Void theory of nucleation in liquids

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Assuming that the liquid state of a system of bound atoms differs from the solid state by the presence of voids inside the system, we consider the growth of the solid nucleus in the liquid as a result of the transport of voids. Establishment of equilibrium between the solid nucleus and surrounding liquid occurs with the formation of a boundary surface that separates these phases; the difference of the chemical potentials on the two sides of this surface creates an effective force that acts on voids in the liquid to move them away from the dividing surface. This leads to growth of the nucleus, at a rate determined by the rate of diffusion of voids to the outside of the atomic system. The parameters of the void diffusion coefficient in condensed inert gases are found from the measured coefficients of atomic self-diffusion in inert gases; these give the rate of growth of the solid nucleus in the liquid near the melting point. The connection is shown between the void-based character of the nucleation process and the saddle-crossing nature of dynamics on the potential energy surface for this system of bound atoms.

I. INTRODUCTION

We begin by assuming that the key difference between the liquid aggregate state and the solid is the presence of empty spaces or voids[1] in bulk liquid systems of bound atoms. We assume here that the atoms interact via a pairwise interaction potential. On this basis, we represent the growth of solid nuclei inside of a bulk liquid as a result of void transport. This concept allows us to determine the rate of nucleation. This follows from general properties of clusters and bulk systems of atoms bound by pairwise interactions. Indeed, introducing the potential energy surface (PES) for such systems, one can describe stable configurations of atoms as minima of the PES. The principal property of the PES of a many-body system is its many local minima in a multidimensional space of atomic coordinates. That these minima could be counted and catalogued was established with the first numerical calculations of cluster energies.[2,3] Simple algorithms for such calculations typically begin with a random configuration of atoms and then move atoms to reach locally stable configurations. Much effort has been focused on finding the global minimal energy.

Unfortunately, such algorithms have relatively limited use because the number of local minima grows unmanageably large, even for clusters of only about 20 atoms. For example, a cluster of 13 atoms with the Lennard-Jones interaction potential was once thought to have 988 local minima on its PES.[2,3] A more detailed and recent analysis[4] yielded 1478 local minima and 17357 saddle points for this PES, but the most recent study found 1505 minima and 25653 first-rank saddles.[5] The number of geometrically distinct local minima increases at least exponentially with the number of cluster atoms.[6,7] For example, the Lennard-Jones cluster consisting of 55 atoms has at least 10^{10} local minima of PES excluding permutational isomers.[8] In addition, there are all of the permutational arrangements of the atoms, roughly $n!$ for each geometric structure (n is the number of cluster atoms). Therefore, a cluster's PES consists of very many local minima separated by barriers or saddle points and lines. This means that the cluster's dynamical behavior can be considered as transitions between neighboring minima of PES (Refs. 9–12 and 5), so-called "saddle-crossing dynamics."[13] For the most part, these transitions proceed slowly in comparison with a typical vibrational relaxation time.[14]

This separation of time scales implies that we can separate two types of cluster excitations, the configurational and the vibrational. Indeed, each local minimum of the PES corresponds to a specific atomic configuration with a definite energy at that minimum, so we can assign each such local state of the cluster a definite configurational energy. Changes of the configuration are thus associated with an identifiable configurational excitation or de-excitation energy. Atoms, of course, also have vibrational motion around the local minimum where they are; the amplitudes of these vibrations reflect the degree of what we shall call the thermal excitation of the cluster. In this way, configurational and thermal or vibrational excitations are separated and can be considered independently.

Now we turn to the mechanism of transport phenomena inside bulk systems of bound atoms. A displacement of an individual atom results from its passage from the region around one minimum to a neighboring well of the PES; this displacement is of the order of the interatomic distance. Therefore, an atomic displacement over large distances has a diffusional character. Hence, we use a diffusional model to describe transport of atoms in condensed system of atoms bound by a pair interaction.

