

Glassy states of clusters with pairwise atomic interactions

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The glassy state of argon is examined from the standpoint that this state of a system is an ensemble of frozen excited configurations. The basis is experimental data for deposition of an argon stream on a very cold substrate; the measurements provide the dependence of the saturated vapor pressure over this system. The immobile state prepared by such deposition is an amorphous argon, and the activation energy for its transition to the crystalline state is found from a theoretical model. A criterion is established for the minimum cooling rate of liquid rare gases to form the glassy state. An analogous glassy state for clusters is analyzed, and a minimum rate of cooling for its formation is also developed. The glassy state of a bulk system of atoms bound by pair interactions, thermodynamically unstable, relaxes to equilibrium by diffusion of voids to the boundary; the corresponding phase change of a cluster can be thought of at least as easily in terms of diffusion of atoms to sites in its lowest-energy, ordered configuration. A common feature of these small systems is the way their counterparts of the glassy state form from fast cooling of liquid aggregate states to become frozen liquid states. © 2003 American Institute of Physics. [DOI: 10.1063/1.1545104]

INTRODUCTION

We begin by distinguishing two kinds of glassy states. The first, which we do not discuss here, is a state of an ensemble of systems that is thermodynamically stable, whose configurations are disordered and very numerous. The second, which we address here for macroscopic and small nanoscale systems, is a metastable state of an ensemble, also with very numerous, disordered configurations, prepared by a mechanism that traps the ensemble kinetically. (The distinction may, in many cases, be a matter of the time scale beyond which we declare a system “in equilibrium.”) From this point, we refer to the latter as a glassy state. Such a glassy state^{1–4} may be formed from an ensemble of systems of bound atomic particles which can exhibit two aggregate states, e.g., liquid and crystalline, so that at high and low temperatures different aggregate states are stable, and the transition between these states requires an activation energy. In such a case, the transition rate depends sharply on the temperature. If the system undergoes relatively fast cooling from a sufficiently high initial temperature, the phase stable at high temperature may undergo only a partial change into the state stable at low temperatures. In such a case, the system’s “final” state is unstable. Because such transitions were initially studied in glasses, the newly formed state is termed the glassy or vitreous state.⁴ However a state with these properties is typical for various types of systems, in particular for condensed rare gases, the simplest system of bound atoms for which interaction between nearest neighbors dominates, and for their clusters. Here, we consider glassylike states of ensembles of bound atoms with pair interactions between atoms and whose conditions for formation of these

“trapped” metastable states may be guided by the behavior of bulk condensed rare gases and Lennard-Jones clusters with completed shells.

GLASSYLIKE STATES OF SIMPLE SYSTEMS OF BOUND ATOMS

In considering a rare gas system, we assume its atoms to be classical and examine two types of excitations, configurational excitation and phonons. Phonons result from vibrational motion of atoms, while configuration excitation corresponds to passage from one local minimum to another on the potential energy surface, i.e., to a change of the atomic configuration around which the system vibrates. For a bulk system, a configurational excitation is typically (but not exclusively) connected with formation of voids.⁵ In thermodynamic equilibrium, the transition between the solid and liquid aggregate states of a bulk rare gas results in a stepwise change in the density of voids in its interior, and with it, a change from a “locked” configuration (with some slow diffusion) to a compliant, mobile system that explores many configurations.

According to the usual definition,^{1–4} a glassy state of a system of bound atoms is a thermodynamically unstable state thermodynamically that has a lifetime growing to infinity if the temperature tends to zero. The rate of decay of this state is expressed by the Arrhenius formula due to the thermal barrier associated with this transition. One can exhibit the nature of glassylike states and transitions occurring during their relaxation for systems of bound atoms with a pair interaction. Such a bulk system can be found in two aggregate states at moderately low temperatures. The liquid state differs from the ordered equilibrium solid primarily because the former includes many voids inside the system;⁵ when solid

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and liquid are in equilibrium, the mean kinetic energies of the two are of course equal. The liquid (fluid) state of this particular bulk system does not exist as a metastable form below the freezing point⁶ because, instead, it transforms into a glassylike state. The glassylike state of this system retains the internal voids of the liquid; its relaxation to thermodynamic equilibrium results from transport of these voids to the outside. Because the void displacement process requires overcoming a barrier, the rate of the void diffusion process decreases strongly with temperature. Hence the glassylike state of this system contains voids frozen in its interior, and the lifetime of the glassylike state with respect to departure of voids to the outside becomes long at low temperatures. Therefore if the cooling process proceeds rapidly, a significant fraction of the voids has insufficient time to escape, and a state with a finite excess above the equilibrium density of voids is realized at low temperatures.

