

Heterophasic oscillations in nanoscale systems

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Both the energy differences between metastable and stable phases and the energy barriers separating these phases decrease with decreasing particle number. Then, for small enough systems, random heterophasic fluctuations of the entire system become an observable form of thermal motion. We discuss mechanisms and observation conditions for these random transitions between phases.

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I. INTRODUCTION

In a macroscopic system, a discontinuous (first order) phase transition is manifested by discontinuity of thermodynamic properties at the phase transition temperature T_λ . For finite systems, these singularities are replaced [1–3] by a continuous change in a transition range ΔT_{tr} of temperatures. This range increases upon diminishing the number N of particles [4], but it has been found [3] rather narrow for systems with a large particle number N : $\Delta T_{tr}/T_\lambda \ll 1$ for $N \gg 1$, thus allowing one to treat the rapid change as a smoothed phase transition, approximately characterized by a transition temperature.

It has been known for a long time that this temperature shifts with diminishing system size [5,6]. More recent detailed studies [2,3,7–19] of finite systems in the transition range of temperatures revealed a rather complex set of behaviors: surface melting, noncrystalline isomers, pattern formation, and properties fluctuations at time scales much larger than particle vibration period. A discussion of size related properties changes, and a list of references on the subject can be found in [9]. The complexity becomes already observable while the phase transition range is still narrow, for $N \sim 10^5$ – 10^7 in three-dimensional and $N \sim 10^4$ – 10^6 in two-dimensional systems. In a condensed system, this particle number corresponds to the nanometer range of sizes. The lower limit here is set by the condition that most particles belong to the bulk, so the bulk dictates the phases of the system, and surface effects can only shift transition parameters. The upper limit depends on the phenomenon; as explained below, in a large enough system the periods of property changes may become too large for observation.

Some of the observed phenomena may be explained by the increased role of the surface in smaller systems [3,7,8]. Surface-related effects can be controlled, for example, by imbedding the system in an appropriate matrix. Other new phenomena reflect features common to all finite systems: the energy differences and energy barriers between different thermodynamic states in finite systems are finite and decreasing when the particle number decreases. Then, heterophasic fluctuations that are small-scale phenomena in macroscopic systems [20] may change the state of the entire finite system. The objective of the current study is to study conditions for observing these fluctuations.

To separate the surface-driven effects from the bulk finite size effects, we first consider a toroidal (periodic) system that has no external surface; systems with an external boundary are then discussed assuming that the system is large enough so that most of the particles belong to the bulk. Toroidal systems are realized in computer simulations under periodic boundary conditions. In recent decades, computer simulations became an increasingly important source of information about finite systems. Three-dimensional (3D) and two-dimensional (2D) systems have been studied [2,3,9–16,19,21] using different simulation algorithms, frequently with the goal of understanding phase transitions in macroscopic systems.

One of the advantages of computer simulations is that simulation algorithms are designed to produce an equilibrium isochoric (NTV, constant particle number N , temperature T , and volume V) or isobaric (NTP, constant N , T , and pressure P) Gibbs ensemble. For real systems, these standard experimental conditions are unambiguous only in the macroscopic limit; in smaller systems, the equilibrium ensemble may depend on the conditions on or near the surface [17,18]. The case discussed in the current paper is a nanosize particle embedded in an inert matrix. In computer simulations, the role of the matrix is played by the cell that is kept at constant shape and size for (NTV) conditions, and is only allowed to change volume to maintain constant pressure for (NTP) simulations.

More complex situations include systems prepared in vacuum with or without a substrate. At times when evaporation can be neglected, these systems can be approximately described by a microcanonical ensemble—see Ref. [3] for a review. These more complex situations are beyond the scope of our paper.

