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PHASE TRANSITIONS IN SIMPLE CLUSTERS

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Formation of the liquid state of clusters with pairwise interactions between atoms is examined within the framework of the void model, in which configurational excitation of atoms results from formation of voids. Void parameters are found from computer simulation by molecular dynamics methods for Lennard–Jones clusters. From that standpoint, phase transitions are analyzed in terms of two aggregate states. This information allows us to divide the entropy jump during a solid–liquid phase transition into two parts: one corresponds to configurational excitation at zero temperature and the other arises from thermal vibrations of atoms. The latter part contributes approximately 40 % for Lennard–Jones clusters consisting of 13 and 55 atoms, increasing to 56 % for bulk inert gases. These magnitudes explain the validity of melting criteria based on thermal motion of atoms, even though the distinctive mechanism of this phase transition results from configurational excitations. It is shown that the void concept allows analyzing various aspects of the liquid state of clusters including the existence of a limiting freezing temperature below which no metastable liquid state exists, and the existence and properties of glassy states that may exist below the freezing limit.

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1. INTRODUCTION

Clusters, being systems of relatively small finite numbers of bound atoms, differ from macroscopic atomic systems in several properties. Their solid states are characterized by sharp, nonmonotonic dependence of their population on the number of component atoms. The most striking aspect is the occurrence of «magic numbers» that corresponds to completed atomic shells, often of polyhedra rather than lattices. In experiments, these favorable structures exhibit heightened populations and stabilities, see, e.g., [1–3]. In the subsequent analysis, we focus on clusters with pairwise interactions between atoms. In this case, the pairwise character and magnitude of the interaction means that the interaction energies between atoms of a cluster are small compared with a typical electronic excitation energy. This criterion is valid for clusters of inert gas atoms and clusters of molecules typically found in a gaseous state under normal conditions. (It does not hold for covalently bound clusters or metallic clusters.) We consider the phase change of clusters between the solid and liquid states and examine how it differs in principle from the traditional melting/freezing transition in macroscopic systems. Indeed, the phase transition in macroscopic systems proceeds by a sharp step in specific properties, and hence, in classical thermodynamics, there are phase transitions of the first and second orders [4–9], depending on the behavior of the derivatives of specific thermodynamical quantities. In the cluster case, computer simulation exhibits coexistence of the solid and liquid phases [10–13] over some finite temperature and pressure band that makes the phase change of clusters richer than for macroscopic systems, and, in a sense, makes the classical thermodynamic classification of phase transitions, based on specific discontinuities, inapplicable here, even while the basic laws of thermodynamics remain completely valid. Because of the coexistence of aggregate states in the phase change of clusters, dividing the phase transitions into sharply divided types loses its sense.

The phase transition is a collective phenomenon that results from simultaneous interaction of many

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atoms. Therefore, simple analytical one-particle models are not suitable for its analysis. In considering the phase change in clusters, we use the results of computer simulation for clusters whose atoms interact through the Lennard – Jones potential. We focus mainly on the liquid state of these systems, whose properties depend monotonically on the number of cluster atoms, in contrast to the solid state, which exhibits its irregular dependence (with magic numbers) on the number of cluster atoms. As a result of melting, the crystalline distribution of atoms is lost, and the liquid state has more or less amorphous structure, although a shell-like distribution of atoms may be conserved to some degree. The aim of this paper is the analysis of some properties of liquid cluster systems on the basis of appropriate models. In constructing our model, we must take the specifics of the cluster liquid state into account. In general, this can follow from the probability of the total kinetic energy of cluster atoms held at constant energy, for example, as was done in [11] for the Lennard – Jones cluster of 13 atoms. Here, this probability has a bimodal form in a range of internal energies near the state of classical melting, i.e., where the chemical potentials of the solid and liquid states are equal. (For convenience, we here refer to this state as the «melting point».) The two maxima of this distribution and their vicinities correspond to two aggregate states, solid and liquid.

In modelling a large liquid cluster with pair interactions between atoms by a spherical liquid drop, we take into account that atoms in this aggregate state occupy a larger volume than in the solid state. Then we can consider the cluster's transition from solid to liquid as a result of formation of voids inside the cluster [14]. We consider a void as an elementary configuration excitation. A void is a perturbed, even a relaxed, vacancy; in contrast to a vacancy in a solid, a void has an indefinite volume and shape that changes in time. On the basis of computer simulation results, we find the average void parameters as they emerge for macroscopic inert gases [15–19] on the basis of their measured parameters. This allows us to analyze various aspects of the phase transitions in condensed inert gases as well as in Lennard – Jones clusters.

Introduction of a void as an elementary configuration excitation is in reality a simplification of a general analysis of the potential energy surface of an ensemble of interacting atoms [20]. In a multidimensional space of atomic coordinates, the potential energy surface for an atomic ensemble with pairwise interactions consists of many potential wells separated by saddles [13, 21–24]. Evolution of this ensemble is described by saddle-crossing dynamics [23]. In particular, a cluster is found near a minimum of the potential energy long enough to equilibrate its vibrations; transition to a neighboring minimum typically proceeds relatively slowly by comparison [25]. (Of course, if there are minima separated by low barriers, equilibration among these may occur on the same time scale as vibrational relaxation, and can be treated appropriately.) First, this leads to a short-range, short-duration order for any amorphous structure of atoms, because each configuration of atoms is preserved for a relatively long time (such that the atomic kinetic energy is not very large). Second, this allows us to introduce an average void by averaging parameters over times that exceed the typical vibrational period but are shorter than typical well-to-well passages. This allows us to separate configuration excitation that is responsible for the phase transition from vibrational excitation associated with an increase of the kinetic energy of the atoms. This fact is of importance for the analysis of the phase transition.

We note that the phase change in clusters is richer and more complicated than in bulk systems. In particular, the sharp onset of a liquid state is absent for Lennard – Jones clusters of 8 and 14 atoms (and others) [26]; these are examples of systems that do not show bimodal distributions of kinetic energies on time scales of vibrational relaxation. In addition, large clusters can exhibit several aggregate states associated with melting of various atomic shells [27, 28]. Below, we focus on clusters with completed atomic shells and consider melting of surface shells. In these cases, the melting process is clearer and more easily distinguished. First, because the surface shell contains a considerable fraction of the cluster's atoms, the statistical weight of configurationally excited states with voids in the surface shell is relatively large, as is the entropy of transition to this state. This leads to a stable liquid state for the surface layer of these clusters, as well as a state composed entirely of liquid. Next, in contrast to the liquid state of bulk systems, where a void differs clearly from the vacancy in a solid, a surface void in a not-so-large cluster can be considered a perturbed vacancy. For example, the energy of formation of a void in the liquid state of a bulk inert gase is approximately half the energy of formation of a vacancy in the solid state of a bulk inert gas [15–17]. In the case of clusters under consideration, the energy difference of formation of surface vacancies and voids is not very large, and hence a void can be considered a perturbed vacancy. This facilitates the analysis.

Because some concepts of classical thermodynamics of macroscopic systems are not valid for clusters, it is necessary to revise some of those concepts in order to apply them to clusters. In particular, the phase of an aggregate state is defined in classical thermodynamics as a uniform distribution of atoms that is restricted by boundaries. From the standpoint of the void concept, this means that the liquid aggregate state as a configurationally excited state has to contain many elementary excitations — voids. To transfer this concept to small clusters, it is necessary to revise the definition, to be done in what follows.