Together with bulk systems of bound atoms, we are considering clusters with filled geometric shells. In principle, clusters can have several aggregate states because different cluster shells can be solid or liquid (e.g., Ref. 7). In the following we restrict ourselves to two aggregate cluster states that correspond to solid and liquid states of the outermost shell. The configurational excitation which leads to formation of the liquid state of this cluster results in transition of atoms of the outermost shell to the cluster surface. Hence, in contrast to bulk systems, we consider here configurationally excited clusters with surface voids. This glassylike state of condensed rare gases and their clusters is the object of the subsequent discussion.

In order to analyze the character of formation and decay of glassylike state of these systems, we need kinetic parameters involving voids. For this purpose, we use measured parameters of processes in condensed rare gases for bulk systems, and the results of computer modeling with bound atoms with a Lennard-Jones pair interaction for clusters. These data will be used in the following for the analysis of kinetics of void diffusion.

THE SATURATED VAPOR PRESSURE OF A NONEQUILIBRIUM RARE GAS

In considering excited states of the system of atoms bound by a pair interaction, we examine nonequilibrium configurational states, so that the degree of configurational excitation of this system (or the concentration of voids) need not conform to its vibrational temperature. We connect the density of voids with the energy of configurational excitation on the basis of the method which we used previously.^{6,8-10} We begin with a bulk solid crystal particle consisting of $n+v$ atoms and remove v atoms to the outside. This system containing n atoms and v vacancies shrinks as a result of relaxation, compressing during a typical atomic time for this system. This system then has n atoms and v voids. Such a state of the system, for which the effective temperatures of the atomic vibrations and configurational excitations may be quite different, admits any number of voids inside the system at any given vibrational temperature.

The degree of configuration excitation of this system of interacting atoms or the concentration of voids can influence

various properties; in the following, we examine the pressure of saturated vapor above the system as a function of its configuration excitation. According to the Clausius–Clapeyron law, the saturated vapor pressure is given by^{11,12}

$$p(v, T) = p_0 \exp\left(-\frac{\epsilon_v}{T}\right), \quad (1)$$

where ϵ_v is the mean binding energy of a surface atom, which is the sublimation energy per atom for a bulk system with a given density of voids v inside it, and the temperature T is expressed in energy units, i.e., as $k_B T$. We assume that the saturated vapor pressures referred to any concentration of voids are identical for the solid and liquid states at the triple point. This gives the preexponential coefficient

$$p_v = p_0 \exp\left(\frac{\epsilon_v - \epsilon_{\text{sol}}}{T_{\text{tr}}}\right), \quad (2)$$

where ϵ_{sol} is the binding energy per atom for the solid state, p_0 is the preexponential factor in formula (1) for the solid state, and T_{tr} is the triple point temperature. It follows from this formula that the preexponential factor in formula (1) drops as the density of voids increases. Of course formula (2) is correct for the liquid state.

From this we have

$$\frac{p(v, T)}{p_{\text{sol}}(T)} = \exp\left[(\epsilon_{\text{sol}} - \epsilon_v)\left(\frac{1}{T} - \frac{1}{T_{\text{tr}}}\right)\right], \quad (3)$$

where $p_{\text{sol}}(T)$ is the saturated vapor pressure over the solid surface at the chosen temperature. In particular, for the metastable liquid state at a temperature T below the triple point, formula (3) gives

$$\frac{p_{\text{liq}}(T)}{p_{\text{sol}}(T)} = \exp\left[\Delta H_{\text{fus}}\left(\frac{1}{T} - \frac{1}{T_{\text{tr}}}\right)\right], \quad (4)$$

where ΔH_{fus} is the fusion enthalpy.