Let us study these elementary configurational excitations of bulk atomic systems in more detail. We consider such a system as a large cluster whose surface contains a relatively small fraction of the atoms, and therefore we ignore the surface phenomena in this system. The global minimum of the PES for this cluster presumably corresponds to a strict vacancy-free crystal lattice of atoms. (Elsewhere we deal with the situation at higher pressures, where this assumption need not be valid, at least for the free energy.[15]) The lowest

configurational excitations of this system correspond to the formation of vacancies when atoms are moved from interior sites to the cluster surface, and holes are formed inside the cluster. One can see that any such configurational cluster excitation must lead to an increase of the volume. When configurational excitations become dense enough such that neighboring vacancies can border with moderate probability, the strict lattice cluster structure is violated because relaxation may occur into the unoccupied volume. Then, the relaxed elementary configurational excitations can be represented as voids,[1] which we distinguish from the single vacancies on isolated lattice sites. The forms and sizes of elementary voids may vary in time, in contrast to an elementary vacancy, so that one can use only average void parameters. Nevertheless, it is convenient to consider a configurational excitation with a given number of voids as a result of relaxation of the cluster with the same number of vacancies. (Of course, during the transition from vacancies to voids, the energy of configuration excitation is changed and the energy so released transfers into the thermal vibrations. But, because we separate these degrees of freedom and make no assumption about equilibrium between them, the energy of each of these degrees of freedom may be arbitrary.) Investigating transport phenomena in condensed inert gases, we use void properties of condensed inert gases in accordance with Refs. 16–18.

The pairwise interatomic interactions, particularly the attractive interactions, assure that the voids show no particular tendency to condense into large bubbles. We can thus assume that the voids are simply the relaxed products of vacancies, and that these occur randomly throughout the structure. This allows us to use average void parameters, as stated above. The void concept is based on observational properties of condensed inert gases that allows us to prohibit the association or fragmentation of voids.

Using this description of the system of bound atoms, one can represent the process of growth of a new phase in an old one as a result of void motion. Indeed, a liquid phase contains a characteristic concentration of voids, while voids are nearly absent in the nearly crystalline solid state. Therefore, growth of a solid phase inside the liquid results in the diffusion of voids away from the region near the surface of the solid nucleus. Hence, we now treat the growth of a solid nucleus inside a liquid phase in terms of void diffusion from that solid nucleus.

II. GROWTH OF A SOLID CLUSTER INSIDE A LIQUID AS TRANSPORT OF VOIDS

We consider growth of a solid phase in a liquid one by assuming the nucleus of the new phase to be a spherical cluster. In bulk systems of bound atoms with a pair interaction between atoms, the liquid and solid aggregate states differ in their concentrations of voids, and therefore the process of growth of a solid nucleus results from transport of voids away from the solid cluster's surface. Thus, we have a growing solid cluster of radius r_o in a bulk liquid at a temperature T below the melting point, and the growth of this cluster results from void diffusion. Our task is to evaluate the rate of

cluster growth. (We do not ask here about the fluctuation that creates the nucleus.)

This problem relates to transport of voids under a weak nonuniformity and in an external field. Then, the void flux is given by

$$j = -D_v N \frac{dc}{dx} + wNc, \tag{1}$$

where N is the number density of atoms, c is the volume fraction of voids (defined as the ratio of the number of voids to the number of atoms in a volume large enough to make this ratio independent of volume), D_v is the diffusion coefficient of voids in this system, and w is the drift velocity of voids. We now consider, just to begin, the one-dimensional case; the first term of this formula corresponds to the diffusion flux, and the second characterizes the hydrodynamic flux. The occurrence of the hydrodynamic flux is associated with the effective force that results from a gradient of the void concentration. This force compels the ensemble of bound atoms to shrink or stretch depending on the position of the nearest minimum of the free energy, and this causes a displacement of voids until this minimum is reached.

