SOLIDS
Structure

Structural Phase Transition in a Large Cluster

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Abstract—The effect of a phase transition between structures in a large cluster with a pair interatomic interaction on the thermodynamic parameters of the cluster is analyzed. The statistical parameters of a cluster consisting of 923 atoms are determined for an icosahedron and a face-centered cubic (fcc) structure. The specific heat and entropy of this cluster are calculated in the case when the transition between the icosahedron and fcc structures has the greatest effect on these parameters, so that at zero temperature this cluster has the structure of an icosahedron, and as the temperature increases to the melting point it assumes an fcc structure. Even with this, the contribution of the excitations of the atomic configurations to the thermodynamic parameters of a cluster is small compared with the excitation of vibrations in the cluster. The contribution of a configurational excitation in the thermodynamic parameters of a cluster becomes substantial for the liquid state of clusters. © 2000 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

We are studying a phase transition between structures for a large cluster with a pair interatomic interaction, where the interaction between nearest neighbors, i.e., a short-range interaction, makes an appreciable contribution to the energy of the cluster. This transition influences the thermodynamic parameters of the cluster, specifically, its specific heat and entropy. Finding these parameters is the subject of the present paper. It would appear that the type of interaction under study, which pertains to systems of inert-gas atoms, is the simplest of the possible interactions. Nonetheless, it has its peculiarities. At zero temperature the macroscopic system of atoms under study forms a close-packed crystal lattice, where each inner atom has twelve nearest neighbors. The crystalline hexagonal and fcc lattices are close-packed structures. For a Lennard–Jones interatomic interaction potential a hexagonal lattice is more advantageous [1, 2], while all solid inert gases (except helium) have an fcc crystal lattice [2–4], though under special conditions the hexagonal structure of solid inert gases is observed in thin films [5–7]. Competition between these structures is possible in systems of coupled atoms with a pair interaction. Clusters, which are systems with a finite number of bound atoms, can also form an icosahedral structure [8], which is characterized by central symmetry and two types of distances between nearest neighbors, differing by 5%. This structure is preferable for small clusters and competes with the fcc structure right up to sizes of the order of a thousand atoms in a cluster [9–14]. Thus, despite its simplicity, the character of the interaction under study permits systems of bound atoms to exist in various forms.

We note that a cluster with a pair interaction between the atoms is a convenient object for computer simulation, which has shown that melting of clusters is fundamentally different from the melting of macroscopic systems of bound atoms [15–23]. In the first place, in a macroscopic system a phase transition between a solid and a liquid occurs at a certain temperature, while for a cluster there exists a temperature range where the solid and liquid phases coexist. In the second place, computer simulation of melting of clusters with closed shells makes it possible to identify several phase transitions corresponding to melting of individual shells [22, 23]. Thus, a cluster is a more complicated system than a macroscopic system of atoms, and the features indicated above must be taken into account when analyzing the properties of a cluster.

Evidently, a phase transition influences the thermodynamic properties of a cluster. This is investigated in the present paper. The greatest effect is observed when a cluster possesses one structure at zero temperature, while heating changes the structure, i.e., different structures correspond to zero and nonzero temperatures of a cluster. In what follows, we shall examine such a case for a cluster containing 923 atoms, so that the icosahedral structure of this cluster is characterized by closed shells, while the fcc structure is characterized by open shells. Let the ground state of this cluster correspond to the structure of an icosahedron and the excitation energy of the fcc structure be relatively small. The energy gap between the structures can be controlled by varying the parameter in the interatomic interaction potential, specifically, the Morse parameter for a Morse potential [24, 25]. The ground state for an fcc structure of a cluster is characterized by a large statistical weight, since the last shell of a cluster is unfilled. For this rea-

son, if the energy gap between the structures is small, heating the cluster makes the fcc structure thermodynamically favorable, i.e., heating changes the structure of the cluster. This affects the thermodynamic parameters of a cluster, and in what follows we shall calculate the specific heat and entropy of a solid cluster as a function of the temperature and energy gap between the icosahedral and fcc structures. These quantities correspond to a configurational excitation of a cluster. The role of transitions between structures in the thermodynamics of a cluster can be determined by comparing the values of these quantities with the corresponding values due to vibrational excitation of a cluster. This is the aim of the present paper.