Let us consider a transition to the ordered solid state as a result of heating of a glassy state, starting from a low temperature, where this glassy state has an indefinitely long lifetime. If this transition starts at a temperature T_1 , finishes at a neighboring temperature T_2 , and the saturated vapor pressure effectively does not vary in this temperature range, we have from the equation $p(v, T_1) = p_{\text{sol}}(T_2)$, on the basis of formulas (1) and (2),

$$\epsilon_v \left(\frac{1}{T_1} - \frac{1}{T_{\text{tr}}}\right) = \epsilon_{\text{sol}} \left(\frac{1}{T_2} - \frac{1}{T_{\text{tr}}}\right). \quad (5)$$

In the following, we analyze the results of an experiment¹³ 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 3×10^{-9} cm/s. We refer to this amorphous form of argon as a glassy state. The heating induces an annealing transition to the crystal state, as is shown in Fig. 1.^{4,13} A typical film thickness in this experiment is about 10 μm , exceeding the

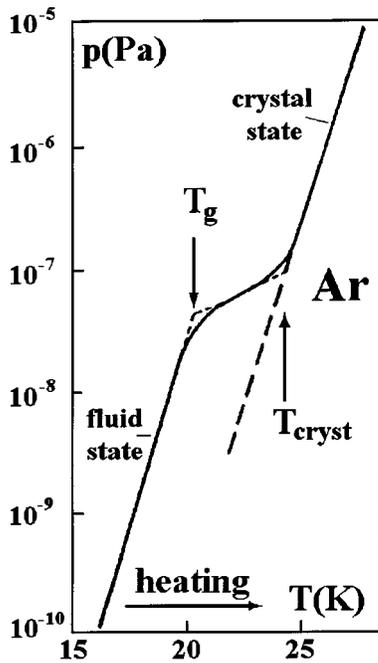


FIG. 1. The temperature dependence of the saturated vapor pressure above a heated amorphous argon formed by deposition of the argon flux on a copper substratum at the temperature 10 K (Ref. 13), and its approximation by the limiting cases (Ref. 4) referred to the glassylike and crystal argon states.

distance between nearest neighbors of bulk condensed argon by more than three orders of magnitude. Hence this film can be considered as bulk condensed argon. The transition to the ordered solid state starts at a temperature $T_1 = 20 \pm 1$ K and finishes at a temperature $T_2 = 24 \pm 1$ K. According to formula (5), this corresponds to the ratio between the binding energies in the glassy and solid states $\epsilon_v / \epsilon_{sol} = 0.78 \pm 0.10$. Note that the ratio of the binding energies ϵ_{liq} and ϵ_{sol} of the liquid and solid states is $\epsilon_{liq} / \epsilon_{sol} = 0.85 \pm 0.10$ for all the rare gases,⁹ and is 0.86 ± 0.02 for argon. One can see that the binding energy per atom of the glassy state ϵ_v which follows from this experiment, coincides with the binding energy per atom ϵ_{liq} for the liquid state within the limits of the accuracy of these data. The liquid state does not exist in the transition temperature range as a metastable aggregate state. (The freezing limit below which the liquid state is not metastable is 52 K for argon⁶.) Hence we deal with the glassy state at such temperatures even though the concentration of voids for this state coincides with its value for the liquid state.

KINETICS OF THE COOLING PROCESS

We now consider the process of formation of a glassy state for a bulk rare gas as it cools, or the decay of such a state as the material warms. We suppose that the transition to a new aggregate state in a homogeneous system occurs adiabatically, so that the rate of the configurational transition coincides with the rate of the temperature variation. In the case we consider, the configurational transition results in diffusion of internal voids to the boundary of the system or from it to the interior. A typical time τ_d of the void diffusion process is

$$\tau_d \sim l^2/d, \tag{6}$$

where l is a typical size of the object or a typical distance from an internal point of the object to its boundary, and d is the diffusion coefficient of voids inside the object. Since the displacement of voids is determined by an inverse displacement of atoms, the diffusion coefficient of voids is

$$d \sim \omega_D a^2 \exp\left(-\frac{E_a}{T}\right), \tag{7}$$

where ω_D is the Debye temperature, a is the lattice constant, T is a current temperature, and E_a is the activation energy for the void displacement that results from displacement of atoms and depends on the concentration of voids or vacancies inside the object. The activation energy drops as the concentration of voids increases.

