

The liquid state of large clusters with pairwise atomic interactions

R.S. Berry^{a,*}, B.M. Smirnov^b

^a *Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, IL 60637, USA*

^b *Institute for High Temperatures, Izorskaya 13/19, Moscow 127412, Russia*

Abstract

Formation of the liquid state for clusters with a pair interaction 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 and from real thermodynamic parameters of the liquid states of condensed inert gases. Phase transitions are analyzed in terms of two aggregate states. This information allows us to divide the entropy jump during the solid–liquid phase transitions in two parts, so that one corresponds to configuration excitation at zero temperature, and the other is a contribution from thermal vibrations of atoms. The latter part contributes from approximately 40% for Lennard-Jones clusters consisting of 13 and 55 atoms up to 56% for bulk inert gases. These magnitudes explain the validity of melting criteria based on thermal motion of atoms, even though this phase transition results from configurational excitation of ensembles of bound atoms. It is shown that the void concept allows us to analyze various aspects of the liquid state of clusters including the existence of the freezing temperature below which no metastable liquid state exists, and the properties of glassy states which may exist below the freezing point.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

We analyze systems of bound atoms bound by pairwise interactions. The pairwise character and magnitude of the interaction means that interaction energies of one atom with other atoms of a cluster is small compared with a typical electronic energy. This criterion holds true for clusters of inert gas atoms and clusters of gaseous molecules normally found in a gaseous state under everyday conditions. For this analysis we will use the results of computer simulation for clusters interacting through the Lennard-Jones potential and the parameters of condensed inert gases for bulk systems of bound atoms. We will focus 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 ‘magic numbers’ of cluster

atoms, that reveal themselves experimentally by heightened populations and stabilities, as, for example [1–3]. Magic numbers correspond typically to completed atomic shells of the favorable structures [4–12]. As a result of melting, the crystal distribution of atoms is lost, and the liquid state has more or less an 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 clusters and bulk systems on the basis of appropriate models.

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 one can consider the cluster’s transition from solid to liquid as a result of formation of voids inside the cluster [13]. A void is a perturbed vacancy; in contrast to a vacancy in a solid, a void has an indefinite volume and shape which change in time. The concept of an average void is useful if the configuration excitation of atoms can

* Corresponding author. Tel.: +1 773 702 7021; fax: +1 773 834 4049.
E-mail address: berry@uchicago.edu (R.S. Berry).

be separated from the vibrational excitation associated with an increase of the kinetic energy of the atoms. Such an assumption follows from the study of the potential energy surface of a system of bound atoms in a multidimensional space of atomic coordinates [14–18] that consists of many potential wells which are separated by saddles. In this phase space a cluster is found long enough near a minimum of the potential energy to equilibrate its vibrations, and transition to the neighboring minimum proceeds relatively slowly by comparison [19]. First, this leads to a short-range, short-duration order for any amorphous structure of atoms, since each configuration of atoms is preserved relatively long (so long as the atomic kinetic energy is not very large). Second, this allows us to introduce an average void by averaging parameters over times which exceed a typical vibrational period. Using the void model for bulk liquid and clusters, we analyze some properties of these systems.

2. Parameters of configurational excitation of clusters

Thus we divide cluster excitation into configuration and vibration parts and consider these parts to be independent. Next, for configurational excitation we use the void model, considering this excitation as a result of formation of voids. Then one can express the parameters of the phase transition and other cluster properties through parameters of forming voids. We start the analysis of configurational excitation from the simplest cluster with completed shells, the icosahedron of 13 atoms. In its state of lowest energy, its first (and only) shell is filled. We find the void parameters from computer simulation of this cluster with Lennard-Jones interaction between atoms. We consider this cluster to be in a microcanonical ensemble [20]. We reduce this analysis to a motion of a point in a phase space of atomic coordinates along a potential energy surface. The potential energy surface for a cluster contains many minima separated by saddles; the number of local minima increases sharply with cluster size [4,5,14,21,22]. Hence one can describe the cluster's evolution as a result of transitions between local minima of the potential energy surface, that correspond to saddle-crossing dynamics [15–18]. Within the framework of this description, the cluster remains near a given minimum of the potential energy surface relatively long, provided its average total kinetic energy is lower than the typical saddle heights. This means that a configurational state of this system can be characterized by the local minimum of the potential energy surface where the cluster is found, and does not depend on the kinetic energy of atoms. In other words, one can separate the configuration and vibration cluster excitations as independent degrees of freedom. Therefore, one can consider the configurational excitation independent of vibra-

tional excitations. This is the basis of the following analysis.