II. PERIODIC SYSTEMS

One expects that in large enough finite systems the kinetics of a discontinuous phase transformation is similar to the nucleation kinetics in macroscopic systems [22]: a change of state parameters from the old to new phase makes the old phase metastable, and then nuclei of the new phase appear in the old phase as fluctuations, reach critical size, and grow to become macroscopic regions in the final equilibrium state. Transient states between the metastable old phase and the stable new phase are then two-phase: part of the system with $N_{new} < N$ particles is in the new phase and the rest of the

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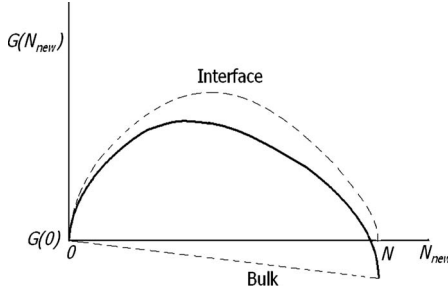


FIG. 1. (NTP)-system: a schematic plot of the nonequilibrium Gibbs energy $G(N_{new})$ (solid line) and of the interface and bulk contributions (dashed lines).

system with $N_{old} = N - N_{new}$ particles is in the old phase. The phases are separated by an interface; we consider here the case when the width of this interface is negligibly small compared to the system size, and the number of interface particles can be neglected in the particle balance. The interface is characterized by surface tension α giving the energy cost of creating a unit area of the interface.

This two-phase approach is widely used in the theory of nucleation and phase transitions kinetics [22,23]. In isotropic models, α is treated as a scalar function of state; when anisotropy is important, the surface tension becomes a function of a point at the interface depending on the local orientation of the interface relative to the anisotropy. Note that we label the phases “new” and “old” as a conventional way to distinguish between phases and to indicate the direction of phase changes when this direction is important.

In an isobaric system at the phase transition point, the Gibbs free energies of the new and old phases coincide. In a macroscopic system, the energy barrier for a heterophasic fluctuation in the entire system is infinitely high, forbidding heterophasic fluctuations of the entire system at any time scale. This barrier becomes finite for a finite supercooling or overheating, but then the energy difference between the old and the new phase in a macroscopic system is macroscopically large, making the transition from metastable to stable state irreversible [9]. Heterophasic fluctuations in the new phase are then local phenomena [20] with a short lifetime. With system size decreasing, the energy difference between the stable and metastable phases decreases, so there is a transition range ΔT_{tr} of temperatures where the probability to find the equilibrium system in either phase is substantial. However, the equilibration time to achieve this two-phase distribution is an exponential function of the interphase barrier energy, and may appear too large for observation. The energy barriers keeping the system in a phase decrease with decreasing particle number N , and in small enough systems, a reverse transition from the new to the old phase can be observed and equilibration achieved on experimental time scales. Then, for these systems heterophasic fluctuations become an observable form of equilibrium thermal motion. The size of the system to observe these fluctuations depends on available observation time; for typical experimental conditions, the characteristic size is in nanometer length-scale. Below, we present a simple model for these fluctuations and discuss conditions for their observation.

Consider a finite system in thermodynamic equilibrium under conditions of constant particle number N , pressure P , and temperature T [(NTP) system]. Near a phase transition, two-phase states with N_{new} particles in the new phase and $N_{old} = N - N_{new}$ particles in the old phase appear as fluctuations. The probability $P(N_{new}) = p(N_{new}) dp(N_{new})$ of finding a state with a number N_{new} of new phase particles in the range $(N_{new}, N_{new} + dN_{new})$ is defined by the minimal work W_{min} of creating this nonequilibrium state [22]. For an (NTP)-system, this minimal work is given by the nonequilibrium Gibbs free energy $G(N_{new})$ [22,23]. We consider a two-phase model for a finite system with $G(N_{new})$ written as a sum of contributions of one-phase regions and the interface [1,2]:

$$p(N_{new}) = Z e^{-W_{min}(N_{new})/k_B T}, \quad Z = \int_0^N p(N_{new}) dN_{new},$$

$$W_{min}(N_{new}) = G(N_{new}) = N_{new} \mu_{new} + (N - N_{new}) \mu_{old} + \alpha \Sigma(N_{new}). \quad (1)$$

In this formula, k_B is the Boltzmann constant, μ_{new} and μ_{old} are the chemical potentials of the new and old phases, α the surface tension, and Σ the area of the interface. Formula (1) assumes that all other modes except for N_{new} are at equilibrium. Then, the entropy related to interface conformations has to be added to the Gibbs energy. Most of this entropy comes from small-scale shape fluctuations (surface waves) of the interface; this part is included in the surface tension. Contributions related to interface position and larger-scale shapes are small and can be neglected. Due to average curvature of the phase-separating interface, pressures in the phases may differ. We are primarily interested in the situation when both phases occupy a significant fraction of the volume, so that the curvature of the interface is small.

