

Phase stability of solid clusters

R. S. Berry^{a)}

Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

B. M. Smirnov

Institute of High Temperatures, Izhor'skaya 13/19, Moscow 127412, Russia

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A solid cluster of 923 atoms bound by pairwise Morse interactions is the model for analyzing thermodynamic properties and phase equilibria in moderately small systems. The range of the potential is chosen so that the free energies of the icosahedral and face-centered cubic (fcc) structures are similar, enough so to allow a phase change between them. Statistical parameters of the cluster are determined for the two structures from their configurational entropies and pair interaction energies. The heat capacity and entropy of this cluster are calculated for conditions in the region of the phase change between the two solid forms, as well as away from this region. The configurational contribution to the thermodynamic properties is small relative to the vibrational contribution, but dominates the differences between free energies of the two phases. The configurational contributions to the thermodynamic properties become relatively more important for liquid clusters.

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INTRODUCTION

One typical kind of phase transition of second order in solids¹⁻³ is that involving a change of lattice symmetry. Its analog for clusters is the transition between different cluster structures.⁴ However the distinction between first and second-order transitions disappears in some cases for small systems.⁴⁻⁶ The reason is that *some* phase changes that become second-order transitions in large systems become so because two local minima (as functions of an order parameter) converge to one as the system is made larger. The sharp phase transitions of bulk materials, with their precise coexistence curves, transform, in their small counterparts, into broad bands of dynamically coexisting forms which are as much like components as they are like phases.⁷ Neither the average internal energy of the clusters in an ensemble, nor the temperature derivative of that energy have sharp discontinuities comparable to those of bulk systems. Nevertheless, since it is possible to see how phase equilibria of bulk systems evolve as the number of particles comprising a cluster increases, this analogy becomes useful for large clusters. We shall refer to transformations between phaselike forms of small systems as “phase changes,” and reserve the term “phase transition” for systems large enough that any coexistence of two or more phases is restricted to a very narrow range of temperatures and pressures, i.e., essentially to a traditional coexistence curve. Here we consider the phase change between the icosahedral and face-centered cubic (fcc) structures for clusters with pair interactions between atoms. We also address the melting process.

In bulk solids, this solid–solid transition occurs in heterogeneous systems, comprised of atoms of different sorts. Here we consider the passages between structures of a cluster whose particles interact through pairwise Morse poten-

tials, specifically when the energies of the icosahedral and face-centered cubic (fcc) structures are similar. Because this transition presumably may occur at low temperatures, conditions for which parameters of any relevant configurationally excited states of the cluster can be determined reliably, the analysis of this transition reveals much about its peculiarities in other cases. We may think of clusters with pair interactions between atoms as models for rare gas clusters. These grow to bulk systems whose crystal structures are close-packed, both face-centered cubic (fcc) and hexagonal structures.^{2,3} In contrast, clusters of atoms with pair interactions typically have structures based on the icosahedron,⁸⁻¹¹ which is not a stable form for a bulk crystal. The competition for stability between icosahedral and close packed structures of clusters is a phenomenon not yet well understood; it takes place in the range of cluster size of hundreds and thousands of atoms.¹²⁻¹⁴ The transition between these structures, as a function of both temperature and cluster size, can be revealing, and the temperature dependence of this phase change becomes a small-system counterpart of a structural phase transition in a solid.

This analogy becomes appropriate if a cluster has one structure at low temperatures and another at higher temperatures. Such a change may take place if the statistical weight of the higher-energy structure is higher than that of the lower-energy structure. Typically, structures with minimum statistical weight are those with filled shells, i.e., magic numbers of atoms. These are generally very low-energy structures as well. Hence we have chosen here to examine the phase change between structures for a cluster consisting of $n=923$ atoms. This is a magic number for an icosahedral cluster, so that the global minimum on the potential surface, the ground-state geometry, is a complete icosahedron. Excited 923 atom Morse clusters may also have locally stable fcc structures. Because, for this number of cluster atoms, the

^{a)}Electronic mail: berry@rainbow.uchicago.edu

outermost shells are not filled, the statistical weight of the fcc structure is large enough at high temperatures to give the fcc structure the lower free energy.

In contrast to bulk systems, where the phase transition occurs along a precise pressure-temperature curve, phase changes in clusters take place throughout a range of temperatures.^{15–17} For clusters of a given size, this range tends to be wider for the transition between structures, if the cluster has two coexisting solid forms, than for the solid–liquid transition. The example considered here was chosen to let us examine the nature of coexistence of solid structures for typical thermodynamic parameters of clusters, and to compare such coexistence with the solid–liquid phase change of the same system.

With Morse interactions between atoms, i.e., $V(R) = D[e^{2\alpha(R-R_0)} - e^{\alpha(R-R_0)}]$, the competition between the relevant structures depends on the range parameter α (or $\rho_0 = \alpha R_0$). In particular, in the commonly studied zero-pressure limit, the energies of the close-packed and icosahedral structures coincide at $\rho_0 = 7.1$.¹⁵ Hence, we use $\rho_0 \leq 7.1$, so that in this range the icosahedral structure generally has lower energy, but the energy gap between structures is not high, and transition between structures proceeds at temperatures well below the melting point. Variation of ρ_0 allows us to analyze the character of this cluster's structural phase change and use it to help us understand structural phase transitions in solids.

There is a useful characteristic of atomic clusters with a pair interaction if the long-range attraction does not extend very far. In this case it is possible to divide the total binding energy of the cluster at zero temperature into three parts:¹⁶ The potential energy of interaction of nearest neighbors, the interaction potential of non-nearest neighbors, and the strain energy. The two latter types of interaction influence the competition among structures, although the much larger first contribution reflects the energy differences associated with changes of configurations in which the total number of nearest neighbors change. Hence, at least for low-lying configurations, one can characterize classes of excited configurational states of such a cluster as those with fewer bonds than in the lowest-energy configuration. Each class is specified by the difference between the number of nearest neighbors or ‘‘bonds’’ in the lowest-energy configuration and the number in that configuration. This categorization simplifies the analysis of low-lying states or low-structural excitations of clusters and allows us to find statistical parameters of a solid cluster which are determined just by its configuration of atoms. With these parameters, we analyze the phase transition between the icosahedral and fcc structures for the solid cluster and the influence of this transitions on cluster thermodynamic parameters. It is straightforward to then include the effects of non-nearest-neighbor attractions and of strain, as corrections to the dominant structural contribution.

