

Melting of clusters with pair interaction of atoms

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Abstract. Analysis of the melting of clusters with pair interaction of atoms by methods of molecular dynamics has revealed special features of the melting process which are useful for the understanding of the microscopic nature of phase transitions in condensed systems. One of these features is the coexistence of solid and liquid phases in a cluster in some temperature range the width of which is inversely proportional to the number of atoms participating in the transition. The melting process is governed by collective motion of cluster atoms, and a potential barrier separates the solid and liquid phases. The physical picture of the melting process has been obtained from computer modeling of clusters. The results demonstrate that the liquid state of clusters with filled shells can be regarded as the lowest excited state with a large statistical weight, and that simple cluster models in which atoms not participating in the transitions are assumed to stay fixed in their lattice sites can describe the melting process only qualitatively.

1. Introduction

Melting of a solid is a phase transition of the first order which leads to the collapse of the long-range order in the arrangement of atoms [1–4] with a stepwise change of the free energy of the atomic system. We shall consider here the simplest condensed system of bound atoms in which the atoms can be represented by rigid or soft spheres. A crystal of such a system has a close-packed structure, with a face-

centred cubic (fcc) or a hexagonal (hcp) lattice. Each atom of this lattice has 12 nearest neighbours at a fixed distance from it, known as the lattice constant.

In the course of melting of this condensed system the size and rigidity of the spheres representing the atoms are not changed, i.e. the character of interaction between neighbouring atoms is conserved. But the volume of the system increases approximately by 10% which leads to the formation of vacancies inside the system. Correspondingly, the number of nearest neighbours of each atom—the coordination number—decreases. The vacancies thus created allow the atoms to change their positions inside the system, and this accords the capacity to flow to the liquid that forms.

The number of nearest neighbours is a parameter which can be used to describe certain properties of the liquid. But such a description is phenomenological, whereas a microscopic description of the melting process must be based on the interatomic potential. In conjunction with modern computer technology, this method allows us to describe the behaviour of a system consisting of many bound atoms. But this still leaves the question how to present and interpret the results. Therefore for the analysis of the microscopic nature of melting of atomic condensed systems it is convenient to consider simple models of such systems and processes that take place in them.

One of such systems is a suspension with a simple interaction between particles [5–7]. By using optical methods one can analyse the transition of particles of a suspension into a bound state and the formation of a crystal structure. Together with a theoretical description of the process, this will provide information useful for the understanding of the nature of the phase transition.

Another simplification of the atomic condensed system consists of examining the two-dimensional case, namely that of surface melting. Indeed, melting of a solid starts from the surface because surface atoms have fewer nearest neighbours than atoms in the interior. This was shown in experiments on

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lead [8] and inert gas crystals [9]. Two-dimensional melting has special features [10], and its investigation is useful for the understanding of the microscopic nature of melting of bound atomic systems. Two-dimensional melting or melting of films on substrata in systems with pair interaction of atoms has been studied in detail both theoretically [11–16] and experimentally [17–24].

But the greatest progress in the understanding of the physics of melting has been achieved by investigating the phase transition in clusters consisting of atoms with pair interaction by the methods of molecular dynamics with the use of modern computers and by creation of new algorithms for calculations. Clusters with pair interaction of atoms have a shell structure, and atoms of the inner shells and of the surface shell have different binding energies. Therefore melting of such clusters starts from the surface shell; at these temperatures the atoms of the inner shells are rigidly locked at their lattice sites. Thus melting of clusters with pair interaction of atoms has an analogy with surface melting.

If the cluster surface shell is filled or almost filled, the melting process is accompanied by the formation of vacancies and migration of some atoms from the surface shell to a free shell, and hence this transition is characterised by a change of the free energy of the system. On the other hand if the cluster surface shell is partially filled, melting of the cluster involves relatively unhindered movement of surface atoms to free sites in the surface shell, i.e. this process proceeds without change of the cluster free energy. Thus, only melting of clusters with a filled (or almost filled) surface shell has an analogy with melting of macroscopic bound systems of atoms. It is this process that will be examined below.

The foundations of computer modeling of cluster properties including the melting process go back to the seventies, when it was shown [25–31] that small clusters can be both in the liquid and in the solid state. In the eighties some principal results for the melting process of clusters were obtained [32–52], which are the basis of our current understanding of this process. Let us consider some of them.

In contrast to the melting of a macroscopic solid where the phase transition has a stepwise character, in clusters the transition from the solid to the liquid state stretches out over an interval of excitation energies, in which the solid and liquid phases coexist. Then at any given excitation energy (or at a fixed temperature if the cluster temperature is controlled by a thermostat) the cluster spends some time in the solid state and some time in the liquid state. Because the transition to the liquid state requires energy, the atom temperatures are different for the solid and liquid states if the cluster is isolated. Otherwise, the phases coexist in a certain range of temperatures. With increase of cluster size and, correspondingly, of the number of atoms in the surface shell, the width of the coexistence region decreases.

Another characteristic feature of the melting of clusters consists in the nature of the transition [46, 47]. It is not a result of amorphisation of the cluster surface when random vibrations of individual atoms reach high amplitudes, such that they leave their sites. The phase transition is due to collective movements of atoms, as a result of which some atoms abandon their sites and attach themselves to the cluster surface from the outside. They can then move freely on the cluster surface and can occupy vacant sites in the

surface shell, which makes the cluster revert to the solid state.

These and other features of the melting of clusters are considered in the present review. The aim here is to analyse the results of computer modeling of the cluster melting process and compare these results with those provided by simple models of the respective cluster properties. This will provide a more accurate description of the process and allow us to select simple and reliable cluster models useful for the understanding of the microscopic nature of the process.

2. Condensed systems of atoms with pair interaction

In the analysis of clusters with pair interaction of atoms, we shall concentrate on inert gas clusters. In choosing an appropriate form of the pair interaction potential of cluster atoms it is convenient to check its validity for inert gas crystals and liquids. Table 1 contains parameters of condensed inert gases expressed as dimensionless quantities. This will allow us to check the validity of scaling laws for these systems.

Table 1. Parameters of diatomic molecules and reduced parameters of condensed inert gases.