Assuming the rate of the temperature variation dT/dt is constant, we obtain for a typical time τ_c of the cooling process

$$\frac{1}{\tau_c} \sim \frac{1}{\Delta T} \frac{dT}{dt} \sim \frac{E_a}{T^2} \frac{dT}{dt}, \tag{8}$$

where $\Delta T = T^2/E_a$ is the temperature range in which the diffusion rate varies weakly. Defining the temperature T_g of the glassy transition by the relation $\tau_d(T_g) = \tau_c$, we have, from formulas (6) and (8),

$$T_g = \frac{E_a}{\ln\left(\frac{\omega_D a^2}{l^2} \frac{T^2}{E_a [dT/dt]}\right)}. \tag{9}$$

Formula (9) connects the parameters of processes that are responsible for the glassy transition. This formula is valid for both cooling and heating processes.

The activation energy E_a for the diffusion process of voids depends on the void concentration. In the limit of low void concentrations, i.e., for the solid state of rare gases, this value is directly related to the activation energy ϵ_a of the process of self-diffusion of atoms in rare gas crystals. We have

$$\epsilon_a = E_a + \epsilon_{sol},$$

because the transition of a crystal atom to a neighboring lattice site is proportional to the probability of a vacancy location in this site, which is $\sim \exp(-\epsilon_{sol}/T)$. Using the activation energy data for the self-diffusion process of atoms in solid argon, $\epsilon_a = 170$ meV,¹⁴ we obtain the activation energy of the vacancy diffusion process in the solid argon:

$$E_a \approx 1000 \text{ K}. \tag{10}$$

The activation energy of the diffusion process drops with an increasing concentration of voids, starting from the concentration $c \approx 1/12$, at which a vacancy on average finds another vacancy as a nearest neighbor in the crystal lattice. At that point, vacancies transform into voids whose shape and volume varies in time in a random way; we characterize voids by their average parameters. Returning to the experiment¹³ probing the transition of argon from the glassy

state to the crystal as a result of heating, we use the experimental parameters $l=10^{-5}$ cm, $dT/dt=2$ K/min. Then from formula (9) we obtain

$$E_a \approx 500 \text{ K.} \quad (11)$$

Thus, the activation energy for void diffusion, when the void concentration is close to its value in liquid argon, is one half of that of the crystalline solid state. This value corresponds to the activation energy of self-diffusion of atoms in liquid argon that is 450 K.¹⁵ Evidently the same behavior of glassy-like states applies to other rare gases.

On the basis of the activation energy (11) for decay of the glassy state of bulk argon and formulas (6) and (8) for the rates of the diffusion and cooling processes, we obtain the criterion $\tau_d(T_m) > \tau_c$ that the argon liquid state is frozen to a glass by fast cooling:

$$l^2 \frac{dT}{dt} > 10^{-3} \text{ K cm}^2/\text{s}; \quad (12)$$

this condition may be fulfilled in reality for thin films. As a result of such cooling, the liquid state is transformed into a thermodynamically unstable disordered state which may be indistinguishable from the glassy state.

Under the experimental conditions,¹³ there is a limiting rate of deposition 3×10^{-9} cm/s or of the flux of attaching argon atoms 8×10^{13} cm⁻² s⁻¹, below which an amorphous structure of argon can be formed. We assume that the heat released from formation of bonds for attaching atoms is transported to the copper substratum by thermal conductivity. Taking the thermal conductivity coefficient of solid argon to be 0.03 W/cm⁻¹ K⁻¹ at a temperature of 10 K, we find that the limiting flux of attaching atoms, which corresponds to a heat flux of 1×10^{-6} W cm⁻², creates a temperature gradient of 3×10^{-5} K/cm. It is apparent that this gradient is small enough that it cannot affect the thermal regime of the argon deposition process. Evidently if this limiting flux for formation of amorphous argon is exceeded, the heat released may influence the new phase growth and hence the structure of the condensed argon as it forms.

Note that the glassy transition differs from a traditional phase transition in a fundamental way. For a system of bound atoms, such as rare gas systems, the glassy transition results from diffusion of voids out of or into the system, and the system remains almost uniform during the course of the transition. The phase transition between the ordered solid and liquid states of this system is thoroughly collective, starting from formation of nuclei of a new phase, and the new phase grows from these nuclei. Thus, the system is nonuniform during the phase transition.