The void concept gives a sufficiently detailed picture of the liquid aggregate state, in comparison with classical thermodynamics, and allows us to resolve its apparent paradoxes. As an example, we consider the criterion of the phase transition for macroscopic systems. According to the widely used Lindemann criterion [29, 30], bulk melting proceeds at the temperature at which the ratio of the atomic oscillation amplitude to the distance between nearest neighbors reaches a certain value (10–15 %). Development of numerical methods for computer cluster simulation gave new variants of this criterion of cluster melting on the basis of the Etters – Kaelberer parameter [31–33] or Berry parameter [12, 34]; these account for pair correlations in positions of atoms. These parameters have jumps at melting and, as with the Lindemann criterion, are connected with thermal motion of atoms, even though the melting results from configurational excitation. Hence, there is an apparent contradiction between the nature of the phase transition in ensembles of bound atoms due to configurational excitation and the practical criteria for this transition based on thermal motion of atoms. The subsequent analysis of numerical parameters of this phase transition exhibits the resolution of this apparent contradiction.

Although vibrational excitation of finite and «infinite» numbers of bound atoms that characterizes thermal motion of atoms is separated from configuration excitation that is responsible for the phase transition, thermal motion of atoms gives a contribution to the entropy jump ΔS at the melting point, because the solid state is more compact than the liquid aggregate state. Reflecting just the thermal (kinetic energy) part of the entropy jump, the vibrational parameters nevertheless simultaneously characterize the phase transition. By exhibiting the connection between the configurational and kinetic-energy aspects, the void analysis justifies applying the melting criteria based on thermal motion of atoms.

The goal of this paper is the analysis of Lennard – Jones clusters with completed shells from the standpoint of the void concept. This consists in obtaining the void parameters from treatment of numerical computer calculations and in the analysis of these data to connect the two kinds of excitation.

2. CHARACTER OF CLUSTER CONFIGURATIONAL EXCITATION

We consider an ensemble of interacting atoms in which the ground electronic state is well separated from electronically excited states, and these excited states do not partake in evolution of the atomic ensemble, i.e., development of this system can be described in terms of motion on the potential energy surface (PES) in a multidimensional space of nuclear coordinates, and this PES corresponds to the electron ground state. The PES has many local minima, which was discovered in first numerical calculations of the cluster energy at zero temperature for a simple character of atomic interactions [35–37]. Early algorithms that made oversimplifying assumptions about the potential landscape led to underestimations of the number of minima, but with increasing the computing power, more elaborate methods made it possible to explore these landscapes fairly thoroughly and to obtain plausible estimates regarding the dependence of the number of minima on the number n of atoms in the cluster. For Lennard – Jones clusters, the number of geometrically distinct minima increases somewhat faster than exponentially with n; there are roughly $n!$ permutational isomers of each of these, and hence the total number increases roughly as $n!\exp(an)$ [21, 36–39]. As a result, cluster evolution consists of transitions between neighboring local minima of PES that correspond to saddle-crossing dynamics [13, 22–24]. This concept is a basis for investigation of various ensembles of interacting atoms, from simple clusters to biological molecules [20, 24].

The character of transitions between neighboring minima of PES is given in Fig. 1, which shows schematic projections of a PES on planes in the space of atomic coordinates where only the coordinate related to a specific transition between two local minima of the PES varies. (These planes are different for each transition.) Energy levels for each well indicate an average atomic energy along the coordinate of the transition. Because this energy is significantly less than the barrier height, such transitions proceed seldom, only when the kinetic energy of atoms in the transition degree of freedom exceeds its average energy adequately. Hence, the system has many oscillations inside a given well until it transfers to another local minimum of the PES. Then

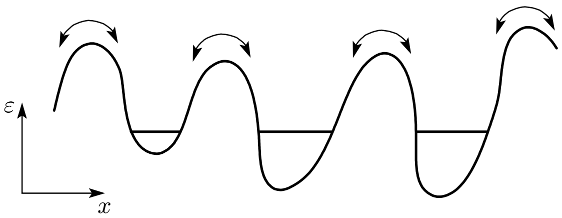

Fig. 1. The evolution of an ensemble of atoms in the ground electron state as the propagation of a point in the phase space of atomic coordinates resulting from transition between neighboring local minima of the potential energy surface

identifying a given local (but not global) minimum of the PES as a configurational excitation of the system of interacting atoms, we can separate it from thermal motion associated with atomic oscillations. This allows us to consider the configurational excitation independently of vibrational excitations and is the basis of the following analysis. Moreover, taking a realistic assumption that a typical time of establishment of the thermodynamic equilibrium for thermal motion of atoms is short compared to a typical time of transition between local minima of the PES, we can introduce the temperature of thermal motion of bound atoms for each configuration excitation.

We use an approach based on the assumption of a large number of local minima on the PES. In particular, the Lennard – Jones cluster of 13 atoms is characterized by 1478 local minima and 17357 saddle points of the potential energy surface [22]; early estimates found only 988 local minima [35, 36]. As noted above, the number of geometrically distinct local minima increases roughly exponentially with increasing the number n of atoms in the cluster [20, 21, 38]. We construct an aggregate state from configurationally excited states. Restricting ourselves to the local minima of the PES that are occupied with a nonnegligible probability in a range of cluster temperatures under consideration, we join the local minima with similar excitation energies into one aggregate state. Because of the large number of such local minima, the aggregate state is characterized by a large statistical weight and, correspondingly, by a large entropy, and hence the probability for a cluster to be found in this aggregate state may be considerable, even when the excitation energy is significantly less than kT. Below, we illustrate this definition of the cluster aggregate state with examples.

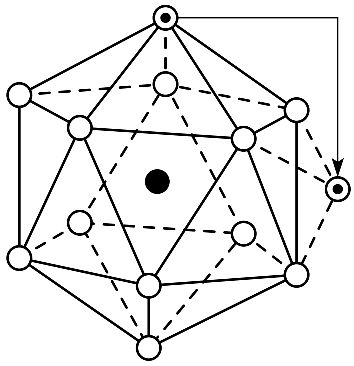

Fig. 2. The character of the lowest configurational excitation in the icosahedral cluster consisting of 13 atoms at zero temperature

3. CONFIGURATIONAL EXCITATION OF THE ICOSAHEDRAL CLUSTER OF 13 ATOMS

Dividing cluster excitations into two parts, configurational and vibrational, we consider these parts independent. Next, for configurational excitation, we use the void model, considering this excitation as a result of formation of voids. Then we can express the parameters of the phase transition and other cluster properties through the parameters of forming voids. We restrict ourselves to clusters with completed shells, which simplifies this analysis because a void, an elementary configurational excitation, is in reality a perturbed vacancy.

We start the analysis of configurational excitation from the simplest cluster with completed shells that has the icosahedral structure and consists of 13 atoms. In the lowest-energy state, its first (and only) shell is filled. Configurational excitation of this cluster consists in transition of one atom from the surface shell to the cluster surface as shown in Fig. 2. After formation of a vacancy on the cluster shell, the atoms around the vacancy are distributed over a larger space due to thermal motion, and the promoted atom moves over the cluster surface more freely than any of the other atoms. As a result of the configurational transition, an excited cluster state has the statistical weight g and the additional entropy ΔS_0 given by

$$g = 12 \cdot 15 = 180, \quad \Delta S_0 = \ln g = 5.2. \qquad (1)$$

Here, the value 12 is the number of shell atoms, any of which can be promoted, and 15 is the number of positions for a promoted atom if it is not in a site bordering the new vacancy. It is important that thermal motion of atoms gives a contribution to these values near the melting point because of the free motion of bound atoms in this configurationally excited state.