Parameter	Ne	Ar	Kr	Xe	Average
$R_c/\text{\AA}$	3.09	3.76	4.01	4.36	
D/meV	3.7	12.2	17.2	24	
$a/\text{\AA}$	3.156	3.755	3.992	4.335	
$\rho_s(0)/\rho_0$	1.06	1.00	0.99	0.98	1.01 ± 0.04
$\rho_s(T_b)/\rho_0$	0.899	0.920	0.926	0.952	0.92 ± 0.02
ρ_l/ρ_0	0.776	0.804	0.800	0.827	0.80 ± 0.02
ρ_b/ρ_0	0.751	0.782	0.791	0.803	0.78 ± 0.02
$(\rho_s - \rho_l)/\rho_0$	0.123	0.116	0.126	0.127	0.123 ± 0.005
$(\rho_l - \rho_b)/\rho_0$	0.025	0.022	0.009	0.022	0.020 ± 0.007
T_m/D	0.57	0.59	0.58	0.58	0.58 ± 0.01
T_b/D	0.63	0.62	0.60	0.59	0.61 ± 0.02
$\Delta H_m/D$	0.94	1.00	0.99	0.99	0.98 ± 0.03
$\Delta H_{\text{sub}}(0)/D$	5.4	6.6	6.7	7.1	6.4 ± 0.7
$\Delta H_{\text{sub}}(T_b)/D$	5.0	5.5	5.4	5.5	5.4 ± 0.2

Let us label the interaction potential of two atoms at a distance R between them as $U(R)$. We shall choose as the main parameters of the interaction potential the equilibrium distance R_c between atoms in a diatomic molecule and the depth of the potential well D , i.e.

$$U'(R_c) = 0, \quad U(R_c) = -D; \quad (1)$$

we shall use m , the atomic mass, as a parameter. One can make up quantities with any dimensionality on the basis of these three parameters, and this is used in Table 1. Apart from the aforementioned parameters of a diatomic molecule and the distance a between nearest neighbours in inert gas crystals at zero temperature, Table 1 contains parameters of two dimensionalities. Energetic parameters are expressed in units of D , with the following notation: T_m and T_b † are the melting and boiling points, ΔH_m is the heat of melting per atom, ΔH_{sub} is the sublimation energy (or the heat of vaporisation) per atom at the boiling point.

†In this paper the temperature is expressed in energetic units.

Parameters of density are expressed in units of $\rho_0 = m\sqrt{2}/R_c^3$ that is the density of a crystal with close-packed structure at zero temperature and distance R_c between the nearest neighbours. Table 1 contains the values of ρ_0 , crystal density at zero temperature; ρ_s , crystal density at the melting point; ρ_l , liquid density at the melting point; and ρ_b , liquid density at the boiling point. The parameters of the interaction potential of inert gas atoms have been taken from Refs [53–66], and the parameters for condensed inert gases have been taken from Refs [57, 67–69] and correspond to atmospheric pressure.

The total binding energy of atoms in a cluster or a condensed system of atoms with pair interaction between them is equal to the sum of the interaction potentials of all the atoms of the system:

$$E = -\frac{1}{2} \sum_{i,j} U(R_{ij}), \quad (2)$$

where i, j are atom numbers, R_{ij} are the distances between corresponding atoms, and $U(R_{ij})$ is the interaction potential of two atoms at a distance R_{ij} between them.

Formula (2) assumes that the interaction potential for two atoms in a system of many bound atoms does not depend on the positions of other atoms. It is valid for systems of weakly interacting atoms, such as atoms with repulsive exchange interaction. This applies to systems of inert gas atoms, systems of alkali metal atoms with the same directions of spin of the valency electrons, etc. In these cases the depth of the attractive well is small compared with typical electron energies of the system, and the ratio of these values is a small parameter. Because this parameter is small, three-body interactions are weak compared with pair interactions, and this ensures the validity of formula (2). Thus atomic systems that are considered in this paper are systems with a weak interaction between atoms, and so they are the simplest systems of this type.

Below we consider two types of interaction potentials—the short-range interaction potential and the Lennard-Jones one. Each of them satisfies relation (1), but the short-range interaction potential acts only between nearest neighbours, whereas the Lennard-Jones potential is a long-range one and has the form:

$$U(R) = D \left[\left(\frac{R_c}{R} \right)^{12} - 2 \left(\frac{R_c}{R} \right)^6 \right]. \quad (3)$$

Let us now analyse the parameters of inert gas crystal on the basis of these interaction potentials.

The optimal distance a between nearest neighbours in a crystal with short-range interaction between atoms is equal to the equilibrium distance between atoms of a diatomic molecule:

$$a = R_c. \quad (4)$$

The atoms form a crystal with close packing where each atom has 12 nearest neighbours. Therefore the crystal sublimation energy ε_{sub} , i.e. the binding energy per atom, is, according to formula (2):

$$\varepsilon_{\text{sub}} = \frac{E}{n} = 6D. \quad (5)$$

Let us determine these parameters for the Lennard-Jones potential, repeating operations reported in Kittel's book [68]. According to formula (2) we have for the

sublimation energy per atom:

$$\begin{aligned} \varepsilon_{\text{sub}} &= -\frac{D}{2} \sum_i \left[\left(\frac{R_c}{R_i} \right)^{12} - 2 \left(\frac{R_c}{R_i} \right)^6 \right] \\ &= -C_1 \frac{D}{2} \left(\frac{R_c}{a} \right)^{12} - C_2 D \left(\frac{R_c}{a} \right)^6. \end{aligned}$$

Here R_i is the distance from the atom under consideration to the i th one, and a is the lattice constant, i.e. the distance between the nearest neighbours. The parameters C_1 and C_2 in this expression for a crystal with an fcc lattice are [68]:

$$C_1 = \sum_k \frac{n_k}{k^{12}} = 12.131, \quad C_2 = \sum_k \frac{n_k}{k^6} = 14.454,$$

where n_k is the number of atoms at a distance ka from the atom under consideration. Optimising this expression for the sublimation energy of the crystal, we obtain [68]:

$$a = \left(\frac{C_1}{C_2} \right)^{1/6} = 0.971 R_c, \quad \varepsilon_{\text{sub}} = \frac{C_2^2 D}{C_1^2} = 8.61 D. \quad (6)$$

Comparison of these values with data in Table 1 shows that the short-range interaction potential is more suitable for describing inert gas crystals than the Lennard-Jones potential.

Note that there are two structures with close packing—the face-centred cubic (fcc) and hexagonal (hcp) lattices (see Refs [68, 70–72]). In both structures each atom has 12 nearest neighbours. For a short-range interaction between atoms both structures have the same energy, whereas for the Lennard-Jones crystal the hcp lattice is more favourable—its binding energy is approximately 0.01% higher than for a crystal with the fcc structure [73, 74]. But in reality all inert gas crystals (Ne, Ar, Kr, Xe) have the fcc lattice. The hexagonal lattice can be produced in films of condensed inert gases by deposition on a special target (see, for example, Refs [75–77]) but even in these cases the fcc lattice is more likely. This confirms again that the Lennard-Jones interaction potential is not suitable for the description of inert gas crystals.