Assuming the motion of atoms to be classical, we represent the energy E of a cluster consisting of n atoms with a pair interaction between them in the form

$$E = U + K = \sum_{i,j} u(\mathbf{r}_{ij}) + \frac{m}{2} \sum_i \left(\frac{d\mathbf{r}_i}{dt} \right)^2. \quad (1)$$

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 $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, so that \mathbf{r}_i , \mathbf{r}_j are the atomic coordinates, and m is the atomic mass. This formula is the basis of our computer simulations of clusters. Let us consider the properties of two terms of this formula, taking into account that thermal equilibrium is established for atomic vibrations as it usually takes place. This allows one to introduce the atomic temperature T , considering the motion of atoms as that of a set of harmonic oscillators. In particular, in the limit of high temperatures, when a typical kinetic energy of atoms significantly exceeds a typical vibrational energy (or the Debye temperature), the Dulong–Petit law is valid, according to which

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

where $n \gg 1$. We will focus on conditions well below this limiting case. The global minimum of the complex potential energy surface corresponds to the cluster's ground state, its equilibrium state at zero temperature. Transitions from the global minimum to other local minima, corresponding to configurational excitations of the cluster, are responsible for a phase transition, whether from one solid form to another or from solid to liquid.

We now analyze the results of computer simulation of the Lennard-Jones cluster of 13 atoms [23], where this cluster is considered as a member of a microcanonical ensemble, i.e. the total cluster energy is conserved during the cluster's evolution. In a particular band of energies, the total kinetic energy of the cluster takes on a bimodal distribution; in that range, one can treat the results of computer simulation [23] in terms of a dynamic equilibrium of two aggregate states. It was fulfilled partially in [12,24,30], and below we give the results of this treatment. The structure of the ground state of this cluster [25] at zero temperature and the character of its configurational excitation in the lowest excited states is shown in Fig. 1. Fig. 2 gives the energies of these states at zero temperature and the values of barriers which separate them [26]. As a result of configurational excitation, an atom transfers from the shell of 12 atoms onto the hollow between three atoms on the cluster surface, as shown in Fig. 1. For this transition an atom must overcome a barrier; likewise, transitions to other positions on the cluster surface are accompanied by overcoming

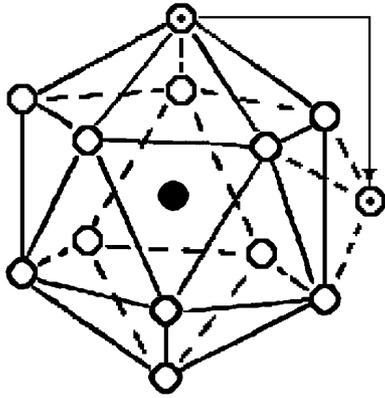


Fig. 1. The character of the lowest configuration excitation in the icosahedral cluster consisting of 13 atoms at zero temperature.

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 transition of one atom are connected in the liquid state, so the system may find all permutations among the atoms of any attainable structure. This follows from the data of Fig. 2.

Let us represent formula (1) in the form

$$E = -E_0 + E_{ex} = U'_{sol} + K_{sol} = \Delta E + U'_{liq} + K_{liq}, \quad (3)$$

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} , U'_{liq} are the average potential energies of the cluster for a given local well of the potential surface, and ΔE is an average excitation energy to produce the liquid aggregate state. Within the framework of this consideration, we join nearby local minima of the cluster potential energy into one aggregate state,

assuming transitions between local minima of the same aggregate state to be more effective than transitions between states which belong to different aggregate states.

We introduce the effective temperature for a given aggregate state of the cluster on the basis of a formula transformed from formula (1):

$$T = \frac{2}{3n - 6}, \quad K = \frac{2K}{33}, \quad (4)$$

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

$$\eta_{sol} = \frac{K_{sol}}{E_{ex}}, \quad \eta_{liq} = \frac{K_{liq}}{E_{ex} - \Delta E} \quad (5)$$

If atomic motion is a combination of harmonic oscillators, we have $\eta = 0.5$. Anharmonicity of the oscillations typically leads to a decrease of this value, and $\eta(E_{ex})$ decreases with an increase of E_{ex} . Fig. 3 gives this dependence which was obtained in [24] on the basis of computer simulation [23]. Note that $\eta_{sol}(E_{ex}) = \eta_{liq}(E_{ex})$ within the limits of their 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 excitation energy because of the increasing role of anharmonicity. Hence the parameter η characterizes 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,

$$\Delta E = \frac{K_{sol} - K_{liq}}{\eta(E_{ex})} = E_{ex} \left(1 - \frac{K_{liq}}{K_{sol}} \right) = 2.49 \pm 0.05. \quad (6)$$

This shows that the entropy jump ΔS_m at the melting point $T_m = 0.29D$ is equal to $\Delta S_m = 8.6 \pm 0.2$ according

