

## Glassy-Like States of Bulk Rare Gases<sup>†</sup>

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**Abstract**—Defining a glassy-like state of a system of bound atoms as a frozen, amorphous, thermodynamically unstable state, we consider a glassy-like state of a condensed rare gas as a configurationally excited state of bound atoms that tends to the thermodynamic equilibrium by diffusion of voids. The criterion for a critical cooling rate is the minimum cooling rate of the liquid state that leads to formation of a glassy-like state. Comparing this glassy-like state with that experimentally obtained by deposition of argon atoms on a cold target, we conclude that glassy-like states are characterized by short-range parameters. On the basis of cluster studies, peculiarities of the liquid aggregate states and glassy-like states are formulated. A glassy-like state of a cluster or a bulk system of bound atoms is a configurationally excited state below the freezing point; the liquid aggregate state exhibits configurational excitations but is characterized by thermal motion of atoms, consistent with the Lindemann criterion. © 2002 MAIK “Nauka/Interperiodica”.

### 1. INTRODUCTION

According to the standard definition [1–4], a glassy state is a frozen, thermodynamically nonequilibrium state of a condensed system that can be formed by sufficiently fast cooling of the system from a fluid state of thermodynamic equilibrium to low temperatures, to attain a persistent state that is not in equilibrium. Peculiarities of these states were first observed and studied for glasses, and we therefore call these states in other systems “glassy-like states.” From this standpoint, we consider a bulk system of bound rare gas atoms, whose liquid state congeals and is not metastable as a fluid below the freezing point [5]; in other words, the liquid state of condensed rare gases can be transformed into a glassy-like state as a result of fast cooling from temperatures above the melting point to temperatures below the freezing point.

A glassy-like state of condensed rare gases can be prepared by two methods [4]. The first method involves a fast cooling of liquid rare gases; in the second, a glassy-like state can be prepared as a result of deposition of individual atoms on a target at a low temperature [4, 6]. Deposited atoms occupy initial positions in a random array, and because the temperature is low, the atoms cannot move from their initial positions enough to attain a distribution in thermodynamic equilibrium. This amorphous spatial distribution of atoms is a glassy-like state of the bulk system. A transition to the crystalline state is possible if the temperature is raised sufficiently high to allow annealing. Of course, parameters of this glassy-like state can differ from those of

systems obtained by fast cooling of the liquid state. Below, we compare these states of bulk rare gases.

In comparing these forms of condensed rare gases, we account for the structures of the liquid and solid aggregate states that differ because of the presence of internal voids [7] in the second case. We define an individual void [8–10] as the result of the relaxation of individual vacancies. When a configurationally excited state of a system of bound atoms is formed from a compact solid state of this system by formation of some number of vacancies, these transform into voids when the system, with its vacancies, relaxes. We therefore characterize configurationally excited states of a bulk system of bound atoms by the concentration of voids and the parameters of an individual void at this concentration. We assume that the voids are the results of individual vacancies and that, if voids do become neighbors, their energies can be computed in the same manner as the energies of individual voids. This allows us to make a quantitative analysis of configurationally excited states, including glassy-like states. This analysis for condensed rare gases is the goal of this paper.

### 2. PROPERTIES AND FORMATION OF GLASSY-LIKE STATES OF RARE GASES

Characterizing configurationally excited states of condensed rare gases by only the number of voids inside it, we prepare our state as follows [8–10]. We take a bulk crystal of a rare gas consisting of  $n + v$  atoms and remove  $v$  atoms to the outside. This system is assumed to be sufficiently large such that almost all the removed atoms come from the inside of the system,

<sup>†</sup>This article was submitted by the authors in English.

**Table 1.** Reduced parameters of the liquid aggregate states for condensed rare gases

$v/n$	$\varepsilon_v/D$	$V_v\sqrt{2}/R_e^3$	$n_c$
$0.320 \pm 0.001$	$3.3 \pm 0.2$	$0.50 \pm 0.06$	$10.2 \pm 0.1$

and surface effects are negligible. After relaxation, this system therefore contains  $n$  atoms and  $v$  internal voids, and according to the definition, an individual void results from the relaxation of an individual vacancy and its immediate environment. At temperatures significantly above 0 K, crystals in equilibrium have a low concentration of voids, but we here deal with quenched systems with much higher concentrations of voids. Under these conditions, the system is in a thermodynamically nonequilibrium state that would tend to equilibrium by migration of voids to the surface of the system. (A nonequilibrium state might also arise, in principle, from a concentration of voids below the equilibrium value.) But considering this system during short time intervals compared to the diffusion times of voids through the system, we can treat thermodynamic-like properties of states with any number of voids. In addition, we assume that the spatial distribution of voids is uniform throughout the system.