We now determine energetic parameters of this transition. In the ground state, each surface atom of this icosahedral cluster has five atoms from the surface shell and the central atom as nearest neighbors. The pairwise interactions therefore yield six «bonds» to these atoms. When this atom is located on the cluster surface, it has only three nearest neighbors. Then the energy of this atomic transition onto the hollow between three atoms on the cluster surface is roughly equal to $3D$, where D is the energy needed to break one bond. (We assume atoms to be classical, and hence the depth of the potential well D for the two-atom interaction coincides with the dissociation energy of a diatomic molecule.) Next, if a surface atom is transferred to a neighboring position on the cluster surface, it retains two bonds between nearest neighbors as it makes the transition between neighboring hollows on the cluster surface. Hence, for this transition, an atom must overcome the barrier whose magnitude is roughly $1D$. Figure 3 gives the energies of these states at zero temperature and the values of barriers that separate them for the Lennard – Jones interaction potential between atoms [40]. We see that the difference between the data in Fig. 3 and the above values is not substantial. Hence, our consideration of an elementary configurational excitation, a void, as a perturbed vacancy is justified.

Figure 3 gives the energies of these states at zero temperature and the values of barriers that separate them [40]. As a result of configurational excitation, an atom transfers from the shell of 12 atoms, as shown in Fig. 2. For this transition, an atom must overcome a barrier; likewise, transitions to other positions on the cluster surface are accompanied by overcoming energetic barriers. Increasing the energy facilitates transitions between different stable positions on the cluster surface, as well as exchanges between a configurationally excited atom and another one. All configurationally excited states with promotion of one atom are connected in the liquid state, and hence the system may find all permutations among the atoms of any attainable structure. This follows from the data in Fig. 3. Thus, all the configurational states with one atom promoted from the outer shell comprise the lowest-energy excited aggregate state.

We now analyze the character of configurational excitation of this cluster in the phase coexistence range where thermal motion of atoms influences the transition parameters. We base this on the results of computer simulation of the Lennard – Jones cluster of 13 atoms [11], in which this cluster is considered a member of a microcanonical ensemble [41], i.e., the total cluster energy is conserved during the cluster's evolution. In a particular band of energies, the probability distribution of the total kinetic energy (or mean kinetic energy per atom) of the cluster becomes the bimodal distribution, which confirms the existence of the aggregate states in the dynamic equilibrium in this case (solid and liquid). Therefore, in this range, we can treat the results of computer simulation [11] in terms of a dynamic equilibrium of two aggregate states. This was fulfilled partially in [42–44], and we give the results of this treatment below.

We now give general formulas of this consideration in which the results of numerical calculations are compared with simple formulas that reflect a simple concept. For the classical motion of bound atoms inside the cluster, we represent the energy E of a cluster consisting of n atoms, with a pair interaction between them, in the form

$$E = U + K = \sum_{i,j} u(\mathbf{r}_{ij}) + \frac{m}{2}\sum_i \left(\frac{d\mathbf{r}_i}{dt}\right)^2. \qquad (2)$$

Here, U is the total potential energy, K is the total kinetic energy of atoms, $u(\mathbf{r}_{ij})$ is the pair interaction potential between atoms at a distance

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j,$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the atomic coordinates, and m is the atomic mass. This formula is the basis of our analysis of cluster computer simulations. We consider the properties of two terms of this formula, taking into account that thermal equilibrium is usually established for atomic vibrations. This allows us to introduce the atomic temperature T, with the motion of atoms treated as that of a set of harmonic oscillators. The cluster temperature is defined from the relation

$$K = \frac{3}{2}nT, \qquad (3)$$

where $n \gg 1$ and the total kinetic energy of atoms is averaged over times much longer than the period of atomic oscillation. A typical oscillation time τ for atoms can be expressed through the Debye frequency ω_D as

$$\tau \sim \frac{1}{\omega_D} \sim \frac{\hbar}{D}. \qquad (4)$$

We note that for a microcanonical ensemble, this definition of the effective temperature, although useful and widely chosen, is not the only one, and different definitions are not equivalent [45].

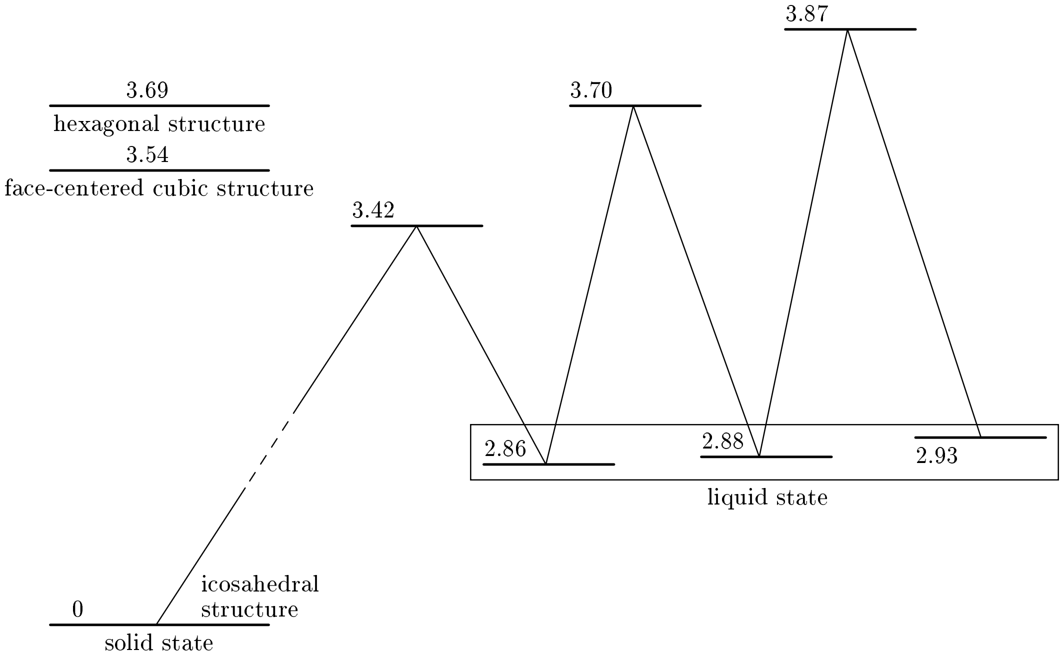

Fig. 3. The energy and barrier positions for the lowest configurational excitations of the Lennard – Jones cluster consisting of 13 atoms according to [40]

The global minimum of the potential energy surface of this cluster has the structure of a regular icosahedron, and it corresponds to the cluster's ground state, its equilibrium state at zero temperature. Transitions from the global minimum to other local minima of the potential energy surface for a 13-atom cluster are responsible for the phase transition to the liquid aggregate state. Figure 3 gives the energies of the lowest configurationally excited states of this cluster at zero temperature and the values of barriers that separate them [40]. As a result of configurational excitation, an atom transfers from the shell of 12 atoms, as shown in Fig. 2. At high temperatures, the lowest configurationally excited state is the liquid aggregate state, which is to be justified below.

