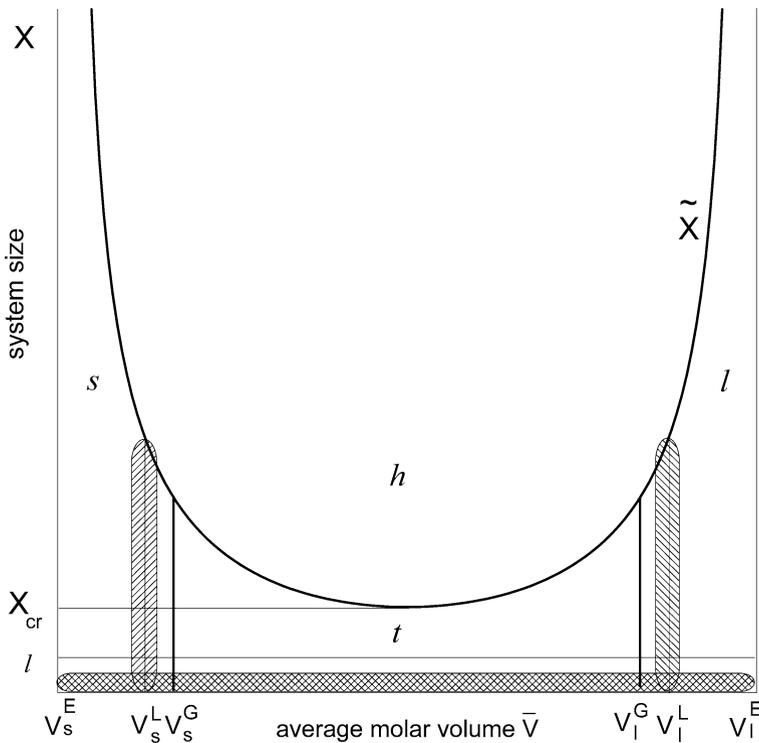

Fig. 3 Size-volume phase diagram of a closed system described in the caption of Fig. 1. Regions of the global stability of the s-solid, l-liquid, t-transition, and h-heterogeneous states. *Shaded areas*—fluctuation regions

curve separates HS from the regions of solid or liquid phase stability and asymptotically approaches $\bar{V} = V_{l(s)}^E$; deviation of the curve from the asymptotes is due to the necessity to accommodate the solid/liquid interface with the energy σ. In the small-system-size limit $(X \to X_{cr})$ the bifurcation curve separates the HS and TS regions of the global stability. Although the critical length X_{cr} is comparable to the interfacial thickness, for $\bar{V} \to V_{l(s)}^G$ one has $\tilde{X} \gg l$. The boundaries $\bar{V} = V_{l(s)}^L$ and $X = 0$ are surrounded by the fluctuation regions where the present method is not valid. Thus if the material conditions of (23), (25) are fulfilled the TS is the globally stable state of the system with the size that satisfies the conditions of (20), see region 't' in Fig. 3.

Although thermodynamically stable, the TS remains mechanically unstable—that is, the isothermal compression of this state is negative, see (7), (8). This does not allow this state to become a bulk phase $(X \to \infty)$ or a phase in an open system (to coexist with another phase) [27]. The negative compression modulus, however, is not an obstacle for the existence of a homogeneous phase in a closed system of a limited size. Indeed, in this case the mechanical instability would cause 'delamination' of the substance from the walls, which is associated with the creation of the free surface and additional free energy. The global stability analysis presented above proves that the latter is not energetically advantageous in small systems. Thus the TS becomes a stable phase for a material system that satisfies (20), (23), (25) and can be observed experimentally.

7 Discussion

We presented the theory which shows that, in a closed system of fixed volume capable of undergoing a phase transition, the transition state can be thermodynamically stable against the bulk phases if a certain material parameters condition is fulfilled. In a small system below the critical size, the transition state turns into a globally stable phase that can be observed experimentally. Such an effect is known to occur in one-component clusters of rare gases and metals [1, 2, 7, 8]. Clusters of tens or hundreds of particles exhibit forms almost precisely analogous to the phases of bulk systems: solid and liquid; but, in a certain range of energies, the most stable structural arrangement turns out to be icosahedral, which is known to be absolutely unstable in the bulk.