STATISTICAL PARAMETERS OF CLUSTER

We construct the cluster partition function like we would that of the bulk, by dividing it into the vibrational and configuration parts. Because we deal with excitation of only a few atoms in a solid cluster, we approximate by taking the vibrational part of the partition function to be identical for

different atomic configurations at each temperature. (This is relatively safe for solid–solid processes, but not for solid–liquid or even for solid-to-surface-melted processes.) Hence, we account for only the configurational part of the partition function which has the form

$$Z = \sum_i g_i \exp\left(\frac{\epsilon_i}{T}\right), \quad (1)$$

where g_i is the statistical weight for the i th configuration of atoms, i.e., the number of different atomic configurations of this symmetry with the excitation energy ϵ_i . Below we treat clusters at low temperatures, at which only a finite number of states contributes to (1). We take the cluster entropy S due to atom configurations to be zero at zero temperature, so that it is

$$S = \ln Z = \ln \sum_i g_i \exp\left(\frac{\epsilon_i}{T}\right). \quad (2)$$

One can introduce an order parameter η for the system under consideration as

$$\eta = \frac{Z_{\text{ico}}}{Z_{\text{ico}} + Z_{\text{fcc}}}, \quad (3)$$

where Z_{ico} and Z_{fcc} are the partition functions for the clusters with icosahedral and fcc structures, respectively. This parameter is one if the cluster has only icosahedral structure and is zero if it is always in the fcc structure. In the example used here, we examine a Morse cluster consisting of 923 atoms whose ground state is icosahedral, but whose excitation energy to the lowest fcc state is relatively small, and for which the entropy of the fcc state is significantly higher than that of the icosahedral form. In this situation, at low temperatures the order parameter varies between one and zero as the temperature increases.

The heat capacity of the cluster due to variation of the atomic configuration is

$$\begin{aligned} C_V &= \frac{\partial E_{\text{exc}}}{\partial T} \\ &= \frac{\partial}{\partial T} \left[\frac{1}{Z} \sum_i \epsilon_i g_i \exp\left(-\frac{\epsilon_i}{T}\right) \right] \\ &= \frac{1}{T^2} \left[\frac{\sum_i \epsilon_i^2 Z_i}{Z} - \left(\frac{\sum_i \epsilon_i Z_i}{Z} \right)^2 \right], \end{aligned} \quad (4)$$

Here $Z_i = g_i \exp(-\epsilon_i/T)$ is the partition function for a given atom configuration, and E_{exc} is the cluster excitation energy. We shall compare this configurational part with the vibrational contribution to the total heat capacity. This latter can be estimated from the Dulong–Petit law $C_o \approx 3n$, where n is a number of cluster atoms or, as we shall do later, from a Debye model. Here and below we express the temperature in energy units. Furthermore we express the configurational excitation energies ϵ_i and temperature in units of D , the dissociation energy of the Morse-bound diatomic, i.e., the energy of one bond.

STATISTICAL PARAMETERS OF THE ICOSAHEDRAL CLUSTER

We begin by calculating the statistical weights of atomic configurations for clusters with pairwise short-range interactions between atoms, specifically including only the interactions between nearest neighbors. If we approximate the pair interaction by the Morse potential, then the corresponding Morse parameter is not small: $\alpha \geq 3$. Thus our first approximation is a cluster dominated by nearest-neighbor interactions.

The second approximation takes into account interaction of non-neighboring atoms and also the strain energy of clusters, the result of displacement of atoms from ideal close-packing distances. This breakdown¹³ has been shown to be useful and is valid for Morse clusters if $\alpha \geq 3$ as well as for other clusters where pair interactions between nearest neighbors dominate.

Within the framework of this scheme, we first characterize the lower states of excitation of a cluster of N atoms by the deviation of the number of cluster bonds (nearest neighbors) from the maximum for that cluster, so that the excitation energy from the ground state of a cluster of a specific N is an integer if the energy is measured in units of the dissociation energy D of a diatomic. We define the statistical weight of this cluster structure as the number of atomic configurations with the same number of bonds between nearest neighbors. Thus, g_i , the statistical weight of the cluster of a given N , is the number of number of structures with i fewer nearest-neighbor bonds than in the ground state. Hence at this level, we assume the vibrational statistics do not change as a result of change of an atom configuration of the cluster, so long as the number of bonds remains constant.

The icosahedral cluster consisting of 923 atoms has 2172 bonds between atoms of neighboring layers and 2730 bonds between atoms in the same layers.¹⁷ This cluster has 561 internal atoms; its surface layer consists of 12 vertex atoms, 150 edge atoms, and 200 atoms located within surface triangles. Each vertex atom has 6 bonds with nearest neighbors, each edge atom has 7 bonds and each surface atom has 9 bonds. One can place an atom in hollows between surface atoms; such an atom has three bonds with nearest neighbors. There are 720 such positions for the cluster under consideration, equal to the number of elemental triangles formed by surface atoms.

The excitations of configurations of cluster atoms considered here correspond to transitions of atoms from the various sites in the cluster surface. We consider only transitions involving excitation of a small number of atoms onto that surface. These excitations determine the thermodynamic parameters of the cluster at low temperatures.

From this it follows that the minimum excitation energy is $\Delta\epsilon=3$ which corresponds to the transition of a vertex atom to a site on the cluster surface, where it has three nearest neighbors. The statistical weight of this excitation is equal $g_3=12 \cdot 715=8580$, large compared to the statistical weight of the ground state for which $g_0=1$. There are also five possible positions on the cluster surface border for such an excited vertex atom; we neglect these because they are so few compared with the total number of available positions.

TABLE I. Statistical parameters of an icosahedral cluster.

ϵ_i	0	3	4
g_i	1	$8.6 \cdot 10^3$	$1.1 \cdot 10^5$
ϵ_i	6	7	8
g_i	$1.7 \cdot 10^7$	$9.3 \cdot 10^8$	$5.2 \cdot 10^9$
ϵ_i	10	11	12
g_i	$3.9 \cdot 10^9$	$8.4 \cdot 10^{12}$	$4.6 \cdot 10^{13}$

The excitation energy $\Delta\epsilon=4$ corresponds to excitation of one edge atom; $\Delta\epsilon=6$ is the energy corresponding to excitation of one surface atom or two vertex atoms. We have

$$g_4 = 150 \cdot 720 = 1.1 \cdot 10^5,$$

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

Thus, we have the following method of calculation of the statistical weight for this cluster. The partial statistical weight which corresponds to a promotion of v atoms from the vertices e atoms from the edges and s atoms from the surface is

$$g_i = C_{12}^v C_{150}^e C_{200}^s C_{720}^k \approx C_{12}^v \frac{150^e}{e!} \frac{200^s}{s!} \frac{720^k}{k!}, \quad (5)$$

where $k=v+e+s$ is the total number of excited atoms, and the energy of this excitation is $\epsilon_i=3v+4e+6s$. This formula is valid for a small number k of excited atoms. We neglect three facts here. First, if an atom is removed from the vertex of a surface triangle, the removed atom cannot be placed in the centers of these triangles because such a site has fewer bonds than other available positions. Second, we cannot allow two promoted atoms to be located in the centers of neighboring triangles because the distance between these centers is only $a/\sqrt{3}$, where a is the distance between nearest neighbors. Third, we neglect formation of bonds between promoted atoms because the number of such atoms is relatively small in the excitations we consider. Thus, formula (5) is approximately valid for weak excitations and allows one to analyze statistical properties of the cluster at low but nonzero temperatures. The statistical weights for first excited states are given in Table I.

