METHODOLOGICAL NOTES

Clusters with close packing

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An analysis is given of the properties of a cluster cut from a face-centered and a body-centered cubic lattice and also from a hexagonal crystalline lattice about a certain center. The clusters have a shell structure and contain tens and hundreds of molecules. The binding energies of molecules and the surface energy of the cluster are shown for different occupation numbers and for three types of structure of the cluster, and also for different temperatures. It is shown that the concept of surface tension is valid for clusters containing tens of molecules, but from the point of view of the binding energy of the surface molecules a cluster consisting of hundreds of molecules is not a macroscopic particle even at relatively high temperatures. An expression is obtained for the surface energy of a cluster.

1. INTRODUCTION

A cluster is a system of bound atoms and molecules. A cluster consisting of a large number of atomic particles, generally speaking, is not a macroscopic system. This means that the parameters of the cluster are not always a monotonic function of the number of particles in it. The sharpest change in the parameters of a cluster occurs in passing through the socalled magic numbers.[1-5] The most stable configurations correspond to the magic numbers, and therefore the extracting clusters from a source cluster with magic numbers of atoms will be characterized by higher currents than clusters with close values of the number of atoms.

It is commonly accepted that the surface atoms of a cluster form a shell and that the magic numbers of atoms in a cluster correspond to the completion of filling a particular shell. With such an approach the different parameters of a cluster as a function of the number of particles in it must have a discontinuity at a magic number of atoms in the cluster and must vary monotonically as the shells are being filled. This is confirmed by various experimental investigations.[6-9] In such a case one can assume that the surface properties of a cluster are determined by the last shell of atoms. In order to understand the degree of validity of this assertion it is necessary to analyze the surface properties of clusters within the framework of different models. In this article such a comparison is carried out for clusters between atoms or molecules of which a short-range interaction exists.

2. SURFACE ENERGY OF A CLUSTER

Let us determine the surface energy of a cluster. We examine first the macroscopic condensed system from which a cluster may be cut out. Then we shall use for the cluster the results obtained for the macroscopic system.

We introduce the surface energy of the macroscopic system as the energy which is expended per unit area in cutting the element of the condensed system. Let N be the density of molecules (or atoms) in the condensed system, and ΔH be the energy expended on converting the condensed body into a gas (vapor) expressed per molecule. We shall calculate this quantity for different models assuming a short-range nature of the interaction between the molecules in the system. Another essential assumption is connected with the fact that in the process of cutting the nature of the distribution of molecules on the surfaces being formed does not change, which holds for the system being considered with short-range interaction between molecules.

We shall use first the random model assuming a random nature of the distribution of the molecules within the system. Then on the surface of area S there are $SN^{2/3}$ molecules on each side of the surface. In each of these molecules half the bonds are broken, i.e., the energy stored in one molecule situated on the surface is equal to $H/2$. From this we obtain the surface energy per unit area for the given model:

$$E_{\text{surf}} = \Delta H \cdot N^{2/3}/4. \tag{1}$$

We now consider a more realistic model when the atoms or molecules of the system form one of the crystals with close packing that has a cubic face-centered lattice.[10-14] In this crystal each of the molecules has 12 nearest neighbors with which it interacts. A cubic face-centered lattice can be composed of two lattices inserted one into the other. In each of these lattices the molecules are situated on parallel planes forming on them a square net with the side of the square being a (a is the distance between neighboring molecules of the structure). The distance between neighboring planes for each of the lattices is equal to $a\sqrt{2}$, and they are shifted with respect to each other in such a way that each of the molecules of one lattice is situated at the center of the parallelepiped (with side of the square a and of height $a\sqrt{2}$) which is the elementary cell of the other crystalline lattice.

Let us determine the specific surface energy of the lattice assuming that the cut has been made between two planes of the lattice. Introducing D the energy of breaking a bond between each pair of nearest neighbors we find $\Delta H = 6D$ since each molecule has 12 neighbors. Each molecule of the surface layer has 8 neighbors, each molecule of the next layer has 12 neighbors. Since the density of the molecules on the surface is equal to $1/a^2$ we obtain $E_{\text{surf}} = 2D/a^2$. Since the

density of the molecules in a face-centered lattice is equal to $\sqrt{2}/a^3$ we obtain from this

$$E_{\text{surf}} = \Delta H N^{2/3}/3 \cdot 2^{1/3} = 0{,}26 \Delta H \cdot N^{1/3}. \qquad (2)$$

We see that this model gives a result close to the result of a random model. Apparently the expression for the specific surface energy is not sensitive to the model.

We use these results for the cluster treating it as a macroscopic system. We assume that the cluster is similar to a drop and has the structure of a cubic face-centered lattice. We note that such a drop model implicitly assumes that the cluster has a closed shell. The total energy of the cluster consisting of n molecules and having the radius r (this energy is expended on converting the cluster into a gas consisting of free molecules) is equal to

$$\varepsilon_n = \Delta H \cdot n - (4\pi r^2 \Delta H/3a^2).$$

Utilizing the connection between the number of molecules in the cluster and its radius $n = 4\pi\sqrt{2}\,(r/a)^2/3$, we have

$$\varepsilon_n = \Delta H \cdot n - (2\pi/3)^{1/3}\Delta H \cdot n^{2/3}. \qquad (3)$$

From this we obtain the binding energy of the nth molecule as

$$\Delta\varepsilon_n = \varepsilon_n - \varepsilon_{n-1} = \Delta H(1 - 0{,}85n^{-1/3}), \quad n \gg 1. \qquad (4)$$

It may be seen from this formula that the contribution of the surface energy to the binding energy of the molecule is significant even in the case of a large number of molecules in the cluster. We note that, in accordance with the model being used, this result takes into account the structure of the shell of the cluster and is a certain average characteristic. Actually the binding energy between the molecule and the cluster depends on the degree of filling of this and other shells of the cluster, and also on the nature of the shell.

3. CLUSTER WITH THE STRUCTURE OF THE FACE-CENTERED LATTICE

In order to determine the roles of different factors in a cluster with an unfilled shell we shall examine the surface effects for a cluster with dense packing which may be cut out from a cubic face-centered lattice. We shall carry out this operation of forming the cluster with the aid of a face-centered lattice in the following manner. We choose one of the molecules of the lattice as the cluster center. Then we include in the cluster only those molecules of the lattice the distance of which to the cluster center does not exceed a definite value. Such a cluster may arise for example in the case of interaction of an ion with atoms of an inert gas. Then the ion is a cluster center, and the atoms interact only with the nearest neighbor, and within the inner region of the cluster each atom has 12 nearest neighbors.