In the macroscopic limit $N \rightarrow \infty$, the condition $\mu_{new} = \mu_{old}$ defines the phase transition line $T = T_\lambda(P)$ in the (T-P)-thermodynamic plane. For finite systems, this condition defines the conventional transition temperature. Near the phase transition temperature along an isobar, the difference $(\mu_{new} - \mu_{old}) \approx -s \Delta T$, where $s = -\partial(\mu_{new} - \mu_{old}) / \partial T$ is the per-particle transition entropy, and $\Delta T = T - T_\lambda(P)$. Chemical potentials and surface tension depend on system size. This results in a size-dependent shift of the transition range. One expects these effects to be small when the size of the system is much larger than the interaction radius of particles. In anisotropic systems, surface tension is a local characteristic depending on the local orientation of the interface. Generalization of our model to include anisotropy is rather straightforward, but it involves new parameters. Qualitatively, effects discussed in the current paper are determined by the rather general features of the Gibbs energy landscape on the N_{new} axis: deep minima at the ends, and a maximum between minimum points. These features are schematically illustrated by Fig. 1.

The Gibbs energy (1) has two end-point minima: $G = G_{new}$ at $N_{new} = N$, and $G = G_{old}$ at $N_{new} = 0$. At these points, the interface area $\Sigma(N_{new})$ and the interface contribution to Gibbs energy vanish. In the Gibbs energy landscape on the N_{new} axis, each minimum is the bottom of an energy basin

associated with corresponding phase. The difference in Gibbs energies between the minima is $G_{new} - G_{old} = N(\mu_{new} - \mu_{old}) \approx -Ns\Delta T$. Between the end points, there is a maximum G_{max} of the Gibbs energy at $N_{new,max} = xN$ ($1 \geq x \geq 0$) separating the two basins. At the maximum,

$$\begin{aligned} \frac{dG(N_{new})}{dN_{new}} &= \alpha \frac{d\Sigma}{dN_{new}} - (\mu_{old} - \mu_{new}) = 0; \\ \frac{d\Sigma}{dN_{new}} &= \frac{\mu_{old} - \mu_{new}}{\alpha} \sim \frac{s\Delta T}{\alpha}. \end{aligned} \quad (2)$$

In a macroscopic system, Eq. (2) describes a critical nucleus [22] of the new phase. This nucleus is a sphere with the radius $R_c \sim [\alpha/(s\Delta T)]$ and the number of particles $N_{new,c} \sim [\alpha/(s\Delta T)]^D$; the surface (the interface area) for this nucleus is $\Sigma(N_{new}) \sim (N_{new})^{(D-1)/D}$, where $D=2$ or 3 is the number of space dimensions. The nucleus becomes very large at small ΔT . At the phase transition $\Delta T=0$, and both the critical radius and the related surface energy are macroscopically large, so there is a macroscopically high excitation energy barrier between phases forbidding heterophasic fluctuations of the entire system. In a finite system, the maximum size, particle number, and interface area of a nucleus are finite, so the energy barrier between phases is also finite. For a periodic system at the conventional phase transition point $\Delta T=0$, the maximum of the Gibbs energy is at $N_{new}=N/2$. The interface area has at this point its maximum value.