In order to connect the drift velocity and the diffusion coefficient, we note that we cannot use thermodynamic relations for voids, although they are valid for atoms, and a void flux in an ensemble of bound atoms causes a back flux for atoms. This leads to a simple relation between the atomic and void transport coefficients. Then, from the Einstein relation between the mobility and diffusion coefficient of atoms, we obtain the ratio between transport coefficients of voids at equilibrium, $j=0$ and $c \sim \exp(-\mu_v/T)$, where μ_v is the chemical potential of voids, i.e., the difference of the Gibbs free energies for a system with a given number of voids and in the absence of those voids. We evaluate this difference for just a single void. This system of bound atoms and voids has a temperature, T, which we express in energy units $k_B T$. From this, we obtain an analog of the Einstein relation between the mobility and diffusion coefficient of a gas that, in the case of voids, has the form

$$w = -\frac{D_v}{T} \frac{d\mu_v}{dx}, \tag{2}$$

where $\mu_v(c)$ is the chemical potential for a void gas, i.e., the free energy of a configurationally excited atomic system per one void, and we neglect the dependence of this free energy on any aggregation of voids.

For the case of a one-dimensional space, we take the boundary conditions such that for $x<0$ the system is solid, and for $x>l$ it is liquid. In an intermediate region $0<x<l$, the void concentration $c(x)$ varies from $c(0)=0$ up to $c(l)=c_{\text{liq}}$, where c_{liq} is the void concentration for the liquid aggregate state. Then, the void flux j inside this system is given by formula (1) and can be represented in the form

$$j = -D_v N \exp\left(-\frac{\mu_v}{T}\right) \frac{d}{dx}\left[c \exp\left(\frac{\mu_v}{T}\right)\right]. \tag{3}$$

Because j=const in a space between planes, this formula can be considered an equation for $c(x)$. Assuming formally that

the chemical potential of voids μ_v depends on c, we obtain for the void flux

$$j = -D_v N \cdot \left(1 + \frac{c}{T}\frac{d\mu_v}{dc}\right)\frac{dc}{dx}. \tag{4}$$

Solving this equation under the above boundary conditions, we obtain the void flux as

$$j = \frac{N}{l}\int_0^{c_{liq}} D_v(c) \cdot \left(1 + \frac{c}{T}\frac{d\mu_v}{dc}\right)dc. \tag{5}$$

Going now from the initial one-dimensional problem to that of the growth of a spherical cluster, we find the total flux of voids J through a sphere of radius r due to diffusion

$$J = 4\pi r^2 j(r) = -4\pi r^2 D_v N\frac{dc}{dr},$$

and this flux is independent of r. Now, we can reduce this problem to the previous one-dimensional case by a change of variable

$$x = \frac{1}{4\pi r}.$$

Then, the variable x varies from $x=0$ for the liquid state up to $x=1/(4\pi r_o)$ for the solid state, where r_o is the current radius of the growing nucleus, and the void flux according to formula (5) is

$$J = 4\pi r_o N\int_0^{c_{liq}} D_v(c) \cdot \left(1 + \frac{c}{T}\frac{d\mu_v}{dc}\right)dc. \tag{6}$$

Thus, we formally express the void flux that determines the rate of growth of a new phase inside the old one, in terms of thermodynamic and kinetic parameters of the matter where voids are located.

III. VOID PARAMETERS FOR THE SOLID AND LIQUID STATES

Thus, we reduce the problem of the growth of a solid nucleus in a liquid at a temperature below the melting point to diffusion and drift of voids away from the growing solid nucleus. In other words, we represent configurational excitation of a system of bound atoms by a diffusive gas of voids inside the system. Taking a bulk cluster, where surface phenomena are not important and practically all of the voids are located inside of the cluster, we denote the number of atoms n in the cluster, the number of voids v for a given configurationally excited state, and introduce the void fraction as $c = v/n$. The triple-point pressure of inert gases is $p \approx 2 \times 10^4 p_o$, where $p_o = D/R_e^3$ is a typical internal pressure, so that D is the well depth for the pair interaction potential between atoms, and R_e is the equilibrium distance that corresponds to the minimum of this pair interaction potential. Because we suppose that the external pressure is small, we neglect its influence on the system of bound atoms. Hence, the Gibbs free energy G of this system is determined by the entropy term and is identical to its Helmholtz free energy F, i.e.,[19,20]
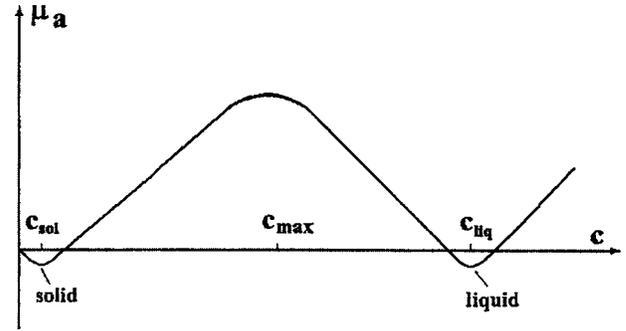