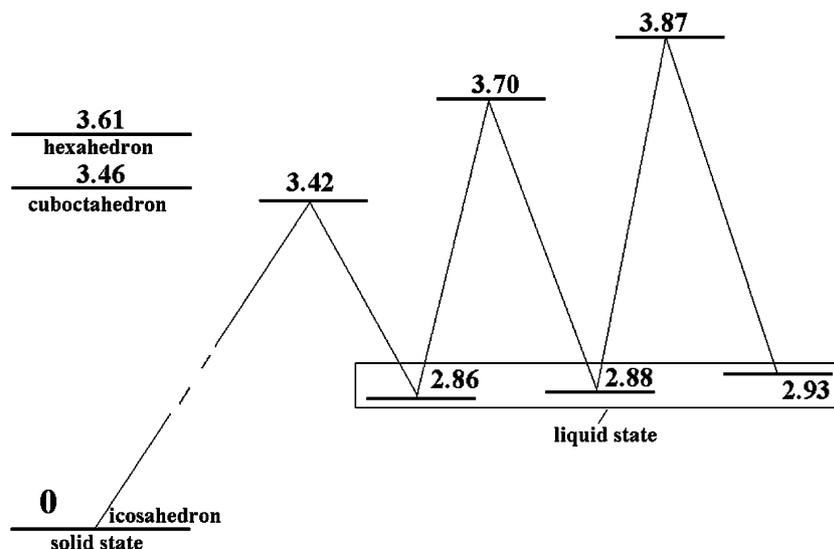


Fig. 2. The energy and barrier positions for the lowest configuration excitations [26] of the Lennard-Jones cluster consisting of 13 atoms.

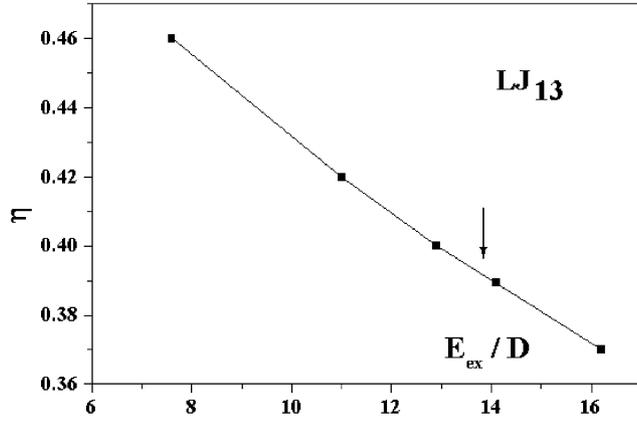


Fig. 3. The dependence on the excitation energy for the energy part related to the kinetic energy of atoms for an isolated Lennard-Jones cluster of 13 atoms. This value is identical for the solid and liquid cluster states. The arrow indicates the excitation energy of the phase transition $w_{\text{sol}} = w_{\text{liq}}$.

to results of computer simulation [23] for this cluster. The effective cluster temperature T_{ef} is determined from equilibrium between the solid and liquid cluster states from the formula

$$\frac{w_{\text{liq}}}{w_{\text{sol}}} = \exp\left(-\frac{\Delta F}{T_{\text{ef}}}\right) = \exp\left(-\frac{\Delta E}{T_{\text{ef}}} + \Delta S\right), \quad (7)$$

where w_{sol} and w_{liq} are the probabilities for the cluster to be found in the solid or liquid states respectively, and ΔF is the free energy jump at melting. The effective cluster temperature tends to the solid temperature in the limit of low temperatures, and to the liquid temperature in the limit of high temperatures.

We now consider one more example of obtaining parameters of the cluster's configurational excitation from the results of computer simulation. As earlier, we assume existence of the two aggregate states [12,24,30] and use the dynamic coexistence of phases in clusters [23,27–29] within a temperature range, i.e. part of time the cluster is found in one aggregate state, and in the remainder it is found in the other state. In addition, while the cluster is in each aggregate state, vibrational equilibrium is established [19], so that the temperature of bound atoms for each aggregate state coincides with the thermostat temperature, if the cluster is in a canonical ensemble [20]. In this case the probability w_{liq} that the cluster is found in the liquid state is given by the formula [30,24,12]

$$w_{\text{liq}} = \frac{p}{1+p}, \quad p = \exp\left(-\frac{\Delta F}{T}\right) = \exp\left(\Delta S - \frac{\Delta E}{T}\right), \quad (8)$$

where T is the cluster temperature which coincides with the thermostat temperature, ΔE is the energy of

configuration excitation, ΔS is the entropy jump as a result of melting, and ΔF is a change of the free energy, and we assume that the cluster is in a canonical ensemble. The parameters of the phase transition ΔE and ΔS determine the behavior the cluster heat capacity, which we connect with the cluster heat capacity that can be calculated in computer simulations. Using the average kinetic energy of atoms for each aggregate state, we characterize each cluster aggregate state by a certain potential energy, i.e. we ignore the broadening of the energy of each cluster state due to fluctuations.