Although strictly the volume and shape of an individual void varies in time, we use average parameters of individual voids that depend only on the void concentration. In Table 1, void parameters are given for the liquid state of condensed rare gases near the triple point [11]. We assume that the interaction inside condensed rare gases is mostly determined by the interaction between nearest neighbors, and that the scaling law is valid for condensed and dense rare gases [11], which allows expressing various parameters of these systems through the atomic mass and two parameters of the pair interaction potential of atoms, the depth of the potential well  $D$  and the equilibrium distance between atoms  $R_e$ , in the same manner. The accuracy of the data given in Table 1 gives the statistical error due to a difference in these parameters for different rare gases.

In Table 1, we give the relative number of voids, the ratio of the number of voids  $v$  to the number of atoms  $n$ , the reduced mean energy  $\varepsilon_v$  of the formation of an individual void, the average reduced volume  $V_v$  of an individual void, and the average number of nearest neighbors for a test internal atom. All these parameters pertain to the liquid state of rare gases near the triple point [11], and we use them in what follows. We assume that parameters of a glassy-like state coincide with parameters of the liquid state if this glassy-like state is formed as a result of a fast cooling of the liquid state.

### 3. KINETICS OF HEATING AND COOLING PROCESSES INVOLVING GLASSY-LIKE STATES

We consider the evolution of the liquid state of rare gases subjected to fast cooling or transformation of an

amorphous state into the crystal as a result of heating. We take the transition rate  $1/\tau$  in the Arrhenius form

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(-\frac{E_a}{T}\right), \quad (1)$$

where the temperature  $T$  is expressed in energy units, i.e., as  $k_B T$ , and  $E_a$  is the activation energy of the process.

Considering the cooling process and assuming the rate of the temperature variation  $dT/dt$  to be constant, we express the typical time  $\tau_c$  of the cooling process as

$$\frac{1}{\tau_c} = \frac{1}{\Delta T} \left| \frac{dT}{dt} \right| = \frac{E_a}{T^2} \left| \frac{dT}{dt} \right|, \quad (2)$$

where  $\Delta T = T^2/E_a$  is the temperature range in which the transition rate varies weakly. This implies that the instantaneous liquid state structure is conserved at temperatures below the melting point if the cooling rate satisfies the relation

$$\left| \frac{dT}{dt} \right| > \frac{T_m^2}{E_a \tau_0} \exp\left(-\frac{E_a}{T}\right). \quad (3)$$

If this criterion is satisfied, subsequent cooling to temperatures below the melting point converts the system into a glassy-like state.

We now consider another scenario, in which a bulk system of bound atoms is prepared in an amorphous state at a low temperature and its heating leads to the transition into the ordered solid (crystalline) state. Considering the amorphous state to be a glassy-like one, we define the glass temperature  $T_g$  by the relation

$$\tau(T_g) = \tau_c.$$

From Eqs. (1) and (2), we then have

$$T_g = \frac{E_a}{\ln\left(\frac{T_g^2}{E_a \tau_0 (dT/dt)}\right)}. \quad (4)$$

Formula (4) relates the parameters of the processes that are responsible for the glassy transition.

We now take into account the nature of transitions involving the aggregate or glassy-like states of a bulk system of bound rare gas atoms as a result of the diffusion of voids in this system to its boundary or from it. The rate of transition between aggregate states of a bulk rare gas system or the rate of the glassy transition in this system is then expressed through the diffusion coefficient  $D_v$  of voids that is related to the self-diffusion coefficient of atoms  $D_a$  by