The energy of an isolated cluster of 13 atoms in the energy range where both solid and liquid may be stable can be represent as

$$E = -E_0 + E_{ex} = U_{sol}^k + K_{sol} = \Delta E + U_{liq}^k + K_{liq}, \quad (5)$$

where E_0 is the binding energy of cluster atoms at zero temperature, E_{ex} is the excitation energy, K_{sol} and K_{liq} are the total kinetic energies of atoms for the solid and liquid cluster states, U_{sol}^k and U_{liq}^k are the average potential energies of the cluster for the kth local minimum of the potential energy surface, and ΔE is the average excitation energy above the energy needed to reach U_{liq}^k required to produce the labile liquid aggregate state. The values in this formula are averaged over times that exceed a typical time of atom oscillations but are less than a typical transition time between cluster aggregate states. Within the framework of this consideration, we join energetically similar local minima of the cluster potential energy into one aggregate state, assuming the transitions between local minima of the same aggregate state to be more effective than transitions between states that belong to different aggregate states. In other words, we assume that the system, although liquid, explores the local minima available to it far more frequently than it returns to the solid with which it is in the dynamic equilibrium on long enough time scales.

We introduce the effective temperature for a given aggregate state of the cluster on the basis of a formula transformed from formula (3):

$$T = \frac{2}{3n-6}K = \frac{2K}{33}, \quad (6)$$

where $n = 13$ is the number of cluster atoms, and the energy fraction η related to the kinetic energy of atoms is

$$\eta_{sol} = \frac{K_{sol}}{E_{ex}}, \quad \eta_{liq} = \frac{K_{liq}}{E_{ex} - \Delta E}. \quad (7)$$

If atomic motion is a combination of harmonic oscillators, we have $\eta = 0.5$. Anharmonicity of the oscillations

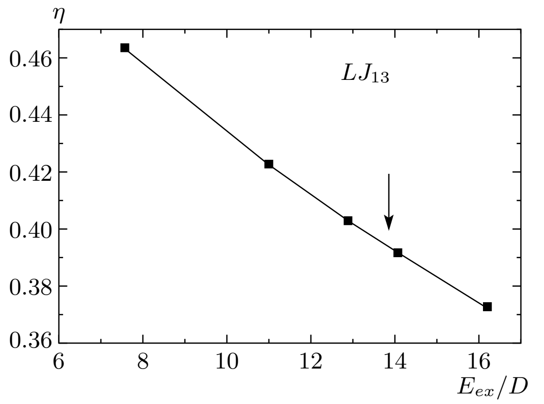

Fig. 4. The dependence on the excitation energy for the energy part related to the kinetic energy of atoms for an isolated Lennard – Jones cluster of 13 atoms. This value is identical for the solid and liquid cluster states. The arrow indicates the excitation energy of the phase transition $w_{sol} = w_{liq}$

typically leads to a decrease of this value, and $\eta(E_{ex})$ decreases with an increase of E_{ex}. Treatment of the results of computer simulation [11] for this cluster by the method in [43] gives the dependence $\eta(E_{ex})$ that is represented in Fig. 4. We note that

$$\eta_{sol}(E_{ex}) = \eta_{liq}(E_{ex})$$

within the limits of the result accuracy, while this quantity has different values for the solid and liquid states at identical temperatures. This value starts from

$$\eta(E_{ex} = 0) = 0.5,$$

where the system can be described in terms of harmonic oscillators and decreases monotonically with increasing the excitation energy because of the increasing role of anharmonicity of the dominant stretching modes[1]. Hence, the parameter η characterizes the influence of the anharmonicity in atomic motion of an isolated cluster as the excitation energy increases.

From these data, we have the excitation energy of the cluster liquid state,

$$\Delta E = \frac{K_{sol} - K_{liq}}{\eta(E_{ex})} = E_{ex}\left(1 - \frac{K_{liq}}{K_{sol}}\right) = 2.49 \pm 0.05. \quad (8)$$

Comparison of formula (8) with the data in Fig. 3 for the excitation energies at zero energy shows that the difference of these energies is not significant. In contrast to this, the ratio of the energy of void formation for bulk inert gases to the vacancy energy formation is approximately one half. The energy of void formation at the melting point $T_m = 0.29D$ allows us to find the entropy jump of the bulk system at the melting point

$$\Delta S_m = \frac{\Delta E}{T_m} = 8.6 \pm 0.2. \quad (9)$$

Comparing this with the entropy jump ΔS_0 of the cluster at zero temperature according to formula (1), we find

$$\frac{\Delta S_0}{\Delta S_m} \approx 0.6. \quad (10)$$

Thus, the different character of atom motion in the solid compact aggregate state and in the liquid aggregate state with its sparser distribution of atoms increases the entropy jump.

An isolated cluster, viewed as a microcanonical ensemble of atoms, is characterized by two temperatures if it can be found in two aggregate states only. These temperatures are determined by formula (6) for each aggregate state, and ignoring the anharmonicity, which gives $\eta = 0.5$, we use formula (8) to obtain the difference of the atomic temperatures T_{sol} and T_{liq} of the solid and liquid aggregate states near the melting point:

$$T_{sol} - T_{liq} = \frac{2\Delta E}{33} \approx 0.15D. \quad (11)$$

Figure 5 gives the values of these temperatures for the Lennard – Jones cluster of 13 atoms as a function of the cluster excitation energy, and these data follow from treatment of the computer simulation results [11] for this cluster. Along with these temperatures, we can introduce the configurational cluster temperature T_{ef} that follows from the equilibrium between the solid and liquid cluster states according to the formula

$$\frac{w_{liq}}{w_{sol}} = \exp\left(-\frac{\Delta F}{T_{ef}}\right) = \exp\left(-\frac{\Delta E}{T_{ef}} + \Delta S\right), \quad (12)$$

where w_{sol} and w_{liq} are the respective probabilities for the cluster to be found in the solid or liquid states and ΔF is the free energy jump at melting. The configurational temperature is determined by populations of the solid and liquid aggregate states. Figure 5 gives

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[1] Some modes, notably bending modes in molecules and, at high energies, high-frequency phonons in large clusters and solids, may have negative anharmonicities. For such systems, this line of reasoning requires further scrutiny. But for clusters of at least several hundred atoms, it is a valid assumption that the anharmonicity reduces the spacing of the relevant modes as the energy increases.

the dependence of the configurational temperature on the cluster excitation energy. The configurational temperature tends to the solid temperature in the limit of low temperatures, and to the liquid temperature in the limit of high temperatures.

4. CONFIGURATIONAL EXCITATION OF THE ICOSAHEDRAL CLUSTER OF 55 ATOMS

We consider a cluster as a member of a canonical ensemble [41], when it is maintained under isothermal conditions. Experimentally [46–49], this condition can be reached when clusters are located in a gas of light (usually, helium) atoms that collide with clusters and metallic walls maintained at a certain temperature. Collisions establish the wall temperature for each cluster if the typical time for equilibration to a gas temperature as a result of collisions with the atomic heat bath is short compared to a typical dwell time of the cluster in each aggregate state. As earlier, we assume the existence of the two aggregate states [42–44] and use the dynamic coexistence of phases in clusters [11, 50–52] within a temperature range; in other words, we assume that part of the time, the cluster is found in one aggregate state and in the remainder, it is found in the other. In addition, while the cluster is in each aggregate state, vibrational equilibrium is established [25], and hence the temperature of bound atoms for each aggregate state coincides with the thermostat temperature if the cluster is in a canonical ensemble [41]. In this case, the probability w_{liq} that the cluster is found in the liquid state is given by the formula [18, 43, 44]

$$\begin{gathered} w_{liq} = \frac{p}{1+p}, \\ p = \exp\left(-\frac{\Delta F}{T}\right) = \exp\left(\Delta S - \frac{\Delta E}{T}\right), \end{gathered} \tag{13}$$

where T is the cluster temperature (which coincides with the thermostat temperature), ΔE is the energy of configurational excitation, ΔS is the entropy jump as a result of melting, and ΔF is a change of the free energy. The parameters of the phase transition ΔE and ΔS determine the behavior of the cluster heat capacity, which we connect with the cluster heat capacity that can be calculated from computer simulations. Using the average kinetic energy of atoms for each aggregate state, we characterize each of those states by the mean potential energy, i.e., we ignore the broadening of the energy of each cluster state due to fluctuations.

