Transition between a cluster and a macroscopic system

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The character of the growth of large inert-gas clusters, whose energy parameters are determined by nearest-neighbor interactions, is studied. It is shown that the optimal structure of a large cluster is based on a truncated octahedron, six faces of which are squares and eight faces are regular or almost regular hexagons. The irregular part of the change in the surface or total energy of a cluster is estimated to be $\sim 10D$, where D is the binding energy of two neighboring atoms, and it is independent of cluster size. The temperature of the transition from a solid cluster to a macroscopic particle, determined by the fluctuations of the total energy of a cluster as a result of the vibrations of its atoms, has been estimated from the behavior of the energy parameters of the cluster. It is shown that a cluster becomes a macroscopic particle when the number of atoms in it exceeds 10^4. © *1995 American Institute of Physics.*

1. INTRODUCTION

A fundamental problem in the physics of small particles is the size at which a particle can be regarded as macroscopic. We shall define a system of bound atoms or molecules as macroscopic if its parameters depend monotonically on the number of constituent particles. Based on this criterion, in what follows we shall examine this problem for clusters of inert gas atoms. It is obvious that for different parameters of a cluster—a system of bound atoms—this transition occurs at different cluster sizes and at corresponding temperatures. In the present paper we shall confine our attention to the binding energy of the atoms in a cluster at low temperature. This problem relates primarily to the determination of optimal configurations of the atoms in a cluster with a fixed number of atoms; this is the main content of the following analysis.

2. INTERATOMIC INTERACTION AND THE STRUCTURE OF A LARGE INERT-GAS CLUSTER

The total binding energy of the atoms in a cluster is the sum of the binding energies for each pair, i.e., the sum of the pairwise interaction potentials of separate atoms. Once the dependence of the total binding energy of the atoms in a cluster on the configuration of the atoms has been determined, the optimal arrangement of the atoms that yields the maximum binding energy of the atoms with a fixed number of atoms in the cluster can be identified. To this end, it is necessary to choose a realistic and convenient interatomic pairwise interaction potential. The interaction potentials of two inert-gas atoms at distances comparable to the equilibrium separation R_e of the atoms in a two-atom molecule are well known and are determined from both data on the elastic scattering of atoms and analysis of different parameters of macroscopic systems of inert gases. For large clusters the long-range part of the interaction potential of two atoms, which corresponds to interatomic separations that are large compared to the equilibrium separation R_e, where the interaction potential of the atoms is relatively small, also becomes important.

In analyzing the energy parameters of inert-gas clusters, we shall choose between two types of interatomic pairwise interaction potentials. The first type, which we term short-range, is identical to the real interaction potential of two atoms at interatomic distances of the order of the equilibrium separation R_e in a diatomic molecule, and vanishes at large distances between the atoms. Based on this, we shall assume that the interaction in a cluster in the case of this interaction potential acts only between nearest neighbors. This greatly simplifies the general problem. First, the distance between nearest neighbors is precisely equal to the equilibrium separation R_e. Second, the total binding energy of the atoms in a cluster is proportional to the total number of bonds between nearest neighbors. We note that our analysis pertains to a cluster at zero temperature. In what follows, we shall measure length in units of the equilibrium separation R_e between atoms in a molecule and energy in units of the dissociation energy D of a diatomic molecule, which is assumed to be classical, i.e., the energy $\hbar\omega$ of a vibrational quantum is relatively low, $\hbar\omega \ll D$. In these units, in the case of the short-range interatomic interaction potential the total binding energy of the atoms in a cluster is equal to the total number of bonds between the nearest neighbors.

Another model interatomic pairwise interaction potential widely employed in computer calculations is the Lennard–Jones potential, which also includes a long-range part. The role of this part of the interaction potential can be assessed, and therefore a choice can be made between the two indicated model potentials by analyzing the parameters of an inert-gas crystal and comparing them with the parameters of a diatomic molecule. Indeed, long-range interaction is manifested in an inert-gas crystal to the same degree as in a cluster. Using the specific binding energy of a crystal with a Lennard–Jones interaction potential,[1] the equilibrium interatomic separation,[1] the optimal structure of the crystal,[2,3] and the melting temperature of the crystal[4] and comparing them with the same characteristics of real crystals,[1,5] we find[6,7] that in all of these cases the Lennard–Jones potential is not as good for describing crystals of inert gases as a short-range interatomic interaction potential. For example, in the units