$$D_v = \frac{n}{v} D_a. \quad (5)$$

**Table 2.** Parameters of void diffusion in condensed rare gases

	Ne	Ar	Kr	Xe	Average
$D$ , K [11]	42	143	200	278	
$E_{\text{sol}}$ , K	$480 \pm 20$	$1900 \pm 100$	$2500 \pm 100$	$3700 \pm 100$	
$E_{\text{sol}}/D$	$11.4 \pm 0.5$	$13.3 \pm 0.7$	$12.5 \pm 0.5$	$13.3 \pm 0.4$	$12.6 \pm 0.9$
$E_{\text{liq}}$ , K [13, 14]	113	352	405	607	
$E_{\text{liq}}/D$	2.69	2.46	2.01	2.18	$2.3 \pm 0.3$
$\varepsilon_{\text{liq}}/D$	2.20	2.29	2.06	2.15	$2.2 \pm 0.1$
$D_0$ , $10^{-2}$ cm <sup>2</sup> /s	2.7	3.7	1.5	2.2	
$l^2 (dT/dt)_{\text{lim}} $ , $10^{-2}$ K cm <sup>2</sup> /s	0.014	0.11	0.15	0.22	

As an activation process, the diffusion of voids is characterized by an activation energy. We note that, for the solid state, the number of vacancies is

$$v \propto \exp(-\varepsilon_v/T),$$

where  $\varepsilon_v$  is the energy of vacancy formation. Hence the activation energies for the self-diffusion coefficient of atoms  $E_a$ , for which the data in Table 2 are taken from [12], and the diffusion coefficients of voids and vacancies ( $E_{\text{sol}}$ ) differ from those of the solid state by the energy  $\varepsilon_v$  of formation of an individual vacancy ( $E_{\text{sol}} = E_a + \varepsilon_v$ ). For the liquid state with  $v \sim n$ , the activation energies for these diffusion processes are identical. Table 2 contains the activation energies for self-diffusion of atoms in the solid ( $E_{\text{sol}}$ ) and liquid ( $E_{\text{liq}}$ ) states. For the liquid state, the diffusion coefficient of voids is given by

$$D_v = D_0 \exp\left(-\frac{E_{\text{liq}}}{T}\right). \quad (6)$$

The parameters of this formula given in Table 2 follow from measurements of the self-diffusion coefficients of atoms in liquid rare gases [13, 14] and Eq. (5). In Table 2, we in addition compare the energy of the formation of an individual void  $\varepsilon_{\text{liq}}$  for the liquid aggregate state near the triple point [11] with the activation energy  $E_{\text{liq}}$  of the diffusion process for voids in the liquid; we find that these values are identical with a suitable accuracy. We can therefore assume that the activation energy  $E_a$  for diffusion of voids in Eq. (1) is equal to the energy of void formation  $\varepsilon_v$ .

For simplicity, we take a condensed rare gas in the form of a plane film located on a target. A typical diffusion time is given by

$$\tau = \frac{l^2}{D_v}. \quad (7)$$

In particular, Eqs. (3), (6), and (7) give the cooling rate for the formation of a glassy-like state of a film as a

result of fast cooling,

$$\left|\frac{dT}{dt}\right| > \left|\left(\frac{dT}{dt}\right)_{\text{lim}}\right| = \frac{T_m^2}{E_{\text{liq}} l^2} D_0 \exp\left(-\frac{E_{\text{liq}}}{T_m}\right). \quad (8)$$

The threshold values of the parameter  $l^2|dT/dt|$  given in Table 2 assure the formation of glassy-like states of rare gases as a result of cooling liquid rare gases.

#### 4. HEATING PROCESS IN THE GLASS TRANSITION

Various parameters of the system can be used in order to distinguish the solid and glassy-like states; guided by the experiment [6], we use the saturated vapor pressure over the plane surface of the system for this purpose. According to the Clausius–Clapeyron law, the saturated vapor pressure is given by [15, 16]

$$p(v, T) = p_v \exp\left(-\frac{\varepsilon(v)}{T}\right), \quad (9)$$

where  $\varepsilon(v)$  is the mean binding energy of a surface atom, which is the sublimation energy per atom for a bulk system with a given number of voids  $v$  inside it. We assume that the saturated vapor pressures referred to any concentration of voids are identical at the triple point, as occurs for the solid and liquid states. For the preexponential coefficient in Eq. (9), this gives

$$p_v = p_0 \exp\left(\frac{\varepsilon(v) - \varepsilon_{\text{sol}}}{T_{\text{tr}}}\right), \quad (10)$$

where  $\varepsilon_{\text{sol}}$  is the binding energy per atom for the solid state,  $\varepsilon_{\text{sol}} = \varepsilon(0)$ ,  $p_0$  is the preexponential factor in formula (9) for the solid state, and  $T_{\text{tr}}$  is the triple point temperature. It follows from this formula that the preexponential factor in Eq. (9) drops as the density of voids increases. Evidently, Eq. (10) is correct for the liquid state.