One can add that the melting point of the Lennard-Jones crystal is equal to $T_m = 0.61D$ [78]. This temperature corresponds to the boiling point of condensed inert gases, and not to their melting point (see Table 1). Note that the Lennard-Jones interaction potential uses two parameters (D and R_c in our notations) whereas the short-range interaction potential is based on three parameters [$D, R_c, U''(R_c)$]. The parameter $U''(R_c)$ determines the width of the attractive well. By adjusting the value of this parameter one can make the melting point of a crystal consisting of atoms with short-range interaction correspond to the melting point of condensed inert gases.

The simplest form of the short-range interaction potential is:

$$U(R) = \begin{cases} -D \exp\left(-\frac{(R-R_c)^2}{2\Delta r^2}\right), & R > R_0, \\ \infty, & R < R_0. \end{cases} \quad (7)$$

It is seen that this interaction potential includes three parameters with dimensions of length: R, R_c, R_0 . But R_0 is not important for a condensed system of atoms. It determines the collision cross section of free atoms. Δr characterises the value of the vibration energy of a diatomic molecule and the phonon spectrum of a condensed system. One can choose it to be proportional

to R_c , i.e. $\Delta r = cR_c$, where the value of c is the same for all inert gases. Then the above scaling laws for condensed inert gases stay valid within the framework of this interaction potential.

Thus the short-range interaction potential describes the behaviour of inert gas crystals better than the Lennard-Jones one [79]. Nevertheless, most computer calculations of the properties of condensed inert gases use the Lennard-Jones interaction potential (3) because of its simplicity. Therefore in what follows both interaction potentials will be used for modeling the properties of inert gas clusters.

The parameters of crystalline and liquid states of condensed inert gases listed in Table 1 allow us to determine the average number of nearest neighbours for liquid inert gases at the melting point. We will use for this purpose the model of a system of bound atoms with fixed lattice points, and we shall also use it later in the investigation of clusters containing vacancies. According to this model, removal of an atom from the system does not affect the positions of the neighbouring atoms. This model is crude, because even a slight excitation will make atoms move towards the vacancy, but its simplicity makes it convenient to use in our analysis.

Using the above model of a system of bound atoms with fixed lattice points, let us isolate a volume V of a solid inert gas containing $\rho_s V/m$ atoms, where m is the atomic mass. Each of these atoms has 12 nearest neighbours, i.e. the total number of bonds in the isolated volume is $6\rho_s V/m$. Denoting the density of the liquid by ρ_l , we obtain the number of vacancies in this volume as $(\rho_s - \rho_l)V/m$. Formation of each vacancy leads to the loss of 12 bonds, i.e. the number of bonds in the volume of the liquid under consideration is $6(2\rho_l - \rho_s)V/m$. This gives for the average number of nearest neighbours in the liquid state:

$$q = 24 - 12 \frac{\rho_s}{\rho_l}. \quad (8)$$

Another way of determining the average number of nearest neighbours in the liquid state at the melting point is based on energetic considerations. Putting $\Delta H_{\text{sub}}(T_m)$ for the energy of atomisation of the liquid state, we find that for the solid state this value is $\Delta H_{\text{sub}}(T_m) + \Delta H_m$, where ΔH_m is the heat of melting. Because each atom partakes in 12 bonds in the solid state, the number of nearest neighbours of atoms in the liquid state is equal to:

$$q = \frac{12}{1 + \Delta H_m / \Delta H_{\text{sub}}(T_m)}. \quad (9)$$

Table 2 contains values of nearest neighbours calculated with the use of this formula. For this calculation we replaced $\Delta H_{\text{sub}}(T_m)$ at the melting point by $\Delta H_{\text{sub}}(T_b)$ at the boiling point which leads to somewhat overestimated

Table 2. The number of nearest neighbours for liquid inert gases and the ratio of the number of atoms to the number of vacancies (in parentheses).

Formula used	Ne	Ar	Kr	Xe	Average
(8)	10.10 (5.74)	10.27 (5.94)	10.11 (5.35)	10.19 (5.63)	10.17 ± 0.08 (5.66 ± 0.25)
(9)	10.07 (5.22)	10.15 (5.49)	10.14 (5.45)	10.19 (5.56)	10.15 ± 0.04 (5.43 ± 0.15)

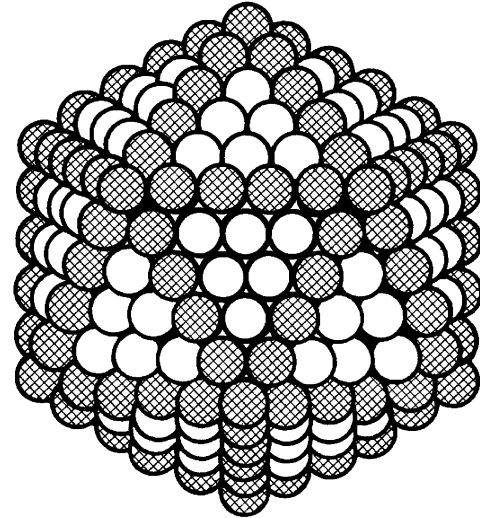


Figure 1. An icosahedral cluster with 561 atoms, i.e. 5 filled shells [81]. Atoms lying on the sides of the triangles forming the surface of the icosahedron are shown cross-hatched.

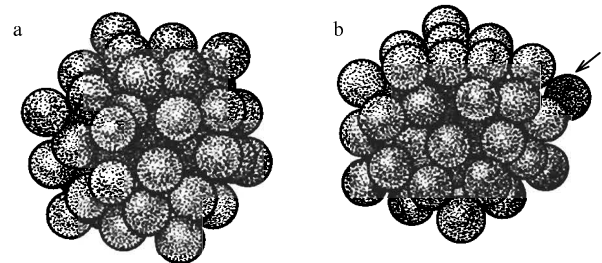


Figure 2. A Lennard-Jones cluster with 55 atoms in the ground (a) and in the lowest excited (b) states according to calculations by Kunz and Berry [52]. In the ground state (a) the cluster has an icosahedral form and its surface consists of 20 regular triangles with 6 atom/spheres in each. In the lowest excited state (b) one atom moves to the cluster surface (this atom is marked by an arrow), and a vacancy is formed in the position it has left, which leads to a displacement of the neighbouring atoms.

values for q . As seen from Table 2, the two methods give similar values for the number of nearest neighbours for liquid inert gases. Averaging over all inert gases and methods of determination, we obtain $q = 10.15 \pm 0.06$. Hence there is one vacancy in liquid inert gases at the melting point per 5.6 ± 0.2 atoms.

3. Clusters with pair interaction of atoms

Let us consider the properties of clusters consisting of atoms with pair interaction. Such clusters of moderate size have an icosahedral structure [80]. The surface of an icosahedron consists of 20 equilateral triangles. An example of an icosahedral cluster with filled shells consisting of 561 atoms is shown in Figure 1 [81]. Figure 2 shows an icosahedral cluster with 55 atoms together with the lowest excited state of this cluster, which corresponds to the transition of one of the atoms on the cluster surface [52].