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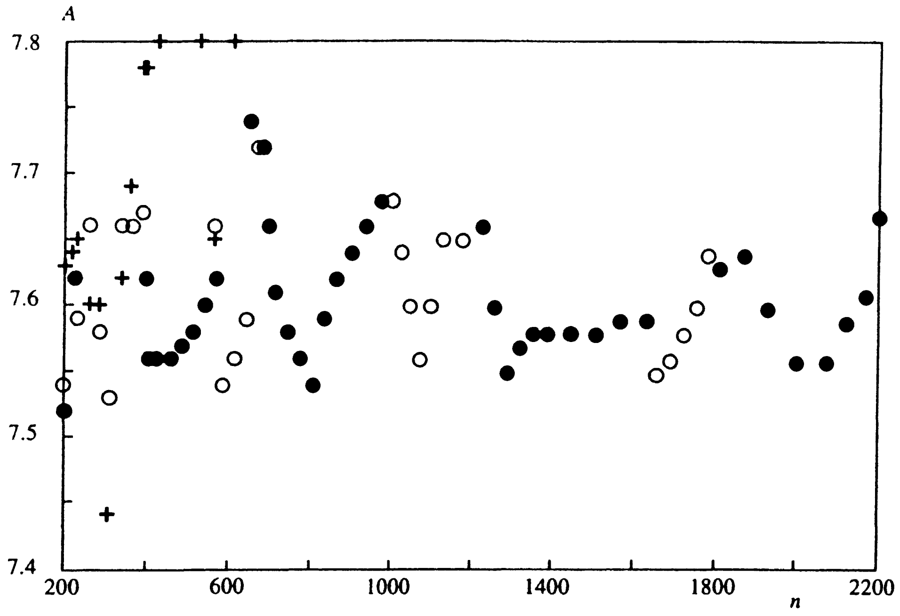

FIG. 1. Specific surface energy A of clusters with short-range interatomic interactions. Filled circles correspond to fcc clusters with a central atom[15]; open circles correspond to fcc clusters without a central atom[15]; crosses correspond to clusters with icosahedral structure (Ref. 12).

adopted here, the specific binding energy of the atoms (the binding energy per atom) is 6 for the short-range interaction potential, 8.41 for the Lennard–Jones crystal,[1] and 6.4±0.7, on the average, for real inert-gas crystals.[8] The distance between nearest neighbors is 1 for the short-range interatomic interaction potential, 0.97 for the Lennard–Jones potential,[1] and 1.00±0.01 for a real crystal.[8] Therefore the short-range interaction potential better describes a system of bound inert-gas atoms[6,7] and we shall employ it below to analyze the properties of inert-gas clusters. Our problem, then, is to determine the optimal structures of a cluster with a fixed large number n of atoms in the cluster in the case of a short-range interaction between the atoms in the cluster.

The optimal structure of clusters with a pairwise interatomic potential is icosahedral for small n and face-centered cubic (fcc) for large n.[9–11] The region of the transition from one optimal structure to another depends on the character of the interatomic pairwise interaction. In the case of a Lennard–Jones interaction potential this transition occurs for $n \sim 1000$,[9–12] and in the case of a short-range interatomic interaction the transition is concentrated in the range $n = 200-500$ (Ref. 12) (see below, Fig. 1). Since the transition to a macroscopic system occurs for $n > 1000$, in what follows we shall study clusters with the fcc structure.

3. LARGE FCC CLUSTERS

Every interior atom of an fcc cluster with a short-range interatomic interaction potential has 12 nearest neighbors, so that the total binding energy of the atoms in a large cluster consisting of n atoms can be represented in the form

$$E = 6n - An^{2/3}. \tag{1}$$

The parameter A is the specific surface energy of the cluster. For large n, the function $A(n)$ for optimal configurations of the atoms in a cluster is concentrated in a range of values that becomes narrower as n increases. We rewrite the expression (1) in the form

$$A(n) = 6n^{1/3} - E/n^{2/3}. \tag{2}$$

We assume that we have determined the total binding energy of the atoms in a cluster for the optimal configuration of the atoms at some given n. Then the function $A(n)$ characterizes the degree of stability of the cluster. The smaller the value of $A(n)$, the more stable the cluster.