We now determine the cluster heat capacity and separate its resonance part due to the phase transition. We have, according to formula (3),

$$E = \frac{K_{\text{sol}}}{\eta_{\text{sol}}} w_{\text{sol}} + \Delta E w_{\text{liq}} + \frac{K_{\text{liq}}}{\eta_{\text{liq}}} w_{\text{liq}},$$

and since the cluster is in a thermostat, $K_{\text{sol}} = K_{\text{liq}}$. Assuming $\eta_{\text{sol}} = \eta_{\text{liq}}$, we obtain the average cluster energy according to formula (1)

$$E = \frac{K_{\text{sol}}}{\eta_{\text{sol}}} + \Delta E w_{\text{liq}} = \frac{K_{\text{sol}}}{\eta_{\text{sol}}} + \Delta E \frac{p}{1+p}. \quad (9)$$

Hence, the cluster heat capacity consists of two parts:

$$C = \frac{dE}{dT} = C_0 + \frac{d(\Delta E w_{\text{liq}})}{dT}, \quad \text{where the first is} \quad (10)$$

$$C_0 = \frac{d(K_{\text{sol}}/\eta_{\text{sol}})}{dT} = \frac{d(K_{\text{liq}}/\eta_{\text{liq}})}{dT},$$

and the resonance part of the heat capacity is

$$C_{\text{res}} = \frac{d(\Delta E w_{\text{liq}})}{dT} = \frac{\Delta E^2}{T^2} \cdot \frac{p}{(1+p)^2}, \quad (11)$$

where we assume the energy of configurational excitation ΔE and the entropy jump ΔS are independent of the temperature. Formula (10) leads to the maximum $C_{\text{res}}^{\text{max}}$ at the melting point T_m defined in this case as $p(T_m) = 1$. We have

$$C_{\text{res}}^{\text{max}} = \frac{\Delta E^2}{4T_m^2} = \frac{\Delta S^2}{4}. \quad (12)$$

Let us introduce the temperature dependence of the entropy jump in the form

$$\Delta S = \Delta S_0 + aT, \quad (13)$$

with ΔS_0 the entropy jump at zero temperature. This gives, at the melting point,

$$a = \frac{\Delta S_m - \Delta S_0}{T_m}, \quad (14)$$

where ΔS_m is the entropy jump at the melting point. Substituting this in formula (12), we get

$$C_{\text{res}}^{\text{max}} = \frac{\Delta S_m^2}{2} - \frac{1}{4} \Delta S_0 \Delta S_m. \quad (15)$$

This formula can be used to determine ΔS_m from other parameters, so we have

$$\Delta S_m = \frac{\Delta S_0}{4} + \sqrt{\frac{\Delta S_0^2}{16} + 2C_{\text{res}}^{\text{max}}}. \quad (16)$$

Thus, we divide the entropy jump at the phase transition into two parts, so that the first, ΔS_0 , is due to configurational cluster excitation at zero temperature, and the second part, $\Delta S_m - \Delta S_0$, is determined by the difference of the entropies of the two aggregate states due to thermal motion of atoms. Formula (16) connects these two contributions to the entropy at the melting point.

Note that the caloric curves give the energy of the phase transitions ΔE as the energy difference between these curves at the melting point. But this leads to an additional error in a comparison with the results of computer simulation at constant cluster energy. Indeed, for the Lennard-Jones cluster of 13 atoms we have $\Delta E = 2.5D$. In the case of isothermal computer simulation, we have for the energy difference

$$\Delta E' = \Delta E + \frac{K_{\text{liq}}(T_m)}{\eta_{\text{liq}}(T_m)} - \frac{K_{\text{sol}}(T_m)}{\eta_{\text{sol}}(T_m)} = 3.7D,$$

so that strong anharmonicity of the liquid state increases the energy difference at the melting point by almost 50%. Thus, simplistic inference of parameters directly from isothermal computer simulation would lead to an additional error.

Let us now analyze the Lennard-Jones cluster of 55 atoms, (LJ)₅₅. First, we obtain the excitation energy of a surface atom by treating it as a transition from the outer shell to the cluster surface, supposing that the excited atom is found far from a forming vacancy. In this way, we neglect interactions between an excited atom and its vacancy. Then the excitation energy is [24] $\Delta \varepsilon = \varepsilon_{56} - \varepsilon_{55}$, where ε_{55} , ε_{56} are the total binding energies of atoms for clusters consisting of 55 and 56 atoms. According to calculations [7] for the ground state energies of these clusters, we have $\Delta \varepsilon = 2.64D$ at zero temperature. The direct calculations for lower excitations of this cluster [31] lead to a minimal excitation energy of $2.63D$. This confirms that an excited atom on the cluster surface can be treated as being far from the forming vacancy. According to computer simulations [32,33], we have the following parameters of the (LJ)₅₅ cluster: $\Delta E = 14\text{--}17$, $T_m = 0.30D$, and $C_{\text{res}}^{\text{max}} = 600\text{--}700$. This gives

$$\Delta S_m = \frac{\Delta E}{T_m} = 52 \pm 5, \quad (17)$$

and the number of atoms that leave the body of the cluster to form voids is

$$v \geq \frac{\Delta E}{\Delta \varepsilon} \approx 5 \quad (18)$$

for this system.