The probability of finding the system described by the equilibrium ensemble (1) in the old basin is $p_{old} \sim \exp[-G_{old}/(k_B T_\lambda)]$, and in the new basin $p_{new} \sim \exp[-G_{new}/(k_B T_\lambda)]$. The condition that the equilibrium ensemble includes significant fractions of both phases is then $G_{new} - G_{old} = N(\mu_{new} - \mu_{old}) \approx -Ns\Delta T \sim k_B T_\lambda$; this defines the transition range of temperatures $\Delta T_{tr} \sim k_B T_\lambda / (sN)$. However, this definition assumes complete equilibrium. In a large enough system, the equilibration time for this ensemble can exceed available times. This time is determined by the energy of creating the critical nucleus. In the critical range of temperatures, the critical nucleus occupies a significant part of the system, and its size is about the system size, so both the surface area of the interface and the energy to create this nucleus grow with increased system size. A supercooling or overheating beyond the transition range results in a smaller critical nucleus and accelerates the transition to the new phase, but then the barrier for the transition back to the old phase includes the energy difference between phases and becomes too large for this transition to happen at experimental time scales. By diminishing the number N of particles in the system, one can arrive at a system size when for the transition range of temperatures the transition from old to new phase happens on observable times. Then, the difference between excitation energies for a transition from the new to old phase and for the transition from the old to new phase become small, and both transitions become observable.

In a macroscopic system the number N of particles is macroscopically large, so the transition range of temperatures vanishes; on approaching the phase transition temperature, the activation energies $G_{max} - G_{new}$ and $G_{max} - G_{old}$ for

an interbasin fluctuation become macroscopically large. Then, the probability to find the system close to the basin-separating maximum becomes negligibly small, and each phase can be unambiguously defined as an ensemble of states belonging to the corresponding basin.

For a finite system in the transition range of temperatures, this phase-basin correspondence becomes conventional: one identifies the phase of the fluctuating system with a basin by convention that for $N_{new} < N_{new,max}$ the system is in the old phase, otherwise the system is in the new phase. The equilibrium ensemble gives now a finite probability to find the system in each of the phases. This two-phase interpretation, based on the phase-basin correspondence, becomes ambiguous when there is a significant probability to find the system close to the basin-dividing barrier. The ambiguity is small when $G_{max} - G_{new}$ and $G_{max} - G_{old}$ are large compared to thermal energy $k_B T$. The same energies define the average times θ_{old} and θ_{new} for the system to continuously keep in the same basin; according to the theory of thermally activated processes, these times can be described by an Arrhenius-like formula:

$$\theta_{old} = \frac{1}{\nu} e^{(G_{max} - G_{old})/k_B T}, \quad \theta_{new} = \frac{1}{\nu} e^{(G_{max} - G_{new})/k_B T},$$

$$G_{max} - G_{old} = \alpha \Sigma_{max} - (N - N_{new}) \mu_{old},$$

$$G_{max} - G_{new} = G_{max} - G_{old} - sN\Delta T, \quad (3)$$

with ν being the frequency of attempts to change the basin; one expects that the time $1/\nu$ is of the order of the vibration period for system particles.

In a metastable macroscopic system, θ_{old} is finite and size-independent while θ_{new} is too large to be observed. The activation energies and the lifetimes θ_{new} and θ_{old} decrease with decreasing particle number N . The condition that both lifetimes are of the same order of magnitude coincides with the condition defining the transition range ΔT_{tr} that there is a significant probability of finding the equilibrium system in any of the phases. Then, in a small enough system in the transition range ΔT_{tr} of temperatures, both the metastable and the stable-metastable transitions can occur at observable times, and random phase changes (heterophasic fluctuations) become a form of thermal motion. The sum $\theta_{new} + \theta_{old}$ gives the average period for these fluctuations. This period depends on N and ΔT ; for a given particle number N , this period as a function of temperature has a minimum when $\Delta T=0$ and $\theta_{new} = \theta_{old}$. The minimal period rapidly increases with increasing particle number. The condition $\theta > \theta_{new} + \theta_{old}$ sets the upper limit $N(\theta)$ for particle number in the system to observe heterophasic fluctuations at time-scale θ .