FIG. 1. The dependence of the chemical potential on the void concentration for a system of bound atoms with a pair interaction between atoms and a void gas inside it. The void concentrations $c_{sol} \approx 0$ and c_{liq} correspond to the solid and liquid aggregate states, the maximum of the chemical potential with respect to the void concentration c_{max}, and the range between c'_{cr} and c_{cr} is not stable, i.e., small uniformities leads to an instability that separates the system in two phases. This dependence relates to the melting point.

$$G = F = -T \ln Z, \tag{7}$$

where Z is the partition function of this system of bound atoms. Introducing the chemical potential $\mu(c)$ of this system as the Gibbs free energy $G(c)$ per atom, we obtain this dependence, as given in Fig. 1.[16–18] Just this chemical potential characterizes the equilibrium between the aggregate states of this system of bound atoms, since the number of voids is not conserved and they can go outside of the system or penetrate into it through the system's boundary.

Note that the chemical potential per atom is connected with the above chemical potential per void by the relation

$$\mu_a(c) = c\mu_v(c), \tag{8}$$

since these chemical potentials are the Gibbs free energies G of the configurationally excited atomic system per atom and void correspondingly.

As indicated in Fig. 1, the chemical potential $\mu(c)$ has two minima at the melting point T_m. (In fact, these two minima exist above and below the point of equal chemical potentials, out to the limits of the spinodal curve.) The solid minimum corresponds to $c=0$, and the liquid minimum is realized at $c=c_{liq}$. The maximum of the void chemical potential at $c=c_{max}$ separates the solid and liquid regions. From the model of a close-packed solid, we take $c_{max}=1/12$. At this concentration, a vacancy in a solid of close-packed structure just finds another vacancy as a nearest neighbor, on average; i.e., at this concentration, vacancies start to interact and transform into voids. Taking a current temperature T below the melting point T_m and assuming it to be constant in space, we have

$$\mu(c_{liq}) > \mu(0). \tag{9}$$

Figure 1 reflects our interpretation of configurational excitation in a system of atoms bound by pair interactions. We characterize such an excitation by assigning the system to a given local minimum of the potential energy surface characterized by its number of voids v. The number of voids, as

TABLE I. Reduced parameters of voids for bulk liquid inert gases (D is the binding energy of two atoms).

	Ne	Ar	Kr	Xe	Average
T_m/D	0.581	0.587	0.578	0.570	0.579 ± 0.007
ϵ_o/D	6.1	6.5	6.7	6.7	6.5 ± 0.3
$\Delta H_{fus}/D$	0.955	0.990	0.980	0.977	0.976 ± 0.017
c_{liq}	0.320	0.319	0.318	0.319	0.319 ± 0.001
$[\epsilon_o-U(c_{liq})]/D$	3.00	3.09	3.05	3.05	3.05 ± 0.04
$s(c_{liq})$	5.16	5.26	5.28	5.35	5.26 ± 0.08
$g(c_{liq})$	55	62	63	68	62 ± 5
a	171	189	193	207	190 ± 15
$g(c_{min})$	15	17	17	18	17 ± 1
α	0.165	0.159	0.151	0.151	0.156 ± 0.007
α/c_{liq}	0.51	0.50	0.48	0.48	0.49 ± 0.02
k	3.26	3.38	3.56	3.58	3.44 ± 0.15

well as the configurational excitation itself, does not stay constant in time. The thermodynamically stable or metastable states of this system refer to the minima of the chemical potential $\mu(c)$ [as well as the minima of the thermodynamical potentials $F(c)$, $G(c)$] as a function of the void concentration. Therefore, although we reduce the problem of configurational excitation to the analysis of a two-component system, composed of bound atoms and voids, such a two-component system is specific, because although the number of atoms is conserved, the number of voids is not.