Let us construct the cluster under consideration. We choose as the z axis the direction perpendicular to the planes of the lattice, and for the x and y axes we choose the directions from the central atom to the atoms closest to it on a plane of the lattice. The cluster under consideration has many planes of symmetry. We divide the possible types of symmetry into two groups. To the first of them we assign the symmetry with respect to the transformation $x \rightleftarrows y \rightleftarrows z$, and to the second the symmetry with respect to the transforma-

tions $x \rightleftarrows -x$, $y \rightleftarrows -y$, $z \rightleftarrows -z$. We choose as the unit of measurement the distance between neighboring planes of the lattice $a/\sqrt{2}$ (in these units the distance between nearest neighbors is equal to $\sqrt{2}$). In virtue of the indicated symmetries the groups of molecules in the cluster form shells in such a way that all the molecules of the appropriate shell are at the same distance and transform into each other under the transformations indicated above.

Table I shows the coordinates of the molecules of the appropriate shell of the cluster in the order of increasing radius of the shell. Coordinates are shown of that molecule for which $z < x < y$ and all the coordinates are positive. Coordinates of other molecules can be obtained from these by appropriate transformations $(x \rightleftarrows y \rightleftarrows z; x \rightarrow -x, y \rightarrow -y, z \rightarrow -z)$.

One can conventionally divide the shells into several types. Shells of one type are characterized by the same symmetry, and also by the same character of filling the shell, including also the number of nearest neighbors in the process of filling the shell. The number of nearest neighbors for molecules of a particular shell and also the surface energy of the cluster after that shell has been filled is contained in Table I. If the nearest neighbors are molecules of the same cell then the number of nearest neighbors for molecules of a given shell varies in the process of it being filled. This is noted in Table I. From an analysis of the data of Table I it follows that the concept of shells of a large cluster does not possess such a categorical character which we have implicitly been assigning to it. Indeed, in this case we depend on an analogy with atoms, the description of the structure of which is based on the shell concept. A change in the structure of the atom as the nuclear charge increases is associated with the filling of a definite shell. For heavy atoms competition between two shells is possible as the charge of their nuclei increases. The number of electron shells participating in the structure of actual atoms can attain values up to 18.

If we take a cluster with the number of molecules running into tens or hundreds, then there will be several shells for which the distances from the center do not differ greatly, and the bonding energy with the molecules of the cluster of molecules of these shells as they are being filled are also close. Thereby the results presented above in confirming the shell concept of a cluster testify concerning the specific properties of this concept in the case of a cluster. On the one hand, in the structure being considered, just as in any shell system, its parameter being investigated—the energy of bonding of the last molecule changes abruptly when the filling of the shell is completed and the transition to filling the next shell is made. On the other hand, competition is possible of several shells at once. This means that sequential filling of individual shells occur in the process of growth of the cluster, but the choice of a particular shell from a number of possible ones can change depending on several factors.

In constructing the cluster under consideration we started from the presence of a center assuming that the interaction with the center selects the sequence of the shells of atoms. In the presence of other factors this sequence may change. For example, in the case of the Ar_n^+ cluster the most suitable structure is considered to be the structure of an icosahedron[10] which has the magic numbers 13, 55, 147, 309, and 561. This is in agreement with experiment[9] for the first three magic numbers. For the cluster under investigation

TABLE I. Parameters of the shells of a cluster with the structure of a face-centered cubic lattice.

Coordinates of the molecule of a shell	Square of the distance to the center	Number of transformations		Number of nearest neighbors	Number of molecules in the cluster	Surface energy (D) in filling the shell
		1 group	2 group			
011	2	3	4	3	13	42
002	4	3	2	4	19	54
112	6	3	8	3 — 5	43	102
022	8	3	4	5	55	114
013	10	6	4	4 — 6	79	138
222	12	1	8	3	87	162
123	14	6	8	5	135	210
004	16	3	2	4	141	222
114	18	3	8	5	165	246
033	18	3	4	5	177	258
024	20	6	4	6	201	258
233	22	3	8	3 — 5	225	306
224	24	3	8	5	249	330
015	26	6	4	4 — 6	273	354
134	26	6	8	5 — 6	321	378
125	30	6	8	5 — 6	369	402
044	32	3	4	5	381	414
334	34	3	8	3 — 5	405	462
035	34	6	4	6	429	462
006	36	3	2	4	435	474
244	36	3	8	5	459	498
116	38	3	8	5	483	522
235	38	6	8	5,6	531	546
026	40	6	4	6	555	546
145	42	6	8	5,6	603	570
226	44	3	8	5	627	594
136	46	6	8	6	675	594
444	48	1	8	3	683	618
055	50	3	4	5	695	630
017	50	6	4	4 — 6	719	654
345	50	6	8	4 — 6	767	702
046	52	6	4	6	791	702

with close packing and a specified center only the first of the magic numbers indicated above are characteristic, and even they correspond to shells of the cluster the binding of the molecules of which with the core of the cluster is not maximal. Thus, we arrive at a conclusion that in the cluster under consideration containing tens and hundreds of molecules competition of many shells occurs.

4. SURFACE PROPERTIES OF A CLUSTER WITH CLOSE PACKING

The results entered in Table I provide complete information on the energy characteristics of the cluster being examined expressed in terms of the energy characteristics of the molecules which are on its surface. This enables one to understand the acceptability of the simple models considered earlier and, if it is possible, to introduce corrective measures into them. We shall note the differences with the model in which a layer of a cubic face-centered lattice is chosen as the surface of the cluster. Since the basis of both models is the same these differences are particularly interesting.

First, having chosen a layer of the face-centered lattice as the surface of the cluster we automatically obtain the result that all the molecules of the inner layers have 12 neighbors, i.e., in the formation of the surface properties of the cluster only the surface layer participates. In the case of a cluster with a center many shells simultaneously determine

its surface properties. For example, for the largest cluster in Table I containing 791 molecules such shells are 046, 055, 345, 017, 444, 136, 226, 145, 026, 116, 235 and 244. The molecules of each of these shells have less than 12 neighbors (but not less than 6).

Another difference between clusters under consideration is associated with the value of the binding energy of the molecule being attached. In filling a layer of a face-centered lattice the molecule being attached has between 4 and 8 nearest neighbors. When the layer has been filled, each molecule of the surface layer has 8 nearest neighbors. This circumstance was used in the expression for the surface energy of the cluster. For the cluster under consideration with a center, the maximum number of nearest neighbors is 6. This is associated with the geometry of constructing the cluster.

The participation of many shells in the creation of surface properties of the cluster makes it more difficult to distinguish clusters with a closed shell. Such a cluster should have maximum stability. Within the framework of the model, where the surface of the cluster is a layer of the face-centered lattice, in the case of a closed shell this layer is totally filled. The numbers of molecules in a cluster with a closed shell should be the most highly distinguished magic numbers of the cluster.