The total binding energy E of the atoms in a cluster with a short-range interatomic interaction and fcc structure can be calculated on the basis of the method of Refs. 8 and 13, which takes advantage of the high symmetry of the cluster. A symmetric fcc cluster possesses O_h symmetry,[14] which includes three four-fold symmetry axes, four three-fold symmetry axes, and three axes of inversion symmetry. The atoms that are carried into one another under these transformations belong to the same shell of a cluster. The maximum number of atoms per shell (the maximum number of elements in the transformation group) is 48. Obviously, the most stable structures of clusters correspond to filled shells. Symmetric cluster figures which are preserved under the given symmetry transformations are special. In what follows, we single out such cluster structures for special attention.

The numbers of atoms in a cluster for which the function $A(n)$ possesses a local minimum are termed magic numbers. The specific binding energy E/n in such a cluster is higher than in a cluster with one atom more or one atom less. Note that these arguments apply to optimal configurations of atoms in a cluster, to which the maximum binding energies of the atoms for fixed n correspond.

Figure 1 displays the function $A(n)$ for fcc clusters with a short-range interatomic interaction obtained in Ref. 15 by the method indicated above. The values of this function for

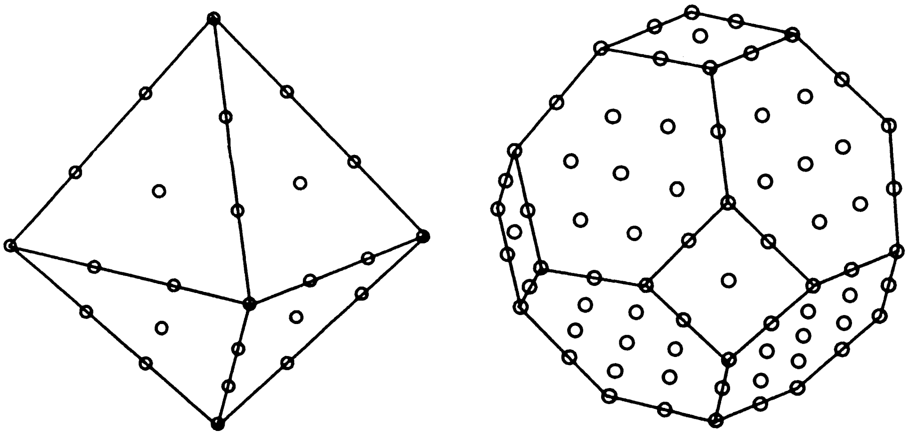

FIG. 2. Geometric figures that correspond to symmetric structures of fcc clusters: a) Octahedron with $m=2$; b) tetradecahedron with $p=2$.

an icosahedral cluster, which were obtained on the basis of Eq. (2) using the energy parameters of an icosahedral cluster calculated in Ref. 12, are also presented there. It follows from this figure that the fcc structure is optimal for a large cluster with a short-range interatomic interaction.

An important conclusion that can be drawn from the data displayed in Fig. 1 is that the function $A(n)$ is oscillatory. This distinguishes the cluster from a macroscopic particle. For large clusters, however, the amplitude of these oscillations becomes relatively small and the thermal fluctuations become quite large, which smears the oscillatory structure of this function. To obtain a criterion for a cluster to be macroscopic, it is necessary to analyze the character of the oscillations of $A(n)$.

Note that in accordance with the general scheme of Ref. 16, a cluster grows by adding atoms to the cluster to cover its flat faces, although over a certain range of n, the added atoms cover separate edges of the cluster. Therefore the starting configurations of the atoms in a cluster are symmetric figures with flat faces.

An fcc cluster can form figures bounded by flat faces with (100), (110), and (111) orientations in the notation adopted in Ref. 17. An atom on a (100) surface has eight nearest neighbors, an atom on a (110) surface has seven nearest neighbors, and an atom on the (111) surface has nine nearest neighbors. Obviously, the most stable symmetric figures of clusters have surface faces with (111) and (100) orientations. The basis of these figures is an octahedron [see Fig. 2(a] bounded by eight (111) planes. The minima of the function $A(n)$ displayed in Fig. 1 correspond to truncated octahedra [(Fig. 2(b)], which can be obtained from an octahedron by slicing off six pyramids whose vertices are also the vertices of the octahedron and whose bases are squares. The truncated octahedra possess the O symmetry of the octahedron, containing all symmetry axes of the O_h group, but not inversion symmetry. This means that the truncated octahedra are unchanged by any transformation of the group O of the octahedron.