THE GLASSYLIKE STATE OF CLUSTERS

By analogy with a bulk system of bound atoms, we define the glassylike state of clusters as a configurationally excited cluster state at low temperatures. Guided by systems of rare gas atoms, we will again consider clusters bound by pair interactions of atoms. Such a cluster, like the bulk solid state, may have several excited aggregate states⁷ which correspond to melting of different cluster shells. As the cluster size in-

creases, only two liquid aggregate states persist, the surface-melted and volume liquid aggregate states. Because of the difference in the binding energies for the internal and surface atoms, these liquid states may be separated and distinguished experimentally.¹⁶ Previously we restricted ourselves only to the volume liquid state of bulk rare gases, while in the following we consider excited cluster states in which the liquid or amorphous character is restricted to the outermost shell.

Configurational excitation of clusters with filled shells that we consider here refers to atomic transitions on the cluster surface. When atoms of the outer cluster shell undergo configurational excitation from the filled or nearly filled outer shell to the cluster's surface, other atoms of this shell can change their positions, and the outer shell "melts." As a result, the binding energy of atoms of the next-inner shell decreases, and the subsequent configurational excitation leads to the melting of this shell. If the liquid cluster is cooled fast enough, so that configurational excitation is preserved, we obtain an analog of the glassy state at low temperatures that has properties of an amorphous glassy system.¹⁷ We analyze this state for the Lennard-Jones cluster consisting of 13 atoms. Strictly, "surface melting" of rare gas clusters appears at a size of about 45 or more atoms, but the analogy of this transformation can be extended to the 13-atom cluster in the sense that there is a range of conditions in which the central atom does not exchange with the others, and hence is not a truly fully melted state.

This is the simplest of rare gas clusters with filled shells. It has icosahedral structure with one central atom and 12 outer atoms located on the sphere around the central atom. If we join atoms on this sphere, we obtain 20 equilateral triangles. We take the Lennard-Jones interaction potential between atoms

$$U(r) = D \left[\left(\frac{a}{r} \right)^{12} - 2 \left(\frac{a}{r} \right)^6 \right], \quad (13)$$

where r is the distance between two interacting atoms, a is the equilibrium distance between them, and D is the potential well depth. Two other structures, both close-packed, the face-centered cubic and hexagonal structures, also have one central atom and 12 atoms on the sphere of radius a around this center. The excitation energy of the face-centered cubic structure is 3.54 D for this cluster, and the excitation energy of the hexagonal structure is 3.69 D .¹⁸

One property of clusters with pair interactions between atoms is the multiplicity of local minima on their effective potential energy surfaces. These local minima are separated by barriers with characteristic saddle points. Hence transitions between adjacent local minima require passage across saddle points. Figure 2 exhibits the positions of the lowest excited states and saddle points for one exemplary configurational excitation of the Lennard-Jones icosahedral cluster of 13 atoms.¹⁹ In particular, in order for the transferring atom to become the nearest neighbor of the initially opposite atom, this atom must pass through two intervening local minima of the potential surface and overcome three barriers. One can consider the cluster's geometry in these excited states as typical configurations of its liquid state. This follows from

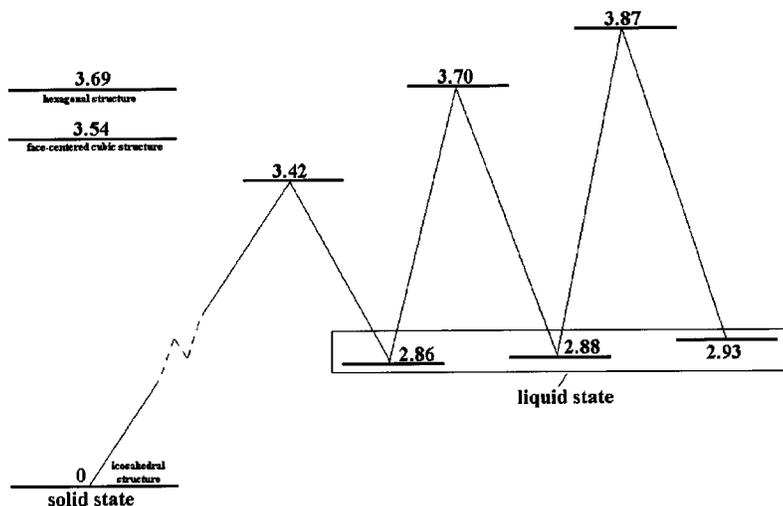


FIG. 2. The lowest excited states of the Lennard-Jones cluster of 13 atoms, and the character of their formation through saddle points (Ref. 19). Values near levels indicate the excitation energies expressed in units of the binding energy D per one bond. The energies of the close-packed structures are taken from Ref. 18. 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 sufficient excitation energy or temperature (Refs. 20–23).

the correlation analysis,^{20–23} and we use this fact. If then the cluster is cooled rapidly to low temperatures, it can remain trapped in one of those local minima. In the following we analyze the possibility of such cluster evolution.