The simplest way of constructing an icosahedral cluster with m filled shells is as follows. Let us draw a sphere of radius mR , where R is the radius of the first sphere, and locate on this sphere 12 atoms such that joining neighbour-

ing atoms produces 20 equilateral triangles. Then each atom is connected to 5 nearest atoms and the distance between these atoms is equal to mR_0 . Divide each of the 30 triangle sides into m parts and place atoms at these points. Draw through these atoms lines parallel to the triangle sides, and place new atoms at the points of intersection. All these atoms are located on the m th shell. This shell contains 12 vertex atoms, $30(m-1)$ atoms on the sides of the triangles, and $10(m-1)(m-2)$ atoms inside the triangles. The number of atoms of the m th filled shell of the icosahedral cluster is $10m^2 + 2$, and the total number of atoms of this cluster with m filled shells is [80]:

$$n = \frac{10}{3} m^3 + 5m^2 + \frac{11}{3} m + 1. \quad (10)$$

Let us now fill the internal cluster shells in the following way. Join the vertices of the cluster with its centre and divide each of the joining lines into m parts. Atoms placed at these these points are vertex atoms of the corresponding shells. The positions of the remaining atoms in each shell are formed by the same operations as those that have been used for atoms of the surface shell.

Recently large clusters have been the subjects of detailed studies (see, for example, monographs [82–88]). Some properties of large clusters consisting of hundreds and thousands of atoms were found to differ from the properties of corresponding bulk systems. This occurs, in particular, in the presence of so-called magic numbers of cluster atoms corresponding to filled cluster shells. Cluster parameters as a function of the number of atoms in the cluster can have an extremum at magic numbers of atoms in a cluster. For example, the binding energy of an atom withdrawn from a cluster with a magic number of atoms is greater than that of an atom withdrawn from clusters with the number of atoms greater or smaller by one than the magic number.

Clusters with pair interaction of atoms have the icosahedral structure when the number of cluster atoms is not large. This means that the magic numbers of such clusters are given by formula (10), which corresponds to filled cluster shells. Let us calculate the number of bonds between nearest neighbours for an icosahedral cluster. The distance between the nearest neighbours of the same shell, R_0 , differs somewhat from the distance R to the nearest neighbours in the adjacent shells [80]:

$$R = 0.951R_0. \quad (11)$$

Each atom of an inner shell has 12 nearest neighbours, as in the case of close packing where the distance between nearest neighbours is fixed.

The close-packed structure is preferable to the icosahedral one for a macroscopic system of bound atoms with pair interaction at zero temperature because of the optimal distance between atoms in the close-packed structure. But in a cluster with icosahedral structure the surface atoms have a greater number of nearest neighbours than in a close-packed one. Therefore clusters of small sizes have the icosahedral structure, which is energetically preferable, while large clusters have a closed-packed structure.

Let us calculate the number of bonds for an icosahedral cluster. As we have seen, there are two types of bonds: between atoms of the same shell, of length R_0 , and between atoms of neighbouring shells, of length R . Each vertex atom has 5 bonds with atoms of the same shell, 1 bond with an

atom of the previous shell and 6 bonds with atoms of the next shell. An atom located on a triangle side has 6 nearest neighbours with atoms of its own shell, 2 with atoms of the previous shell and 4 with atoms of the next shell. An atom located inside a triangle has 6 bonds with atoms of its own shell, and 3 bonds each with atoms of the previous shell and the next shell. From this it follows that an icosahedral cluster with m filled shells has A bonds of length R and B bonds of length R_0 , where [89]:

$$A = 10m^3 + 2m, \quad B = 10m^3 + 15m^2 + 5m. \quad (12)$$

For clusters with short-range interaction this allows us to determine the total binding energy of atoms at zero temperature [63]:

$$E = -A U(R) - B U(R_0), \quad (13)$$

where $U(r)$ is the pair interaction potential for a distance r between the two atoms. It has a minimum $-D$ at the distance R_e —the equilibrium distance for a diatomic molecule [see formula (1)]. Assuming lengths of both bonds to be close to the equilibrium distance R_e , we can expand formula (13):

$$E = (A + B) - \frac{1}{2} U''(R_e) [A(R - R_e)^2 + B(R_0 - R_e)^2]. \quad (14)$$

Optimising this expression, i.e. choosing interatomic distances which correspond to the maximum binding energy, we obtain:

$$A(R - R_e) \frac{\partial R}{\partial R_0} + B(R_0 - R_e) = 0. \quad (15)$$

Taking account of equation (11) we obtain:

$$\frac{R_0}{R_e} = \frac{0.951A + B}{0.904A + B} = 1 + \frac{0.047A}{0.904A + B},$$

$$E = (A + B) - 1.2 \times 10^{-3} \frac{ABR_e^2 U''(R_e)}{0.904A + B}. \quad (16)$$

Note that the second term reduces to zero if $R = R_0 = R_e$. Because these values are close, the second term of the total binding energy given by expression (16) is small compared with the first term. For example, in the case of the truncated Lennard-Jones interaction potential† the second term amounts to 2.3 % of the first one for clusters of large size.

Thus clusters with pair interaction of atoms have icosahedral structure when their size is small and close-packed structure when their size is large. The transition from one structure to the other one takes place when the number of cluster atoms is around 1000 [90].

Because in what follows we shall be concerned with small clusters with filled shells we list in Table 3 the values of the sublimation energy (binding energy per atom) for clusters with filled shells with icosahedral structure for the Lennard-Jones potential ($\epsilon_{\text{sub}}^{\text{LJ}}$) [90–94] and the short-range interaction potential ($\epsilon_{\text{sub}}^{\text{sh}}$) [89], that is the truncated Lennard-Jones potential. In addition, Table 3 also gives

†The truncated Lennard-Jones interaction potential corresponds to the Lennard-Jones potential of interaction between nearest neighbours, and when the distances between atoms are large this potential tends to zero.

the ratio η of the total binding energies of atoms in clusters with fcc structure [76, 86, 92] to those in clusters of the same size with icosahedral structure for the two types of interaction potential.

Table 3. The binding energy of cluster atoms per atom (in units of D) for the Lennard-Jones interaction potential ($\epsilon_{\text{sub}}^{\text{LJ}}$) [90–94] and the short-range interaction potential ($\epsilon_{\text{sub}}^{\text{sh}}$) [79, 89] for icosahedral clusters with filled shells, and the ratio of the binding energies for fcc and icosahedral structures for short-range (η_{sh}) and Lennard-Jones interaction potentials (η_{LJ}) between atoms.

m^*	n^*	Sublimation energy of an icosahedral cluster		Ratio of the sublimation energies of clusters	
		$\epsilon_{\text{sub}}^{\text{sh}}$	$\epsilon_{\text{sub}}^{\text{LJ}}$	η_{sh}	η_{LJ}
1	13	3.171	3.410	0.873	0.922
2	55	4.165	5.076	0.943	0.961
3	147	4.632	5.962	0.958	0.977
4	309	4.900	6.495	0.985	0.984
5	561	5.072	6.848	0.996	0.990
6	923	5.192	7.099	1.003	0.995
7	1415	5.281	7.286	1.007	0.997
8	2057	5.349	7.4295	1.010	0.999

* m is the shell number of the icosahedral cluster; n is the number of cluster atoms.