Table I gives the thermodynamic parameters of inert gases[21,22] and voids[17,18,23,24] obtained from measured parameters of liquid inert gases. In Table I, D is the binding energy for a classical dimer of inert gas atoms, T_m is the melting point at the triple point with the temperature expressed in energy units through this paper (k_BT), ϵ_o is the binding energy per atom (or per vacancy) for the solid state, and ΔH_{fus} is the enthalpy of melting per atom; other notations are given below. By taking a configurationally excited state of a system of bound atoms of inert gases as a gas of voids inside a bulk cluster, one can use classical thermodynamic relations. In particular, the reduced Gibbs free energy or the chemical potential of this system, with the pressure contribution neglected, has the form

$$\mu(c) = -\frac{T \ln Z}{n} = c \cdot [\epsilon(c) - Ts(v)] = c \cdot [\epsilon(c) - T \ln g(c)],$$

$$(10)$$

where Z is the partition function of the void gas, $\epsilon(c)$ is the energy of formation of one void at a given void concentration, $s(c)$ is the entropy of formation of one void, $g(c)$ is the statistical weight of an individual void, and the energy of formation of one vacancy is $\epsilon_o = \epsilon(0)$. Although we consider a gas of voids, i.e., we suppose the individual voids inside the cluster to be independent, the interaction of voids is taken into account by the dependence of the energy of their formation on the void concentration. At small void concentration,

when they are assumed to be essentially vacancies, we have also $g(c) = 1$.

Considering an individual void as a quasiparticle, we construct thermodynamic parameters of a gas of voids, including the range of parameters of configurational excitation for which such excitations are not favorable thermodynamically. This operation is described in Refs. 17, 18, 23, and 24 for bulk inert gases on the basis of their thermodynamic parameters, and we now use these results. In particular, the energy of formation of an individual void has the form

$$\epsilon = \epsilon_o - U(c), \qquad (11)$$

where U is the effective interaction potential of voids, ϵ_o is the energy of formation of one vacancy in the crystal, i.e., when $v = 0$ ($\epsilon_o = 6D$ for a short-range interaction potential, if D is the binding energy per bond). The form of this interaction potential must yield two minima of the chemical potential (see Fig. 1). The simplest form of this is the following one:

$$U(c) = \epsilon_o \left[\exp\left(-\frac{\alpha}{c}\right) - \exp\left(-\frac{k\alpha}{c}\right) \right], \qquad (12)$$

and the parameters of this interaction potential are given in Table I. In addition, the statistical weight of an individual void is taken in the form

$$g(c) = 1 + ac, \qquad (13)$$

and values of the parameter a are also given in Table I. All of this allows us to construct the chemical potential of voids. In particular, the maximum value of the chemical potential between the solid and liquid minima, averaged over different inert gases, is equal to $\mu(T_m, c_{max}) = 0.15\pm0.01$, and $\mu(T_m, c_{max})/T_m = 0.26\pm0.02$, where $c_{max} = 1/12$.

IV. DIFFUSION OF VOIDS

We now determine the diffusion coefficient of voids in a region with a given concentration of voids. Diffusion of voids is achieved by elementary void jumps; an individual jump of a void corresponds to transition from one atomic configuration to a nearby one. From the standpoint of the PES, such a jump is a transition between neighboring local minima. This process has an activation character. Hence, the diffusion coefficient for a void can be represented in the form

$$D_v = d_o \exp\left(-\frac{E_a}{T}\right), \qquad (14)$$

where E_a is the activation energy of this process. In the limiting cases, for the solid and liquid aggregate states, one can express the void diffusion coefficient D_v through the self-diffusion coefficient of atoms D_a by the relation

$$|D_v c| = |D_a|. \qquad (15)$$

It is clear that a displacement of a void is simultaneously the same displacement of an atom in the opposite direction.