3. Phase transition in clusters with pair interactions between atoms

Thus, we consider the configurational excitation of a cluster as formation of voids; an individual void is formed by the relaxation of the vacancy when a particle moves to the surface. We distinguish the terms ‘void’ and ‘vacancy,’ so that they are only approximately equivalent for solid clusters, in which relaxation is slight. Such a configurational excitation is the physical basis of the cluster’s liquid state, and we use this concept to analyze the solid–liquid phase transition in these clusters. Note that formation of a void is characterized by a very large increase of entropy (or a void is characterized by a large statistical weight). Therefore the transition into configurationally excited states is thermodynamically favorable at available temperatures. For simplicity, we consider the case of a single liquid state of the cluster, i.e. a state corresponding to a definite number of voids. This relates to the two-state approximation for cluster aggregate states [30]. For large clusters or bulk systems, this number of voids is dictated by the thermodynamic requirements, whereas for clusters of moderate sizes this assumption may be violated; we return below to this problem.

The nature of the order–disorder phase transition for an ensemble of bound atoms may be understood on the basis of the lattice model (for example [34–36]). Within the framework of this model, atoms are located in 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, while 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 compared to 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 corresponding distribution. This order–disorder phase transition models the solid–liquid phase transition for an ensemble of bound atoms, so that the ordered state is analogous to the solid state, and the disordered state, to the liquid state. Since this phase transition leads to a change of atomic configuration, it results from configurational excitation of an ensemble of bound atoms. One can see that the lattice model for configurational excitation of a system of bound atoms is a simplified void model that we consider here where a void is considered equivalent to a vacancy and additional assumptions are used. Therefore the conclusions which follow from the lattice model relate also to the void model of configuration excitation.

Assuming one liquid state, we introduce the melting temperature according to the definition

$$w_{\text{liq}} = w_{\text{sol}} = \frac{1}{2}. \quad (19)$$

Note that for an isolated cluster, with constant energy, these temperatures which are expressed through the kinetic energy of cluster atoms, are different for the solid and liquid states. We consider one aspect of this problem. In practice, it is convenient to use the Lindemann criterion [37,38] for the melting point of an ensemble of bound atoms. According to this criterion, the melting starts if the ratio of the amplitude of atomic oscillations to the distance between nearest neighbors reaches the value 0.10–15. With computer modeling of clusters, more precise criteria of the phase transition were created with the correlations in positions of two cluster atoms. In particular, this correlation function can use the Eters–Kaelberer parameter [39–41] or the Berry parameter [42,43]. These parameters are proportional to the fluctuation of the distance between two atoms and vary in time in a different manner for the solid and liquid states, that allows us to distinguish a cluster state. These parameters are connected with thermal motion of atoms, while the melting results from configurational excitation of an ensemble of bound atoms.

One can see an apparent contradiction between the nature of the phase transition in ensembles of bound atoms due to configurational excitation and the practical criteria of this transition which are based on thermal motion of atoms. This contradiction can be removed if we account for the influence of thermal excitation on the entropy of this transition in accordance with formula (13). The second part of this formula accounts for the apparent paradox of the thermal motion in the entropy jump, and if we understand the origin of the paradox, the above criterion of the phase transition becomes natural. The nature of this term results from the lower density of atoms in the liquid state, that leads to the associated larger entropy from the atomic vibrations. Naturally the entropy jump due to vibrations of atoms increases with increasing 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.

Thus, one can find separately the entropy jumps ΔS_0 and ΔS_m at zero temperature and at the melting point that are given in Table 1 for the clusters considered here. The statistical weight of configurational excitation of a

cluster consisting of 13 atoms (see Fig. 1) is equal $g_0 = 12 \times 15$, where the first factor is the number of surface atoms that can be promoted, and the second factor is the number of positions to which the promoted atom can go on the cluster surface, if the new vacancy and the excited atom are not adjacent. Correspondingly, the entropy jump for this transition is $\Delta S_0 = \ln g_0 = 5.2$. We note that the contribution from thermal vibrations $\Delta S - \Delta S_0$ to the total entropy jump ΔS increases with increasing temperature, as does the anharmonicity of vibrations, which is given in Fig. 3. Evidently, the vibrational anharmonicity gives a contribution to the entropy jump also.