4. Statistics of the liquid state of cluster A_{13} near the melting point

The liquid state and the solid–liquid transition in the Lennard-Jones cluster A_{13} have been subjected to detailed analysis by the methods of molecular dynamics. In this section we shall consider separately the liquid state of this cluster and the nature of its melting.

Figure 3 shows the distribution function of atoms in cluster A_{13} according to their kinetic energies E_{kin} for different cluster excitation energies E_{ex} [34]. The cluster excitation energy is the difference between the total binding energies of cluster atoms at zero temperature and the temperature in question. Figure 3 shows the main features of cluster melting. The solid and liquid cluster states are clearly separated. The observation time is substantially longer than the typical time of the cluster staying in one of these states, which in turn greatly exceeds the transition time from one state to the other. This makes it possible to separate the solid and liquid states and provides the means for their coexistence.

In identifying the ground state of the cluster with the solid state and the excited state with the liquid state, we start from the assumption that in the ground state the cluster has a filled shell, and in the excited state one atom migrates to the unoccupied shell and can move freely on it. Exchanges between the excited and nonexcited atoms involve in this process all the surface atoms of the cluster. This fact can be confirmed by numerical para-

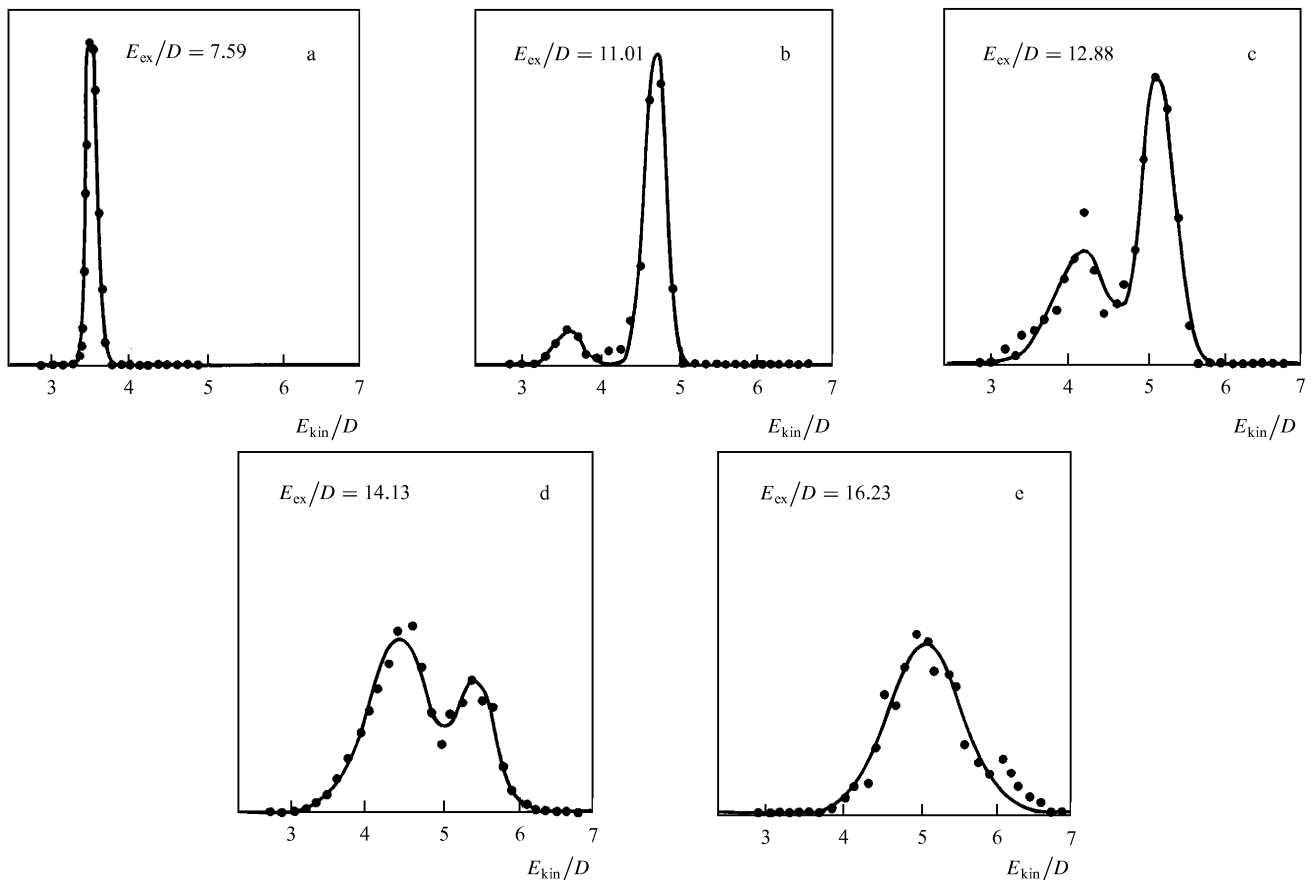


Figure 3. The distribution function of atoms in the Lennard-Jones cluster A_{13} according to their total kinetic energies E_{kin} averaged over a short time [34]. The excitation energies (E_{ex}) are shown in the respective boxes.

meters which are traditionally used to ascertain whether the cluster state is solid or liquid. One of these parameters is the root mean square of bond length fluctuation,

$$\delta = \frac{2}{n(n-1)} \sum_{i < j} \left[\frac{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}{\langle r_{ij} \rangle^2} \right]^{1/2}, \quad (17)$$

where r_{ij} is the distance between the i th and the j th atoms, averaging is made over the paths of the atoms over a long period of time, and n is the a number of cluster atoms. Figure 4 gives the temperature dependence of δ in the region of the melting point of cluster A_{13} . When the cluster is in the ground state, atoms are fixed at their lattice sites and the value of δ in expression (17) is determined by the amplitude of vibrations of atoms about their equilibrium positions. If during the observation time the cluster can switch from the liquid state and back many times, the value of δ is determined by the cluster size and becomes greater.