With diminishing system size and all other factors kept constant, $N_{new,max}$ increases towards its largest possible value $N_{new}/2$. At $\Delta T=0$, $G_{max} - G_{old} = G_{max} - G_{new} = \alpha \Sigma_{max} \sim (N)^{(D-1)/D}$. Using Eq. (3) one gets the upper limit $N_{up}(\theta)$ for the particle number in a system fluctuating at $\Delta T=0$ between the old and new basins at time-scales $t < \theta$:

$$N_{up}(\theta) \sim \left(\frac{1}{p} \ln \frac{\theta}{\tau} \right)^{D/(D-1)}, \quad p = \frac{r_0^2 \alpha}{k_B T},$$

$$\begin{aligned} G_{max} - G_{old} &= G_{max} - G_{new} \\ &= \alpha \Sigma_{max} \sim r_0^2 \alpha N^{(D-1)/D} \sim k_B T_\lambda \ln \frac{\theta}{\tau}, \end{aligned} \quad (4)$$

r_0 is the interparticle distance. The ratio $p = r_0^2 \alpha / (k_B T_\lambda)$ is a nondimensional materials characteristic.

When $\Delta T \neq 0$, the old phase is metastable. The average lifetime θ_{new} of the system in the new phase is now larger than that in the old phase. The ratio $\theta_{new} / \theta_{old} = \exp[(G_{old} - G_{new}) / k_B T] \geq 1$ is of the order of unity in the transition range of temperatures and becomes very large beyond this range. Increasing supercooling or overheating of the old phase results in increasingly asymmetric heterophasic switches: the system stays a long time in the new phase and for a short time visits the old one. When θ_{new} becomes larger than the observation time, the transition is essentially irreversible. For a system yielding the condition (4), the reverse transition is observable at time-scale θ in the temperature range $\Delta T_{hp}(\theta)$,

$$\Delta T_{hp}(\theta) = \frac{k_B T_\lambda}{sN} \ln \frac{\theta}{\tau}. \quad (5)$$

Note that the transition range of temperatures ΔT_{tr} is defined by the condition that in the equilibrium ensemble, the probabilities to find the system in the old as well as in the new phase are of the order of unity; this equilibrium can be reached only at times much larger than $\theta = \theta_{new} + \theta_{old}$. The ratio θ / τ may be very large, so the range $\Delta T_{tr}(\theta)$ of temperatures where the heterophasic fluctuations are observable may be larger than the transition range $\Delta T_{tr} \sim k_B T_\lambda / (sN)$, but the asymmetry of phase change rapidly increases when $|\Delta T| > \Delta T_{tr}$.

With decreasing particle number N , the average period for heterophasic fluctuations decreases and the probability $P_{inter} \sim \exp[-\alpha \Sigma_{max} / k_B T] \sim \theta / \tau$ of finding the system close to the activation barrier increases. In a small enough system, the phase-basin correspondence and the description of the system in terms of phases can become ambiguous. The condition $P_{inter} \sim \theta / \tau \gg 1$, assumed by the two-phase approach, limits the system size from below; when this condition is violated, the two-phase picture is not applicable.

An (NTP)-system large enough to justify the phase-basin correspondence is with a high probability occupied by the old or the new phase. In contrast to that, a macroscopic or very large (NTV)-system (constant N , T , and volume V) has a range of densities $n = N/V$ where two coexisting phases coexist at equilibrium while having different densities. The number N_{new} of particles in the new phase, and thus volumes occupied by phases, are determined by the condition that the pressure in the system equals the phase transition pressure $P = P_\lambda(T)$. The minimal work of preparing a state with a non-equilibrium value of N_{new} is now the free energy $F(N_{new}) = G(N_{new}) - PV$, it has a deep minimum [see a schematic plot of $F(N, T, V, N_{new})$ in Fig. 2] at the equilibrium value of N_{new} . There are also two end-point minima, both metastable, de-