In considering the configurationally excited cluster state, we join the first excited states into one liquid aggregate state in accordance with Fig. 2. This is valid if the transitions among excited states of this group occur much more frequently than between these and the lowest configurational state of the cluster, as is the case for this system. This criterion is fulfilled well enough to justify using this approximation for simplicity. For this 13-atom Lennard-Jones cluster we use the melting point (point of equal free energies) $T_m \approx 0.31 D$;²² the excitation energy is $\Delta \epsilon \approx 2.5 D$,²² and from the definition of the melting point

$$g \exp\left(-\frac{\Delta \epsilon}{T_m}\right) = 1. \quad (14)$$

The statistical weight g of the cluster's excited state is $g \approx 3 \times 10^3$.^{9,24} For this classical system of bound atoms, the statistical weight of the liquid state with respect to the ground state takes into account that the effective vibrational frequencies for a transiting atom in the ground and excited states are different. Thus, from analysis of computer modeling of the Lennard-Jones cluster of 13 atoms,^{20–23} one can define the “surface-melted” liquid state of this cluster as the group of lowest configurationally excited states (and the saddles that link them), and estimate kinetic parameters for transitions from these states on the basis of this modeling.

We use the principle of detailed balance⁹ that connects the rates of cluster excitation ν_{ex} and quenching ν_q as a result of thermal motion of bound atoms; this has the form

$$\nu_{\text{ex}} = \nu_q g \exp\left(-\frac{\Delta \epsilon}{T}\right). \quad (15)$$

For the rate of excitation of a classical atom of this cluster we take

$$\nu_{\text{ex}} = 12 \epsilon_D \exp\left(-\frac{E_b}{T}\right) \cdot \alpha, \quad (16)$$

where ω_D is the Debye frequency, a typical frequency of atomic oscillations; the factor 12 takes into account that each surface atom can partake in this transition, E_b is the barrier energy for this transition from the ground state, and α is the geometrical factor, i.e., the range of solid angles for atomic motion that determines this transition. For definiteness, we take $12\alpha = 1$, and we obtain our estimate for the cooling rate at which the excited cluster state may be frozen:

$$\frac{dT}{dt} > \frac{T_m^2 \omega_D}{E_a g} \exp\left(-\frac{E_a}{T_m}\right). \quad (17)$$

We use formula (8) and take the probability of quenching to be maximal at the melting point; the activation energy is $E_a = E_b - \Delta \epsilon \approx 0.56 D$ ²² in this case.

Comparing the criterion (17) with the criterion of formation of the glassy state for a bulk system of bound atoms $T_g > T_m$, where T_g is given by formula (9), we find that the difference of the criteria for bulk systems and clusters is twofold. First, the activation energy is higher for a bulk system because more energy is required to change the position of an internal crystal atom than that to move a surface atom. On the basis of formula (11) we have $\exp(E_a/T_m) = 400$ in the case of bulk argon; the corresponding energy is only 8 for the Lennard-Jones cluster of 13 atoms. Second, the criterion (9) for formation of the glassy state of a bulk system contains an additional large factor l^2/a^2 in comparison with the cluster; this factor is responsible for diffusion of voids to the boundary. On the other hand, the character of cluster cooling is simpler than for a bulk system, because this process proceeds from the cluster surface, and the cluster has a developed surface. Hence one can reach high rates of cooling dT/dt by inserting a cluster into a cold gas. Now we estimate the critical density of a cold gas that would provide cooling fast enough for the cluster to “freeze in” its excited configurational state.