To analyze the Lennard-Jones cluster of 55 atoms whose global minimum structure is a completed icosahedron, we use formulas (17) and (18). The data from computer simulations [32,33] give us the entropy jump ΔS_0 at zero temperature separately for each number of new voids, if, according to formula (18), we take $v = 5-7$. We assume that atoms can transfer not only from the icosahedron's vertices, but also from the edges; we ignore the difference of the energy changes when an atom goes from a vertex or from an edge to the cluster surface, and we assume that transferring atoms are not adjacent to the vacancies they leave. A new vacancy on a cluster edge or surface has six neighboring atoms, and a vertex vacancy has only five. Then we have that $v \cdot (5-6)$ positions on the cluster surface are lost for atoms transferred from any of 80 positions on the cluster surface, if v transferring atoms on the cluster surface do not border vacancies on the cluster shell. From this we found the entropy jump for this configurational excitation of the cluster at zero temperature which results from v atoms moving from the outermost cluster shell of 42 atoms. We have this value

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

where

$$m = 80 - v \cdot (5-6)$$

is the number of positions for floaters on the cluster surface, when floaters do not border new vacancies. From this we have $\Delta S_0 = 28.2-28.7$ for $v = 5$, $\Delta S_0 = 31.2-32.0$ for $v = 6$, and $\Delta S_0 = 31.6-33.0$ for $v = 7$. This gives the average value

$$\Delta S_0 = 31 \pm 2, \quad (20)$$

and from formula (16) we obtain the entropy jump at the melting point

$$\Delta S_m = 45 \pm 2. \quad (21)$$

Using formulas (17) and (21) for the entropy jump at the melting point, we take its average value $\Delta S_m = 48 \pm 4$ that is given in Table 1. From Table 1 it follows that the contribution of thermal motion to the entropy jump at the melting point is identical approximately for the Lennard-Jones clusters consisting of 13 and 55 atoms.

Table 1
Parameters of melting for atomic clusters and bulk systems

	LJ ₁₃	LJ ₅₅	Bulk inert gases
T_m/D	0.29	0.31	0.58
$\Delta E/D$	2.5	16 ± 1	0.98 <i>n</i>
ΔS_0	5.2	31 ± 2	0.73 <i>n</i>
ΔS_m	8.6	48 ± 4	1.68 <i>n</i>
$\Delta S_0/\Delta S_m, \%$	60	65 ± 10	44

LJ_{*n*} is a cluster consisting of *n* atoms with the Lennard-Jones interaction potential; *D* is the depth of the potential well.

The last example relates to bulk systems of bound atoms for which we use the parameters of condensed inert gases. The entropy jump at zero temperature is equal in this case to

$$\Delta S_0 = \ln C_{n+v}^v = n \ln \frac{n+v}{n} + v \ln \frac{n+v}{v}, \quad (22)$$

where n is a number of ensemble atoms, v is a number of vacancies, C_{n+v}^v is a number of ways to remove v atoms from the initial lattice containing $n+v$ atoms. We have for condensed inert gases [44–47] $n/v = 3.12 \pm 0.01$, which gives $\Delta S_0/n = 0.73$ (see Table 1). The reduced entropy jump in inert gases near the triple point is [24,12,48] $\Delta S_m/n = 1.68 \pm 0.03$, so that the contribution to the entropy jump due to thermal motion of atoms is $(\Delta S_m - \Delta S_0)/\Delta S_m = 56 \pm 1$.

4. Peculiarities of configurational excitation for ensembles of bound atoms

Thus, the void concept is useful for the analysis of the liquid state of ensembles of bound atoms. We now consider other aspects of this problem. Looking now at a bulk system of bound atoms with a pair interaction, we can simplify the problem of configurational excitation by restricting the treatment to internal voids only. Because most internal voids can be considered identical, one can optimize this case, specifically by finding the optimal number of voids in the liquid aggregate state [44–46], using parameters of condensed rare gases. This gives the number of internal voids; the entropy of formation of individual void $\Delta s = \Delta S/n$, where ΔS is the total entropy jump at the phase transition, n is the total number of atoms and the energy of formation of an individual void at melting is approximately one-half of that of an individual vacancy in a solid inert gas.