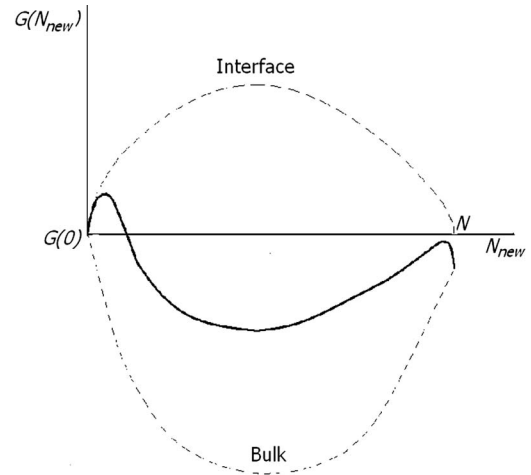


FIG. 2. (NTV)-system: a schematic plot of the nonequilibrium free energy $F(N_{new})$ (solid line), and of the interface and bulk contributions (dashed lines).

scribing nuclei of corresponding phases. When the particle number N is decreased, the free energy landscape becomes more shallow, and fluctuations of the relative numbers $x = N_{new} / N$ and $1 - x = N_{old} / N$ increase. The phase coexistence picture is justified by the same condition $\theta / \tau \gg 1$ as the phase-basin approximation.

III. NONPERIODIC SYSTEMS

The simple model of a finite system under periodic boundary condition, used above to discuss system size limitations for observation of heterophasic fluctuations, does not account for many factors. A more realistic model has to include additional system-specific fluctuating characteristics, for example, local anisotropy in crystals and liquid crystals. However, one expects that under periodic boundary conditions, the two-phase picture and the qualitative predictions of the simple model still apply.

Boundary conditions other than periodic introduce a new component, the external boundary of the system, which needs to be included in the model. The external boundary contribution to the Gibbs free energy describes a thin layer near the surface where the local structure is perturbed by the presence of the boundary and possible direct interactions with the imbedding matrix. The width δr of this layer is expected to be about the width of the phase-separating interface; as described, we study systems of a size much larger than this width, so the bulk contribution is much larger than the surface contribution. However, close to a phase transition the difference in Gibbs energy between phases is also small, so the surface contribution may become important.

In a system with a boundary, a nucleus can have part of its surface at the interface between phases, and part at the external boundary. The surface tension at the boundary depends on the phase of the adjacent material, so for a two-phase state there are the surface tensions α_{new} and α_{old} for the new and old phases at the external boundary and the surface tension α at the interface between phases. The minimal work to create a critical nucleus at the boundary is usually smaller, and thus

the probability of nucleation at the surface (heterogeneous nucleation) is much larger, than that in the bulk. The difference $\zeta = \alpha_{old} - \alpha_{new}$ characterizes the surface-related bias towards the new phase.

Consider a two-phase state with N_{new} particles in the new phase, $0 < N_{new} < N$, and external boundary parts belonging to the new and old phase meeting at the junction with the phase-separating interface. The surface part of the Gibbs energy includes now the energies of the interface and all parts of the external surface and of their junction. The geometry of the two-phase system at given N_{new} is determined by the condition of minimum Gibbs energy. In particular, the angles of contact between surfaces at their junction are determined by the condition of mechanical equilibrium [22]. This, in turn, determines the shape of the two-phase system. The Gibbs energy can be then calculated from the system geometry defined by the angles of contact and N_{new} . For a system confined in a matrix that has a fixed form and can only change the volume to maintain constant pressure, the shape of the external surface is determined by the matrix.

For the general case, the formula for the Gibbs free energy becomes rather cumbersome, although the dependence of this energy on N_{new} is qualitatively similar to that of a system with periodic boundary conditions: in the transition range of temperatures there are two end-point minima corresponding to the stable and metastable phase, and a maximum describing the barrier energy G_{max} for heterophasic fluctuations. Details depend on the bias $\zeta = \alpha_{old} - \alpha_{new}$. Qualitatively, changes in phase transition behavior due to bias can be understood from general considerations.

With bias $\zeta > 0$ towards the new phase increasing, the contact angle decreases, thus forcing a small new phase region to be more and more layerlike. The conventional phase transition temperature and the phase transition range of temperatures shift towards the old phase due to surface energy gain in transition [5,6]; this effect is proportional to the fraction of the system at the surface and thus is larger for smaller systems. The energy barrier for nucleation decreases, so the frequency of heterophasic fluctuations increases.