From this one can calculate the partial partition function Z_i for a given excitation energy

$$Z_i = \sum g_i \exp\left(-\frac{\epsilon_i}{T}\right),$$

where the summation is taken over the different ways to achieve a given excitation energy, and the cluster temperature T is expressed in units of the binding energy D of one bond. Below we evaluate the cluster entropy $S=\ln Z$ for the solid cluster state up to its melting point; for this cluster the melting point $T_m \approx 0.44$ according to Ref. 18. (Here and elsewhere we take T_m to mean the temperature at which the liquid and solid clusters have equal free energies, to correspond to the bulk melting temperature. Just as the solid-liquid equilibrium for clusters actually occurs in a band and not simply along a curve of $p(T)$, so do the solid and liquid

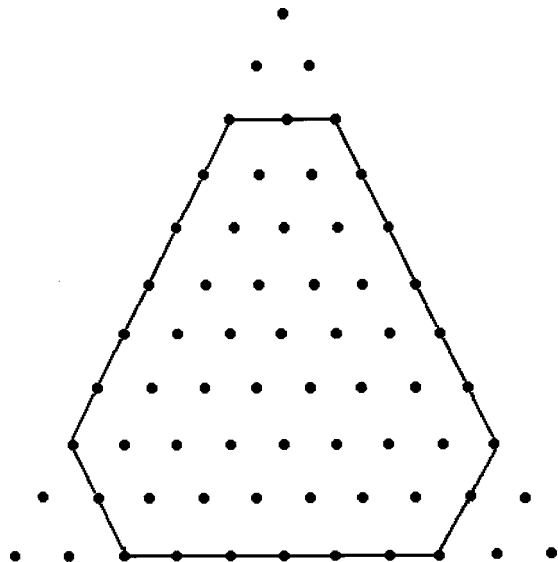


FIG. 1. The filled $\{111\}$ facet of the fcc cluster consisting of $n = 861$ atoms. This cluster has the structure of a truncated octahedron and is formed from an octahedral cluster consisting of 891 atoms. Positions of atoms of this cluster whose $\{111\}$ facets are regular triangles are shown in this figure. Solid lines restrict the boundary of the facet for the cluster consisting of 861 atoms.

clusters coexist away from the curve of equal free energies.⁷⁾ The values of key statistical parameters of this cluster are given in Table I.

The method of the analysis of the Morse cluster used by Cheng *et al.*¹⁵ allows us to determine the statistical weight for the lowest states of the solid cluster. Below we apply this to a cluster with an fcc structure. The optimal shape of closed-shell clusters with fcc structure is a truncated octahedron whose surface consists of 8 hexagons and 6 squares.¹⁹ First we construct the ground state of the cluster with fcc structure. Because this operation for the ground and lowest excited states is cumbersome, we describe it in detail. The basis of this cluster in the ground and lowest excited states is the structure of the truncated octahedron. The filled octahedral cluster of about the size of interest contains 891 atoms and has 4620 bonds between nearest neighbors. Its surface consists of 8 regular triangles, and each of 12 its edges contains 11 atoms, including those at vertices. Cutting 6 pyramids near each cluster vertex, we obtain a truncated octahedron which includes 861 atoms with 4476 bonds between nearest neighbors.²⁰ Each of removed pyramids contains 5 atoms and has edges of 2 atoms. The surface of the cluster so formed consists of 8 hexagons with alternating side lengths and 6 squares, each incorporating 9 atoms. The long edges of each hexagon contain 7 atoms, including vertices. Squares have the directions $\{100\}$ and hexagons have directions $\{111\}$ in usual notation.² Figure 1 shows positions of the surface atoms of a hexagon.

The growth of this cluster transpires by filling of its $\{111\}$ facets. The first stage of the growth process consists of filling positions in the centers of surface triangles. Figure 2 shows positions of the surface atoms when the new layer of this facet is filled. The layer of one facet contains 46 atoms and increases the number of bonds between nearest neigh-

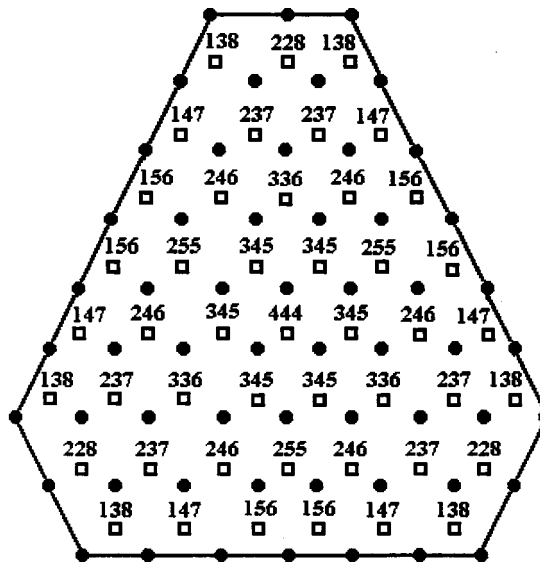


FIG. 2. The character of filling of the $\{111\}$ facet for the fcc cluster with the structure of a truncated octahedron. The basis is the cluster consisting of 861 atoms and positions of its surface atoms are marked by dark circles, while the positions of the new layer are marked by clear squares. Notations of shells to which atoms belong are given above their positions, and numbers klm in these notations label coordinates zxy of an atom of this shell in units $a/\sqrt{2}$, where a is the distance between nearest neighbors, and the origin is the symmetry center for completed cluster shells.

bors by 252. Here we use the convenient notation of expressing the atom position coordinates in units of $a/\sqrt{2}$, where a is the distance between nearest neighbors, and values $|x|$, $|y|$, $|z|$ are given in increasing order of these values. Then atoms with identical quantities of these values form a shell; the values for nearest neighbors coincide, and two others differ by unity.