These void parameters may be used to analyze other properties of liquid inert gases. Below the melting point the liquid state becomes metastable. The number of voids in a system is not conserved because voids can diffuse out of a cluster or diffuse in from the surface as they form. As a consequence, within a band of temperatures and pressures, the cluster's free energy has two minima as a function of the number of voids, corresponding to the stability conditions for the solid and liquid states. One of these states, stable or metastable, is realized after relaxation of a cluster when a certain number of voids is created inside it. The void model shows [50] that this takes place above a certain temperature, which we call the freezing limit. Below this temperature, the free energy has no minimum corresponding to the liquid, as a function of the number of voids. Hence the liquid state of condensed inert gases does not exist as a metastable one below the freezing limit. Likewise, there is an upper bound to the temperature range within which the free

energy has a minimum corresponding to the solid. Above the melting limit, the temperature at which that minimum does not exist, there is no solid form, metastable or stable.

At low temperatures the liquid state of condensed inert gases may convert into a glassy state, which is strictly an unstable state with a long lifetime. The glassy state, an amorphous state of atoms, has been created experimentally with argon [49] by deposition of argon atoms on a cold target surface. This state is converted to the crystalline solid by heating, as demonstrated by the experiment [49]. This behavior follows from the void model of the glassy state in condensed inert gases [51,52] since a long lifetime of a glassy state is a consequence of the barrier character of void diffusion in condensed inert gases. Thus, the void concept of configurational excitation of a bulk system with pair interactions between atoms gives new understanding of some phenomena exhibited by these systems.

Considering a void as a relaxed vacancy, at zero temperature the vacancy and void become equivalent if we neglect the vacancy–atom interaction. Real parameters of voids take into account this interaction and hence the effect of the thermal motion of atoms on configurational excitation. The lower the temperature, of course the less is the configurational excitation and the less is the vibrational excitation as well. Evidently, the separation of the configuration 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 for especially 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 total kinetic energy is distinctly bimodal [23,53] for an isolated cluster. The occurrence and persistence of these two aggregate states allows us to use the approach of two aggregate states [30], which is an analogue of the solid and liquid aggregate states for bulk systems. Note that in reality one can observe several types of configurational excitations which correspond to excitation of different cluster shells [33,54].

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 [53], because only a small entropy 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 clusters with pair interactions between atoms 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 the clusters with a pairwise atomic interaction.

5. Summary

The solid–liquid phase transition in clusters and bulk systems can naturally be interpreted in terms of configurational excitation of a collection of bound atoms. Configurational excitation is separated from excitation of the thermal vibrations of the atoms, as follows from the multi-basin topographies of the multidimensional potential energy surfaces for such systems. Nevertheless, some of the most useful criteria of this phase transition, starting from the Lindemann criterion, are based on the nature of the thermal motion of atoms. The void concept for configurational excitation of such systems, interpreted with the help of the results of computer simulations and thermodynamic parameters of condensed inert gases, shows that the origin of this apparent paradox lies with the very significant contribution of the changes of thermal vibrations of atoms to the entropy jump at this phase transition. The void concept of configurational excitation is useful also for understanding other phenomena involving these atomic ensembles.

Acknowledgments

This paper is supported partially by RFBR-grant 03-02-16059. R.S.B. wishes to acknowledge the support of a Grant from the National Science Foundation.