For a large bias $\zeta > \alpha$, no contact angle can satisfy the mechanical equilibrium condition at the junction; in this special case, the entire external surface is always in the new phase because this lowers the Gibbs energy by at least the energy $\delta G = (\zeta - \alpha)\Sigma(0)$ of creating a double-layer with the new phase at the surface. Here, $\Sigma(0)$ is the external surface area.

Note that the surface tensions, and thus the bias, depend on temperature. In an orientation order model of melting [24], a thin layer of melt appears at the surface at a temperature close to the bulk melting temperature. The appearance of this layer corresponds to the condition $\zeta > \alpha$. As already mentioned, the scalar two-phase model of the current paper applies to the crystalline phase only quantitatively. Below, we discuss the case $\zeta > \alpha$ in more detail.

For $\zeta > \alpha$, the minimum of the Gibbs free energy at given N_{new} assumes that the external boundary always belongs to the new phase, and the interface area $\Sigma(N_{new})$ is a monotonously decreasing function of N_{new} , with a maximum $\Sigma(0)$ at $N_{new} = 0$. Consider a spherical 3D particle of radius R , $\Sigma(0) = 4\pi R^2$. The old phase occupies a sphere of radius R_{old} so

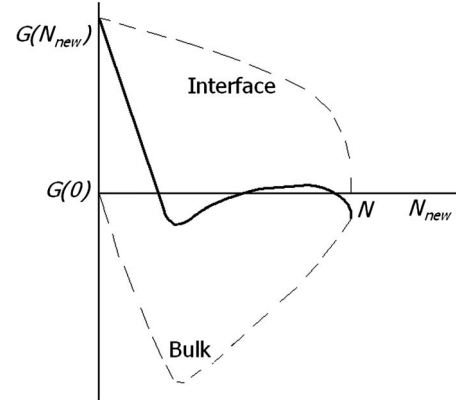


FIG. 3. (NTP)-system with very high surface bias: nonequilibrium Gibbs energy $G(N_{new})$ (solid line); interface and bulk contributions (dashed lines).

that its surface area and volume are $\Sigma(N_{new}) = 4\pi R_{old}^2$ and $V_{old} = (4/3)\pi R_{old}^3$. The number of particles in the new phase is $N_{new} = (N - N_{old}) = (N - n_{old}V_{old})$, where n_{old} is the particle number density of the old phase. The Gibbs free energy for the spherical system has the form

$$G(N_{new}) = G(N) + 4\pi\alpha \left[\frac{3}{4\pi n_{old}} (N - N_{new}) \right]^{2/3} - (N - N_{new})s(T_\lambda - T). \quad (6)$$

Here, $G(N)$ is the Gibbs free energy for $N_{new} = N$. The conventional (bulk) transition temperature T_λ is defined by the condition $\mu_{new} = \mu_{old}$, and the higher temperature phase is the new phase [for the opposite choice, the sign of the last term in Eq. (6) has to be changed]. Note that due to different densities of phases, the external radius R depends on N_{new} . Below, we assume that this density difference is small, and neglect this effect.

The Gibbs energy (6) is schematically shown in Fig. 3. The slope of the interface energy is negative and has a singularity at $N_{new} = N$. Deep in the temperature range ($T < T_\lambda$) of the old phase, the bulk part of the Gibbs energy as a function of N_{new} has a large constant positive slope. The Gibbs energy has end-point minima at $N_{new} = 0$ and $N_{new} = N$ and a maximum at $N_{new,max}$,

$$N_{new,max} = N - \frac{4\pi}{3n_{old}^2} \left[\frac{2\alpha}{s(T_\lambda - T)} \right]^3. \quad (7)$$