It might seem that a closed shell must be characterized by the maximum binding energy of the surface molecules.

We shall introduce it in such a manner that the binding energy of the last molecules included in the cluster is equal to $6D$ (i.e., they have 6 nearest neighbors). We note the conventional aspect of the definition that has been used. For example, in the case of a cluster with the last shell being 035 (429 molecules) that falls under this definition, the molecules of the preceding shell 334 have 5 nearest neighbors each; in the case of a cluster with the last shell being 046 (791 molecules) any molecule of the cluster has no less than 6 nearest neighbors.

According to Table I the binding energy of the molecule being attached is an irregular function of the number of molecules in the cluster even for large values of these numbers. Being averaged over several shells within the limits of a single closed shell, this quantity has a relatively large amplitude of fluctuations, which does not permit the use for it of monotonic dependences as functions of the number of molecules, as is the case in the simplified models (cf., formula (4)). Naturally this quantity should grow with an increase in the number of molecules in the cluster. However, for example, for the 7th closed shell 125 the average binding energy of the molecule being attached is equal to 5.5 D, while for the 12th shell, which includes the 444, 055, 017 shells, when the cluster contains twice as many molecules this quantity is equal to 4.64 D. The difference between these values is close to the amplitude of the change of the average binding energy of a molecule for the occupation numbers under consideration (naturally, without taking into account the first shell).

The conclusion that we have reached confirms the thesis that a cluster containing even a large number of molecules is not a macroscopic system. Its parameters as a function of the occupation numbers are jumpwise discontinuous functions whose values are of an irregular nature. There is therefore no point in representing these parameters in the form of a monotonic function of the occupation numbers as this would have occurred for a macroscopic system. One can only speak of a certain average value of the corresponding parameter. Thus, for the cluster under examination the average value of the binding energy of the last molecule amounts to 4.8 + 0.3 D if the number of molecules in it is less than 429, and is equal to 5.1 + 0.4 D if it contains less than 791 molecules. In carrying out this averaging we did not take into account the first shell of the cluster.

Here one can expect that the surface energy of the cluster is with a certain degree of accuracy a regular function of the number of molecules in it since a large number of molecules belonging to different shells of the cluster make a contribution to it. Thus for a cluster with the external shell 046 which contains 791 molecules 12 shells of the cluster containing 356 molecules, i.e., nearly half of the molecules of the cluster participate in the formation of the surface energy. Table I provides values of the surface energy of clusters with closed shells. These values are approximated by the formula $(8.2 \pm 0.2)n^{2/3}$ where n is the number of molecules in a cluster and the surface energy is expressed in units of the binding energy between two nearest neighbors. We note that formula (3) for the model of a face-centered lattice gives in these units for the surface energy the expression $7.7n^{2/3}$, and this coincides with the previous result within the limits of its accuracy. Within the framework of a random model in accordance with formula (1) the surface energy of the cluster is equal to $\pi r^2 \cdot \Delta H \cdot N^{2/3}$, where r is the radius of the cluster,

and N is the density of molecules in it. In terms of the units used earlier we obtain for the surface energy of the cluster $7.2n^{2/3}$ which agrees with the results of other models.

5. CLUSTER WITH OTHER STRUCTURES

The basic virtue of the method under consideration is its simplicity. It might seem that an analysis of a cluster containing tens or hundreds of molecules is possible only on the basis of numerical methods using computers. However, as can be seen from the material presented a cluster containing hundreds of molecules with pairwise interaction and having a given crystalline structure can be constructed by simpler mathematical methods. This provides simple possibilities to "touch" the cluster and study its individual properties. This will permit one to understand the general regularities of the physics of clusters. In particular, one of the fundamental questions in the physics of clusters which is being discussed here is whether a cluster including tens and hundreds of molecules is a macroscopic particle or not. It is clear that conclusions from an analysis of such a cluster will be more convincing if they refer to different structures of a cluster.

The methodology presented above enables one to construct clusters with different crystalline structures. Below we shall carry out these operations for a cluster with a body-centered lattice.[11-14] This lattice can be constructed from two cubic lattices inserted into one another so that each molecule of one of them turns out to be at the center of the cube formed by the other lattice (Fig. 1). Each molecule has 8 nearest neighbors.

It is convenient to choose for the unit of length one half the constant of each of the cubic lattices. In terms of these units the distance between nearest neighbors is equal to $\sqrt{3}$. The convenience of such units consists of the fact that in terms of them the three coordinates of each molecule are integers and they are either all even or all odd. This simplifies the procedure of constructing the cluster which includes shells in the order of their distance from the center. The parameters of a number of shells of the cluster are shown in
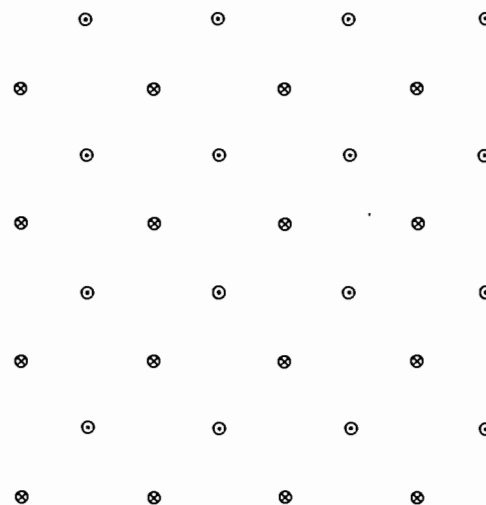

FIG. 1. Cubic body-centered lattice. Circles with a dot inside indicate positions of molecules of one layer, circles with a cross inside correspond to the position of molecules of another layer. Then the layers alternate. The distance between adjacent layers is equal to $a/\sqrt{3}$, the edge of a square of a layer is $2a/\sqrt{3}$.