4. CLUSTERS—TRUNCATED OCTAHEDRA

We now determine the parameters of the truncated octahedra—the total number of n of atoms in the filled structure of a cluster and its surface energy $E_{\text{sur}} = 6n-E$. For a cluster with a short-range interatomic interaction, the total binding energy of the atoms is

$$E=\sum_k n_k k/2,$$

where n_k is the number of atoms with k nearest neighbors. This formula takes into account the fact that every bond links two atoms. Hence, the surface energy of the cluster is

$$E_{\text{sur}}=\sum_k (6-k/2)n_k. \tag{3}$$

It follows from this formula that only the surface atoms contribute to the surface energy, because $k=12$ for the interior atoms.

We first calculate the parameters of an octahedral cluster. Let m be the number of the octahedron in a family. Then each of the 19 edges of the octahedron contains $m+1$ atoms, two of which are vertex atoms. The octahedral cluster therefore contains six vertex atoms, $12(m-1)$ nonvertex edge atoms, and $4(m-1)(m-2)$ surface atoms located inside the eight surface triangles, i.e., the octahedron contains $4m^2+2$ surface atoms. From the relation

$$n_m=n_{m-1}+4m^2+2,$$

where n_m is the number of atoms in the mth octahedral cluster, we find[18] (in what follows the index m is dropped)

$$n=\frac{2m^3}{3}+2m^2+\frac{7m}{3}+1. \tag{4a}$$

To find the surface energy, we note that a vertex atom has four nearest neighbors, an interior edge atom has seven nearest neighbors, and an interior atom of a surface triangle has ten nearest neighbors. Then, on the basis of Eq. (3), we obtain for the surface energy of an octahedral cluster[18]

TABLE I. Filled structures of fcc clusters with short-range interatomic interactions.

n	A	m, k in Eq. (5)	n	A	m, k in Eq. (5)
201*	7.519	6, 2	1000	7.680	– –
260	7.659	7, 3	1072*	7.561	11, 3
314*	7.533	7, 2	1126	7.650	11, 2
338	7.666	7, 1	1139	7.647	12, 5
369	7.814	– –	1157	7.785	– –
405	7.563	8, 3	1289*	7.548	12, 4
459*	7.562	8, 2	1385	7.581	12, 3
538	7.801	– –	1504	7.587	13, 5
586*	7.540	9, 3	1654*	7.550	13, 4
640	7.594	9, 2	1750	7.602	13, 3
664	7.699	9, 1	1804	7.693	13, 2
675	7.719	– –	1865	7.643	– –
711	7.607	10, 4	1925	7.561	14, 5
807*	7.545	10, 3	2075*	7.561	14, 4
861	7.624	10, 2	2171	7.622	14, 3
885	7.746	10, 1	2190	7.614	15, 6
952	7.812	– –	2225	7.710	14, 2
976	7.561	11, 4	2406*	7.552	15, 5

The asterisk indicates local minima of the function $A(n)$; dashes refer to structures obtained from truncated octahedra by removing some edges and vertices.

$$E_{\mathrm{sur}}=6(m+1)^2. \tag{4b}$$

Slicing off six identical regular pyramids with edge length k from the mth octahedron, we obtain a truncated octahedron characterized by the indices m and k. The method employed yields the following expressions for its parameters:

$$n=\frac{2m^3}{3}+2m^2+\frac{7m}{3}+1-k(k+1)(2k+1),$$

$$E_{sur}=6(m+1)^2-6k(k+1). \tag{5}$$

The truncated octahedron is bounded by 14 planes, so that six of its (100) faces are squares and eight (111) faces are hexagons. If these hexagons are regular, we obtain a regular figure—a tetradecahedron,[19] which possesses a higher symmetry than O_h. Denoting by p the number of the figure in the family of tetradecahedra, we have in this case $m=3p$ and $k=p$. This gives for the parameters of the tetradecahedron[20]

$$n=16p^3+15p^2+6p+1,$$

$$E_{\mathrm{sur}}=48p^2+30p+6. \tag{6}$$

Each tetradecahedron corresponds to a local minimum of $A(n)$ as a function of the magic numbers for a cluster with a short-range interatomic interaction.