We use the simple model presented previously⁹ for an exchange of energy between a colliding atom and a cluster, so that the average energy of an atom before collision is $\frac{3}{2}T_0$, where T_0 is the gas temperature expressed in energetic units

(of $k_B T$); after collision, the atom's energy is $\frac{3}{2}T$, where T is the cluster temperature. Then the heat balance equation of the cluster has the form

$$c_p \frac{dT}{dt} = \frac{3}{2}(T_0 - T)Nv_T\sigma, \quad (18)$$

where c_p is the cluster's heat capacity, N is the number density of gas atoms, v_T is the average atomic velocity, and σ is the cross section of atom-cluster collisions. Assuming the cluster atoms to be classical, we use the Dulong–Petit formula for the heat capacity $c_p = 3n$, where n is the number of cluster atoms. Using the liquid drop cluster model for collisional processes,⁹ we have $\sigma = \pi r_W^2 n^{2/3}$, where r_W is the Wigner–Seitz radius. Under these conditions, the criterion (17) takes the form

$$\frac{dT}{dt} > n^{1/3} \frac{T_m^2}{E_a(T_m - T_0)} \cdot \frac{\omega_D}{v r_W^2} \exp\left(-\frac{E_b}{T_m}\right), \quad (19)$$

where $v = \sqrt{2\pi T_0/m}$ and m is the atomic mass; we use the relation (14) and $E_b = E_a + \Delta\epsilon$.

For definiteness, we use this estimate for the argon Lennard-Jones cluster of 13 atoms ($T_m = 44$ K) inserted into helium at a temperature of 20 K. Then formula (19) gives the number density of helium atoms

$$N \gg 3 \times 10^{17} \text{ cm}^{-3}, \quad (20)$$

a criterion that may be tested in experiments.

Although this example may not yet be convenient for real experimental conditions because of difficulties of detecting configurationally excited argon clusters, this demonstrates the possibility of conserving a cluster's configurational excitation by cooling it rapidly enough from its liquid state. Since excited configurational states of metallic clusters may possibly be detected, one may be able to study the glassylike cluster state when a liquid metallic cluster is inserted into a cold gas, for example, by fragmentation patterns,²⁵ collisional ionization with a metallic surface, or photoionization. Determination of radial density distributions for clusters bound primarily by pair interactions may also become a way to probe densities of vacancies.¹⁶

Thus the configuration excitation of small clusters, via transition of surface atoms from the outermost completed shell to the cluster's surface, is an analog of formation of a bulk glassy state. Although such an excitation involves only single-atom transitions, the freezing transition involves the collective character of the system because of the collective character of the cluster's initial liquid state. Therefore from the thermodynamic standpoint, the frozen liquid states of clusters at low temperatures are analogs of the glassy states of bulk systems of bound atoms.

PECULIARITIES OF CONFIGURATIONALLY EXCITED CLUSTERS

Thus, moving from bulk systems to clusters with pair interactions between atoms, we define a glassylike state of a cluster as a configurationally excited and frozen cluster state. This requires an additional analysis of cluster states and a more detailed definition of aggregate and glassylike states. It

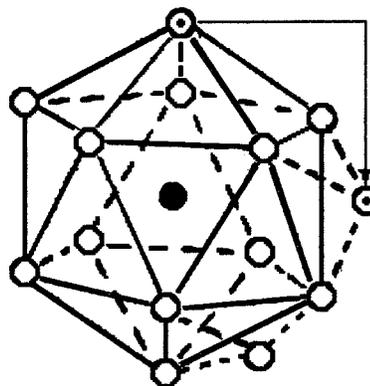


FIG. 3. Configuration excitation of a cluster of 13 atoms with a pair atom interaction. The arrow shows transition of a vertex atom to a free positions over a triangle formed by surface cluster atoms.

is productive to analyze cluster properties in terms of behavior on a complex potential energy surface in a multidimensional space of atomic coordinates, a surface with many local minima separated by barriers.^{18,26–30} From this standpoint, a cluster with pair interactions between atoms at moderate or low temperatures remains for long intervals near a single local minimum, and, from time to time, undergoes transitions to neighboring energy minima. With this perspective, we define a cluster *aggregate* state as a sum of local energy minima with similar energies if a cluster remains for extended periods within this set of minima and ventures outside this set only infrequently. A cluster of 13 atoms can be a simple case to demonstrate this. The lowest configuration excitation of this cluster is given in Fig. 3 and within the framework of the cluster shell model results from one-atom configurational promotion from the completed shell to the cluster surface. Figure 2 gives the excitation energies and saddle-point energies at zero temperature in the case of the Lennard-Jones interaction between atoms. All the transitions of one atom of Fig. 3 are joined in the liquid aggregate state near the melting point.