Now we construct the configuration of cluster atoms for $n = 923$. We start from the configuration in which one facet is filled according to Fig. 2, and another contains a surface hexagon which includes 19 atoms. This configuration of surface atoms is shown in Fig. 3. The addition of the surface hexagon of 19 atoms increases the number of bonds between nearest neighbors by 99. Thus, the fcc cluster of 926 atoms in its ground state has 4827 bonds between nearest neighbors. Let us consider the statistical weight of this configura-

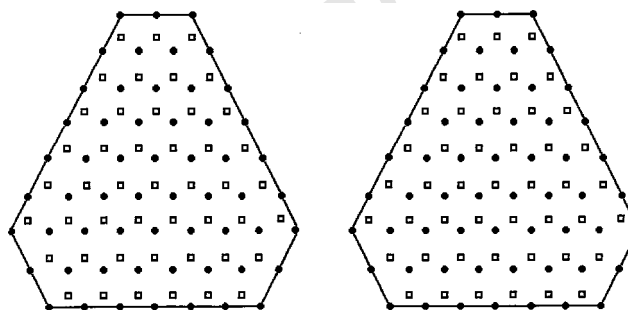


FIG. 3. Filling of the $\{111\}$ facets for the fcc cluster of 926 atoms in the ground configuration. Positions of surface atoms of filled facets are marked by dark circles and positions of atoms of the filling layer are indicated by clear squares. The number of bonds between nearest neighbors for this cluster is equal 4827 compared to 4914 for the icosahedral cluster with $n = 926$.

tion. Choosing the filled facet and the partially filled facet in an arbitrary way, we obtain $7 \cdot 8 = 56$ versions. Next, the regular triangle on the surface of the partially filled facet can be chosen in 10 ways, which makes the statistical weight $g = 560$ for the fcc cluster of 926 atoms in its ground state.

In order to transform this cluster into the lowest-energy fcc configuration of the cluster of 923 atoms, we must remove 3 atoms from it. The high-energy sites from which we take these are in the edges of the nonregular hexagon of a filled facet or in the regular polygon of the partially filled facet. When these atoms are removed, 17 bonds between nearest neighbors are lost, leaving 4810 bonds in the ground state of the fcc cluster of 923 atoms. The statistical weight of this cluster is equal to the product of a number of operations for construction of the cluster of 926 atoms and numbers of operations for removal of 3 atoms from it. If only symmetric states in which all three atoms are removed from the same kind of site, this number is

$$g_o = 8 \cdot 7 \cdot (3 \cdot 10 + 3 \cdot 10 + 3 \cdot 13) = 5544.$$

The first term in parentheses corresponds to removal of 3 atoms from the filled facet; the second term, to removal of the upper edge and two lower lateral edges from the regular surface hexagon of the partially filled facet, and the third term, to removal of the lower and two upper lateral edges from the regular surface hexagon of the partially filled facet. Thus, even without consideration of unsymmetrical states in which the three atoms are removed from different kinds of sites, the statistical weight of this structure is large compared to that of the filled icosahedral cluster.

Now we formulate our general, second-order approach to the analysis of the Morse clusters. The total number of bonds between nearest neighbors of the fcc cluster in the ground state is 4810, while for the icosahedral cluster of 923 atoms the total number is 4902. We divide the interactions between cluster atoms into the interactions between nearest neighbors, the interactions between non-nearest neighbors and the strain interactions.¹⁶ The total binding energies of the icosahedral and fcc structures of the Morse clusters coincide if the Morse parameter $\alpha = 7.1$.¹⁵ The largest contribution to the total binding energy is of course that of the interactions between nearest neighbors, but because the difference between the numbers of bonds in the two structures is small, the two other contributions to the total binding energy are important in the competition between these structures, specifically the strong sensitivity of this competition to the form of the pair interaction potential between atoms.^{15,17,21-23} In contrast, to analyze the excitation energy one need consider only the nearest-neighbor interactions, expressing the excitation in terms only of the difference between numbers of bonds in the ground and excited states.

Let us analyze excited configurational states of the 923 atom fcc cluster. As above, we express the excitation energy in terms of the number of bonds that are broken to produce the excited configuration from that of lowest energy. The lowest of these states corresponds to the excitation energy $\Delta\epsilon = 1$ which results from the promotion of one atom from a vertex of any hexagon to a free hexagon edge, so that this atom forms two bonds with atoms of the hexagon edge. The

statistical weight of this excitation is the sum of several terms. The contribution to the statistical weight by the formation of a vacancy in the filled facet in the transformation of the 926 atom fcc cluster into the 923 atom cluster (see Fig. 3) and the placement of the transiting atom onto the filled facet is

$$\frac{g'_1}{8 \cdot 7} = 3 \cdot 10 \cdot (10 \cdot 2 + 2 \cdot 1).$$

Here the first factor accounts for the number of positions for vacancies when three atoms are removed from the fcc cluster of 926 atoms to make the cluster of 923 atoms, and the second factor is the number of positions of the regular hexagon on the surface of an unfilled facet. The first term in parentheses describes the case in which the initial position of the promoted atom is not the vertex of an edge to which this atom is finally attached, and the second corresponds to a vertex position. Each term in parentheses is the product of the number of initial positions of the promoted atoms in vertices of hexagons and final positions of this atom near hexagon edges.

In the second option the vacancy is also created in a filled facet, but the promoted atom is then attached to an edge of the regular hexagon of the unfilled facet. This gives a contribution into the statistical weight of this excited state of

$$\frac{g''_1}{8 \cdot 7} = 3 \cdot 10(10 \div 11) \cdot (6 \div 12) \sim 3000.$$

Here the first factor is the number of possible vacancies in the completed facet in the course of the transformation of the fcc cluster of 926 atoms into the cluster of 923 atoms, the second factor is the number of possible positions of the regular hexagon on the surface of the unfilled facet during this operation, the third term is the number of possible positions of the promoted atom as a vertex of a hexagon, and the last term is the number of free positions for this atom near an edge of a small surface hexagon.