The method for calculating the binding energy of the atoms in an fcc cluster [8,13] makes it possible to find the optimal configuration of atoms for a given number of atoms in a cluster, and the corresponding binding energy of the atoms. Some results of such calculations are presented in Table I.[15] The table includes the symmetry configurations of the atoms in a cluster when the cluster forms a figure that is preserved under every transformation in the group O of the octahedron. Clearly, the minima of the function $A(n)$ correspond to truncated octahedra, which subsume all of the tetradecahedra'.

5. GROWTH OF A LARGE CLUSTER AND ITS MACROSCOPIC NATURE

We now analyze the character of the oscillations of the function $A(n)$ according to Fig. 1 and Table I. We define the location of the lth minimum of the function $A(n)$ in the form

$$n_{\mathrm{min}}=\frac{16}{27}(l+\alpha)^3, \tag{7}$$

so that tetradecahedra are described by this formula. The function (7) therefore has the correct asymptotic form. Statistical analysis of the data in Fig. 1 and Table I yields for the parameter in this formula $\alpha=1.03\pm0.08$, if it is assumed that $n=201$ corresponds to the number of the minimum $l=6$. If in the size range of the clusters presented in Table I only the parameters of the tetradecahedra are used, statistical analysis of their positions gives $\alpha=0.96\pm0.01$. Next, using Eq. (6) for the largest tetradecahedra gives $\alpha=15/16=0.938$. Therefore the parameter α in Eq. (7) is close to 1.

As one can see, the filled structure of an fcc cluster with a short-range interatomic interaction consists of a tetradecahedron or a figure which is nearly a tetradecahedron in which the six (100) faces are squares and eight (111) faces are either regular hexagons or hexagons with almost the same edge length. Starting with this figure and filling its faces with atoms, we now analyze the change in the surface energy of a cluster. For the analysis it is most convenient not to add but rather to remove surface atoms of the figure. If all atoms of the same surface square are removed from the surface of the p-th tetradecahedron, then the decrease Δn in the number of atoms and the surface energy ΔE_{sur} of the cluster will be

$$\Delta n=(p+1)^2, \quad \Delta E_{\mathrm{sur}}=2p+2. \tag{8a}$$

If all atoms on the same surface hexagon are removed, then these parameters turn out to be

$$\Delta n=3p^2+3p+1, \quad \Delta E_{\mathrm{sur}}=6p+3. \tag{8b}$$

If atoms on an adjacent square and hexagon are removed, then these parameters of the cluster decrease by

$$\Delta n=(2p+1)^2, \quad \Delta E_{\mathrm{sur}}=4(2p+1). \tag{8c}$$

When the atoms on a square and two hexagons adjoining the square but not bounding one another are removed, these parameters are

$$\Delta n=7p^2+6p+1, \quad \Delta E_{\mathrm{sur}}=14p+6. \tag{8d}$$

On the basis of these expressions, we arrive at the following conclusions. The change in the specific surface energy of a cluster accompanying the removal of separate elements of the surface of a cluster is

$$\Delta A=\frac{E_{\mathrm{sur}}-\Delta E_{\mathrm{sur}}}{(n-\Delta n)^{2/3}}-\frac{E_{\mathrm{sur}}}{n^{2/3}}=A\left(\frac{2\Delta n}{3n}-\frac{\Delta E_{\mathrm{sur}}}{E_{\mathrm{sur}}}\right), \tag{9}$$

where A corresponds to the filled figure whose parameters are given by Eq. (6). On the basis of each of Eqs. (8), in the limit of large p we have $\Delta A \sim 1/p^2$, i.e., the amplitude of the oscillations of the surface energy of a cluster relative to the average value does not depend on the cluster size in the limit of a large number of atoms in the cluster.