An interesting application of the theory can be found in the case of melting/ freezing/amorphization transition. As known [28–31], amorphization of multi-component materials has strictly kinetic origin—that is, at least one internal relaxation time crosses an experimental time scale. Such materials do not possess any kind of thermodynamic stability and may be understood as liquids that have lost their ability to flow. They have been quite properly called glasses or glassy states. However, there is another category of materials where the amorphous states appear to have some kind of thermodynamic stability with respect to crystallization or melting; particularly interesting among them are pure substances: carbon [32–34], semiconductors [35, 36], one-component metals [37, 38], and water [39]. Such states may be called *amorphous phases*. A number of experimental data indicate that the stability of the amorphous phases in pure substances may be a size effect [32–39].

In the framework of the multiparticle potential energy $\Phi(\mathbf{r}_i)$ the thermodynamic stability of the amorphous phase upon cooling is explained as trapping of the system in one of the shallow basins. How can one describe an amorphous phase within the framework of the Landau theory? One may, of course, suggest a complicated free energy with at least one more additional minimum for the amorphous phase ("dig a hole on the peak"). However,

there are significant theoretical advantages in attempting to describe the amorphous phase with the simple free energy with only two minima (Ockham's razor principle). We have demonstrated above that in a closed system of the size below the critical one there is a material parameter criterion under which the transition state has less free energy than any bulk phase or a heterogeneous combination (mixture) of the two. That is, the homogeneous transition state can be globally stable in such a system. Stabilization of the transition state in small systems of limited resources allows us to conjecture that this state corresponds to an amorphous phase of pure substances.

A typical amorphization path involves a high-temperature stage of preparation and a low-temperature stage of analysis or usage [28–38]. Our stability analysis is relevant to the high-temperature stage of preparation of the amorphous phases of pure substances. Once it is exposed to the ambience, according to the analysis, such phase should lose its stability. Observability of this phase in open systems may be explained by the slow kinetics of its decomposition at low temperatures.

The transition state can be stabilized only if the material conditions, (23), (25), are satisfied. They should be used in the material selection process for the experimental verification of the effect. These conditions favor hard materials (small β^E) with large transformation strain. There are only a handful of systems described in the literature where the conditions, (23), (25), can be verified. We found that for the MD-aluminum system at $T = 700$ K, $V_s^E = 17.05$ A^3/atom, $V_l^E = 17.85$ A^3/atom, $\beta_l^E = 2.18 \times 10^{-11}$ m^2/N [38]. For the interfacial thickness we used the estimate $l \approx 3$ nm, which can be obtained from the E-plot for the liquid/γ-phase interface because the liquid/solid one was not available. For the surface energy the value $\sigma = 0.103$ J/m^2 was obtained from Ref. [40]. These data allowed us to estimate $l_{fl} \approx 0.32$ nm and $l_{cr} \approx 6.4$ nm, which means that, although the Landau method is applicable to that system, the transition state of the free energy, (17), cannot be made stable there. Taking into account that the numerical factor in (23) depends on the coefficients of $G(P, \eta)$ in (17), it is conceivable that this criterion will be fulfilled if another function $G(P, \eta)$ is chosen to describe the system.

The isochoric conditions are not unique in their property to stabilize the transition state in small systems of limited resources. Earlier [41], we considered a similar problem in a small closed system of fixed energy (microcanonical ensemble) and obtained a similar result. There are reasons to expect similar stabilization in small isolated particles of fixed compositions. In the present paper we consider a case of a thin film where the phase separation is permitted only parallel to the plane of the film. Although there may be special physical reasons why only this type of transformation is permitted, one may argue that a film can break down into phase domains with the interfaces perpendicular to the plane of the film. This can tip the balance in favor of the heterogeneous state. In this case our calculations still hold true for 3D nanosystems (nanoparticles) because for them the surface-to-volume ratio (2D/X) increases with the increase of the dimensionality D. We believe that it may also be possible to observe the effect of dynamical coexistence in small systems if the fluctuations are properly accounted for in the system of dynamical equations. The Landau method will also help analyze the second-order phase transition in nanosystems.

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