In the third case the vacancy created by transformation of the 926 atom fcc cluster into the 923 atom cluster is formed in a small hexagon. Its contribution in the statistical weight of the excited state is

$$\frac{g'''_1}{8 \cdot 7} = 6 \cdot 10(10 \div 13) \cdot (10 \div 11) \cdot (6 \div 12) \sim 6000.$$

Summarizing the above contributions, we obtain for the statistical weight of the excited state of the cluster with $\Delta\epsilon = 1$

$$g_1 \sim 100g_o.$$

The set of excited states with $\Delta\epsilon = 2$ can be obtained from the ground state by promotion of one atom from a vertex of a surface hexagon onto the surface of a square where the promoted atom has four nearest neighbors. This gives

$$g'_2 = 12 \cdot 24 \cdot g_o,$$

where the first factor is the number of hexagon vertices and the second factor is the number of positions on the surfaces of squares. An additional contribution gives transitions of an atom from an edge of a hexagon to a free edge of a hexagon. The total statistical weight of this excited state with $\Delta\epsilon=2$ is

$$g_2 \sim 500g_o.$$

The excited states with $\Delta\epsilon=3$ can result from transitions of an atom from vertices of incomplete hexagons on the surfaces of free hexagonal facets. This gives a contribution to the statistical weight of such an excited configuration of

$$g'_3 = 12 \cdot 6 \cdot 92g_o = 6.6 \cdot 10^3 g_o,$$

where 12 is the number of hexagon vertices, 6 is the number of free hexagon facets, and 92 is the number of possible positions of a promoted atom on the surface of a free facet. An additional contribution arises from promotions from edges of surface hexagons to square facets

$$g''_3 = 20 \cdot 24g_o \sim 600g_o,$$

where 20 is the number of atoms located on edges of surface hexagons. One more way to obtain excited states with $\Delta\epsilon=3$ is by promotion of a bound pair of surface atoms to the square surface, where one of atoms occupies a vertex of a surface hexagon, and the other becomes its neighboring atom on an edge. This operation contributes a statistical weight of excited states

$$g'''_3 = 24 \cdot 24g_o \sim 600g_o,$$

where the first factor is the number of positions for the bound pair of atoms and the second factor is the number of positions for this pair on the surface of squares. One last contribution to the statistical weight arises from transitions of hexagon atoms on partially filled hexagon facets. As a result, we have for the total statistical weight of excited states with $\Delta\epsilon=3$

$$g_3 \sim 8000g_o.$$

“Noncompleted structures” complicate the calculation of the statistical weights of still higher excited states of the fcc cluster. We estimate these approximately. One can create excited states with $\Delta\epsilon=4$ by excitation of two vertex atoms of incomplete hexagons to the surface of a square in the form of a bound pair; the number of such possible excitations is

$$g_4 = C_{12}^2 \cdot 24g_o \sim 1600g_o,$$

where the first factor is the number of ways to choose two vertex atoms of surface hexagons.

The first way to obtain an excited states with $\Delta\epsilon=5$ corresponds to transition of one internal atom of a surface hexagon to the surface of a square. This has a statistical weight

$$g'_5 = 30 \cdot 24g_o \sim 700g_o,$$

where the first factor is the number of internal atoms in incomplete surface hexagons and the second factor is the number of available positions on the surfaces of squares. The second way to create an excited states with $\Delta\epsilon=5$ is excita-

tion of a bound pair of atoms consisting of one vertex and one edge atom of an incomplete hexagon on the surface of a free hexagonal facet. This gives

$$g''_5 \sim 24 \cdot 92 \cdot 6 \cdot \frac{1}{2}g_o \sim 4 \cdot 10^4 g_o.$$

Here the first factor is a number of initial positions of atomic pairs, the second and third terms are the numbers of final positions for one of these atoms, the fourth factor accounts for the number of positions for the second atoms with respect to the first on the surface of a filled facet, and finally the factor of 1/2 takes into account that permutation of the two promoted atoms does not change the state. One more way to obtain an excited state with $\Delta\epsilon=5$ is excitation of one vertex atom of an incomplete hexagon onto the surface of a square facet. Still another puts the atom onto the surface of a filled hexagon facet. These operations lead to the statistical weight of excited states

$$g'''_5 \sim C_{12}^2 \cdot 24 \cdot 6 \cdot 92 \cdot g_o \sim 8.7 \cdot 10^5 g_o,$$

where the first factor is the number of ways to choose two transiting atoms located on vertices of incomplete hexagons, the second factor is the number positions on square facets, and the two subsequent factors give the numbers of positions on the surfaces of free hexagonal facets. The fourth way to create excited states with $\Delta\epsilon=5$ arises from excitation of an internal atom of an incomplete hexagon on the surface of a free hexagon facet. It has a statistical weight of

$$g''''_5 = 30 \cdot 6 \cdot 92g_o \sim 1.6 \cdot 10^4 g_o.$$

From this we obtain the total statistical weight for all the kinds of excitations with $\Delta\epsilon=5$

$$g_5 \sim 9.3 \cdot 10^5 g_o.$$

Excited configurations with $\Delta\epsilon=6$ are formed as a result of transitions of two vertex atoms of incomplete hexagons or a pair of bound vertex and edge atoms on the surface of free hexagonal facets in which the promoted atoms do not form a bond each with other. This operation leads to the statistical weight of excited states with $\Delta\epsilon=6$

$$g_6 \sim (C_{12}^2 + 24) \cdot C_{552}^2 \cdot g_o \sim 1.4 \cdot 10^7 \cdot g_o.$$

A full analysis of all the low-lying excited states of the 923 atom cluster is too complex to be practical. Here we have restricted our analysis to enumerating the states which give the main contributions to the statistical weights of states defined by a given coarse-grained excitation energy, specifically to the breaking of a specified number of bonds. Among subsequent excited states we extract those with $\Delta\epsilon=9$ which are formed as a result of excitation of three vertex atoms of incomplete surface hexagons to the surfaces of free hexagonal facets; their statistical weight is

$$g_9 \sim C_{24}^3 \cdot C_{552}^3 \cdot g_o \sim 5.6 \cdot 10^{10} \cdot g_o.$$

In the same way we estimate the statistical weight of excited states which result from transition of four vertex atoms of incomplete surface hexagons onto free hexagonal facets

$$g_{12} \sim C_{24}^4 \cdot C_{552}^4 \cdot g_o \sim 4.1 \cdot 10^{13} \cdot g_o.$$

If statistical weights of other intermediate levels of configurational excitation were desired for estimating thermodynamics properties, it would be sufficient for many purposes to estimate them by interpolation from the values given here. These values of statistical weights of the fcc cluster under consideration are used below for evaluation of its thermodynamical parameters.