2. STATISTICAL PARAMETERS OF AN EXCITED SOLID CLUSTER

To determine the statistical and thermodynamic parameters of a solid cluster consisting of atoms with a pair interaction, we shall divide the energy of a cluster into three parts [26]: the first part is determined by the interaction between nearest neighbors, the second part is determined by the interaction between atoms which are not nearest neighbors, and the third part refers to the stress energy. We shall consider the case where the interaction between the nearest neighbors makes an appreciable or the main contribution to the energy of a cluster. This is a common case, specifically, the popular Lennard–Jones interaction potential pertains to this case. Under these conditions, to a first approximation, we construct a cluster on the basis of a short-range interaction of atoms, so that the state of the cluster is characterized by the number of bonds between nearest neighbors. In the second approximation we include in the analysis the interaction of nonnearest neighbors and the stress energy in a cluster, which is related with the displacement of the equilibrium distances between nearest neighbors as a result of a long-range interaction. This scheme is convenient for analyzing the competition between fcc and icosahedral structures [24, 25]. In this scheme, the long-range interaction of atoms is important for the competition between structures, since the number of bonds between the nearest neighbors for these structures is close. Conversely, the long-range interaction is not important for the excitation of a cluster. Indeed, the excitations considered are related with a change in the positions of one or several atoms, so that the long-range interaction in a cluster changes little with such transitions, and the excitation can be characterized by the change in the number of bonds between the nearest neighbors.

Thus, in the present scheme the excitation of a cluster is characterized by the number of broken bonds between the nearest neighbors, i.e., the excitation energy, measured from the energy of the ground state of a cluster with a given structure, is expressed in units of the energy required to break one bond and is an integer. The statistical weight g_i of the excited state of a cluster

with a given structure is equal to the number of configurations of atoms in the cluster that correspond to the number i of broken bonds with respect to the ground state of this structure. As one can see, in this case we assume that the vibrational and configurational excitations separate, since the configurational excitation is relatively weak.

We shall determine the statistical parameters of our cluster with an icosahedral structure. A cluster consisting of 923 atoms possesses filled shells. It is characterized by 2172 bonds between nearest neighbors, belonging to neighboring layers, and 2730 bonds between nearest neighbors in the same layer [15]. This cluster has 561 inner atoms, and the surface layer of this cluster includes 12 vertex atoms, 150 edge atoms, and 200 atoms inside surface triangles. Each vertex atom possesses six nearest neighbors, each edge atom possesses seven nearest neighbors, and each atom on the inner surface of a cluster possesses nine nearest neighbors. If a new atom is placed on the surface of this cluster in a cavity between the surface atoms, the atom will have three nearest neighbors. There are 720 such positions, which is equal to the number of triangles that can be formed from the surface atoms.

The excitation of the configurations of atoms in a cluster corresponds to transferring surface atoms into the centers of the surface triangles. In what follows, transitions with the participation of a small number of atoms, which determine the thermodynamic parameters of a cluster at low temperatures, will be considered. The minimum excitation energy of our cluster with an icosahedral structure is $\Delta\varepsilon = 3$ and corresponds to transferring a vertex atom to the surface of the cluster. The statistical weight for such an excitation is $g_3 = 12 \times 715 = 8580$ and is much greater than the statistical weight for the ground state $g_0 = 1$. We shall take account of the fact that five positions on the surface of a cluster lie next to the vertex atom undergoing a transition, and in what follows we shall neglect this compared with the total number of surface cavities. Further, the excitation energy $\Delta\varepsilon = 4$ of a cluster corresponds to a transition of one edge atom, and $\Delta\varepsilon = 6$ corresponds to the excitation of one surface atom or two vertex atoms. We have

$$g_4 = 150 \times 720 = 1.08 \times 10^5,$$

$$g_6 = \frac{12 \times 11}{1 \times 2} \times \frac{720^2}{2} + 200 \times 720 = 1.7 \times 10^7.$$