The two minima of the Gibbs energy become equal at $T = T_{\lambda,new}$,

$$T_{\lambda,new} = T_\lambda - \frac{4\pi\alpha}{sN} \left(\frac{3N}{4\pi n_{old}} \right)^{2/3},$$

$$N_{new}(T_{\lambda,new}) = N \left[1 - \left(\frac{2}{3} \right)^3 \right] \sim 0.70N. \quad (8)$$

The temperature $T_{\lambda,new}$ is the new phase transition temperature; in the macroscopic limit $N \rightarrow \infty$, the shift $\Delta T_\lambda = T_\lambda - T_{\lambda,new}$ of the phase transition temperature towards the biased phase vanishes as $N^{-1/3}$. With temperature increasing

towards T_λ , the maximum position $N_{new,max}$ shifts to smaller values, reaching zero at $T=T_{sp}$,

$$T_{sp} = T_\lambda - \frac{3\alpha}{s} \left(\frac{4\pi}{3n_{old}^2 N} \right)^{1/3}. \quad (9)$$

At temperatures $T > T_{sp}$ the Gibbs energy becomes a monotonously decreasing function of N_{new} ; the only minimum at $N_{new}=N$ corresponds to the biased new phase.

As in the case of a system in periodic boundary conditions, the form of the Gibbs energy with two end-point minima and a maximum leads to random heterophasic fluctuations as a form of thermal motion observable in small enough systems; the average period of these fluctuations is given by Eq. (3). A fluctuation from the old to the new phase moves the interface from the external surface towards the center of the system through the critical configuration at maximum of the Gibbs energy; a fluctuation from new to old phase involves nucleation of an old phase nucleus in the new phase and its fluctuational growth to reach the same critical configuration. At the new transition temperature $T_{new,\lambda}$, the Gibbs energy has the maximum at $N_{new}=N_{new,max}(T)$, and the activation energy ΔG to reach this critical configuration from any of the phases is

$$\begin{aligned} \Delta G = G_{max} - G(N) &= 4\pi\alpha \left(\frac{3N}{4\pi n_{old}} \right)^{2/3} \left[\left(\frac{2}{3} \right)^2 - \left(\frac{2}{3} \right)^3 \right] \\ &\sim 0.72\alpha \left(\frac{N}{n_{old}} \right)^{2/3}. \end{aligned} \quad (10)$$

This excitation energy is lower than in a corresponding periodic system, and decreases with increasing bias.

IV. SOME REMARKS

The transition most studied in finite systems is the melting-crystallization phase transition. Due to the anisotropy of the crystalline packing, the crystal surface energy depends on the direction of the interface relative to the crystalline axes. The typical nucleus is then not spherical (not circular for 2D systems). Generalization of the simple scalar model (1) to include anisotropy is rather a straightforward

task. The simple scalar model (1) is expected to describe melting only qualitatively. However, heterophasic oscillations are determined by qualitative features of the Gibbs energy that are common in isobaric finite systems in the phase transition range of temperatures.

In Ref. [15], random density oscillations with periods $\sim 10^3 \tau$ in a two-dimensional (NTP)-system of $N=4096$ Lennard-Jones particles have been reported. When the size of the system was increased to 36 864 or more particles, these oscillations have not been seen, and the transition became irreversible at the available simulation time scale. Although this is in line with the above theory, applicability of the two-phase description to 2D systems may impose additional size limitations.

A necessary condition for the validity of the two-phase picture is a small width of the interface compared to the system size. For phase transitions characterized by large discontinuity of properties, the interface is only few interparticle distances wide, so the two-phase picture is expected to hold at least qualitatively when $N \gg 1$. However, in some systems, for example, in systems that are close to a critical point, the differences between phases are small and phase transitions are almost continuous. In a near-critical state, the correlation radius of fluctuations and the width of the interface between phases become large [23].

Data presented in [15] and other publications are consistent with the assumption that the width of the crystal-melt interface in the 2D Lennard-Jones system is much larger than the interparticle distance. Then, a system with particle number $N \gg 1$ (for example, $N=2500$ or 4096) may still be too small to host a critical nucleus. In this case, a spatially homogeneous phase change involving excited local structures may have lower excitation energy than the two-phase mechanism.

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