STRUCTURAL TRANSITIONS AND THE THERMODYNAMIC PARAMETERS OF THE SOLID CLUSTER

The above analysis allows us to evaluate parameters governing the phase transition between the icosahedral and fcc cluster structures. Expressing the temperature in units of the binding energy of one bond, we find that the cluster excitations start to appear at $T \approx 0.2$. The above statistical weights allow us to analyze cluster states up to temperatures $T \approx 0.35$; the melting point for this 923 atom cluster is $T_m = 0.44$.⁸ Phase coexistence of the icosahedral and fcc solid structures of the cluster may emerge from the low-temperature condition of sole stability of the ground icosahedral state if the free energy develops a second minimum for the fcc structure; this is how the thermodynamic parameters allow the onset of the finite-system analog of a bulk phase transition.^{7,24} The parameters that determine whether such a “new” minimum appears in the free energy are of course the excitation energy Δ and the statistical weights of the accessible states of both structures. Note that we can change the value of Δ by varying the Morse parameter α , particularly in the vicinity of $\alpha = 7.1$, the value at which the energies of structures.

The temperature at which the two phases have equal free energies, which is the precise analog of the temperature of the bulk phase transition T_{tr} between the two solid structures, is determined by the condition of equality of the partition functions of the two phases. For convenience, we refer to T_{tr} as the “central temperature” of the phase change. At this point,

$$Z_{ico} = Z_{fcc} g_o \exp\left(-\frac{\Delta}{T_{tr}}\right), \quad (6)$$

where Z_{ico} is the partition function (1) for the icosahedral state, $Z_{fcc} = Z/g_o$, so that Z is the partition function of the fcc cluster with no weighting for the multiplicity of the icosahedral structure, and $g_o = 5544$ is the statistical weight of its ground icosahedral state. (This equation is of course an approximation insofar as it does not recognize the contributions of excited configurations of the two forms.) From formula (6) we obtain an approximate central temperature of the phase change,

$$T_{tr} = \frac{\Delta}{\ln g_o + \ln Z_{fcc}/Z_{ico}} = \frac{0.116\Delta}{1 + 0.116 \ln Z_{fcc}/Z_{ico}}. \quad (7)$$

From this equation, it follows that coexistence, with equal probability or frequency, of the two solid phases of the 923 atom cluster occurs if $\Delta < 4$, so long as $T_{tr} < T_m$.

The heat capacity has a peak at the central temperature T_{tr} of the phase transition, and the “excess” contribution to

the heat capacity above the smooth contribution from each single phase follows directly from the partition function of Eq. (6):

$$C_{tr} = \left(\frac{\Delta}{2T_{tr}}\right)^2 \exp[-\alpha(T - T_{tr})^2], \quad \text{where } \alpha = \left(\frac{\Delta}{2T_{tr}^2}\right)^2. \quad (8)$$

In the tacitly implied pressure range, i.e., low enough that the effects of pressure on structure may be disregarded, the difference between the heat capacities at constant pressure and volume is relatively small. Hence we assume these values to be identical and denote them as C . If $\Delta < 2$, formulas (7) and (8) give the maximum value of the heat capacity owing to the phase transition $C_{max} = (\ln g_o/2)^2 \approx 19$. For higher values of Δ , the jump in the heat capacity is greater but remains close to the above value. However this value is small in comparison with the vibrational contribution to the heat capacity, which, in the classical limit according to the Dulong–Petit formula, is $C = 3n \approx 3000$, where n is a number of cluster atoms.

The width of the peak in the heat capacity is relatively small. Indeed, if we define this width as $\Delta T = 1/\alpha$, we obtain from formula (8)

$$\Delta T \equiv \frac{2T_{tr}^2}{\Delta} = \frac{2T_{tr}}{\ln g_o + \ln Z_{fcc}/Z_{ico}}, \quad (9)$$

and for this cluster we have $\Delta T/T_{tr} = 1/5 \div 1/4$.

Let us now extend formula (4) for the cluster heat capacity to allow the cluster to have two structures whose ground states are separated by the energy difference Δ . In this case, expression (4) gives the cluster heat capacity

$$C = \frac{Z_1}{Z} C_1 + \frac{Z_2}{Z} C_2 + \frac{1}{T^2} \frac{Z_1 Z_2}{Z^2} (g \bar{\epsilon}_1 - \bar{\epsilon}_2 - \Delta)^2, \quad (10a)$$

Here Z_1 and Z_2 are the total partition functions for the corresponding cluster structures, $Z = Z_1 + Z_2$; C_1 and C_2 are the heat capacities for each cluster structure when the other cluster structure is absent; $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ are the average excitation energies for a given cluster structure where the ground configuration of this structure corresponds to zero energy.

Expression (10a) exposes the character of the “resonance” of the cluster’s heat capacity that occurs when both structures contribute significantly to the mean cluster energy. Indeed, let us suppose in this formula that $\bar{\epsilon}_1 \ll \Delta$ and $\bar{\epsilon}_2 \ll \Delta$, so that the maximum corresponds to $Z_1 = Z_2 = Z/2$. This gives the maximum heat capacity C_{max}

$$C_{max} = \frac{1}{2} (C_1 + C_2) + \left(\frac{\Delta}{2T}\right)^2, \quad (10b)$$

that corresponds to Eq. (8).

Figure 4 contains the dependence of the cluster heat capacity on the energy gap Δ between the ground states of the icosahedral and fcc structures at the temperatures $T = 0.25$ and 0.3 . One can see the resonant character of the heat capacity at the temperature $T = 0.25$ which becomes less sharp at $T = 0.3$.

Next we examine the entropy $S = \ln Z$ associated with the configurational freedom of cluster atoms. (Note that we are

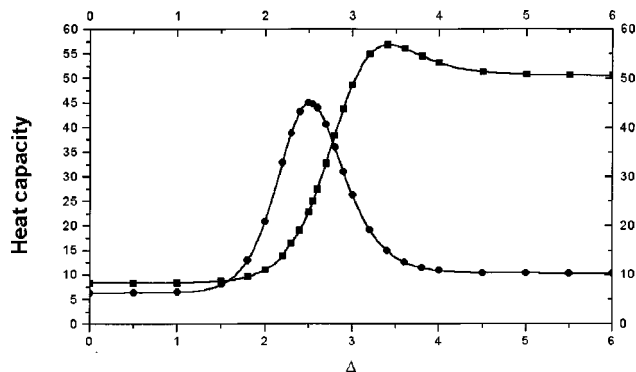


FIG. 4. The heat capacity of the solid cluster of $n=923$ at the temperatures $T=0.25$ and $T=0.3$ as functions of the energy gap Δ between ground states of the icosahedral and fcc structures of the cluster.

using dimensionless units, equivalent to setting $k_B=1$.) This function is of course very close to zero at low temperatures because the cluster is found virtually exclusively in the ground state of the filled icosahedral structure. (If we had chosen an open-shell cluster as our example, the configurational freedom even at very low temperatures would complicate this issue, but nevertheless one can expect to be able to invoke quantum symmetry-breaking to retain validity of the Third Law even in such cases.)