Table II gives the parameters of formula (14) for the diffusion coefficient of voids, determined on the basis of for-

TABLE II. The parameters of diffusion of voids for solid and liquid inert gases.

	E_{sol}/D	E_{sol}/ϵ_o	d_{sol}, 10^{-4} cm^2/s	E_{liq}/D	E_{liq}/ϵ_{liq}	d_{liq}, 10^{-3} cm^2/s
Ne	5.3±0.5	0.9±0.1	3	2.7	0.9	2.6
Ar	6.8±0.7	1.0±0.1	3	2.5	0.8	3.6
Kr	5.8±0.5	0.9±0.1	2	2.1	0.7	1.5
Xe	6.6±0.4	1.0±0.1	1	2.2	0.7	2.2

TABLE III. The parameters of growth of a solid nucleus in liquid inert gases.

	c_{liq}	c_{cr}	δ_{sol}, 10^{-5} cm^2/s	α_{sol}	δ_{liq}, 10^{-8} cm^2/s	α_{liq}
Ne	0.31	0.25	8.2	8.0	$10 \times 10^{\pm 0.4}$	16±2
Ar	0.32	0.25	17	7.2	$1 \times 10^{\pm 0.5}$	20±2
Kr	0.32	0.26	14	6.3	$3 \times 10^{\pm 0.4}$	17±2
Xe	0.31	0.25	17	6.8	$0.4 \times 10^{\pm 0.3}$	20±1

mula (15) and experimental data from Ref. 25 for the self-diffusion coefficient of atoms in solid inert gases and from Refs. 26–28 for liquid inert gases. Comparison between the activation energies of the diffusion process of voids and energies of formation of vacancies and voids is given also in Table II for the solid and liquid aggregate states of inert gases and shows the correspondence of these values. Thus, the activation energy of the void diffusion process can be expressed through the energy of vacancy or void formation, whose values are given in Table I.

V. CHARACTER OF VOID TRANSPORT INSIDE A NONUNIFORM SYSTEM OF BOUND ATOMS

The above formulas allow us to describe transport of voids during nucleation, i.e., as a new phase grows inside an old one. Let us consider the character of this process. We first examine a uniform void distribution inside a bulk cluster. Guided by Fig. 1, one can see that if the void concentration inside the system is initially below c_{max}, the subsequent development of this cluster leads to formation of the solid aggregate state, i.e., all of the voids disappear from the cluster by moving to its boundary. In contrast, if $c > c_{max}$, the cluster evolves to the liquid state, so that if $c < c_{liq}$, voids go into the cluster and the void concentration increases up to c_{liq} to terminate the relaxation process. In this case, the nucleus disappears. If the cluster temperature differs from the melting point and the system is macroscopic in size, one of these states is stable and the other one is only metastable. (This is because the thermodynamically unfavored form is so unfavored, in a large system, that it will probably not be observable. This is not the case for small systems.) Of course, we assume that the cluster temperature does not differ strongly from the melting point, and the chemical potential for a void gas has two local minima, similar to those of Fig. 1.

In the course of the nucleation process, a bulk cluster under consideration is nonuniform and contains nuclei of a new phase. Under the conditions of most interest to us here, the new phase is stable and the old phase is metastable. For definiteness, we consider the case in which a spherical solid phase grows inside the liquid one, and the temperature is below the melting point, so that the solid state is stable and liquid state is metastable. (We do not consider here the possibility of diffusion-limited aggregation and dendritic growth.) Let us analyze formula (6) for transport of voids in this process. From this formula, it follows that the concentrations of voids at which

$$1 + \frac{c}{T} \frac{d\mu_v}{dc} < 0 \qquad (16)$$

are not realized because transport of voids at these concentration would be directed opposite to a void gradient. In a nonuniform system, the effective force due to the chemical potential gradient drives the movement of voids. Where the chemical potential decreases as a function of void concentration, this force causes a void flux that tends to increase the void concentration gradient. In the range of void concentration according to formula (15), this flux exceeds the diffusion void flux. As a result, the void gradient increases and leads in the end to the formation of a dividing surface, so that void concentrations are different on two sides of this surface. Table III gives the value of the critical void concentration c_{cr} near the liquid minimum that is the boundary of the void stability. In accordance with formula (16), this concentration satisfies the relation