Coordinates of the molecule of a shell	Square of the distance to the center	Number of transformations		Number of bonds of a molecule of the shell	Number of moleules in the cluster	Surface energy of the cluster (D) as the shell is filled
		1 group	2 group			
111	3	1	8	1	9	28
002	4	3	2	4	15	28
022	8	3	4	2	27	52
113	11	3	8	3	51	76
222	12	1	8	4	59	76
004	16	3	2	4	65	76
133	19	3	8	2	89	124
024	20	6	4	4	113	124
224	24	3	8	3	137	148
115	27	3	8	4	161	148
333	27	1	8	4	169	148
044	32	3	4	2	181	172
135	35	6	8	3	229	220
244	36	3	8	4	253	220
006	36	3	2	4	259	220
026	40	6	4	4	283	220
335	43	3	8	3	307	244
226	44	3	8	4	331	244
444	48	1	8	4	339	244
155	51	3	8	2	363	292
117	51	3	8	4	387	292
046	52	6	4	4	411	292
246	56	6	8	3	459	340
137	59	6	8	4	507	340
355	59	3	8	4	531	340
008	64	3	2	4	537	340
337	67	3	8	3	561	364
028	68	6	4	4	535	364
446	68	3	8	4	609	364
228	72	3	8	4	633	364
066	72	3	4	2	645	388
157	75	6	8	3	693	436
555	75	1	8	4	701	436
266	76	3	8	4	725	436
048	80	6	4	4	749	436
119	83	3	8	4	773	436
357	83	6	8	3	821	484
248	84	6	8	4	869	484

Table II. The number of nearest neighbors of the molecule in a shell shown in Table II uniquely determines the binding energy of the molecules on being attached to the cluster. Just as before, we assume that only the short-range interaction between nearest neighbors is significant. Therefore the binding energy of the molecule is equal to the product of the number of nearest neighbors with which it establishes a bond and the binding energy of the dimer D. It can be seen that the number of nearest neighbors in the attachment of a molecule does not exceed 4.

Figure 2 shows the surface energy of a cluster with the structure being considered containing 400–800 molecules.
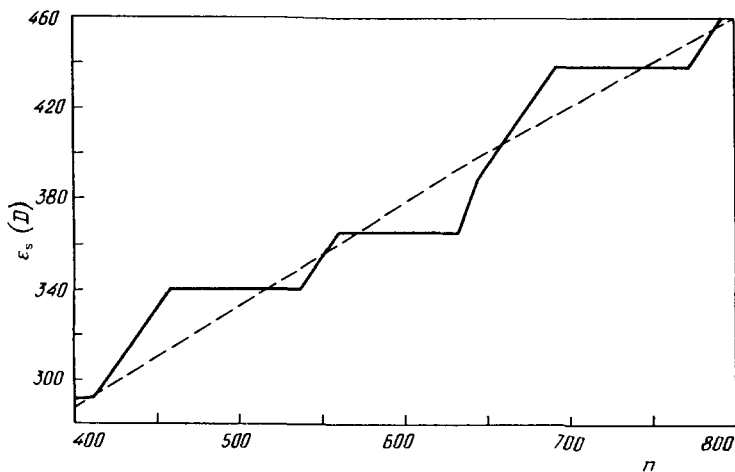

FIG. 2. Surface energy of a cluster with the structure of a face-centered cubic lattice as a function of the number of molecules in it (solid line). The dotted curve corresponds to the approximation formula (5).

The average value of the surface energy in units of D amounts to $(5.3 \pm 0.2)n^{2/3}$ where n is the number of molecules in the cluster. This formula is applicable starting with tens of molecules in the cluster.

The results that are shown confirm the general conclusion. There is no point in expressing individual parameters of the molecules of the cluster as a function of the occupation numbers, in particular, the binding energy of the molecule being attached. This quantity experiences jumps after filling of the appropriate shell. As regards the surface energy, it is determined for the cluster just as for a macroscopic particle.

To analyze the expression for the surface energy of a cluster we consider one more close packed structure–the hexagonal lattice.[11-14] If we consider the molecules of this structure situated on one of the planes then each of the molecules in the plane has 6 nearest neighbors forming a regular hexagon. The molecules are situated along parallel lines, so that the distance between them along the line is equal to a, the distance between nearest neighbors, and the distance between the lines is equal to $a\sqrt{3/2}$, and the molecules of the next line are displaced with respect to the molecules of the preceding line by a distance $a/2$. The molecules of the next plane are situated within the hollows of the preceding one, while the molecules of the third layer are situated above the molecules of the first layer. If one models the molecules by spheres of radius $a/2$ then each of the spheres touches 12 others, six of which are in the same layer, three in the layer lying above it, and three in the layer lying below it. The distance between the layers is equal to $a\sqrt{3/2}$.

A cluster cut out from the lattice under consideration possesses a symmetry on being rotated through the angle $2\pi/3$ about an axis perpendicular to the planes in which the molecules are situated, and also on reflection with respect to that one of these planes in which the center is located and also to the plane perpendicular to it that passes through the center. Fig. 3a shows positions of molecules in the cluster containing 347 molecules, and also the square of the distance of these molecules to the center (in units of a). Layers are picked out which are situated above the layer in which the center is situated and which is designated as the zeroth layer. From symmetry considerations the same disposition of molecules also occurs in four layers of cluster lying below the zeroth layer. The number of molecules of the corresponding shell of the cluster and the number of molecules in the cluster, if this shell is the last one, are shown in Table III.

Having counted the number of nearest neighbors that each molecule has we will find the surface energy of the cluster. For a cluster containing $n = 347$ molecules we find that 194 molecules situated within 18 shells have fewer than 12 nearest neighbors. In units of the binding energy of the dimer D the surface energy is equal to $\varepsilon_s = 394$. For a cluster consisting of $n = 257$ molecules on the surface (i.e., with incompleted bonds) there are 164 molecules belonging to 16 shells. The surface energy is equal to $\varepsilon_s = 338$. Approximating the surface energy in the standard manner we find $\varepsilon_s = (8.16 \pm 0.18)n^{2/3}$

We write a general expression for the surface energy of a cluster basing ourselves on the results obtained for three types of structures. We represent the surface energy of a cluster in the form

$$\varepsilon_s = A\Delta H \cdot n^{2/3}.$$

The values of the coefficient A obtained for clusters of the examined structures are shown in Table IV. Summarizing these results we obtain the following expression for the surface energy:
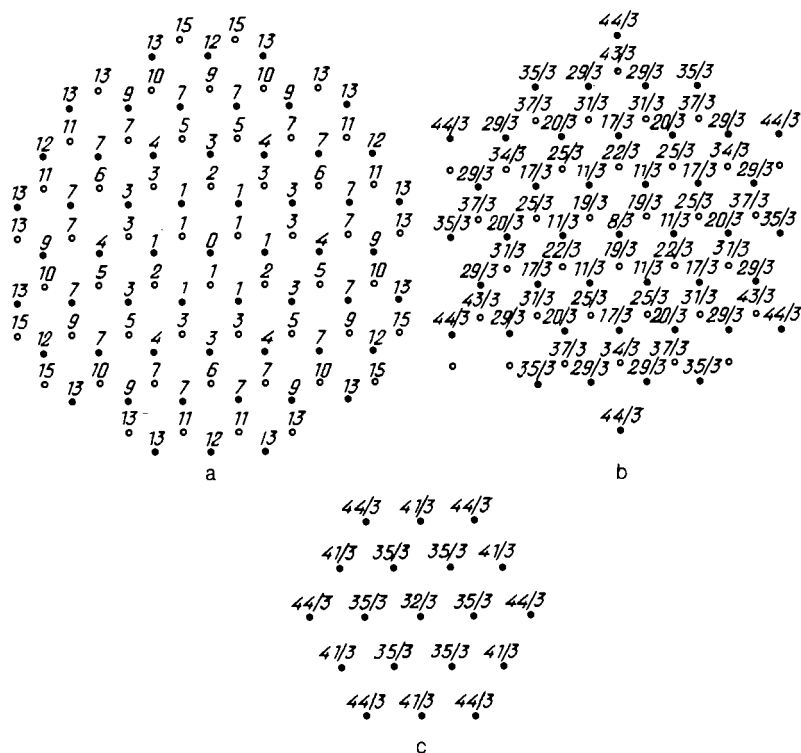