Thus, the partial statistical weight for the excitation of v atoms from vertices, e atoms from edges, and s atoms from the surface is

$$g_i = C_{12}^v C_{150}^e C_{200}^s C_{720}^k \approx C_{12}^v \frac{150^e}{e!} \frac{200^s}{s!} \frac{720^k}{k!}, \qquad (1)$$

where $k = v + e + s$ is the total number of excited atoms and the energy of this excitation is $\varepsilon_i = 3v + 4e + 6s$. This formula is valid for a small number k of excited

atoms. We shall neglect the following circumstances. First, the displaced atoms cannot occupy a vertex of a surface triangle in which one of the vertex atoms has been removed. Second, two displaced atoms cannot be placed at the center of neighboring triangles, since the distance between these centers is $a/\sqrt{3}$, where a is the distance between the nearest neighbors. Third, we neglect the possible bonds between the displaced atoms, since the number of such atoms is relatively small. Thus, the expression (1) is valid for weak excitations and makes it possible to determine the statistical properties of a cluster at low temperatures. The statistical weights of the first few excitations of our cluster are presented in Table 1.

We note that if the excitation corresponds to a transition of several atoms, the excitation of edge atoms makes the main contribution to the statistical weight of the cluster. For example, the statistical weight for the excitation $\Delta\varepsilon = 12$ is $g' = 3.5 \times 10^{13}$ for edge atoms, $g'' = 5.2 \times 10^9$ for surface atoms, and $g''' = 5.5 \times 10^{12}$ for vertex atoms.

The method for analyzing clusters with a Morse interatomic interaction potential [24, 25] makes it possible to determine the statistical weight of the lower states of a solid cluster consisting of 923 atoms and possessing an fcc structure. The optimal figure for a cluster with fcc structure is a regular truncated octahedron, whose surface includes eight hexagons and six squares [27]. We shall present the ground state of a cluster with an fcc structure consisting of 923 atoms. The basis for it is a cluster-octahedron with filled shells, which consists of 891 atoms and has 4620 bonds between nearest neighbors. Its surface consists of eight regular triangles, and each of the 12 edges contains 11 atoms (including vertex atoms). Cutting off six pyramids near each vertex, we obtain a truncated regular octahedron, containing 861 atoms with 4476 bonds between nearest neighbors [28]. Each of the removed pyramids contains five atoms and possesses edges consisting of two atoms. The surface of the cluster formed consists of eight irregular hexagons and six squares, containing nine atoms each. The long edge of the hexagon contains seven atoms (including vertex atoms). Using the standard designations [5], the squares have {100} directions, and the hexagons have {111} directions.

Growth of a given cluster occurs by filling of its faces with direction {111}. A new layer on one face contains 46 atoms and increases the number of bonds between the nearest neighbors by 252. To construct a cluster consisting of $n = 923$ atoms, we start with a cluster consisting of 926 atoms, which contains a new layer on one face, and the other face contains a regular hexagon consisting of 19 atoms. This configuration of the surface atoms is shown in Fig. 1. The addition of a hexagon consisting of 19 atoms increases the number of bonds between the nearest neighbors by 99. Thus, an fcc cluster consisting of 926 atoms possesses in the ground state 4827 bonds between nearest neighbors. To

Table 1. Statistical weight of the excited states of a cluster with 923 atoms and an icosahedral structure

| ε_i	g_i	ε_i	g_i	ε_i	g_i
0	1	6	1.7×10^7	10	3.9×10^9
3	8.6×10^3	7	9.3×10^8	11	8.4×10^{12}
4	1.1×10^5	8	5.2×10^9	12	4.0×10^{13}

find the statistical weight of this state, we note that the faces which we are considering can be filled in $7 \times 8 = 56$ ways. Further, a regular hexagon can be placed on the surface of a face in 10 different ways, which gives a statistical weight $g = 560$ for the ground state of an fcc cluster containing 926 atoms.