References

- [1] O. Eicht, K. Sattler, E. Recknagel, *Phys. Rev. Lett.* 94 (1981) 54.
- [2] O. Eicht et al., *Ber. Bunsenges. Phys. Chem.* 86 (1982) 860.
- [3] J. Xie, J.A. Northby, D.L. Freemann, J.P. Doll, *J. Chem. Phys.* 91 (1989) 612.
- [4] M.R. Hoare, P. Pal, *Adv. Phys.* 20,24 (1971) 161.
- [5] M.R. Hoare, *Adv. Chem. Phys.* 40 (1979) 49.
- [6] J.W. Lee, G.D. Stein, *J. Phys. Chem.* 91 (1987) 2450.
- [7] J.A. Northby, *J. Chem. Phys.* 87 (1987) 6166.
- [8] J. Farges, M.F. deFeraudi, B. Raoult, G. Torchet, *Adv. Chem. Phys.* 70 (1988) 45.
- [9] B.W. Van de Waal, *J. Chem. Phys.* 90 (1989) 3407.
- [10] J. Farges, M.F. deFeraudi, B. Raoult, G. Torchet, *Philos. Mag.* 60B (1989) 881.
- [11] J.A. Northby, J. Xie, D.L. Freemann, J.P. Doll, *Z. Phys. D* 12 (1989) 69.
- [12] B.M. Smirnov, *Clusters and Small Particles in Gases and Plasmas*, Springer, New York, NY, 1999.
- [13] H. Reiss, H.L. Frisch, J.L. Lebowitz, *J. Chem. Phys.* 31 (1959) 369.
- [14] D.S. Corti, P.G. Debenedetti, S. Sastry, F.H. Stillinger, *Phys. Rev.* 55E (1997) 5522.
- [15] K.D. Ball, R.S. Berry, *J. Chem. Phys.* 111 (1999) 2060.
- [16] R.S. Berry, in: J. Jellinek (Ed.), *Theory of Atomic and Molecular Clusters*, Springer, Berlin, 1999, p. 1.
- [17] T. Komatsuzaki, R.S. Berry, *J. Chem. Phys.* 110 (1999) 9160.
- [18] D.J. Wales, J.P.K. Doye, M.A. Miller, P.N. Mortenson, T.R. Walsh, *Adv. Chem. Phys.* 115 (2000) 1.
- [19] B. Vekhter, R.S. Berry, *J. Chem. Phys.* 106 (1997) 4644.
- [20] D. Ter Haar, *Elements of Thermostatistics*, Addison-Wesley, New York, 1966.
- [21] F.H. Stillinger, T.A. Weber, *Phys. Rev.* 25A (1982) 978.
- [22] F.H. Stillinger, T.A. Weber, *Phys. Rev.* 28A (1983) 2408.
- [23] J. Jellinek, T.L. Beck, R.S. Berry, *J. Chem. Phys.* 84 (1986) 2783.
- [24] B.M. Smirnov, *Phys. Uspekhi* 37 (1994) 1079.
- [25] S.N. Khanna, P. Jena, *Phys. Rev. Lett.* 69 (1992) 1664.
- [26] D.J. Wales, R.S. Berry, *J. Chem. Phys.* 92 (1990) 4283.
- [27] G. Natanson, F. Amar, R.S. Berry, *J. Chem. Phys.* 78 (1983) 39.
- [28] J. Jellinek, T.L. Beck, R.S. Berry, *Chem. Phys. Lett.* 107 (1984) 227.
- [29] R.S. Berry, *Chem. Rev.* 93 (1993) 2379.
- [30] R.S. Berry, B.M. Smirnov, *J. Chem. Phys.* 114 (2001) 6816.
- [31] D.J. Wales, *Chem. Phys. Lett.* 166 (1990) 419.
- [32] H.P. Cheng, R.S. Berry, *Phys. Rev.* 45A (1992) 7969.
- [33] R.E. Kunz, R.S. Berry, *Phys. Rev.* 49E (1994) 1895.
- [34] W. Bragg, H.J. Williams, *Proc. Roy. Soc. A* 145 (1934) 699.
- [35] R. Kubo, *Statistical Mechanics*, North Holland, Amsterdam, 1965.
- [36] J.M. Ziman, *Models of Disorder*, Cambridge University, Cambridge, 1979.
- [37] F.A. Lindemann, *Zs. Phys.* 11 (1910) 609.
- [38] J.P. Hansen, L. Verlet, *Phys. Rev.* 184 (1969) 151.
- [39] R.D. Eppers, J.B. Kaelberer, *Phys. Rev. A* 11 (1975) 1068.
- [40] R.D. Eppers, J.B. Kaelberer, *J. Chem. Phys.* 66 (1977) 5512.
- [41] J.B. Kaelberer, R.D. Eppers, *J. Chem. Phys.* 66 (1977) 3233.
- [42] R.S. Berry, T.L. Beck, H.L. Davis, J. Jellinek, *Adv. Chem. Phys.* 90 (1988) 75.
- [43] Y. Zhou, M. Karplus, K.D. Ball, R.S. Berry, *J. Chem. Phys.* 116 (2002) 2323.
- [44] B.M. Smirnov, *JETP* 85 (1997) 1010.
- [45] B.M. Smirnov, *Inorg. Mater.* 35 (1999) 562.
- [46] B.M. Smirnov, in: J.W.P. Schmelzer, G. Röpke, V.B. Priezhev (Eds.), *Nucleation Theory and Applications*, JINR, Dubna, 1999, p. 355.
- [47] R.S. Berry, B.M. Smirnov, in: J.W.P. Schmelzer, G. Röpke, V.B. Priezhev (Eds.), *Nucleation Theory and Applications*, JINR, Dubna, 2002, p. 340.
- [48] B.M. Smirnov, *Phys. Uspekhi* 44 (2001) 1229.
- [49] A. Kouchi, T. Kuroda, *Jpn. J. Appl. Phys. Part 2* 29 (1990) L807.
- [50] R.S. Berry, B.M. Smirnov, *JETP* 93 (2001) 541; *ZhETF* 120 (2001) 889.
- [51] R.S. Berry, B.M. Smirnov, *JETP* 95 (2002) 255; *ZhETF* 122 (2002) 298.
- [52] R.S. Berry, B.M. Smirnov, *J. Chem. Phys.* 118 (2003) 5979.
- [53] T.L. Beck, J. Jellinek, R.S. Berry, *J. Chem. Phys.* 87 (1987) 545.
- [54] R.E. Kunz, R.S. Berry, *Phys. Rev. Lett.* 71 (1993) 3987.