FIG. 3. Position of molecules in layers of a hexagonal lattice. a–Empty circles (e.c.)–position of molecules of the initial layer, dark circles (d.c.)–position of circles of the first layer. b–D.c. and e.c.–positions of molecules of the second and third layers respectively. c–D.c.–position of molecules of the fourth layer. The numbers indicate the square of the distance from the corresponding molecule to the center in units of distance between nearest neighbors and are placed above the corresponding points.

TABLE III. Position of the molecules in the cluster cut out from a hexagonal crystalline lattice.

Layer	Square of the distance to the center	Number of molecules	Number of molecules in the cluster
0	1	6	—
1	1	6	13
1	2	6	19
2	8/3	2	21
0	3	6	—
1	3	12	39
2	11/3	12	51
0	4	6	57
1	5	12	69
2	17/3	12	81
1	6	6	87
3	19/3	6	93
2	20/3	12	105
0	7	12	—
1	7	12	129
3	22/3	6	135
3	25/3	12	147
0	9	6	—
1	9	6	159
2	29/3	24	183
1	10	12	195
3	31/3	12	207
4	32/3	2	209
1	11	12	221
3	34/3	6	227
2	35/3	12	—
4	35/3	12	251
0	12	6	257
3	37/3	12	269
0	13	12	—
1	13	12	293
4	41/3	12	305
3	43/3	6	311
2	44/3	12	—
4	44/3	12	335
1	15	12	347

$$\varepsilon_s = (1,35 \pm 0,02)\Delta H \cdot n^{2/3}. \tag{5}$$

It is convenient to use this formula for a cluster or a drop the nature of the interaction between molecules of which on the surface is the same as inside.

We note another special feature that refers to the surface energy of a cluster. Clearly a real cluster that has one of the structures being examined can contain a small number of vacancies or impurity molecules. This will affect the parameters of the individual molecules situated near them. Correspondingly the vacancies and the impurities can determine such parameters of a cluster as the ionization potential, the affinity energy, the resonance energy of photons, etc. However, the surface energy is determined by the large number of

TABLE IV. Values of the parameter $A = \varepsilon_s/(\Delta H \cdot n^{2/3})$ for clusters cut out from different crystalline lattices.

Type of lattice	A
Cubic face-centered	1,33 ± 0,07
Cubic body-centered	1,33 ± 0,5
Hexagonal	1,36 ± 0,03
Average	1,35 ± 0,02

molecules so that the influence of these factors on the surface energy of the cluster is not great.

One more remark refers to the principle according to which the cluster was assembled. Specifically, it included molecules the distance of which from the center does not exceed a certain value. This had a determining influence on the shape of the cluster close to spherical. The existence of a surface tension of the cluster justifies its spherical shape, and thereby also the method of constructing it. From the point of view of the shell structure of a cluster such a method of constructing a cluster guarantees its optimal energy characteristics corresponding to the minimum surface energy of the cluster containing a given number of molecules. This refers to zero temperature when the sequence of filling the shells by adding molecules to the cluster is determined by the binding energy of the molecules so that those shells are being filled for which the binding energy is higher. At a finite temperature holes are formed in the inner shells, but this does not alter the general natue of the structure of a cluster.

6. SURFACE ENERGY OF A DROP

The above analysis of clusters with close packing shows that the surface of a cluster has a complicated topography. As the cluster grows the parameters associated with individual elements of this topography, such as the binding energy of an individual molecule, the ionization potential, the energy of affinity to an electron, etc. vary in an irregular manner experiencing sudden jumps after the corresponding shell has been filled. This does not allow one to determine reliably the dependences of these parameters on the number of particles in a cluster, one can only determine their average values with a certain error. Conversely, the surface energy which is produced by all the molecules that can emerge on the surface of the cluster is insensitive to the topography of the cluster surface. Therefore in determining the surface energy of the cluster one can treat it as a macroscopic particle and conversely, in analyzing the macroscopic particle one can use the results obtained for a cluster. On this basis we use the results obtained earlier for the analysis of a macroscopic drop.

Utilizing formula (5) for the surface energy we define the surface tension E_s as the ratio of the surface energy to the area of the surface of the cluster. We obtain a formula close to (1):

$$E_s = 0,28\Delta H \cdot N^{2/3}, \tag{6}$$

where ΔH is the energy of converting the macroscopic system to gas evaluated per molecule, and N is the density of molecules in this condensed system which we consider to be isotropic. We shall use this formula for systems of arbitrary structure. On the basis of this formula we have for the surface tension of mercury and water 0.36 and 0.23 J/m² respectively. The real values of these quantities are respectively 0.48 and 0.07 J/m². The general conclusion from this comparison and from general considerations consists of the fact that the relations that we have obtained are not suitable for systems in which the interaction of the molecules on the surface differs from their interaction within the system. In particular, the obtained formulas are not suitable for polar liquids and solutions. These results can be used for systems with a strong interaction between atoms and molecules in which the interacting particles retain to a certain extent their

TABLE V.

n	40	80	100	200	400	800	1000
x	8	12	14	22	34	52	60
y	16	25	29	46	73	116	135

individuality. In particular, this refers to metals and oxides. In so doing we should expect an accuracy which we obtained for the surface tension of mercury.

Macroscopic particles[1] of not very great size have a high surface energy. We shall use expression (5) for the surface energy obtained for clusters treated as being closely packed which contain n molecules:

$$\varepsilon_s = 1{,}35 \Delta H \cdot n^{2/3}. \qquad (7)$$

We introduce the specific area of the surface of a particle S which is the ratio of the area of the surface of the particle to its mass:

$$S = 3/r\rho,$$

where r is the radius of the particle. ρ is the density of the matter in it. From this we obtain for the specific surface energy:

$$\varepsilon_s = 0{,}27 (\rho/m_0)^{2/3} \Delta H \cdot S, \qquad (8)$$

where m is the mass of the particle, and m_0 is the mass of an individual molecule.