We first determine the cluster heat capacity and separate its «resonance» part, the peak due to the phase transition. According to formula (5), we have

$$E = -E_0 + \frac{K_{sol}}{\eta_{sol}} w_{sol} + \Delta E w_{liq} + \frac{K_{liq}}{\eta_{liq}} w_{liq}, \tag{14}$$

and because the cluster is in a thermostat, $K_{sol} = K_{liq}$. Assuming that $\eta_{sol} = \eta_{liq}$, we obtain the average cluster energy according to formula (14),

$$E = \frac{K_{sol}}{\eta_{sol}} + \Delta E w_{liq} = \frac{K_{sol}}{\eta_{sol}} + \Delta E \frac{p}{1+p}. \tag{15}$$

We first consider the Lennard – Jones cluster of 13 atoms in a thermostat. We note that the anharmonicity of atomic oscillations affects the degree of the configurational excitation. Indeed, because the anharmonicity is greater for the liquid than for the solid cluster, the density of vibrational states increases faster with energy than does that of the solid, and therefore the average potential energy for the isothermal liquid cluster is higher than that for the solid. If the melting temperatures for the isolated and isothermal clusters are approximately equal (as they are for clusters of ca. 100 atoms or more), we find a special excess change of the cluster's potential energy in the isothermal case that does not appear in the constant-energy case. Taking the melting point $T_m = 0.29D$ for both cases and the corresponding kinetic energies at this temperature to be

$$K_{sol}(T_m) = K_{liq}(T_m) \approx 2.9D,$$

we find the excess excitation energy $\Delta E'$ as a change of the average potential energy per atom given by

$$\begin{gathered} \Delta E' = \Delta E + \frac{K_{liq}(T_m)}{\eta_{liq}(T_m)} - \frac{K_{sol}(T_m)}{\eta_{sol}(T_m)} = \Delta E + \\ + K_{sol}(T_m)\left[\frac{1}{\eta(15.3D)} - \frac{1}{\eta(11.7D)}\right] = 3.1D, \end{gathered} \tag{16}$$

where $\Delta E = 2.5D$ is the energy difference for aggregate states of an isolated cluster at the melting point. We here assume that the anharmonicity parameter η is identical for both aggregate states of an isolated cluster, and its dependence on the excitation energy is given in Fig. 4. Next, the dependence of the temperature of a given aggregate state on the excitation energy is represented in Fig. 5, and, as indicated in formula (16), the excitation energies of isolated clusters correspond to the temperature $0.29D$ for each aggregate state. Therefore, the anharmonicity of the solid aggregate state under isothermal conditions is higher than that for an isolated cluster, whereas for the liquid state, we have a different relation between these values. As a result, the

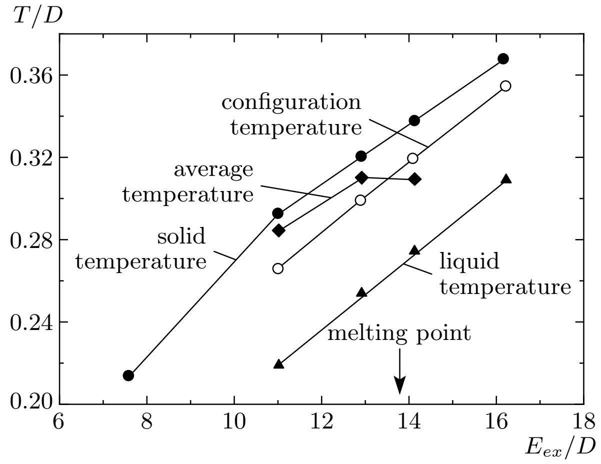

Fig. 5. Temperatures of the Lennard – Jones cluster of 13 atoms depending on the excitation energy (the temperatures of the solid and liquid aggregate states, average transversal temperature, and configuration temperature)

isothermal phase transition requires a greater change of potential energy than that at constant energy, due to interactions between atoms for the Lennard – Jones 13-atom cluster. Due to the anharmonicity, the energy change for an isothermal cluster exceeds that of the isolated cluster approximately by 20 %.

We next analyze the temperature dependence of the heat capacity under isothermal conditions. We represent the cluster heat capacity in the isothermal case as [53, 54]

$$C = \frac{dE}{dT} = C_0 + \frac{d\left(\Delta E w_{liq}\right)}{dT}, \tag{17}$$

where the first term characterizes the cluster's heat capacity in the absence of the phase transition,

$$C_0 = \frac{d\left(K_{sol}/\eta_{sol}\right)}{dT} = \frac{d\left(K_{liq}/\eta_{liq}\right)}{dT}, \tag{18}$$

and the resonance part of the heat capacity is

$$C_{res} = \frac{d\left(\Delta E w_{liq}\right)}{dT} = \frac{\Delta E^2}{T^2}\,\frac{p}{(1+p)^2}. \tag{19}$$

We here assume that the energy of configurational excitation ΔE and the entropy jump ΔS are independent of the temperature. Formula (19) leads to the maximum C_{res}^{max} at the melting point T_m defined in this case as $p(T_m) = 1$. We have

$$C_{res}^{max} = \frac{\Delta E^2}{4T_m^2} = \frac{\Delta S^2}{4}. \tag{20}$$

To account for the temperature dependence of the entropy jump, we represent it as

$$\Delta S = \Delta S_0 + aT, \tag{21}$$

where ΔS_0 is the entropy jump at zero temperature. At the melting point, this gives

$$a = \frac{\Delta S_m - \Delta S_0}{T_m}, \tag{22}$$

where ΔS_m is the entropy jump at the melting point. On the basis of formulas (13) and (19), we obtain the resonant part of the heat capacity:

$$C_{res}^{max} = \frac{\Delta E}{(1+p)^2}\frac{dp}{dT} = \Delta E\frac{p}{(1+p)^2} \times \left(\frac{d\Delta S}{dT} + \frac{\Delta E}{T_m^2}\right) = \frac{\Delta S_m^2}{2} - \frac{1}{4}\Delta S_0 \Delta S_m. \tag{23}$$

Because numerical calculations by the molecular dynamics method allow one to determine the heat capacity maximum, this relation can be used for evaluating the entropy at zero temperature as

$$\Delta S_0 = 2\Delta S_m - \frac{4C_{res}^{max}}{\Delta S_m}. \tag{24}$$

We now use this formula for the Lennard – Jones cluster of 55 atoms. As our basis, we take computer simulations of this cluster in [28, 55, 56], which give the parameters characterizing the phase transition within the ranges

$$\Delta E = 15 \pm 1, \quad \frac{T_m}{D} = 0.31 \pm 0.01, \quad C_{res}^{max} = 650 \pm 50.$$

From this, we have

$$\Delta S_m = \frac{\Delta E}{T_m} = 48 \pm 5. \tag{25}$$

On the basis of formula (24), we have

$$\Delta S_0 = 36 \pm 15. \tag{26}$$

The large uncertainty here makes this result relatively uninformative. We need a way to do better.