This is true only of filled faces. We now demonstrate this for a surface square. If the (100) face of a cluster is removed, removing atoms of a square with edge $i \gg 1$ so that one vertex of this square is also a vertex of the figure, we obtain for the desired parameters of the cluster, to within $1/i$,

$$\Delta n = i^2, \quad \Delta E_{\mathrm{sur}} = 2i. \tag{10}$$

Then, on the basis of Eqs. (9) and (6), we have to within $\sim 1/p$

$$\Delta A = A \frac{i^2 - ip}{24p^3}.$$

The minimum of this quantity corresponds to $i = p/2$:

$$\Delta A_{\min} = -(4 \cdot 2^{1/3} n^{1/3})^{-1} = -0.2 n^{-1/3}. \tag{11}$$

Over the range $n \sim 10^3 - 10^4$ the corresponding variation in the surface energy $(0.2n^{1/3})$ does not exceed the characteristic fluctuations in this quantity when individual atoms are added, so that in what follows we shall neglect this effect.

On the basis of the foregoing analysis, we take the amplitude of fluctuations in the surface energy of a cluster about the mean to be $\Delta E_{\mathrm{sur}} \sim 10$. This estimate was obtained from Eqs. (8) for large n for the case when the number of atoms removed from the surface of the cluster is approximately one-half the number of surface atoms and all atoms can be collected from the different figures taken into account in Eqs. (8).

Two circumstances are pertinent here. First, changing the number of the octahedron from which the desired figure is obtained by unity corresponds to the removal or attachment of four surface triangles, which corresponds for the given figure to the removal or attachment of four hexagons. Therefore our estimate also includes fluctuations in the specific surface energy accompanying a transition to a new number of the optimal figure of the cluster. Second, a transition from magic to nonmagic filling numbers results in a change in the specific surface energy by a quantity of order unity. The present estimate covers the magnitude of irregular variations produced in the surface energy of a cluster by different mechanisms.

Thus, irregular variations in the surface energy of a cluster as the cluster grows, which characterize the difference of the surface energy of the cluster from a monotonic function of the number of atoms, are $\Delta E_{\mathrm{sur}} \sim 10$. These deviations obviously distinguish a cluster from a macroscopic particle, for which the dependence of the surface energy on the number of constituent atoms is approximately monotonic. A cluster can therefore be regarded as a macroscopic particle if the fluctuations in its surface energy are greater than the indicated quantity. The fluctuation of the total energy of a solid cluster as a result of the motion of its atoms is $T\sqrt{s}$, where T is the temperature of the cluster expressed in energy units, and s is the effective number of cluster vibration modes. Therefore the criterion for a cluster to be macroscopic has the form

TABLE II. Maximum temperatures T_m (in units of D) for inert-gas clusters.

	Element			
n	Ne	Ar	Kr	Xe
10^3	0.60	0.34	0.23	0.18
10^4	0.38	0.21	0.14	0.11

$$s \gg \left(\frac{\Delta E_{sur}}{T} \right)^2 = 100 \frac{D^2}{T^2}, \tag{12}$$

where D is the energy required to break the bond between nearest neighbors, or the dissociation energy of a diatomic molecule, and which was used above as the unit of energy.

We use the Debye approximation[21] for the modes of a cluster, and assume that the Debye temperatures of the cluster are the same as those of inert-gas crystals for longitudinal and transverse modes. We then obtain for the effective number of modes in the cluster

$$s = 3nT^3/\Theta_D^3,$$

where Θ_D is the mean Debye temperature for an inert-gas crystal, and $\Theta_D \gg T$. Expressing the irregular part of the variation in the surface (and total) energy of a cluster in conventional units as $\sim 10D$, we obtain the following estimate for the temperature at which the cluster can be regarded as a macroscopic particle:

$$T^5 \gg T_m^5 = 30D^2\Theta_D^3/n. \tag{13}$$

In this formula we employed the relation $\Theta_D^3 = \Theta_L \Theta_t^2$, where Θ_L and Θ_t are the Debye temperatures for longitudinal and transverse modes, and the values of these quantities for inert-gas crystals were taken from Ref. 22. Table II contains the value of T_m for inert-gas clusters at two cluster sizes.

We emphasize that we regard a system of many bound atoms to be macroscopic if its energy fluctuations exceed the irregularities in the energy variations accompanying the addition of new atoms. On the basis of this definition, an almost-filled large flat surface is not a macroscopic system at zero temperature, since the filling of the surface gives rise to an additional jump in its energy. However, even at low temperatures, a large surface satisfies the definition employed above for a macroscopic system. This definition of a macroscopic system can be formulated differently: an individual atom in the system makes a small contribution to the investigated part of the system's energy by comparison with all of the other atoms. We assumed above that the fluctuations in the internal energy of the cluster are due to the vibrations of the atoms. Transitions of atoms to excited shells can make a definite contribution to this quantity.