It is convenient to use this formula for porous systems. In particular, representing the aerogel SiO_2 in the form of a set of spheres bound together, we find that its specific internal energy is equal to $\varepsilon_s / Sm = 2$ J/m^2 (m is the mass of an individual particle; the value[15] $\Delta H = 133$ kcal/mole has been used). From this, in particular, it follows that for an aerogel with a typical value of the specific area of the internal surface $S = 1000$ m^2/g the specific internal energy is equal to 2kJ/g. This energy is comparable with the specific energy of gunpowder (2.5–5 kJ/g).

Let us consider the liberation of energy on the coalescence of two drops or clusters. They then form a new drop with a lower surface energy. We assume that the coalescence of the drops occurs relatively rapidly and the excess of energy is spent on evaporating a portion of the molecules in the drop, each of which contains n molecules, while x molecules evaporate. Then in accordance with formula (7) we have the following equation for the energy balance:

$$2{,}7 \Delta H \cdot n^{2/3} = 1{,}35 \Delta H \cdot (2n - x)^{2/3} + \Delta H \cdot x.$$

We see that this equation does not depend on the binding energy of an internal molecule and can be written in the form

$$x = 2{,}7 n^{2/3} - 1{,}35 (2n - x)^{2/3}. \qquad (9)$$

In Table V we provide solutions of this equation. For comparison we also give there values of the number of molecules $y = 1.35 n^{2/3}$ which can evaporate drawing on the surface energy of one of the drops. This energy, for example, is liberated when the drop attaches to a plane surface.

7. THERMODYNAMICS OF CLUSTERS WITH CLOSE PACKING

Let us make more precise the basic assertion of the paper, which follows from an analysis of constructed clusters,

which consists of the fact that the surface energy of the cluster can be defined with a certain degree of accuracy as a function of the number of particles in the cluster, while for the binding energy of the molecule being attached such a dependence has no meaning. The binding energy of the molecule being attached $\Delta \varepsilon_n$ is the derivative of the total energy of the cluster with respect to the number of particles, so that $\Delta \varepsilon_n$ is related to the surface energy. If one traces how the surface energy of a cluster increases as new molecules are added to it (cf., Fig. 2) it is possible to establish that each molecule attached to the cluster leads to an increase in the surface energy by an amount $\Delta H - \Delta \varepsilon_n$. We see that the derivative of the surface energy with respect to the number of molecules in a cluster is not a regular function of the number of molecules. Therefore those problems where it is essential to know the total energy of the cluster (for example, energy liberation on the coalescence of two clusters), the cluster can be regarded as a macroscopic particle. In those problems where the derivative of the surface energy is essential, the macroscopic approaches are inapplicable. The reason for the difference between a cluster and a macroscopic particle consists of the fact that in the very method of constructing the cluster the crystalline structure has already been imbedded. Therefore the binding energy of the molecule being attached may assume definite discrete values and this refers to clusters of any size. However these assertions refer to zero temperature. Obviously thermal motion of the molecules may alter this situation.

First let us determine how the structure of a cluster changes as a result of thermal excitation. Even at low temperatures the excitation energy of a cluster is quite high. Indeed, we shall regard the vibrations of molecules in a cluster as classical ones. Then the energy $3(n - 2)T/2$ which significantly exceeds the binding energy of an individual molecule (T is the temperature expressed in energy units) is concentrated on the vibrational degrees of freedom of the cluster which contains n molecules. This energy can be utilized for forming vacancies in a cluster and transfer of molecules from filled shells of the cluster to more distant unfilled shells.

Basically vacancies arise on the surface of the cluster and from there the molecules go over to the external unfilled shells of the cluster. This effect disturbs the previously discussed closed structure of the cluster when one of the shells of the cluster is filled sequentially and after it has been filled the building of the next shell occurs. The temperature effect makes the cluster "full of holes" so that it acquires several unfilled shells with different binding energies of the molecules. This effect is stronger the larger the cluster. Figure 4 shows the number of vacancies in the surface shells of the cluster containing a number of molecules close to 791 and which has the structure of a face-centered lattice. We designate as surface shells of the cluster under discussion, which contains a number of molecules in the neighborhood of 791, the shells 017, 345, and 046 where the binding energy of the
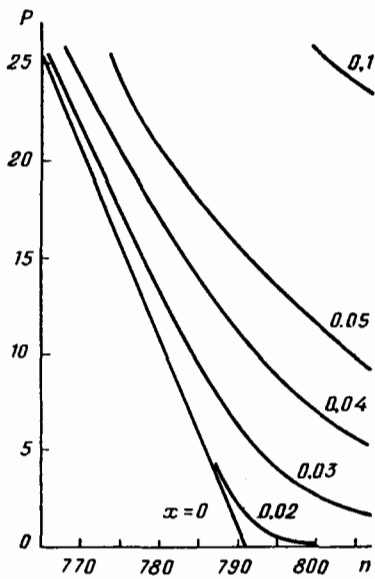
FIG. 4. Number of vacancies in the surface shells of a cluster with the structure of the face-centered cubic lattice as a function of the number of molecules in the cluster (the values of the parameter $x = T/\Delta H$ are shown).

molecules is equal to $6D$. The total number of molecules in these shells is equal to 96. At low temperatures $(x = T/\Delta H \rightarrow 0)$ as new molecules are added to the cluster containing $n < 791$ molecules they occupy the vacant places in the surface shells, and for $n = 791$ the surface shells are completely filled and the external shells are completely vacant. As the temperature increases the external shells begin to become filled even before the surface shells have been filled. Therefore in the surface shells there are vacancies even for $n > 791$. Their number is greater, the higher the temperature.

Among the external shells of the cluster under consideration containing a number of molecules close to 791 the most

important are the shells 336, 127, and 225 with the binding energy of molecules in them being $5D$ and the total number of molecules which can be situated in the shells being equal to 96. These shells are the ones that are being filled most effectively. Figure 5 presents the population of these external shells depending on the number of molecules in the cluster at different temperatures.

The temperature effect under consideration leads to an increase in the surface energy of the cluster (Fig. 6) and to a smoothing out of the energy parameters of the cluster as a function of the number of molecules contained in it. Indeed, at low temperatures as one shell is being filled and another one is beginning to be filled the binding energy of the molecule being attached experiences a jump. As the temperature increases the new shell begins to be filled before the preceeding shell has been completely filled. And this makes the change in the binding energy of the molecule more smooth.