Increasing the temperature increases the entropy monotonically, as it must. It happens in this system because increased temperature increases the population of excited icosahedral configurations and the phase change occurs into states of the fcc structure. The entropy also increases with any decrease of the energy gap Δ between the ground states of the icosahedral and fcc structures. In particular, Fig. 4 shows the dependence of the cluster's heat capacity S on the gap Δ between the icosahedral and fcc ground states. In the limit of large values of Δ , the entropy is simply that of the icosahedral cluster; at $T=0.3$ it is equal $S=0.53$. In the limit of small Δ the entropy comes overwhelmingly from the contribution of the fcc structure and is equal $S\approx 11$. These entropy values are equal to 0.7 and 9.8 at the temperature $T=0.25$ in the limits of large and small Δ correspondingly, and also 0.003 and 9.2 at the temperature $T=0.2$. Because the fcc cluster structure is that of an open shell, the number of its low-lying configurations is large. That is what makes the differences in the entropy values of the fcc and icosahedral forms so large. However the contribution to the total entropy from atomic vibrations is large compared with any of these values. In particular, in the classical limit we may estimate this contribution from the Debye model, for which the entropy is¹

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

where ω_D is the Debye frequency (the maximum or cut-off frequency in the model); n is a number of cluster atoms. For the 923 atom cluster, this formula gives $S_{\text{vib}} \sim 1000$.

A temperature increase leads to increase of the number of populated excited states, which in turn determine the thermodynamic properties of the cluster. In particular, from the

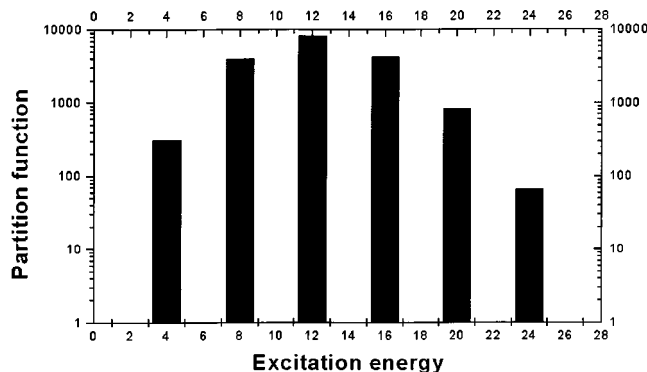


FIG. 5. The partition functions which correspond to excitation of edge atoms for the solid icosahedral cluster consisting of 923 atoms at the cluster melting point.

statistical weights of all the excited configurations, we may estimate these properties up to temperatures $T \approx 0.35$. In the next higher temperature range, up to the melting point $T_m = 0.44$, where the thermodynamic properties increase still further, we evaluate them a bit more crudely, by restricting the estimation to include only excitations of edge atoms. This can be justified because such excitations give a large proportion of the total statistical weight of all the available excitations. According to formula (5) we have, for the partition function of configurations produced by excitation of k edge atoms to the cluster surface

$$Z_k = \frac{(150 \cdot 720)^k}{(k!)^2} \exp\left(-\frac{4k}{T}\right).$$

Values of these partition functions are shown in Fig. 5. At the melting point the total partition function due to these excitations is $Z = \sum Z_k = 165$, corresponding to an entropy of $S=5.1$. In addition, restricting the estimate to these excitations, we obtain the cluster heat capacity at the melting point: $C=141$. One can be sure that including other excitations would increase these parameters, but the orders of magnitude are established by this estimate; we have $S \sim 10, C \sim 100$ for the solid icosahedral cluster of $n=923$ at the melting point. For the cluster of this size, the entropy of the fcc form is greater and the heat capacity is less than for the icosahedral cluster, but the orders of magnitude of these quantities are the same for both forms. Thus, the contributions to the total entropy and heat capacity of the solid cluster owing to excitation of atom configurations are less than the contributions due to atomic vibrations.

Despite the greater magnitude of their vibrational contributions, the differences between the entropies and heat capacities of the two solidlike phases are due largely to the differences in their configurational parts, at the level of this model, the Debye approximation. Only if we were to explore the differences in force constants associated with different configurational excitations, i.e., with sites having different numbers of nearest neighbors, would the change of the vibrational contributions affect the results. Even at that level, the contributions of vibrations to the difference between partition functions of icosahedral and fcc structures is essentially second order, because it is only in the differences in the

numbers of local configurational excitations that in turn govern the differences in the vibrational contributions to the entropies and heat capacities; a given local excitation produces roughly the same change in vibrational frequencies in the two structures. This is especially true because we consider only structures with a small number of excitations, so that the long-range contributions to the thermodynamic properties remain almost unchanged.

THERMODYNAMIC PARAMETERS DUE TO CLUSTER MELTING

The thermodynamic parameters of a cluster change substantially when the cluster melts. To estimate these changes, we take the fusion enthalpy per atom ΔH_{fus} for this cluster to be that of a condensed rare gas which, in our dimensionless units, is $\Delta H_{\text{fus}}=0.98$. From this, we obtain the entropy change due to the melting of the cluster

$$\Delta S = \frac{\Delta E}{T_m} = \frac{n\Delta H_{\text{fus}}}{T_m} = 2060,$$

which exceeds the entropy of the solid cluster at this temperature by two orders of magnitude and is comparable to that due to atomic vibrations at the melting point. Thus, the configurational contribution to the entropy is an important part of the free energy of the liquid state of the cluster, but is relatively unimportant for its solid state. Note that the melting point of bulk condensed rare gases is $T_m=0.58$ and exceeds that for the cluster considered here, for which $T_m=0.44$. Therefore, the bulk heat of fusion is clearly too high to be an accurate estimate of the enthalpy of fusion of our cluster. Nevertheless, the above estimations are close enough to fix the magnitudes and the essential conclusions are valid. In addition, the parameters of the liquid state of condensed rare gases are based entirely on excitations of internal atoms, with no consideration of pure surface effects. In clusters of even several thousand particles, the surface excitations are important to the entropy, enthalpy and heat capacity.