It then follows that

$$\frac{p(v, T)}{p_{\text{sol}}(T)} = \exp\left[(\varepsilon_{\text{sol}} - \varepsilon(v))\left(\frac{1}{T} - \frac{1}{T_{\text{tr}}}\right)\right], \quad (11)$$

**Table 3**

	$T_g$ , K	$T_*$ , K	$\varepsilon(v)$ , K	$E_a$ , K
Experiment [6]	$20 \pm 1$	$24 \pm 1$	$730 \pm 90$	$330 \pm 20$
Theory for liquid	21	23	790	350

where  $p_{\text{sol}}(T)$  is the saturated vapor pressure over the solid surface at a given temperature. In particular, for the metastable liquid state at a temperature  $T$  below the triple point, Eq. (11) gives

$$\frac{p_{\text{liq}}(T)}{p_{\text{sol}}(T)} = \exp\left[\Delta H_{\text{fus}}\left(\frac{1}{T} - \frac{1}{T_{\text{tr}}}\right)\right], \quad (12)$$

where  $\Delta H_{\text{fus}}$  is the specific fusion enthalpy.

Along with the temperature of the glassy transition given by Eq. (4), which characterizes the equality of the rate of heating and the process of void diffusion, we introduce the temperature  $T_*$  from which the subsequent growth of the saturated vapor pressure can proceed. For heating of an amorphous state of a rare gas, this temperature is defined by the relation

$$p(v, T_g) = p_{\text{sol}}(T_*),$$

and in accordance with Eq. (11) we have

$$\varepsilon(v)\left(\frac{1}{T_g} - \frac{1}{T_{\text{tr}}}\right) = \varepsilon_{\text{sol}}\left(\frac{1}{T_*} - \frac{1}{T_{\text{tr}}}\right). \quad (13)$$

We now use these formulas to analyze the results of the experiment [6] in which amorphous argon was prepared by deposition of an argon stream on a copper substrate at a temperature of 10 K; the triple point of bulk argon is  $T_{\text{tr}} = 83.7$  K. Amorphous argon is formed under these experimental conditions if the deposition rate is less than  $3 \times 10^{-9}$  cm/s. We refer to this amorphous form of argon as a glassy state. Warming leads to an annealing transition to the crystal state [6, 4]. A typical film thickness in this experiment is 10  $\mu\text{m}$ , exceeding the distance between nearest neighbors of bulk condensed argon by more than three orders of magnitude. This film can therefore be considered as bulk condensed argon. The heating rate  $dT/dt \approx 2$  K/min leads to the glassy transition at  $T_g = 20 \pm 1$  K and the saturated vapor pressure starts to grow from the temperature  $T_* = 24 \pm 1$  K. In Table 3, the results of this experiment are compared with the above formulas, with the amorphous state assumed to be structurally analogous to the liquid state and the experimental data treated on the basis of Eqs. (4) and (13). This comparison shows that the amorphous state of argon obtained by deposition of atoms on a cold target is identical to the glassy-like state that we have described as a frozen liquid state at low temperatures.

## 5. PECULIARITIES OF LIQUID AGGREGATE STATES AND GLASSY-LIKE STATES

Assuming a kind of structure for condensed rare gases allowed us to formulate the concept of glassy-like states on the basis of elementary configurational excitations in this system. Because this understanding starts from the study of clusters, systems of a finite number of bound atoms, we consider the concepts of the glassy-like and liquid aggregate states for clusters simultaneously. On the one hand, taking a cluster to the limit of very many constituent particles makes it into a bulk system, allowing us to use and modify the cluster concepts for bulk systems. On the other hand, the cluster is a convenient vehicle for computer modeling, and the results for clusters give important information about the glassy and phase transitions for bulk systems. Next, considering clusters bound by pair interactions between atoms, we assume that these atoms can be treated as classical and examine excitations of two types, configurational excitations and phonons. Phonons of course result from vibrational motion of atoms, while a configuration excitation leads to a change of the atomic configuration. Both the true solid-liquid phase transition and the glassy transition result primarily from transitions involving configurationally excited states of the cluster. Computer modeling of clusters allows us to understand these phenomena in detail.