To convert this cluster into a cluster consisting of 923 atoms, three atoms must be removed from it. This operation can be performed with both filled and partially filled faces. As a result, 17 bonds between nearest neighbors will be lost, i.e., 4810 bonds correspond to the ground state of an fcc cluster containing 923 atoms. The statistical weight of this cluster is equal to the product of the number of operations required to form a cluster consisting of 926 atoms by the number of operations to remove three atoms from it:

$$g_0 = 8 \times 7 \times (3 \times 10 + 3 \times 10 + 3 \times 13) = 5544. \quad (2)$$

The first term in parentheses corresponds to the removal of three atoms from the filled face, the second term corresponds to the removal of the top edge or two bottom side edges of a regular hexagon of the face being filled, and the third term describes the removal of the bottom edge or two top side edges of a regular hexagon. As one can see, the statistical weight of an fcc cluster is much greater than for an icosahedral cluster with filled shells.

We shall now formulate the general properties of the our cluster on the basis of our approach. The total number of bonds between nearest neighbors in the case of
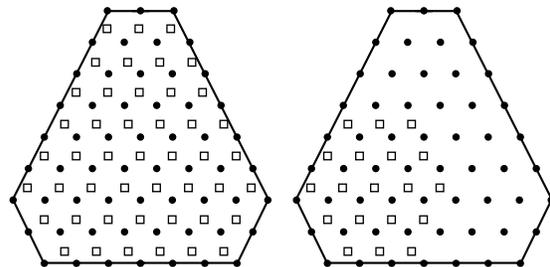
Fig. 1. Filling of the {111} faces of a cluster of an fcc structure, containing 926 atoms, in the ground state. The positions of the atoms on the filled layers are indicated by filled circles, and the positions of the atoms on the layers being filled are marked by open squares. The number of bonds between the nearest neighbors of a cluster is 4827 (for an icosahedral cluster with $n = 926$ the number of bonds is 4914).

Table 2. Statistical weights for the lower states of an fcc cluster with 923 atoms

i	g_i/g_0	i	g_i/g_0
1	100	5	9.3×10^5
2	500	6	1.4×10^7
3	8000	9	5.6×10^{10}
4	1600	12	4.1×10^{13}

an fcc structure is 4810, while for a cluster with icosahedral structure, where the distances between the nearest neighbors are suboptimal, it is 4902. As a result of the closeness of these quantities, the crossing of the energy levels for different structures is determined by the interaction of the non-nearest neighbors. Specifically, for a Morse interatomic interaction potential the energies of clusters for our structures are identical for the Morse parameter in the pair interaction potential $\alpha = 7.1$ [24, 25]. Thus, the cluster energy is determined mainly by the interaction between the nearest neighbors, but the competition between the structures and the parameters of the crossing of the energy levels are sensitive to the form of the interatomic interaction potential [10–15]. Specifically, the greater the contribution of the interaction of non-nearest neighbors to the cluster energy is, the larger the clusters for which crossing of energies occurs for fcc and icosahedral structures. However, in analyzing the lower excited states of a cluster, the interaction of non-nearest neighbors can be neglected, as was done above.

The statistical weight of the bottom excited states of an fcc cluster containing 923 atoms can be found by the same method as for the ground state. This method becomes more complicated as the excitation increases (Table 2 contains the values of the statistical weights of a cluster for $\varepsilon_i \leq 6$). For subsequent excitation of a cluster, we obtain a statistical weight that is all the larger, the larger the number of atoms that move on its surface. Specifically, for $\varepsilon_i = 9$ the transfer of three vertex atoms on its surface, where there are 552 free positions, so that the statistical weight of this excitation is

$$ g_9 \sim C_{24}^3 C_{552}^3 g_0 \sim 5.6 \times 10^{10} g_0, $$

makes the main contribution. Similarly, we find the statistical weight of the excitation when 12 bonds are broken. These results are included in Table 2, where the data make it possible to determine the thermodynamic parameters of fcc clusters up to temperatures $T = 0.3$–0.35.