We now determine the entropy jump at zero temperature from another standpoint. The energy of formation of one vacancy at zero temperature can be found by comparing the total binding energies of atoms ε_{55} and ε_{56} for the Lennard – Jones clusters of 55 and 56 atoms. On the basis of calculations in [57] for ε_{55} and ε_{56}, we have [43]

$$\Delta\varepsilon = \varepsilon_{56} - \varepsilon_{55} = 2.64D$$

at zero temperature. The direct calculations for lower excitations of this cluster [58] lead to the minimal excitation energy $2.63D$. The proximity of these values confirms that an excited atom transferred onto the cluster surface can be treated as being well removed from the vacancy from which it came. Evidently, the energy of void formation, the relaxed form, is less than the energy $\Delta\varepsilon$ of formation of the initial vacancy. This implies that the number of atoms leaving the body of the cluster to form voids is

$$v \geq \frac{\Delta E}{\Delta\varepsilon} \approx 5. \qquad (27)$$

Taking the number of voids in the liquid state of the Lennard – Jones cluster of 55 atoms to be $v = 5$–7, we determine the entropy jump at zero temperature ΔS_0 as we treat the solid–liquid transition to be a consequence of transitions of atoms from the outer cluster shell onto its surface. Because of the icosahedral structure of this cluster, its outermost shell consists of 42 atoms, and there are 80 positions with 3-atom «hollows» on the surface for atoms promoted from the outer shell. A new vacancy on the cluster edge or surface has $l = 6$ neighboring atoms, and a vertex vacancy has only $l = 5$. Therefore, if v atoms transfer onto the cluster surface, then vl bonds are lost in the cluster surface for atoms transferred to any of the 80 positions on the cluster surface if we assume that v transferring atoms on the cluster surface do not border vacancies on the cluster shell. From this, for the configurational excitation of the cluster at zero temperature, we find the entropy jump that results from v atoms moving from the outermost shell,

$$\Delta S_0 = \ln C_m^v C_{42}^v,$$

where $m = 80 - vl$ is the number of positions on the cluster surface for transition of atoms from the outermost cluster shell. This formula implies that the entropy jump at zero temperature is

$$\Delta S_0 = 28.5 \pm 0.3 \quad \text{for} \quad v = 5,$$

$$\Delta S_0 = 31.6 \pm 0.4 \quad \text{for} \quad v = 6,$$

$$\Delta S_0 = 32.3 \pm 0.7 \quad \text{for} \quad v = 7.$$

Thus, the entropy jump at zero temperature depends weakly on the number of transferred atoms, and the average value of the entropy jump at zero temperature is

$$\Delta S_0 = 31 \pm 2. \qquad (28)$$

One can see that this value is well within the range in formula (26). Because the accuracy is higher in this case than in formula (26), we use formula (24) for determination of ΔS_m. Then formula (24) gives

$$\Delta S_m = \frac{\Delta S_0}{4} + \sqrt{\frac{\Delta S_0^2}{16} + 2C_{res}^{max}}, \qquad (29)$$

and on the basis of formula (28) and the calculated maximal heat capacity

$$C_{res}^{max} = 650 \pm 50,$$

we obtain

$$\Delta S_m = \frac{\Delta E}{T_m} = 45 \pm 2. \qquad (30)$$

This result, together with its validity range, is consistent with formula (25), but we now have a result with greater precision and presumably with greater accuracy. Thus the analysis of computer simulations of these clusters by molecular dynamics allows us to determine some thermodynamical parameters of the phase transition within the framework of a simple scheme. Below, we analyze these results together with the microscopic nature of the phase transitions.

5. CHARACTER OF PHASE TRANSITIONS IN SIMPLE ENSEMBLES OF BOUND ATOMS

The nature of the order–disorder phase transition for an ensemble of bound atoms may be understood on the basis of the lattice model (see, e.g., [6, 59, 60]). Within this model, atoms are located at sites of a crystal lattice and interaction occurs only between nearest neighbors. Then the ordered state is a compact distribution of atoms, which leads to a maximum number of bonds between nearest-neighbor atoms, and the disordered state with a random distribution of atoms corresponds to a maximum entropy and to a loss of some of the bonds between nearest neighbors that occur in the ordered state. The phase transition between these states proceeds by a stepwise change of the total atomic binding energy and the entropy of the evolving distribution. This order–disorder phase transition models the solid–liquid phase transition for an ensemble of bound atoms, with the ordered state being analogous to the solid state and the disordered state analogous to the liquid state. Because this phase transition involves a change of the atomic configuration, the passage to the disordered state occurs by configurational excitation of the system. One can see that the lattice model for configurational excitation of such a system is a simplified void model, in which a void is considered equivalent to a vacancy and additional assumptions are used. Thus, the conclusions following from the lattice model generally apply also to the void model of configuration excitation.

In considering a phase change of clusters, we invoke a certain hierarchy of times for establishment of the various equilibria along the path to the overall transition. We now exhibit the validity of the hierarchy of times in clusters that was the basis of the argument. We assume that a typical time to establish thermal (vibrational) equilibrium in clusters, τ_0, is short compared to a typical time of transition between aggregate states. Roughly, we have $\tau_0 \sim 1/\omega_D$, where ω_D is the Debye frequency. To estimate the time needed for an atom promoted to the cluster surface to move from one position to another or to its ground-state location, we assume for simplicity that all atom positions are separated by identical barriers. Moreover, we take the barrier height to be $U_0 = 0.56D$, as it is at zero temperature (see Fig. 3), even though a temperature increase leads to a decrease of these barriers. A transition of an atom in a three-contact hollow on the cluster surface may proceed in one of the three directions through a triangular transition state, joined there to two nearest neighbors. With τ denoting the transition time to a neighboring position on the cluster surface, we find the mean transition time to the ground state to be 9τ. Thus, under these assumptions, we infer that transitions between different configurational states proceed faster by an order of magnitude than a transition from the surface to a vacancy in the outer shell, normally occupied in the solid state. This allows us to join all the different configurational excitations for promotion of one atom from the outermost shell onto the cluster surface in one liquid aggregate state.

We now estimate the time τ of transition between neighboring positions on the cluster surface on the basis of the Frenkel model [61], according to which the transition occurs if the atomic oscillation energy exceeds the barrier height. Assuming for simplicity that the barrier has an axial symmetry, we take it in the form

$$U(\rho) = U_0 + \frac{1}{2}\frac{d^2U}{d\rho^2}\rho^2,$$

where ρ is the distance from the point of the barrier minimum in the saddle plane. From this, we find the transition rate

$$\nu = \frac{1}{\tau_0}\frac{1}{4\pi R^2}\int\limits_0^\infty 2\pi\rho\,d\rho\,\exp\left[-\frac{U(\rho)}{T}\right] = \\ = \frac{T}{2R^2\dfrac{d^2U}{d\rho^2}}\exp\left(-\frac{U_0}{T}\right), \quad (31)$$

where T is the current temperature and R is the distance between an atom and the saddle point. Taking

$$\frac{d^2U}{d\rho^2} \sim \frac{D}{R^2}$$

for an estimate, we obtain

$$\tau = \frac{1}{\nu} \sim 50\tau_0 \quad (32)$$

at the melting point $T_m = 0.29D$. Thus, the hierarchy of times is as we used above.