The potential energy surface of a typical cluster of more than very few particles bound by pair interactions between atoms has many local minima, determined by the configuration of atoms; this is possibly the principal characteristic of such systems [17–20]. Each local minimum corresponds to a specific configurational excitation of a cluster, and neighboring local minima are separated by saddle points of the potential energy surface. During its evolution at low temperatures, a cluster is therefore most often found at those local minima, and spends only a very small fraction of time in intermediate positions. We base our approach on the supposition that the cluster aggregate state is a group of configurationally excited states with very similar excitation energies. Within this definition, each cluster aggregate state is characterized by a certain energy and entropy that corresponds to the classical thermodynamic state in the limit of large cluster size. But the analysis of the cluster phase transitions on the basis of local minima of the potential energy does not include the Lindemann criterion [21, 22], which has proved itself very useful for real systems, and according to which the phase transition proceeds at the temperature at which the mean amplitude of atomic oscillations reaches a certain value. From the analysis of computer simulations of the phase transition in clusters, the compatibility of these two perspectives can be seen.

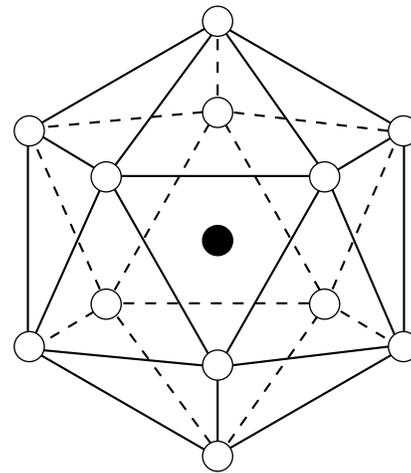
We consider a cluster consisting of 13 atoms bound by the Lennard-Jones interactions  $LJ_{13}$ . This cluster has icosahedral structure in its ground configurational state, as shown in Fig. 1. The lowest configurational excita-

tion of this cluster corresponds to the transfer of one atom from an icosahedron vertex to a surface face; the total number of such configurational excitations, and hence its statistical weight, is  $g = 180$  (15 positions on the cluster surface times 12 vertex atoms). There are three positions of an excited atom on the cluster surface that correspond to different excitation energies; the parameters of these excitations are given in Fig. 2 [23]. Naturally, neighboring stable positions of a test atom are separated by barriers. The barrier character of the cluster potential surface can be understood in the simplest case where only the nearest neighbors interact. A test atom then has six bonds with nearest neighbors and three bonds if it transfers to the icosahedron surface; in this case, the excitation energy is  $3D$ , where  $D$  is the depth of the Lennard–Jones well. But in the course of a transition between these states, at the lowest potential maximum along such a path (the saddle point), the test atom has bonds to only two atoms, and this transition is therefore characterized by the barrier height  $1D$ . The long-range contributions to the total interaction in the Lennard–Jones interaction coming from nonnearest neighbors smooth this picture such that the excitation energy and the barrier threshold slightly decrease in this case. We note that these data for atom excitations (Fig. 2) pertain to zero temperature and hence include no vibrational contributions to the energy.

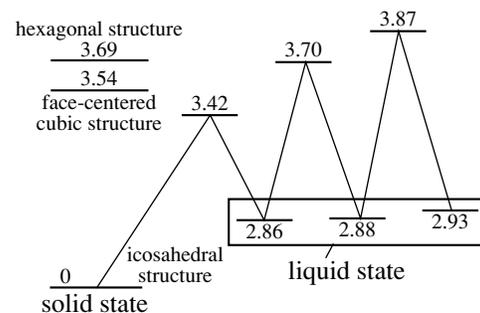
We now analyze the phase transition that occurs when this cluster is heated. The important special property of any phase change in clusters is the coexistence of the phases (e.g., solid and liquid) within some non-zero temperature range [24–27], in contrast to bulk systems where any phase transition occurs at a specific temperature (both at a given pressure, of course). This follows from the cluster consisting of a relatively small, finite number of particles, and we now focus on the parameters of the liquid state of this cluster in the range of the phase transition [24–27]. We note that because the liquid state is analyzed on the basis of various correlations between cluster atoms, it can be reliably separated from the ordered solid state. In accordance with the previous computer simulations [24–27], the temperature range of the phase coexistence for  $LJ_{13}$  is  $(0.29–0.31)D$ , the excitation energy of the liquid state is  $\Delta\epsilon \approx 2.5D$  on average, and the statistical weight of the liquid state with respect to the solid state of this cluster is approximately