We consider one more parameter of the cluster under examination. The distribution of clusters among shells corresponds to the Fermi–Dirac case, so that the parameter of the cluster is the chemical potential μ_n which is determined from the relation

$$\sum_k n_k [1 + \exp(\Delta\varepsilon_k - \mu_n)/T)]^{-1} = n, \qquad (10)$$

where n_k is the number of states in the k th shell, and $\Delta\varepsilon_k$ is the binding energy of the molecule in the shell when n molecules are present in the cluster. As the shell is being filled and a transition occurs to a new shell the chemical potential changes from the binding energy of the molecule in the shell being filled to the binding energy in the new shell. This transition becomes smoother the higher the temperature (Fig. 7).

8. THE CLUSTER MODEL OF THE CONDENSATION

The dependence of the surface energy on the number of molecules in the cluster, which has a stepwise nature at low temperatures and becomes smoothed out as the temperature
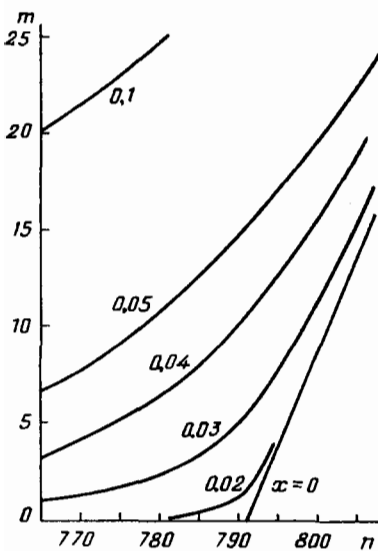

FIG. 5. Number of molecules in the external shells of a cluster where the binding energy of the molecule is equal to $5D$, at different temperatures (the values of the parameter $x = T/\Delta H$ are shown).
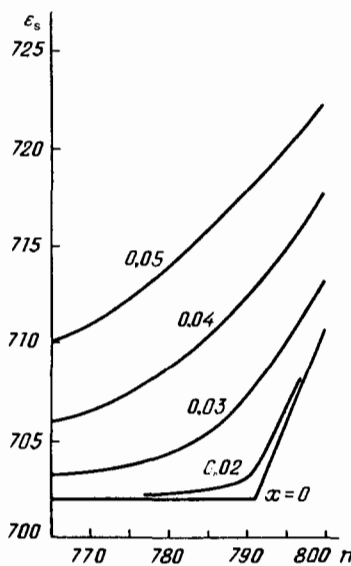

FIG. 6. Surface energy of the cluster under consideration as a function of the number of particles in it at different temperatures (values of the parameter $x = T/\Delta H$ are shown).
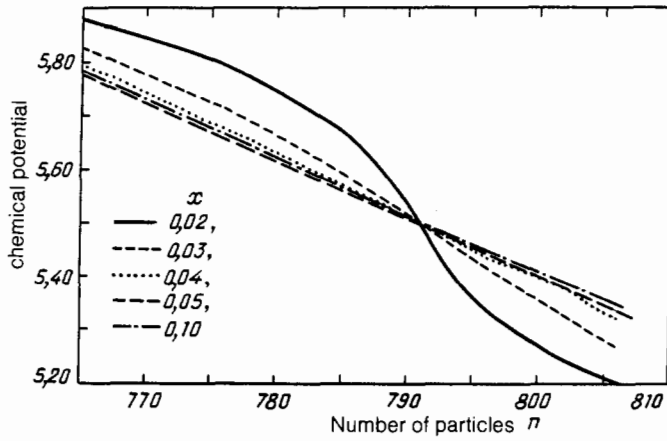
FIG. 7. The chemical potential of a cluster as a function of the number of particles in it expressed in units of D. Values of the parameter $x = T / \Delta H$ are shown.

increases, affects the nature of the processes associated with the attachment of molecules to the cluster and the evaporation of molecules belonging to the cluster. We briefly consider one of such processes corresponding to condensation of molecules in a supersaturated vapor which occurs through the formation and growth of nuclei, with the nuclei being clusters. Our aim is to understand how the parameters of the clusters affect the rate of condensation.

We give a sketch of the general theory of the condensation being examined assuming that the growth and decay of nuclei is associated with the addition of molecules to the cluster and evaporation of molecules. We examine the kinetic regime when the mean free path of the molecules is large compared to the size of the cluster. We write the time of evaporation of molecules from the cluster in the form $\tau_0 \exp(\Delta \varepsilon_n / T)$ where $\Delta \varepsilon_n$ is the binding energy of the nth molecule in the cluster, and the rate of capture of free molecules by the cluster is equal to $j\sigma_n$ where σ_n is the cross section for the capture of molecules by the cluster which is proportional to the cross section of the cluster; the flux of incident molecules is equal to

$$j = N(T/2\pi m)^{1/2},$$

where N is the density of the molecules in the gas phase, and m is the mass of a molecule. We introduce the pressure of the saturated vapor $P_{sat}(T)$ in such a way that at the density of molecules corresponding to it the times of evaporation and capture of a molecule are equal to one another for clusters of a large size. The degree of supersaturation of the gas or vapor (p is the gas pressure) is equal to:

$$S = p/P_{sat} = j\sigma_n\tau_0\exp(-\Delta H/T). \quad (11)$$

We write down the kinetic equation for the density of clusters N_n containing n molecules. We have:

$$dN_n/dt = -N_n\exp(-\Delta\varepsilon_n/T)/\tau_0$$
$$+ N_{n-1}j\sigma_{n-1} + N_{n+1}\exp(-\Delta\varepsilon_{n+1}/T)/\tau_0 - N_n j\sigma_n, \quad (12)$$

where σ_n is the cross section for the capture of a molecule by a cluster containing n molecules. We then concentrate our attention on the principal elements of the process and therefore we shall neglect the dependence of the parameters τ_0 and $\Delta\varepsilon_n$ on n. Equation (12) has a steady-state solution:

$$N_{n-1}/N_n = 1/S \exp[-(\Delta H - \Delta\varepsilon_n)/T]. \quad (13)$$

Using Eq. (13) we analyze the classical theory of condensation where the binding energy of a molecule $\Delta\varepsilon_n$ is a monotonic function of the number of particles in the cluster. Using for the binding energy of the nth molecule of the cluster an expression of the type (4) we have, taking into account (5):

$$\Delta\varepsilon_n = \Delta H - 2A\Delta H \cdot n^{-1/3}/3.$$

The relation (12) assumes the form:

$$N_{n-1}/N_n = (1/S)\exp(2A\Delta H/3n^{1/3}T).$$

From this we obtain the critical number of molecules in the cluster

$$n_{cr} = (2A\Delta H/3T \ln S)^3, \quad (14)$$

which corresponds to minimum population. Clusters of smaller size will evaporate, clusters of greater size will grow.