The partial partition function Z_i for a given excitation energy ε_i and statistical weight g_i of this excitation and the total partition function Z can be calculated on the basis of the parameters obtained:

$$ Z_i = g_i \exp\left(-\frac{\varepsilon_i}{T}\right), \quad Z = \sum_i Z_i. \tag{3} $$

Here and below we express the temperature T in energy units. Introducing the separate partition functions Z_{ico} and Z_{fcc} for the icosahedral structure and the fcc structure, we have $Z = Z_{ico} + Z_{fcc}$. Then the probability η of an icosahedral structure being realized follows from the formula

$$ \eta = \frac{Z_{ico}}{Z_{ico} + Z_{fcc}}. \tag{4} $$

We note that the partition function can be divided into configurational and vibrational parts. Since we are dealing with weak excitations, the vibrational part of the partition function does not depend on the excitation of configurations and can be separated from it. Correspondingly, we shall analyze below only the configurational part of the partition function. The specific heat C and S of a cluster which correspond to the configurational excitations are

$$ C = \frac{\partial E_{exc}}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{Z}\sum_i \varepsilon_i Z_i\right) $$

$$ = \frac{1}{T^2}\left[\frac{1}{Z}\sum_i \varepsilon_i^2 Z_i - \left(\frac{1}{Z}\sum_i \varepsilon_i Z_i\right)^2\right] = \frac{\overline{E^2}}{T^2} - \left(\frac{\overline{E}}{T}\right)^2, \tag{5} $$

$$ S = \ln Z + \frac{\overline{E}}{T} = \ln \sum_i Z_i + \frac{1}{TZ}\sum_i \varepsilon_i Z_i. \tag{6} $$

Here E_{exc} is the configurational excitation energy of a cluster, and $\overline{E}$ and $\overline{E^2}$ are the average and mean-square values of the excitation energy of a cluster. At low pressures the difference between the specific heats of a cluster at constant pressure and volume is relatively small, so that we shall assume that they are the same and denote them by C. The energies ε_i of the configurational excitation and temperature of a cluster can be expressed in reduced units, i.e., in terms of the energies required to break one bond.

3. STRUCTURAL TRANSITIONS AND THERMODYNAMIC PARAMETERS OF A SOLID CLUSTER

We shall use the general formulas presented above to determine the thermodynamic parameters of our cluster. The ground state of the cluster possesses an icosahedral structure and is separated from the ground state of the fcc structure by an energy gap, which we denote as Δ. The excited states contribute to the partition function, starting at the temperatures $T \approx 0.2$, and the statistical weights presented in Tables 1 and 2 make it possible to determine the thermodynamic parameters of a cluster up to $T \approx 0.3$–0.35, while the melting temperature is $T_m = 0.44$ [29] for a cluster containing $n = 923$ atoms. A phase transition between icosahedral

and fcc structures is possible if the cluster in the ground state possesses an icosahedral structure and the energy gap Δ is small. We note that the energy gap can be regulated by varying the parameter of the interatomic interaction potential, specifically, for the Morse potential the gap is zero for a cluster when the Morse parameter $\alpha = 7.1$ [24, 25].

We shall now determine the temperature T_{tr} of a transition between structures using the relation $Z_{ico}(T_{tr}) = Z_{fcc}(T_{tr})$, and for $\Delta \sim 1$, when a transition occurs at low temperatures, we have $T_{tr} = \Delta/\ln g_0 = 0.116\Delta$, where the statistical weight g_0 of the ground for the fcc structure is determined by equation (2). A structural transition leads to resonance in the specific heat of a cluster, and its maximum value is $C_{max} = (\ln g_0/2)^2 \approx 19$. But this value is small compared with the specific heat of a cluster due to the vibrations of the atoms, specifically, according to the Dulong–Petit formula, the latter is $C = 3n \approx 3000$ (n is the number of atoms in a cluster). The relative width of a resonance in the temperature dependence of the specific heat of a cluster is small, and for small Δ it is

$$\Delta T = \frac{2T_{tr}^2}{\Delta} = \frac{2T_{tr}}{\ln g_0} = 0.23 T_{tr}, \qquad (7)$$

i.e., this resonance is not sharp.