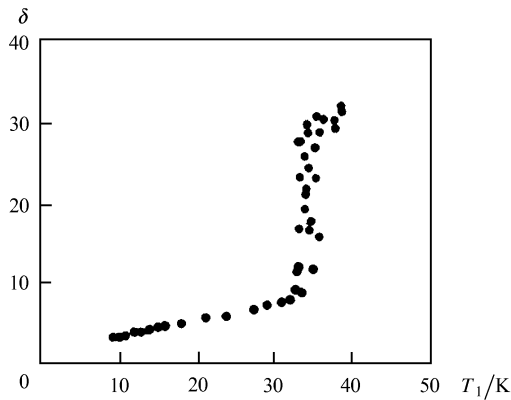


Figure 4. Values of δ , the square root of the fluctuations of the bond length [formula (17)] for the Lennard-Jones cluster A_{13} on averaging over long periods of time [34].

Another characteristic of the cluster state is the mean square displacement of cluster atoms:

$$\langle r^2(t) \rangle = \frac{1}{nk} \sum_{i=1}^n \sum_{p=1}^k [r_i(t_p + t) - r_i(t_p)]^2. \quad (18)$$

Here i is the number of the atom, t_p is the initial time, k is the number of initial times over which the average is taken, and $r_i(t)$ is the coordinate of the i th atom at time t .

Fig 5 shows the dependence of the mean square displacement of atoms on time for two excitation energies: in the first case the cluster A_{13} is in the solid state and in the second case it is in the liquid state. In the first case cluster atoms in the ground state are located at their lattice sites, and the mean square displacement of atoms is determined by the amplitude of their vibrations and does not depend on time. In the second case the variation of the mean square displacement of atoms with time is related to their diffusion to vacant sites in the cluster. Therefore it is proportional to time as long as this time is not very large, and is much greater than in the first case. This behaviour is seen in Fig 5.

Thus, the above parameters allow us to establish whether the cluster state is solid or liquid. This conclusion conforms to our analysis of the cluster structure. Thus, the cluster with a filled surface shell is the solid one, and the excited state with the formation of a vacancy in the surface

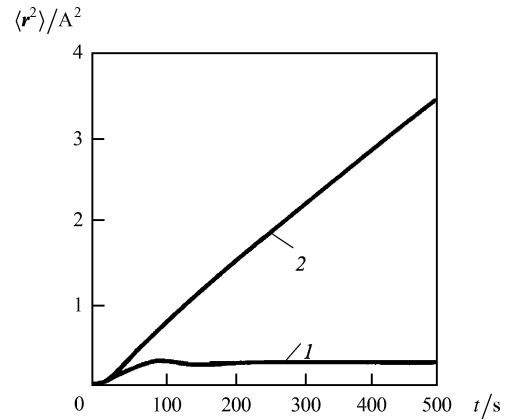


Figure 5. Mean square of atom displacement for the Lennard-Jones cluster A_{13} versus time at the following cluster excitation energies: (1) $7.59D$ (solid state); (2) $16.23D$ (liquid state) [34].

shell and the transition of atoms to free shells is the liquid state. Below we shall be guided by this fact.

Let us make use of the data shown in Fig 3. The liquid and solid phases coexist in the excitation energy range from $E_{\text{ex}}^l = 10.5D$ to $E_{\text{ex}}^m = 16.0D$. One can relate the average kinetic energy of atoms in the solid state \bar{E}_{kin} to the cluster temperature T by the relation:

$$\bar{E}_{\text{kin}} = (3n - 6) \frac{T}{2}, \quad (19)$$

where n is the number of cluster atoms; the degrees of freedom related to rotation and translation of the cluster as a whole are excluded from consideration. From this we have for cluster A_{13} :

$$\bar{E}_{\text{kin}} = 33 \frac{T}{2}. \quad (20)$$

In the same way we can introduce the temperature for the liquid state of the cluster through the total kinetic energy of the atoms E_l . Because the total cluster energy is conserved in the transition from the solid to the liquid state, i.e. it takes place at a fixed excitation energy E_{ex} , the atom temperatures for the solid and liquid states are different.

We shall introduce the ratio

$$\eta = \frac{\bar{E}_{\text{kin}}}{E_{\text{ex}}}. \quad (21)$$

If cluster atoms move as harmonic oscillators, $\eta = \frac{1}{2}$. The values of η and other parameters which characterise the phase transition are given in Table 4 for the Lennard-Jones cluster A_{13} . The excitation energy of the liquid state can be defined as

Table 4. Parameters of the solid and liquid states for the Lennard-Jones cluster A_{13} . The energies are expressed in units of D .

E_{ex}	E_{kin}	η	E_l	$\Delta\epsilon$	f_l/f_s
7.6	3.48	0.46	—	—	0
11	4.63	0.42	3.56	2.5	0.1
12.9	5.11	0.40	4.15	2.4	0.4
14.1	5.44	0.39	4.48	2.5	1.8
16.2	6.0	0.37	5.07	2.5	4.0

$$\Delta\varepsilon = \frac{\bar{E}_{\text{kin}} - E_1}{\eta}.$$

Note that in fact we have here the distribution over excitation energies, and the quantity $\Delta\varepsilon$ characterises this distribution, corresponding to the maximum of the distribution function. In addition, Table 4 contains the ratio of the maxima of distribution functions over kinetic energies of atoms for the cluster in the liquid state (f_l) and in the solid state (f_s). This ratio is smaller than the ratio of probabilities for the cluster to be in the liquid state (w_l) and the solid state (w_s) because the distribution function for the liquid state is wider than for the solid one.

We shall compare the data in Table 4 with simple cluster models describing cluster statistics for the solid and liquid states. Further we shall regard the liquid state as the lowest excited state, with a large statistical weight and, of course, exhibiting the properties of the liquid state. Because of the large statistical weight of the liquid state, the transition to this state occurs at temperatures that are low compared with the excitation energy and this results in a narrow temperature range in which these states coexist.

We shall denote by g the ratio of the statistical weights of the liquid and solid states (we shall call it the statistical weight of the excited state applying to a cluster with filled shells). Then we have for the probabilities of the cluster being in the solid and liquid states:

$$w_s = \left[1 + g \exp\left(-\frac{\Delta\varepsilon}{T}\right) \right]^{-1},$$

$$w_l = g \exp\left(-\frac{\Delta\varepsilon}{T}\right) \left[1 + g \exp\left(-\frac{\Delta\varepsilon}{T}\right) \right]^{-1}. \quad (22)$$

One can define the melting point of the cluster by the relation $w_s(T_m) = w_l(T_m)$, which gives:

$$T_m = \frac{\Delta\varepsilon}{\ln g}. \quad (23)$$

Using the cluster excitation energy [34] $\Delta\varepsilon = 2.5D$ and the melting point of the Lennard-Jones argon cluster A_{13} $T_m = 0.31D$, we have for the statistical weight of the excited state of this cluster $g = 3 \times 10^3$.