$$\left(\frac{d\mu_v}{dc} \right)_{c_{cr}} = -\frac{T}{c_{cr}}. \qquad (17)$$

Formation of the dividing surface creates a specific character of growth of the solid nucleus in this case. Indeed, because of different values of the chemical potential, that is, $\mu_{sol} \equiv \mu(c_{sol})$ and $\mu_{liq} \equiv \mu(c_{liq})$ on different sides of the dividing surface, the forming force creates a drift velocity of voids that is proportional to the chemical potential gradient in accordance with formula (2). In the case of a spherical nucleus, we take the distribution of distances from this nucleus for the force such that the total void flux through each spherical surface does not depend on its radius. This leads to the difference of the chemical potentials $\Delta\mu(r)$ at a given distance r from the nucleus center

$$\Delta\mu(r) = \frac{(\mu_{liq} - \mu_{sol})r_o}{r}, \qquad (18)$$

where r_o is a current nucleus radius. From this and formula (2), we determine that the radius of the growing nucleus changes with time as

$$\frac{dr_o}{dt} = \frac{D_{liq}}{r_o} \frac{(\mu_{liq} - \mu_{sol})}{T}, \qquad (19)$$

where D_{liq} is the diffusion coefficient of voids for the liquid state. Thus, in accordance with a general principle of thermodynamics,[19,20] equality of the atom chemical potentials is fulfilled under equilibrium conditions on the dividing

surface that separates two phases. In the case considered here, of growth of a new phase, this equality is violated, and the difference of the chemical potentials from two sides of the dividing surface creates a force which causes motion of voids and displacement of the dividing surface.

We now evaluate the rate of growth of the solid nucleus in the case in which the temperature T is close to the melting point T_m. Then, we have $\mu_{liq} - \mu_{sol} = (T_m - T)s$, where s is the transition entropy per atom, and formula (19) gives the time dependence of the change of area of the nucleus:

$$\frac{dr_o^2}{dt} = \delta_{sol} \frac{(T_m - T)}{T} \exp\left[-\alpha_{sol} \frac{(T_m - T)}{D}\right],$$

$$\delta_{sol} = \frac{1}{2} D_{liq}(T_m)s, \quad \alpha_{sol} = \frac{E_{liq}D}{T_m^2}. \quad (20)$$

Table III contains the values of parameters $\delta_{liq}, \alpha_{liq}$ for inert gases.

In considering this problem, we do not take into account any contribution of surface effects to the chemical potential. Therefore, we neglect the critical phenomena during nucleation,[20,29] and suppose that the nuclear radius significantly exceeds the critical radius at all times described by this model. Furthermore, we concentrate here on the growth of a solid nucleus inside a liquid that results from the effective force induced by a difference between the chemical potentials for the solid and liquid aggregate states. This effective force acts on each void independently and compels it to move from the dividing surface. Hence, the rate of expansion of the solid nucleus does not depend on the void concentration and is determined by friction experienced by the moving voids, so that the frictional force is expressed through the diffusion coefficient of voids in this system. Therefore, the growth of the liquid nucleus in a solid will proceed by the same scenario, and the rate of an increase of the radius of the liquid nucleus inside a solid, by analogy with formula (19), is given by

$$\frac{dr_o^2}{dt} = \delta_{liq} \frac{(T_m - T)}{T} \exp\left[-\alpha_{liq} \frac{(T_m - T)}{D}\right],$$

$$\delta_{liq} = \frac{1}{2} D_{sol}(T_m)s, \quad \alpha_{liq} = \frac{E_{sol}D}{T_m^2}. \quad (21)$$

For condensed inert gases, the parameters of this formula are

represented in Table III. They are expressed through parameters given in Tables I and II. One can see that the growth rate for the liquid nucleus is lower than that for the solid because the void coefficient diffusion in solids is lower than that in liquids.