For a structural transition it is convenient to separate in equation (5) the terms referring to the icosahedral and fcc structures. We have

$$C = \frac{Z_{ico}}{Z}C_{ico} + \frac{Z_{fcc}}{Z}C_{fcc}$$

$$+ \frac{1}{T^2}\frac{Z_{ico}Z_{fcc}}{Z^2}(\overline{\varepsilon_{ico}} - \overline{\varepsilon_{fcc}} - \Delta)^2. \qquad (8)$$

Here Z_{ico} and Z_{fcc} are the partition functions for the corresponding structure of a cluster, $Z = Z_{ico} + Z_{fcc}$, C_{ico} and C_{fcc} are the specific heats for each structure of the cluster in the absence of the other structure, and $\overline{\varepsilon_{ico}}$ and $\overline{\varepsilon_{fcc}}$ are the average energies of the configurational excitation for a given structure, if zero energy corresponds to the ground state of this structure. Figure 2 shows the temperature dependence of the specific heat of a cluster for different values of the energy gap Δ between the ground states of the icosahedral and fcc structures. The resonance character of these curves is due to the effect of a structural phase transition on the specific heat of a cluster. Figure 3 displays the caloric curves for the states of the cluster under study. We note that a change in the energy gap shifts the energy of the fcc structure, and near the melting temperature of a cluster the contributions of the icosahedral and fcc structures to the excitation energy of a cluster from the ground state of the given structure are comparable.
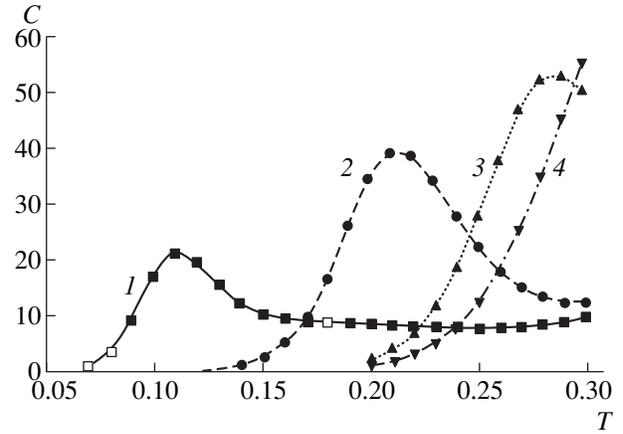
Fig. 2. Temperature dependences of the specific heat of a solid cluster consisting of $n = 923$ atoms, which is associated with the configurational excitation, for the following values of the energy gap width Δ between the ground states of the icosahedral and fcc cluster: $\Delta = $ (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4.
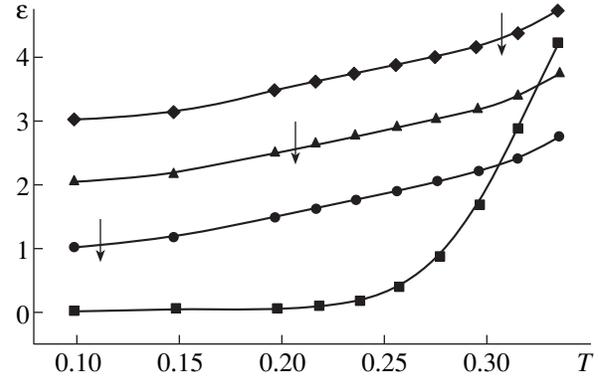
Fig. 3. Caloric curves for icosahedral and fcc structures of a cluster with 923 atoms. The arrows on the curves indicate the positions of a phase transition between the icosahedral and fcc structures.

The expression (8) shows the character of the resonance of the specific heat of a cluster that occurs when both structures make the same contribution to the specific heat. Indeed, let us take in this expression $\overline{\varepsilon_{ico}} \ll \Delta$ and $\overline{\varepsilon_{fcc}} \ll \Delta$, so that the maximum corresponds to $Z_{ico} = Z_{fcc} = Z/2$. This gives for the maximum specific heat

$$C_{max} = \frac{1}{2}(C_{ico} + C_{fcc}) + \left(\frac{\Delta}{2T}\right)^2, \qquad (9)$$

where T is the temperature of the structural phase transition. In the limit of small Δ, when $C_{ico} = C_{fcc} = 0$ and $T = T_{tr} = \Delta/\ln g_0$, we have $C_{max} = (\ln g_0/2)^2$, as was obtained above.