$$g_{\text{liq}} = \exp(\Delta\epsilon/T_{\text{eq}}) \approx 4 \times 10^3,$$

where  $T_{\text{eq}} = 0.30D$  is the classical melting point for this cluster, the (approximate) temperature at which the free energies of the solid and the liquid are equal. (The pressure is assumed to be zero.) We note that the model for the liquid state of this icosahedral cluster is based on one-atom configurational transitions. Comparing these data with the data at zero temperature, we find that only the statistical weight of the excited state varies signifi-



**Fig. 1.** The structure of the icosahedral cluster consisting of 13 atoms [30].

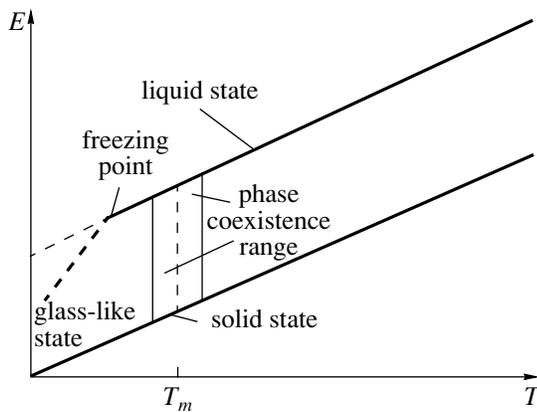


**Fig. 2.** The lowest excited states of the Lennard–Jones cluster of 13 atoms and the character of their formation through saddle points [23]. Values near levels indicate the excitation energies expressed in units of the binding energy  $D$  per one bond. The energies of the close-packed structures are taken from [17]. The lowest excited cluster states may be linked to the cluster’s liquid state in which the clusters spend most of the time if they begin with a sufficient excitation energy or temperature [24–27].

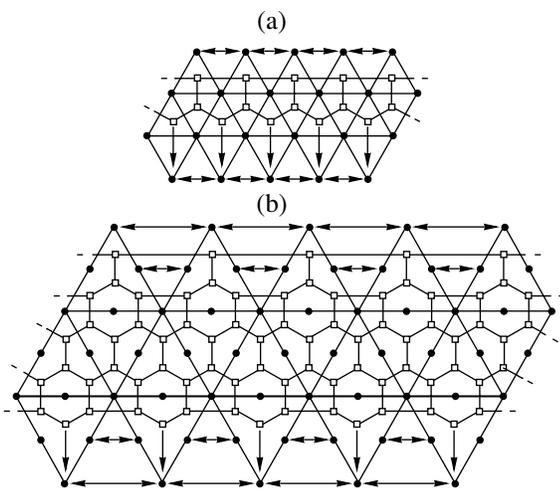
cantly, whereas changes of other parameters of the cluster excited state are not very important.

This implies that heating of the Lennard–Jones cluster of 13 atoms from zero temperature to the melting point changes the statistical weight of one-atom excitation from 180 to  $4 \times 10^3$ , and the entropy of this transition therefore changes from  $\Delta S = 5.2$  to  $\Delta S = 8.3$ . The latter corresponds to the specific entropy change  $\Delta s = \Delta S/13 = 0.64$ . We note that the specific entropy change for bulk rare gases is  $\Delta s = 1.68$  at the melting point.

From this consideration, it follows that, as a result of cluster heating, the statistical weight contributed by vibrations of individual atoms also increases with temperature, making the conditions still less stringent for the phase transition. This is why the Lindemann criterion is valid for the phase transition, although the phenomenon results overwhelmingly from the configura-



**Fig. 3.** The caloric curve for a cluster or bulk system with two aggregate states.



**Fig. 4.** The developed view of the surface of the icosahedral cluster with the completed layers consisting of 13 (a) and 55 (b) atoms. Solid circles are the surface cluster atoms, and the open squares are positions of an atom located on the cluster surface; transitions of this atom on the cluster surface are shown by solid lines, and the boundaries of the surface cluster triangles are denoted by fine solid lines. Arrows show transitions of a test atom into the ground state, and double arrows relate to the same atom of the three-dimensional structure; dotted lines connect identical positions for the three-dimensional cluster.

tional excitation of the system. We also note the example of a solid–solid phase transition in a large cluster [28, 29] in which the vibrational contribution to the thermodynamic parameters is quite small, although this contribution is significant in the case of the solid–liquid phase transition.