The foregoing analysis applies to solid clusters. For liquid clusters the energy fluctuations are stronger, since the sinusoidal nature of the oscillatory motion of the surface atoms is destroyed. Therefore, on the basis of the estimate

(13), it follows that liquid clusters of inert gases with $n > 10^3$ are macroscopic particles in any case (the melting point of the inert-gas clusters is $0.58D$ [Ref. 8)].

Note that in actuality the temperature of the clusters cannot be low. Indeed, clusters are usually formed when an expanding gas condenses. Clusters are therefore initially hot, and they subsequently cool, both as a result of collisions between the clusters and the atoms of the cooled gas, and as a result of evaporation of individual atoms from them. The characteristic rates of cooling as a result of these processes decrease rapidly with decreasing temperature, so that low-temperature clusters are quite difficult to obtain, since their lifetime is limited. Taking this circumstance into account and using the data in Table II, it can be concluded that in real inert-gas clusters with $n > 10^4$ are macroscopic particles.

6. CONCLUSIONS

The foregoing analysis shows that the growth of large clusters of an inert gas, which are maintained by short-range interatomic interactions, amounts to the filling of the individual faces of a tetradecahedron. Irregular fluctuations in the surface and total energies of a cluster are estimated to be of the order of $10D$, where D is the binding energy of two neighboring atoms in a cluster. From the standpoint of the behavior of the total energy of a cluster as a function of the number of constituent atoms, an inert-gas cluster can be regarded as a macroscopic particle with $n > 10^4$, since the temperature of the cluster cannot be very low. For other cluster parameters, the transition from a cluster to a macroscopic particle can start at different filling numbers.

[1] C. Kittel, *Introduction to Solid State Physics*, John Wiley, New York (1986).

[2] T. Kihara and S. Koba, J. Phys. Soc. Jpn. **7**, 348 (1952).

[3] B. W. Van de Waal, Phys. Rev. Lett. **67**, 3263 (1991).

[4] J. G. Broughton and G. H. Gilmer, J. Chem. Phys. **79**, 5095 (1983).

[5] A. J. Moses, *Practicing Scientist's Handbook*, Van Nostrand and Reinhold, New York (1978).

[6] B. M. Smirnov, Usp. Fiz. Nauk **164**, 1165 (1994).

[7] B. M. Smirnov, Phys. Scripta **51**, 402 (1995).

[8] B. M. Smirnov, Usp. Fiz. Nauk **162**, 97 (1992) [Sov. Phys. Usp. **35**, 1052 (1992)].

[9] J. W. Lee and G. D. Stein, J. Phys. Chem. **91**, 2450 (1987).

[10] B. W. van de Waal, J. Chem. Phys. **90**, 3407 (1989).

[11] J. Xie, J. A. Northby, D. L. Freemann, and J. P. Doll, J. Chem. Phys. **91**, 612 (1989).

[12] B. M. Smirnov, Chem. Phys. Lett. **22**, 395 (1995).

[13] B. M. Smirnov, Usp. Fiz. Nauk **162**, 119 (1992) [Sov. Phys. Usp. **35**, 37 (1992)].

[14] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Nonrelativistic Theory)*, 3rd ed., Pergamon Press, New York (1977).

[15] B. M. Smirnov, Zh. Éksp. Teor. Fiz. **107**, 2080 (1995) [JETP **80**, 1151 (1995)].

[16] U. Naher, U. Zimmermann, and T. P. Martin, J. Chem. Phys. **99**, 2256 (1993).

[17] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Rinehart and Wilson, New York (1976).

[18] S. W. Wang, L. M. Falikov, and A. W. Searcy, Surf. Sci. **143**, 609 (1984).

[19] B. Raoult, J. Farges, M. F. de Feraudy, and G. Torchet, Phil. Mag. B **60**, 881 (1989).

[20] B. M. Smirnov, Usp. Fiz. Nauk **163**, 29 (1993).

[21] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Pergamon Press, New York (1980).

[22] N. Schwentner, E. E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases*, Springer-Verlag, Berlin (1985).

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