Since the entropy, according to equation (6), is determined by the excited configurations of the atoms

Table 3. Entropy of a cluster in the limit of small and large widths of the energy gap between the icosahedral and fcc structures of a cluster

T	$\Delta \longrightarrow 0$	$\Delta \longrightarrow \infty$
0.2	11.3	0.05
0.25	12.8	0.88
0.3	14.0	5.85
0.35	16.5	15.6

in a cluster, it is zero at zero temperature, since the cluster is in the ground state of the filled structure of an icosahedron. A temperature increase and phase transition increase the entropy, which increases monotonically with increasing temperature and with decreasing energy gap Δ between the ground states of the structures studied. This can be demonstrated in the limit of small values of Δ, when the phase transition occurs at low temperature in accordance with equation (7). In this case, only the ground configurational states of atoms for these structures determine the parameters of a cluster Z and $\bar{E}$ near the phase-transition temperature, and the entropy in this temperature range is

$$S = \ln(1 + g_0 e^{-\Delta/T}) + \frac{\Delta}{T} \frac{g_0 e^{-\Delta/T}}{1 + g_0 e^{-\Delta/T}},$$

$$\frac{dS}{dT} = \frac{\Delta^2}{T^3} \frac{g_0 e^{-\Delta/T}}{(1 + g_0 e^{-\Delta/T})^2}. \tag{10}$$

It follows from the last equation that $dS/dT > 0$, i.e., the entropy is a monotonic function of temperature. The derivative of the entropy itself has a maximum at the phase-transition point $T_{tr} = \Delta/\ln g_0$, where the derivative is

$$\frac{dS}{dT}(T_{tr}) = \frac{\Delta^2}{4T_{tr}^3} = \frac{\ln g_0^3}{4\Delta}. \tag{11}$$

This gives for the entropy at the phase-transition points

$$S(T_{tr}) = \ln 2 + \frac{\Delta}{2T_{tr}} = \ln \sqrt{\frac{g_0}{2}} \approx 4.0. \tag{12}$$

Far from a phase transition, where $g_0 \exp(-\Delta/T) \gg 1$, the entropy is

$$S = \ln g_0 - \frac{\Delta}{2T}.$$

Thus, in the limit of small values of Δ and high temperatures, the entropy approaches the limit $S = \ln g_0 = 9.6$. This limit corresponds to the entropy of the ground state of the fcc structure.

It is possible to determine the dependence of the entropy of a cluster on the width Δ of the energy gap between the structures. Then, in the limit of small Δ the

entropy is determined by the fcc structure of the cluster, while its statistical weight is relatively large, and in the limit of large Δ the entropy corresponds to the icosahedral structure. The values of the entropy at different temperatures for these limiting cases are given in Table 3.

Let us compare the contribution of excitations of the configurations of atoms in a cluster and excitations of vibrations of a cluster to the thermodynamic parameters of a solid cluster. The contribution of excitations of configurations to the entropy is relatively small. Specifically, in the classical limit the entropy of a cluster due to excitation of its vibrations is determined by the expression [30]

$$S_{vib} = 3n\left(\ln\frac{T}{\hbar\omega_D} - 1\right), \quad T \gg \hbar\omega_D, \tag{13}$$

where ω_D is the Debye frequency and n is the number of atoms in a cluster. For the cluster under study, this formula gives $S_{vib} \sim 1000$, which is much greater than the entropy due to the configurational excitation of a cluster. For example, using the approximate method, described above, for determining the partition function for a cluster with an icosahedral structure, when only transitions of atoms from an edge of this figure are taken into account, we obtain for the configurational part of the entropy at the melting temperature of the cluster $T_m = 0.44$ [29] the partition function $Z = 165$, specific heat $C = 141$, and entropy $S = 32$. These values attest to a small contribution from configurational excitation to the parameters, under study, of the solid cluster.