In order to determine the rate of condensation it is necessary to solve the system of equations (12). The problem is simplified due to the fact that at each transition the number of molecules in the cluster changes by unity. Since the values of n which determine the rate of the process are great, considering n as a continuous parameter one can reduce the system of equations (12) to the Fokker-Planck equation:

$$\frac{\partial N_n}{\partial t} = \frac{\partial}{\partial n}(a_n N_n) + \frac{\partial}{\partial n^2}(b_n N_n), \quad (15)$$

where

$$a_n = \exp(-\Delta\varepsilon_n/T)\{S\exp[(\Delta\varepsilon_n - \Delta H)/T] - 1\}/\tau_0,$$
$$b_n = \exp(-\Delta\varepsilon_n/T)\{S\exp[(\Delta\varepsilon_n - \Delta H)/T] + 1\}/2\tau_0.$$

In the case of the classical theory of condensation we obtain that for $n = n_{cr}$ we have $a_n = 0$. The time of condensation on attainment of the critical parameters is determined by the quantity $b(n_{cr}) = \exp(-\Delta\varepsilon_n/T)/\tau_0$, with it being basically expended on going through the range of Δn determined by the relationship

$$\frac{1}{T}\frac{d\Delta\varepsilon_n}{dn}\Delta n \sim 1. \quad (16)$$

By the same token the time of condensation after attaining the critical parameters amounts in order of magnitude to $\tau\Delta n^2$, where $\tau = ta_0\exp(\Delta\varepsilon_n/T)$ is the time of evaporation
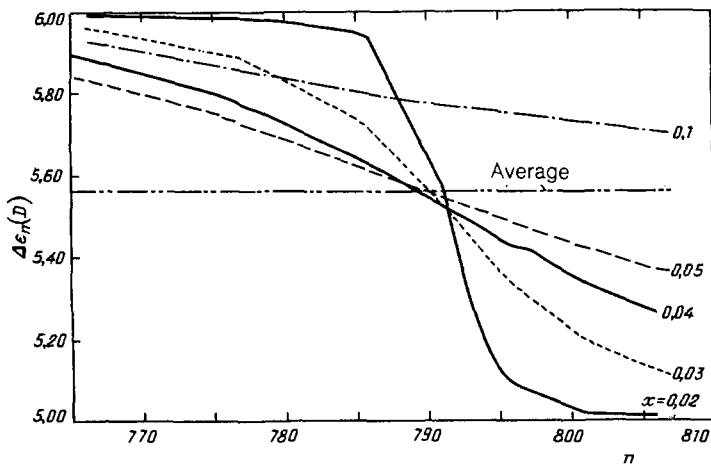
FIG. 8. The binding energy of the molecule being added to the cluster as a function of the number of particles in it, expressed in units of D. Values of the parameter $x = T/\Delta H$ are shown. The dotted line characterizes the average value of the binding energy in accordance with formula (5).

of a molecule from a cluster of critical size.

Now on the basis of the relationships obtained above we present the general picture of the process of condensation, taking into account the properties of real clusters. In doing this it is essential that the binding energy of the molecules to the cluster is a nonmonotonic function of the number of molecules in the cluster, with this feature of being nonmonotonic being preserved as the temperature is increased. From this it follows that the distribution of clusters with respect to size in the process of condensation has the following form. The maximum population corresponds to clusters with a partial filling of a closed shell for which the binding energy of the molecule being attached is equal to ΔH or is close to this value. Thus at low temperatures clusters are picked out with a closed shell being filled, and an increase in the temperature smooths out this effect but preserves it. The distribution function of the clusters with respect to the number of molecules contained in them has sharp dips coresponding to the filling of shells that are not closed. This has a significant effect on the nature of condensation which is sharply slowed down in the case of filling of shells of the cluster that are not closed.

To demonstrate this fact Fig. 8 presents the dependence of the binding energy of the molecule being added to the cluster $\Delta\varepsilon_n$ on the number of particles in it in the region of filling of the closed shell with $n = 791$. We see that these dependences do not correspond to the averaging of binding energy inherent in the classical theory of condensation. For values of the parameter $x = \Delta\varepsilon_n / T = 0.02 - 0.05$ which are of interest for condensation, the change in the factor $\Delta\varepsilon_n /T$ as the shell is being filled amounts to a few units, and this corresponds to a change in the population of the clusters by orders of magnitude. By this token the distribution function of the clusters with respect to the number of molecules in them is essentially nonmonotonic. We note that these conclusions follow from an analysis of relatively large clusters, i.e., they are valid for different regimes of condensation.

As a result of the nonmonotonic dependence of the binding energy of the molecule being added to the cluster on the number of molecules in it the picture of condensation becomes more complicated than in the classical case. In this case the cluster theory may be constructed based on the Fokker–Planck equation (15), but taking into account real

values of $\Delta\varepsilon_n$. We see that in this case the condensation time will be determined by the passage through the shells with the lowest values of the binding energy of the molecules $\Delta\varepsilon_n$. There can be many such shells, with the temperature effects being able to smooth out only partially the stepwise nature of the dependence of $\Delta\varepsilon_n$ on n, but not to change it. By the same token the classical theory of condensation turns out to be unsuitable, and the validity of the simplified variants of the cluster theory of condensation can be checked by means of numerical calculations taking into account the Fokker-Planck equation (15) and the real dependences of the energy of attachment of a molecule to the cluster on the number of molecules in it and on the temperature.

9. CONCLUSION

An analysis of clusters cut out from the face-centered, body-centered and hexagonal crystalline lattices around a certain center enables one to formulate a number of assertions concerning the physics of clusters. At low temperatures a cluster containing tens and hundreds of molecules cannot be regarded as a macroscopic system because a number of the parameters of the cluster cannot be defined as a monotonic function of the number of particles in it. This refers, in particular, to the binding energy of a molecule being attached to the cluster, which depends on the structure of the cluster—shell in which it is situated, and the shells that have been filled. The binding energy of a molecule in a cluster experiences jumps as the cluster grows—as one shell is filled and the next shell starts growing. A similar stepwise behavior should be expected for other parameters of the cluster associated with the behavior of a single molecule— the ionization potential, the affinity energy, the energy of electron excitation, etc.

The surface energy of the cluster is produced by a considerable or a greater part of the molecules of the cluster. This quantity is insensitive to the topography of the surface of the cluster—to the structure of its shells. Therefore for the surface energy a cluster containing tens and more molecules is a macroscopic particle. For it one can utilize such a concept as surface tension.

In conclusion we note that the method that has been used for constructing a cluster by cutting it out from a crystalline lattice can be applied to lattices of different symmetry

and is convenient in analyzing different properties of clusters and processes in which they participate.

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[1] We see the terms cluster, drop, macroscopic particle for systems containing tens and more molecules have the same meaning in examining surface energy.

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