We shall compare these values with the results obtained by using simple models of clusters. The Lennard-Jones cluster A_{13} has icosahedral structure. We shall consider the excitation of this cluster to be the result of detachment of an atom from cluster A_{13} and its reattachment to the surface shell far from the vacancy. Then the cluster excitation energy is:

$$\Delta\varepsilon = \varepsilon_{13} - \varepsilon_{14}, \quad (24)$$

where ε_n is the atom binding energy for a cluster with n atoms. Using the results of calculations reported in Refs [91, 96], we find the excitation energy of the Lennard-Jones cluster A_{13} to be $\Delta\varepsilon = 2.84D$ at zero temperature. This coincides with the results of direct calculations of the excitation energy [37] according to which the Lennard-Jones cluster A_{13} has three tightly spaced excited states with excitation energies of $2.85D$, $2.88D$, and $2.93D$.

The existence of three excited states in this cluster with tightly spaced excitation energies can be readily explained. At zero temperature, an excited cluster A_{13} contains an excited atom over the middle of the triangle formed by surface atoms. An icosahedral cluster A_{13} with one vacancy in the surface shell has a symmetry with respect to rotation around the cluster axis by an angle $2\pi/5$. This axis passes through the cluster centre and the vacancy. Therefore the 15 surface triangles that are not adjacent to the vacancy can be divided into three groups. On rotation about the symmetry axis triangles of one of the other groups come into positions previously occupied by the first group. Hence, the same excitation energies apply to the positions of an excited atom over triangles of each group. When the atom is over triangles belonging to different groups, the cluster excitation energy differs because of long-range interaction of the atoms. Therefore, there are three different excitation energies for the lowest excited cluster states at zero temperature. They are close to $3D$ for the short-range pair interaction potential.

Fig. 6 shows atom configurations for the Lennard-Jones cluster A_{13} at zero temperature [42], and Fig. 7 shows saddle atom configurations through which the cluster

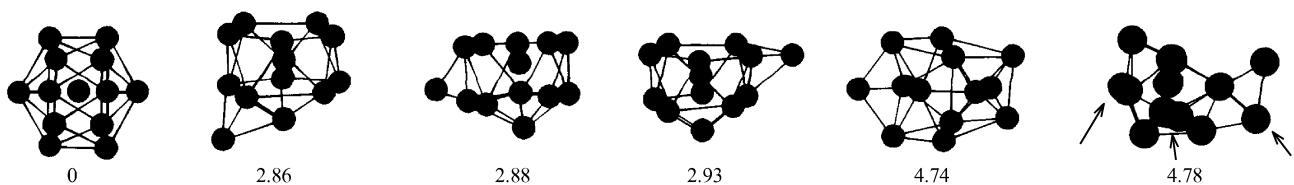


Figure 6. Structures of low excited states of the Lennard-Jones cluster A_{13} at zero temperature [42]. The excitation energy, in units of D , is given below each structure. The arrows indicate atoms the projections of which in the plane of the figure coincide or almost coincide.

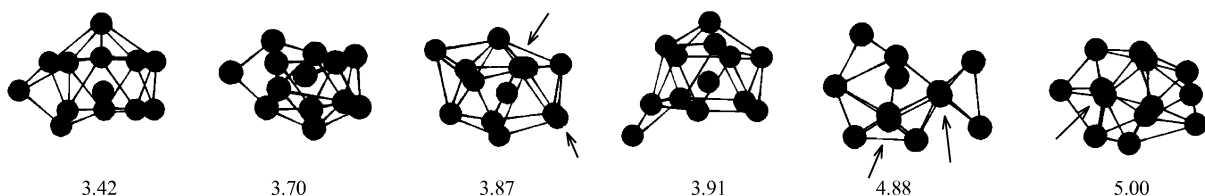


Figure 7. Saddle structures through which the excitation of the Lennard-Jones cluster A_{13} takes place [42]. The excitation energy, in units of D , is given below each structure. This is the height of the barrier through which the transition to an excited state proceeds. The arrows indicate atoms the projections of which in the plane of the figure coincide or almost coincide.

passes on excitation at zero temperature [42]. These atom configurations relate to single-atom excitations. At the melting point these configurations get blurred and lose their clearly defined structure.

Alongside with single-atom excitations of a cluster, there are excitations that involve transitions of groups of atoms. Such excitations with small excitation energies are not included in Figs 6 and 7 (see also Ref. [37]). The most important of these is the excitation of cubo-octahedral cluster structure with an excitation energy of $3.45D$ [90–94]. Evidently, interaction between this structure and the icosahedral structure is responsible for the excitation of the liquid state of the cluster.

Let us evaluate the barrier height for an atom located on the surface of the Lennard-Jones cluster A_{13} and moving from its site in one triangle to a site in an adjacent triangle. We shall define the height of the potential barrier as the energy difference for two states: in the first the atom is located over the centre of one of the triangles at an optimal distance from its three atoms, and in the second the atom is situated over a common side of the triangles at an optimal distance from its atoms and symmetrically with respect to the remaining two atoms of these triangles. Assuming the long-range interaction with other cluster atoms to be conserved in this transition and the distance from atoms common to the triangles to be optimal, we obtain for the barrier height:

$$\Delta U = -U(R_c) - U(1.687 R_c) + 2U(1.437 R_c) = 0.66D .$$

This value must be compared with the minimal barrier height of $0.56D$ for transitions represented in Figs 6 and 7. Note that the barrier height for icosahedral clusters with filled shells that are next in sequence (A_{55} , A_{147}) is smaller than for cluster A_{13} .

Thus the excitation energy of the Lennard-Jones cluster A_{13} , which is close to $2.84D$ at zero temperature, corresponds to the excitation of the liquid state of the cluster, and at the melting point it amounts to approximately $\Delta\epsilon = 2.5D$. The difference between the above values can be attributed to the thermal excitation of atoms. Therefore at the melting point the excited state of the cluster is no longer related to a single configuration of atoms in the cluster but to a combination of several structures with close excitation energies. Transitions between these excited states lead to the transport of atoms from their lattice sites to other sites. Therefore the sum of these excited states represents the liquid state by its definition.

Let us now evaluate the statistical weight of cluster A_{13} on the basis of a simple cluster model as an atomic system with fixed lattice points. According to this model, the cluster starts by having an icosahedral structure, and after transition of one atom the remaining atoms retain their positions in the new atomic configuration. Obviously, the lower the temperature, the better this model works. Within the framework of this model, at zero temperature the lowest excited state corresponds to the transition of one of the surface atoms to the free shell, and the statistical weight of this state is determined by the number of sites for vacancies on the filled surface shell (12) and the number of sites inside the surface triangles which are formed by the remaining surface atoms (15). Thus the statistical weight of the excited state of the cluster within the framework of this model is 180. Because as a result of a transition 3 bonds between nearest neighbours are lost, the excitation energy is close to

Table 5. Parameters of excitation of the icosahedral cluster A_{13} with short-range interaction between atoms.