This conclusion is incorrect for melting of a cluster, and we shall analyze it for condensed inert gases. The liquid state is characterized by the formation of voids inside the system [31], and condensed inert gases can be viewed as a macroscopic system of atoms with short-range interatomic interaction [32], i.e., when only nearest neighbors interact. This makes it possible to use the parameters presented above for condensed inert gases to analyze the melting in a system of bound atoms with a short-range interaction. Specifically, in the units employed, the melting energy per atom for condensed inert gases is $\Delta H_{fus} = 0.98$ [32], so that the change in entropy on melting of a cluster is

$$\Delta S = \frac{\Delta E}{T_m} = \frac{n\Delta H_{fus}}{T_m} = 2060. \tag{14}$$

Here ΔE is the change in the internal energy of a cluster as a result of melting, T_m is the melting temperature, and $n = 923$ is the number of atoms in the cluster. It was assumed that the specific energy of melting is the same for a cluster and a macroscopic system. As one can see, the entropy jump on melting of a cluster is comparable to the entropy due to vibrations of atoms in a cluster. Thus, the configurational part of the entropy is substantial for the liquid state of a cluster and negligible for its solid state. We note that the melting temperature for condensed inert gases $T_m = 0.58$ [32] is greater than the melt-

ing temperature for our cluster $T_m = 0.44$ [29]. Therefore, we shall employ the overestimated values for the specific melting energy of a cluster. The estimates made and the conclusions drawn are nonetheless valid.

This conclusion also pertains to the specific heat of a cluster. Indeed, we shall employ the relation between the partition functions for liquid (Z_{liq}) and solid (Z_{sol}) states

$$\frac{Z_{liq}}{Z_{sol}} = \exp\left(-\frac{\Delta E}{T} + \Delta S\right). \qquad (15)$$

Assuming the internal energy E_{vib} of a cluster due to excitation of the vibrations of the cluster to be a smooth function of the temperature, we represent the total internal energy of a cluster in the form

$$E = E_{vib} + \Delta E w_{liq},$$

where $w_{liq} = Z_{liq}/(Z_{sol} + Z_{liq})$ is the probability of finding a cluster in the liquid state. Hence we obtain for the specific heat $C = \partial E/\partial T$ of a cluster near a phase transition, by analogy to equation (8),

$$C = C_0 + \left(\frac{\Delta E}{2T_m}\right)^2 \exp[-\alpha(T - T_m)^2],$$

$$\alpha = \left(\frac{\Delta E}{2T_m^2}\right)^2, \qquad (16)$$

where the specific heat C_0 is related with the vibrations of the cluster. For the cluster parameters employed, we obtain for the maximum specific heat $(C_V)_{max} = 1.1 \times 10^6$ and $\alpha = 5.5 \times 10^6 \, K^{-2}$, i.e., the width ΔT of the transition region is $\sim 10^{-3}$ K. As one can see, in this region the specific heat due to the configurational excitation of a cluster is two orders of magnitude greater than the contribution due to vibrations in a cluster.

The fundamental difference between the excitation of the configurations of a cluster at a structural phase transition and accompanying melting lies in the character of this excitation. In the case of a structural phase transition, the configurational excitation corresponds to a change in the positions for one or several atoms, while all atoms participate in a vibrational excitation. On melting the number of voids formed is comparable to the number of atoms in a cluster, so that this transition is stronger and changes the thermodynamic parameters of the cluster.

4. CONCLUSIONS

The method used for clusters with a pair interatomic interaction, where the interaction between nearest neighbors makes an appreciable contribution to the energy of a cluster, makes it possible to determine the thermodynamic parameters of a cluster taking account of the phase transition between structures. The effect of a phase transition is strongest for a cluster with 923 atoms, in which the shells are filled for the icosahedral

structure and unfilled for the fcc structure, for two reasons. First, the energy gap between the ground and first excited states is larger in an icosahedral cluster with filled shells than in an fcc cluster with an unfilled shell. Second, the statistical weights for the ground and first excited states of an fcc cluster are appreciably larger than for an icosahedral cluster. On account of this difference between the structures, the phase transition is reflected in the thermodynamic parameters of this cluster much more strongly than for clusters with other sizes. A phase transition between structures leads to a resonant temperature dependence of the specific heat of a cluster, and a phase transition between the solid and liquid has a much stronger effect on the properties of the cluster.

The contribution of a configurational excitation to the specific heat and entropy of a solid cluster is small compared with the contribution of the vibrations of the atoms in a cluster, even in the presence of a phase transition between the structures. For this reason, a configurational excitation has only a negligible effect on the thermodynamic parameters of a solid cluster. Conversely, the configurational part of the excitation in the liquid state of a cluster is has a large effect.

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