Consequently, we have three typical times that are of importance near the melting point, where the rates of the phase transition in both directions are similar. These times are the time τ_0 of equilibrium establishment for transversal degrees of freedom, during which a definite vibrational temperature is established depending on the aggregate state; the typical time τ for transition between neighboring configurationally excited states; and the typical time of transition between aggregate states. The last is the longest one, but during the time τ, an equilibrium is established within the liquid state. This reflects the lability of that state. We note that from the standpoint of void formation, the case of a 13-atom cluster is special because the liquid aggregate state involves formation of only one void in this case. For larger clusters, the time of transition between the aggregate states is increased in comparison with times of transition between neighboring configurationally excited states. We demonstrate this for a 55-atom cluster, assuming that the number of voids $v = 6$ is the optimal one for the liquid state. This means that the total probability for the cluster to be in any of the configurationally excited states with $v = 5$ is less than for $v = 6$, and for $v = 4$ is still less than that for $v = 5$. To reach the solid aggregate state starting from the liquid, this cluster must pass through configurationally excited states with small probabilities of occurrence, and hence, in most histories, the cluster returns to its initial liquid state many times and eventually reaches the other, solid aggregate state. This means that a typical time of transition between aggregate states is very long compared with the time for passage between neighboring configurationally excited states, particularly in the case of large clusters. Thus, the dynamic coexistence of phases in clusters proceeds such that the vibrational temperature is established fast, next an equilibrium is established between configurationally excited states of the liquid phase, and then the phase transition can proceed during longer times.

At zero temperature, the vacancy and the relaxed void become equivalent if we neglect the vacancy–atom

Parameters of melting for atomic clusters and macroscopic inert gases

	LJ_{13}	LJ_{55}	bulk inert gases
T_m/D	0.29	0.31	0.58
$\Delta E/D$	2.5	16 ± 1	$0.98n$
$(T_{sol} - T_{liq})/T_m$	0.22	0.31 ± 0.02	0.56
ΔS_0	5.2	31 ± 2	$0.73n$
ΔS_m	8.6	48 ± 4	$1.68n$
$\Delta S_0/\Delta S_m$, %	60	65 ± 10	44

interaction. Real parameters of voids take this interaction into account, and hence the relaxation has its effect on the thermal motion of atoms upon configurational excitation. Of course, the lower the temperature, the less is the configurational excitation and the less is the vibrational excitation as well. Evidently, the separation of the configurational excitation from thermal vibrations of atoms that we have used is valid only at low to moderate temperatures, and is better for clusters with completed outer shells than for others. Therefore, we use the void concept primarily for clusters with complete shells, such as those consisting of 7, 13, 19, 55, 147, … atoms. In these cases, there is a solid–liquid coexistence region of temperature and pressure within which the probability distribution of the total kinetic energy is distinctly bimodal [11, 26] for an isolated cluster. The occurrence and persistence of these two aggregate states allows us to use the approach of two aggregate states [44], which is an analogue of the solid and liquid aggregate states for bulk systems. We note that in reality, several types of configurational excitations can be observed that correspond to excitation of different cluster shells [27, 28].

Next, for some clusters with incomplete outer shells, thermodynamically stable states of configurational excitation are absent, in particular, for clusters consisting of 8 and 14 atoms [26], because only a small entropy (and free energy) jump separates the states; this is much the same situation as occurs with excited states of atoms with open shells. Therefore, the real behavior of excitations of open-shell clusters with pair interactions may be more complicated than that within the framework of the void model of a cluster with two aggregate states. Nevertheless, this model is useful for understanding and description of the clusters with a pairwise atomic interaction.

The table presents some parameters for the liquid states of Lennard–Jones clusters consisting of 13 and 55 atoms, which we obtained from the analysis of the results of molecular dynamics computer simulations. In this table, LJ_n is a cluster consisting of n atoms with the Lennard–Jones interaction potential, D is the depth of the potential well, T_m is the melting point, ΔE is the phase transition energy for an isolated cluster at the melting point, T_{sol} and T_{liq} are the effective (kinetic-energy-based) temperatures of the solid and liquid states for an isolated cluster at the melting point, and ΔS_0 and ΔS_m are the respective entropy jumps for the phase transition at zero temperature and the melting point. In determining the difference $T_{sol} - T_{liq}$, we assume the heat capacity for each aggregate state to be given by the Dulong–Petit law.

In the table, we also include the parameters of bulk inert gases consisting of n atoms, which were found [15–17, 19] on the basis of measured parameters of condensed inert gases and are averaged over classical inert gases (Ne, Ar, Kr, Xe). Then the reduced entropy jump in inert gases near the triple point is

$$\Delta S_m/n = 1.68 \pm 0.03$$

[18, 43, 62]. Considering the entropy jump at zero temperature as a result of vacancy formation in a solid, we then obtain

$$\Delta S_0 = \ln C_{n+v}^{v} = n \ln \frac{n+v}{n} + v \ln \frac{n+v}{v}, \qquad (33)$$

where n is the number of atoms in the system, v is the number of vacancies, and C_{n+v}^{v} is the number of ways to remove v atoms from the initial lattice containing $n+v$ atoms. For condensed inert gases [15–17, 19], we have

$$n/v = 3.12 \pm 0.01,$$

which gives

$$\Delta S_0/n = 0.73$$

as included in the table.

It follows from the data in the table that in all the cases under consideration, the atomic thermal motion makes a very large contribution to the entropy jump at the melting point. This effect is very important because it holds down the temperature of the phase transition or even makes it possible at all, in principle. In addition, the thermal contribution to the entropy jump can solve the paradox of the phase transition, which we now consider. In practice, it is convenient to use the Lindemann criterion [29, 30] for the melting point of an ensemble of bound atoms. According to this criterion, melting starts if the ratio of the amplitude of atom oscillations to the distance between nearest neighbors reaches a value in the range 0.10–0.15. With computer modelling of clusters, more precise criteria of the phase transition were introduced, using the correlations in positions of two cluster atoms. In particular, this correlation function can use the Etters – Kaelberer parameter [31–33] or the Berry parameter [12, 34]. These parameters are proportional to the mean fluctuation of the distance between two atoms, which, similarly to the Lindemann index, falls into different ranges for the solid and liquid states; this difference allows us to distinguish a cluster's state. These parameters are connected with thermal motion of atoms, while the melting, i.e., the lability of the liquid, results from configurational excitation of an ensemble of bound atoms.

One can see an apparent contradiction between the nature of the phase transition that we attribute to configurational excitation and the practical criterion signifying this transition, which is based on thermal motion of atoms. This contradiction disappears when we account for the influence of thermal excitation on the entropy of this transition in accordance with formula (21). The second part of this formula accounts for the apparent paradox of the thermal motion in the entropy jump, and hence, if we understand the origin of the paradox, the amplitude-based criteria of the phase transition become natural. The nature of this term results from the lower density of atoms in the liquid state and from the associated larger entropy of the atomic vibrations. Naturally, the entropy jump due to vibrations of atoms increases with increasing the temperature. Thus, although the method of calculation separates configurational excitation from the thermal motion of the bound atoms, the latter gives a contribution to the entropy change of the transition.

We conclude that because thermal motion of atoms gives a significant contribution to the entropy jump, this effect improves conditions of the phase transition or can even be a required condition for the phase transition. When we consider a bulk system of bound atoms, we base our argument on the model in which the liquid state is formed from the solid state by removal of internal atoms. Then the system relaxes to the liquid state by shrinking, such that vacancies of the crystal lattice are transformed into voids. The entropy of this configurational excitation follows from this intermediate state with vacancies, and the void concept [14] describes the phase transition. Using the void concept for the analysis of the phase transitions allows one to understand its nature more deeply.