One can see the difference between this definition of the liquid aggregate state and that of classical thermodynamics, in which the bulk phase or aggregate state corresponds to an uniform distribution of atoms in some spatial region restricted by boundaries. This means that a phase of bulk matter includes many elementary configurational excitations while in the case of a 13-atom cluster this state can result from a single elementary configurational excitation. Of course, for the liquid cluster state (or an excited aggregate state) it is necessary to apply additional criteria for correlations between two-atom positions that differ for the solid and liquid states.^{31,22,32} From this it follows that the cluster aggregate states have additional peculiarities in comparison with bulk systems, and one of these is phase coexistence.^{19,22,31,32} This means that a cluster may exhibit a dynamic equilibrium between two or more phaselike forms within some range of temperature and pressure, rather than just along a coexistence curve. Thus, for clusters, it is necessary to extend the concepts of classical thermodynamics beyond those of aggregate states of bulk systems. Within this framework, we consider the glassylike cluster states as fro-

zen liquid states at low temperatures below the melting point, or as configurationally excited cluster states at low temperatures.

We note one more peculiarity of clusters which allows us to use the cluster shell model.^{9,33–35} Transitions in clusters bound by short-range, predominantly pairwise forces, including their excitations, can be considered as configurational transitions of individual atoms between cluster shells. The cluster shell model is similar in some respects to the electronic shell model of atoms. We may formulate the relation between these models. Indeed, we use the electronic shell model to provide a qualitative description of atomic transitions and atomic processes, but additional information is required (for example, spectroscopic data), if we want to make quantitative estimates of these processes. In the same manner, one can use a one-atom shell model for a qualitative description of cluster processes, while it is necessary to account for simultaneous interactions of many atoms for a quantitative cluster description.¹⁹ Figures 2 and 3 show this for a 13-atom cluster. The configuration excitation of Fig. 3, the transition of one atom between the completed and free shells of this cluster, allows us to interpret the character of the solid–liquid and glassy transitions of this cluster. But for quantitative description of these transitions, one must account for interactions among various atoms in the course of the transitions. Considering the analogy of the atomic shell model of clusters and the electronic shell model of atoms, we note that the cluster shell model is richer and allows us to understand such phenomena as the solid–liquid and glassy transitions in clusters.

CONCLUSION

On the basis of the above-presented 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 traditional definition,⁴ the bulk glassy state is a thermodynamically unstable configurational state of bound atoms formed by fast cooling of the system, specifically if extremely slow cooling would yield a true phase transition, requiring an activation energy, between two aggregate states. The transition for glasses to relax to ordered solids involves the change of positions of some constituent particles, so that finally the system take on a crystalline structure as it undergoes “infinitely” slow cooling. One characteristic of this transition is the difference of densities of structures of the initial and final states. Therefore together with restructuring of the particle positions, voids must diffuse to the system’s boundary or into the systems.

This approach is complementary to a more traditional free-volume model, in which detailed attention is directed toward the change in available free volume as a system goes between liquid and glass.^{36,37} Here our emphasis is on the change of the kinetics with temperature, specifically on the way reducing temperature rapidly inhibits passage over saddles while the free volume remains relatively unchanged. In this sense, this treatment differs in emphasis but is not inconsistent with a model that emphasizes relatively small but perhaps important changes in the volumes of vacancies at the glass transition.

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 glassylike state of such a system may 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 formation of a random distribution of atoms.

In the case of clusters, systems exhibiting a finite number of locally stable, configurationally excited states formed by transition of atoms from completed cluster shells to the surface conform to the model of a glassy state. This corresponds to formation of surface voids, and annihilation of voids results in transition of atoms from the cluster surface to the outermost shell. This glassylike state may be considered also from the standpoint of cluster configurational excitation as a result of transition to local minima on the potential energy surface. Because neighboring local minima of the cluster’s configurational energy are separated by barriers,^{28,30} transitions from the ground cluster shell to excited configurations have an activation character. This activation requires significantly more energy than passage among the configurationally excited states, so the states in this set appear together. Thus, known excited structures of simple systems of bound atoms conform to the definition of the glassy state. Based on the concept that glassylike states of simple systems form as a result of creation of voids, one can analyze these states in some detail.

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