VI. CONCLUSION

It is convenient to consider configurational excitation of a system of atoms bound by a pair interaction as a result of formation of voids (or vacancies) inside this system. Transitions between configurationally excited states are characterized by variation of the number of voids in a two-component system consisting of atoms and voids. Then, the nucleation process results from transport of voids inside this system between a growing nucleus and its environment. From the standpoint of the behavior of the PES of this system, an elementary displacement of a void is the transition of the system between two neighboring local minima of the PES. The analysis shows a thermodynamically instability of configurational excitations of this system in some range of void concentrations between those corresponding to the mean void concentrations in the solid and liquid aggregate states. This phenomenon makes impossible a *continuous* transition between the solid and liquid aggregate states that might be induced by variation of the number of voids. Therefore, in the case of coexistence of the solid and liquid states inside the system, a situation that takes place in nucleation processes, the dividing surface appears that separates the solid and liquid phases. When a nucleus of a new phase grows inside of an old phase, the difference of the chemical potentials on two sides of the dividing surface creates an effective force that acts on voids of an old phase and drives them to facilitate the nucleus' growth of the new phase. The rate of the nucleus' growth is expressed through the coefficient of self-diffusion of atoms in this system.

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[1] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).
[2] M. R. Hoare and P. Pal, Adv. Phys. **20**, 161 (1971); *ibid.* **24**, 645 (1975).
[3] M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).
[4] K. D. Ball and R. S. Berry, J. Chem. Phys. **111**, 2060 (1999).
[5] D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, UK, 2003).
[6] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).
[7] D. S. Corti, P. G. Debenedetti, S. Sastry, and F. H. Stillinger, Phys. Rev. E **55**, 5522 (1997).
[8] D. J. Wales and H. A. Scheraga, Science **285**, 1368 (1999).
[9] F. H. Stillinger and T. A. Weber, Phys. Rev. A **28**, 2408 (1983).
[10] O. M. Becker and M. Karplus, J. Chem. Phys. **106**, 1495 (1997).
[11] R. S. Berry, *Theory of Atomic and Molecular Clusters*, edited by J. Jellinek (Springer, Berlin, 1999), pp. 1–26.
[12] D. J. Wales , J.P.K. Doye, M. A. Miller, P. N. Mortenson, and T. R. Walsh, Adv. Chem. Phys. **115**, 1 (2000).
[13] T. Komatsuzaki and R. S. Berry, J. Chem. Phys. **110**, 9160 (1999).
[14] B. Vekhter, K. D. Ball, J. Rose, and R. S. Berry, J. Chem. Phys. **106**, 4644 (1997).

[15] R. S. Berry and B. M. Smirnov, Phys. Rev. B **71**, 144105 (2005).

[16] B. M. Smirnov, JETP **85**, 1010 (1997).

[17] B. M. Smirnov, *Clusters and Small Particles in Gases and Plasmas* (Springer, New York, 1999).

[18] B. M. Smirnov, Inorg. Mater. **35**, 562 (1999).

[19] D. Ter Haar, *Elements of Thermostatics* (Addison–Wesley, New York, 1966).

[20] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980), Vol. 1.

[21] B. M. Smirnov, Phys. Usp. **37**, 1079 (1994).

[22] B. M. Smirnov, Phys. Usp. **44**, 1229 (2001).

[23] B. M. Smirnov, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev (JINR, Dubna, 1999), pp. 355–367.

[24] R. S. Berry and B. M. Smirnov, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev (JINR, Dubna, 2002), pp. 340–366.

[25] B. M. Smirnov, Sov. Phys. Usp. **21**, 331 (1978).

[26] J. Naghizadeth and S. A. Rice, J. Chem. Phys. **36**, 2710 (1962).

[27] L. Bewilogua, L. Gladun, and B. Kubsch, J. Low Temp. Phys. **4**, 299 (1971).

[28] W. Schmidt, *Liquid State Electronics of Insulating Liquids* (CRC Press, Boca Raton, 1997).

[29] I. Gutzow and J. Schmelzer, *The Vitreous State* (Springer, Berlin, 1995).