6. CONCLUSIONS

The void concept for configurational excitation of ensembles of bound atoms is the basis for their analysis. This concept follows from a general approach of local minima of the potential energy surface for an ensemble of interacting atoms [20]; a simplified version of this approach allows us to analyze the results of cluster computer simulations by molecular dynamics. On the basis of this analysis, we can understand some aspects of the behavior of ensembles of bound atoms at the phase transition in detail. In particular, there is a difference in the transition parameters for an isolated cluster at constant energy and a similar cluster in a thermostat. The entropy jump of the phase transition includes two contributions, both of which are important: the thermal, virational motion of atoms (because the solid state is characterized by a more compact distribution and correspondingly by a lower entropy than the liquid aggregate state at this temperature) and the configurational excitation that introduces the voids, providing the basis of the fluidity of the liquid. The thermal effect in the entropy jump at the phase transition provides the validity of melting criteria based on thermal motion of atoms, whereas the «nature» of the phase transition consists in the configurational excitation.

The void concept for configurational excitation of ensembles of bound atoms, interpreted with the help of the results of computer simulations and thermodynamic parameters of condensed inert gases, gives a deepened understanding of the phase transition in these ensembles.

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REFERENCES

1. O. Echt, K. Satler, and E. Recknagel, Phys. Rev. Lett. **94**, 54 (1981).
2. O. Echt et al., Ber. Bunsenges. Phys. Chem. **86**, 860 (1982).
3. J. Xie, J. A. Northby, D. L. Freemann, and J. P. Doll, J. Chem. Phys. **91**, 612 (1989).
4. K. Huang, *Statistical Mechanics*, Wiley, New York (1963).
5. R. Brout, *Phase Transitions*, Benjamin Inc., New York (1965).

6. R. Kubo, *Statistical Mechanics*, North Holland, Amsterdam (1965).

7. D. Ter Haar and H. Wergeland, *Elements of Thermodynamics*, Addison-Wesley, New York (1966).

8. R. P. Feynman, *Statistical Mechanics*, Benjamin Inc., Massachusetts (1972).

9. L. D. Landau and E. M. Lifshits, *Statistical Physics*, Vol. 1, Pergamon Press, Oxford (1980).

10. R. S. Berry, J. Jellinek, and G. Natanson, Phys. Rev. A **30**, 919 (1984).

11. J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986).

12. R. S. Berry, T. L. Beck, H. L. Davis, and J. Jellinek, Adv. Chem. Phys. **90**, 75 (1988).

13. R. S. Berry, in *Theory of Atomic and Molecular Clusters*, ed. by J. Jellinek, Springer, Berlin (1999), p. 1.

14. H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

15. B. M. Smirnov, Zh. Eksp. Teor. Fiz. **112**, 1847 (1997).

16. B. M. Smirnov, Inorg. Mater. **35**, 562 (1999).

17. B. M. Smirnov, in *Nucleation Theory and Applications*, ed. by J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev, JINR, Dubna (1999), p. 355.

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

19. R. S. Berry and B. M. Smirnov, in *Nucleation Theory and Applications*, ed. by J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev, JINR, Dubna (2002), p. 340.

20. D. Wales, *Energy Landscapes*, Cambridge Univ. Press, Cambridge (2003).

21. D. S. Corti, P. G. Debenedetti, S. Sastry, and F. H. Stillinger, Phys. Rev. E **55**, 5522 (1997).

22. K. D. Ball and R. S. Berry, J. Chem. Phys. **111**, 2060 (1999).

23. T. Komatsuzaki and R. S. Berry, J. Chem. Phys. **110**, 9160 (1999).

24. D. J. Wales, J. P. K. Doye, M. A. Miller, P. N. Mortenson, and T. R. Walsh, Adv. Chem. Phys. **115**, 1 (2000).

25. B. Vekhter and R. S. Berry, J. Chem. Phys. **106**, 4644 (1997).

26. T. L. Beck, J. Jellinek, and R. S. Berry, J. Chem. Phys. **87**, 545 (1987).

27. R. E. Kunz and R. S. Berry, Phys. Rev. Lett. **71**, 3987 (1993).

28. R. E. Kunz and R. S. Berry, Phys. Rev. E **49**, 1895 (1994).

29. F. A. Lindemann, Z. Phys. **11**, 609 (1910).

30. J. P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).

31. R. D. Etters and J. B. Kaelberer, Phys. Rev. A **11**, 1068 (1975).

32. R. D. Etters and J. B. Kaelberer, J. Chem. Phys. **66**, 5512 (1977).

33. J. B. Kaelberer and R. D. Etters, J. Chem. Phys. **66**, 3233 (1977).

34. Y. Zhou, M. Karplus, K. D. Ball, and R. S. Berry, J. Chem. Phys. **116**, 2323 (2002).

35. M. R. Hoare and P. Pal, Adv. Phys. **20**, 161 (1971).

36. M. R. Hoare and P. Pal, Adv. Phys. **24**, 645 (1975).

37. M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).

38. F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).

39. F. H. Stillinger and T. A. Weber, Phys. Rev. A **28**, 2408 (1983).

40. D. J. Wales and R. S. Berry, J. Chem. Phys. **92**, 4283 (1990).

41. D. ter Haar, *Elements of Thermostatics*, Addison-Wesley, New York (1966).

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

43. B. M. Smirnov, Uspekhi Fiz. Nauk **37**, 1079 (1994).

44. R. S. Berry and B. M. Smirnov, J. Chem. Phys. **114**, 6816 (2001).

45. R. S. Berry, submitted to Israel J. Chem. (2004).

46. M. Schmidt, R. Kusche, W. Krommüller et al., Phys. Rev. Lett. **79**, 99 (1997).

47. M. Schmidt, R. Kusche, B. von Issendorf et al., Nature **393**, 238 (1998).

48. M. Schmidt, R. Kusche, T. Hippler et al., Phys. Rev. Lett. **86**, 1191 (2001).

49. M. Schmidt, T. Hippler, J. Donges et al., Phys. Rev. Lett. **87**, 203402 (2001).

50. G. Natanson, F. Amar, and R. S. Berry, J. Chem. Phys. **78**, 39 (1983).

51. J. Jellinek, T. L. Beck, and R. S. Berry, Chem. Phys. Lett. **107**, 227 (1984).

52. R. S. Berry, Chem. Rev. **93**, 2379 (1993).

53. R. S. Berry and B. M. Smirnov, Zh. Eksp. Teor. Fiz. **120**, 889 (2001).

54. R. S. Berry and B. M. Smirnov, Zh. Eksp. Teor. Fiz. **125**, 414 (2004).

55. P. Labastie and R. L. Whetten, Phys. Rev. Lett. **65**, 1567 (1990).

56. H. P. Cheng and R. S. Berry, Phys. Rev. A **45**, 7969 (1992).

57. J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).

58. D. J. Wales, Chem. Phys. Lett. **166**, 419 (1990).

59. W. Bragg and H. J. Williams, Proc. Roy. Soc. A **145**, 699 (1934).

60. J. M. Ziman, *Models of Disorder*, Cambridge Univ. Press, Cambridge (1979).

61. Ya. I. Frenkel, *Kinetic Theory of Liquids*, Oxford University Press, Oxford (1946).

62. B. M. Smirnov, Uspekhi Fiz. Nauk **44**, 1229 (2001).