Returning to the problem under consideration, we conclude that the liquid and glassy-like cluster states have virtually identical structural nature, but are characterized by different statistical weights or entropies because the liquid state, corresponding to higher temperatures than glassy-like states, has significantly

higher vibrational entropy (which reflects the mobilities and higher frequency motions of the atoms of the liquid). The caloric curve for a bulk rare gas system is schematically represented in Fig. 3. The liquid state is a thermodynamically stable or metastable aggregate state above the freezing point; in the course of a temperature decrease, it is transformed into a glassy state. For a cluster, this picture can be more complicated because a cluster can have several aggregate states, e.g., those based on different aggregate states of its shells (see, e.g., [31]). Considering a bulk system of bound atoms for which surface effects are not essential, we obtain only one kind of configurational excitations in the form of internal voids, and the caloric curve therefore takes a simple form.

In contrast to a bulk system, the transition of a cluster from a glassy-like state, or cluster relaxation, proceeds rapidly, because the elementary excitation does not become entangled inside the system, as it can in the case of the void diffusion inside a bulk. Nevertheless, this tendency occurs in clusters if their size increases. Figure 4 contains a developed view of clusters with the icosahedral structure consisting of 13 and 55 atoms; these clusters have completed shells of atoms in their ground configurational states. Elementary configurational excitations of these clusters correspond to transitions of one vertex atom (or several atoms) to the cluster surface, such that, in glassy-like states, a promoted atom drifts over the cluster surface, and the cluster relaxation corresponds to a transition of an atom to a free vertex position. Because all the positions of an excited atom on the cluster surface are almost identical, such an atom can have random displacements on the surface, similarly to a diffusion process. Thus, as a cluster increases in size, the character of the relaxation process for glassy-like states becomes identical to that of a bulk system.

From this analysis for the simplest bulk systems of bound atoms and clusters, it follows that the glassy and phase transitions have a common feature that consists in a change of configurational excitation in such transitions. The difference between these phenomena is such that thermal excitation of bound atoms influences the phase transition, e.g., as demonstrated by the Lindemann criterion. For glassy-like states of a system of bound atoms, the thermal motion of atoms is not very important.

## 6. CONCLUSIONS

On the basis of the above analysis, the glassy state concept can be carried over from complex (i.e., bulk macroscopic) systems to simple ones, specifically to atomic clusters. According to the definition [4], the glassy state is a thermodynamically unstable configurational state of bound atoms formed by fast cooling of a system for which extremely slow cooling leads to a transition, with an activation energy, between two truly stable aggregate states. For glasses [1–4], this transition

involves the change of positions of some constituent particles, and the system finally takes a crystalline structure as it undergoes an “infinitely” slow cooling. One more peculiarity of this transition is the difference in densities of the structures for the initial and final states. Together with restructuring of the particle positions, relaxation to the equilibrium therefore requires that voids must diffuse to the system boundary or into the system.

Focusing now on simple bulk systems of bound atoms, such as condensed rare gases, we find no need to invoke restructuring of chemical bonds in such systems, but transport of voids proceeds by analogy with glasses and has an activation character. The glassy-like state of such a system can be prepared by two methods, by fast cooling of the liquid aggregate state or by deposition of an atom flux on a substratum at low temperatures below the melting point with the formation of a random distribution of atoms.

In the case of clusters, the systems exhibiting a finite number of locally stable configurationally excited states formed by the transition of atoms from completed cluster shells to the surface conform to the model of a glassy state according to its definition. This corresponds to the formation of surface voids; the annihilation of voids results in a transition of atoms from the cluster surface to the outermost shell. This glassy-like state can also be considered from the standpoint of the concept of the cluster configurational excitation as a result of the transition to local minima of the potential energy surface of this cluster. Because neighboring local minima of the cluster configurational energy are separated by barriers [19, 20], transitions from the ground cluster shell to excited configurations have an activation character. Thus, the known excited structures of simple systems of bound atoms conform to the definition of the glassy state. Based on the nature of the glassy-like states of simple systems as a result of formation of voids, one can analyze these states in more detail.

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