Now let us examine the behavior of the heat capacity in the melting range for the 923 atom cluster. We simplify and aggregate by using the two-level approximation for the solid and liquid states, so that the ratio of the liquid Z_{liq} and solid Z_{sol} partition functions is

$$\frac{Z_{\text{liq}}}{Z_{\text{sol}}} = \exp\left(-\frac{\Delta E}{T} + \Delta S\right), \quad (11)$$

where $\Delta E = n\Delta H_{\text{fus}}$ is the transition energy. Assuming the internal cluster energy E_{vib} due to atom vibrations to be a smooth function of temperature, we represent the total internal cluster energy in the form

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

where $w_{\text{liq}} = Z_{\text{liq}} / (Z_{\text{sol}} + Z_{\text{liq}})$ is the probability that the cluster be found in the liquid state. From this we obtain the heat capacity $C = \partial E / \partial T$ near the melting point $T_m=0.44$ by analogy with formula (8)

$$C = C_o + \left(\frac{\Delta E}{2T_m}\right)^2 \exp[-\alpha(T - T_m)^2], \quad \text{where } \alpha = \left(\frac{\Delta E}{2T_m^2}\right)^2, \quad (12)$$

where C_o is the contribution from atomic vibrations. With the parameters of the 923 atom cluster, we find the maximum of the heat capacity $(C_V)_{\text{max}} = 1.1 \cdot 10^6$ and $\alpha = 5.5 \cdot 10^6$ (in units of the reduced temperature T^{-2}), so that the width of the transition range is $\Delta T \sim 10^{-3}$. In contrast to the solid-solid phase change, for which the configurational contributions are only a small but crucial part of the heat capacities of the phases, within this range the contribution to the solid-to-liquid heat capacity due to excitation of atomic configurations exceeds that for atomic vibrations by more than two orders of magnitude.

CONCLUSION

The method used here, representing clusters with a pair interaction between atoms with interaction between nearest neighbors dominating the cluster energy, allows one to determine the thermodynamic parameters of the cluster that account for its structural phase change between fcc and icosahedral structures. This simplification is justified because only few-particle configurational excitations are sufficient to describe the two solid-phases structures considered here; the contributions of non-nearest-neighbor interactions to the total energies are very similar for the two forms in such cases. The peculiarities of this problem are made especially vivid for the Morse cluster consisting of 923 atoms by two considerations which follow from the fact that the lowest-energy icosahedral structure of this system has a closed-shell structure, while the lowest fcc structure of this size has no completed outer shell. First, the cluster with the filled shells has a significant energy gap between its ground and excited configurations, whereas the corresponding gap for the fcc cluster with unfilled shells is significantly smaller. Second, the statistical weights of the ground and first excited states of the fcc cluster are much larger than those for the icosahedral cluster. This difference of the structures leads to such different values of thermodynamical parameters that the phase change between these structures emerges with more dramatic characteristics than for clusters of other comparable sizes. For rare-gaslike potential parameters, the phase change between the icosahedral and fcc structures has associated with it a marked peak in the heat capacity due to excitation of cluster configurations at low temperatures. However, if the range of the Morse potential is made significantly longer, so that the transition between the two solid structures occurs near the melting point, this influence is less pronounced.

The contribution of excitations of atomic configurations to the heat capacity and entropy of solid clusters is small compared to the contribution due to atomic vibrations, even in the region of the phase change between solid structures. Thus, excitation of atomic configurations is not a very important factor in the cluster's heat capacity and cluster entropy, even when the phase transition between the icosahedral and fcc structures of this solid cluster occurs at a low temperature. In contrast, the configurational parts of the cluster heat capacity and entropy are of importance for the liquid state of the cluster.

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- ¹L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Vol. 1 (Pergamon, Oxford, 1980).
- ²N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976).
- ³C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986).
- ⁴A. Proykova, R. Radev, F.-Y. Li, and R. S. Berry, *J. Chem. Phys.* **110**, 3887 (1999).
- ⁵R. Radev, A. Proykova, F.-Y. Li, and R. S. Berry, *J. Chem. Phys.* **109**, 3596 (1998).
- ⁶R. Radev, A. Proykova, and R. S. Berry, *Internet J. Chem.* **1**, Article 36, <http://ijc.chem.niu.edu/articles/1998v1/36/> (1998).
- ⁷R. S. Berry, in *Theory of Atomic and Molecular Clusters* (Springer-Verlag, Berlin, 1999), p. 1.
- ⁸J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, *J. Chem. Phys.* **78**, 5067 (1983).
- ⁹J. Farges, M. F. deFeraudy, B. Raoult, and G. Torchet, *J. Chem. Phys.* **84**, 3491 (1986).
- ¹⁰B. Raoult, J. Farges, M. F. deFeraudy, and G. Torchet, *Philos. Mag. Suppl.* **60**, 881 (1989).
- ¹¹J. Jellinek J., T. L. Beck, and R. S. Berry, *J. Chem. Phys.* **84**, 2783 (1986).
- ¹²J. W. Lee and G. D. Stein, *J. Phys. Chem.* **91**, 2450 (1987).
- ¹³B. W. Van de Waal, *J. Chem. Phys.* **90**, 3407 (1989).
- ¹⁴J. Xie, J. A. Northby, D. L. Freemann, and J. P. Doll, *J. Chem. Phys.* **91**, 612 (1989).
- ¹⁵H.-P. Cheng, X. Li, R. L. Whetten, and R. S. Berry, *Phys. Rev. A* **46**, 791 (1992).
- ¹⁶R. E. Kunz and R. S. Berry, *Phys. Rev. E* **49**, 1895 (1994).
- ¹⁷A. L. Mackay, *Acta Crystallogr.* **15**, 916 (1962).
- ¹⁸R. S. Berry, B. M. Smirnov, and A. Yu. Strizhev, *JETF* **85**, 588 (1997).
- ¹⁹J. P. K. Doye, D. J. Wales, and R. S. Berry, *J. Chem. Phys.* **103**, 4234 (1995).
- ²⁰B. M. Smirnov, *Chem. Phys. Lett.* **232**, 395 (1995).
- ²¹A. Rytönen, S. Valkealahti, and M. Manninen, *J. Chem. Phys.* **106**, 1888 (1997).
- ²²S. W. Wang, L. M. Falikov, and A. W. Searcy, *Surf. Sci.* **143**, 609 (1984).
- ²³B. M. Smirnov, *Phys. Scr.* **52**, 710 (1995).
- ²⁴B. M. Smirnov, *Phys. Usp.* **37**, 1079 (1994).