Character and type of excitation	Excitation energy/ D	Statistical weight			
		n_v	n_a	g	
Single-atom excitations	2.96	12	15	180	
	3.91	12	25	300	
	3.91	12	5	60	
Atom-pair excitations	a, c^*	4.17	30	16	480
	a, d	4.88	30	50	1500
	b, c	5.17	36	16	586
	b, d	5.88	36	50	1800
	a, e	5.90	30	39	1170
	a, f	6.87	30	171	5130
	b, e	6.87	36	35	1260
	b, f	7.86	36	155	3580

*The following classification of the position of vacancies and excited atoms is used: a —vacancies are adjacent; b —vacancies are not adjacent; c —excited atoms are located over the centres of adjacent triangles; d —excited atoms are located over the centres of nonadjacent triangles; e —excited atoms are located over the centres of common sides; f —excited atoms are located over the centres of sides that are not common.

$3D$. Clearly, we would obtain a similar result for clusters with short-range interaction. The appropriate parameters for excited states of cluster A_{13} with a truncated Lennard-Jones interaction potential between atoms are given in Table 5.

The above model describes a cluster as a system of bound atoms that interact with each with other independently. It relates to zero temperature and gives a more or less accurate value for the excitation energy but a strongly understated value for the statistical weight of the cluster. Let us consider another cluster model assuming the binding energy of an excited atom to be relatively small. We take it that an excited atom can move freely on the cluster surface. Then the number of states of an excited atom corresponding to its motion along the cluster surface is equal to

$$g_{\text{ex}} = \frac{11}{12} \int \exp\left(-\frac{p^2}{2mT}\right) \frac{dp dr}{(2\pi\hbar)^2} = \frac{11mTR_0^2}{6\hbar^2} .$$

Here R_0 is the cluster radius, and the factor $11/12$ accounts for the presence of a vacancy on the cluster surface. If we assume that atom vibrations do not contribute to the statistical weight of the cluster and take the number of vacancies into account, we obtain for the ratio of statistical weights of the cluster in the ground and excited states:

$$g = \frac{22mTR_0^2}{\hbar^2} . \quad (25)$$

It is seen that the scaling law is violated in this case for clusters consisting of atoms of different kinds because the statistical weight of the cluster contains one more parameter—the Planck constant \hbar . According to formula (25) the ratio of the statistical weights of the liquid and solid states for the Lennard-Jones cluster A_{13} is equal to 1200 for Ne, 11 000 for Ar, 38 000 for Kr, and 98 000 for Xe.

In the case of the argon cluster considered here it is seen that also this model yields an excessive value for the

statistical weight of the cluster as compared with the results obtained by computer modeling of the cluster by the methods of molecular dynamics. The example of the Lennard-Jones cluster A_{13} demonstrates that the single-atom excitation model of a cluster with fixed lattice sites allows us to determine the excitation energy of the liquid state of the cluster with an accuracy to within the thermal energy of the excited atom, but for the statistical weight of the liquid state of the cluster at the melting point yields a value that is about two orders of magnitude lower than that obtained by computer modeling. Conversely, the assumption that the excited atom can move freely on the surface of the cluster leads to an excessive value for the statistical weight of the liquid state. The true value is somewhere between the values yielded by the two single-atom excitation models under consideration here, i.e. the excited atom moves on the surface of the cluster, but its displacements depend on the positions of other atoms. Such understanding of the nature of the liquid state of cluster A_{13} will be helpful in the analysis of larger clusters.

Thus the liquid state of cluster A_{13} is a mixture of excited cluster states which ensures that it has a large statistical weight. Such a large statistical weight cannot be the result of harmonic vibrations of atoms about their sites. This means that the transitions of atoms between potential wells are of principal importance for the liquid state. This limits the usefulness of single-atom excitation models for describing the cluster phase transition and makes numerical methods of molecular dynamics more convenient and reliable in studying this phenomenon.

5. The liquid state of clusters

We shall consider special features of the liquid state of the cluster as the lowest excited cluster state with a large statistical weight. The statistical weight of the liquid state sharply increases with increase of the cluster size. Let us consider as an example cluster A_{55} with the icosahedral structure and calculate the number of single-atom excitations within the framework of the cluster model with fixed lattice sites, as used in the derivation of Table 5. This cluster contains 42 surface atoms (12 at vertices and 30 in the middle of the sides of 20 surface triangles). Because an excited atom at the surface of the cluster must not border a vacancy, the statistical weight of the lowest single-atom excitation with the excitation energy $3D$ is equal, within the framework of the cluster model with fixed lattice sites, to

$$g_{55} = 12 \times 75 = 900 .$$

If we compare this with the statistical weight of the corresponding state of cluster A_{13} we shall see its steep increase with increasing number of surface atoms. In the case of the icosahedral cluster A_{147} which contains 92 surface atoms the statistical weight of the lowest single-atom excitation (with excitation energy of $3D$) is

$$g_{147} = 12 \times 175 = 2100 .$$

Correspondingly, the statistical weight of single-atom excitation of a cluster with icosahedral structure and m filled shells is:

$$g_m = 12(20m^2 - 5) ,$$

since each of the 20 triangles on the surface of the icosahedron can be divided into m^2 small triangles over the

centre of each of which an excited atom is located. Small triangles with a vacancy forming at their apexes must be excluded from consideration. Because the surface shell of this cluster includes $n_{\text{sur}} = 10m^2 + 2$ atoms, we obtain for the ratio:

$$\frac{g_m}{n_{\text{sur}}} = 24 - \frac{108}{10m^2 + 2} , \quad (26)$$

i.e. the statistical weight of single-atom excitation of the cluster is approximately proportional to the number of surface atoms.

Let us determine the probability of simultaneous excitation of two and more atoms. On the basis of data in Table 5 for cluster A_{13} with short-range interaction of atoms we have that at the cluster melting point $T_m = 0.31D$ the probability of excitation of two atoms is 20 times less than the probability of single-atom excitation. Let us make the same comparison for a large cluster. Neglecting interaction of an excited atom with a vacancy and assuming the number of vacancies n_v and the number of possible sites of an excited atom n_a to be large, we have for the relative probability of single-atom excitation within the framework of the cluster model with fixed sites:

$$w_1 = n_v n_a \exp\left(-\frac{\Delta\varepsilon}{T}\right) , \quad (27)$$

where $\Delta\varepsilon$ is the excitation energy of one atom. The relative probability of excitation of two atoms is

$$w_2 = \frac{n_v(n_v - 1)}{2} \frac{n_a(n_a - 1)}{2} \exp\left(-\frac{2\Delta\varepsilon}{T}\right) , \quad (28)$$

i.e. $w_2 = w_1^2/4$. Therefore in this approximation the relative probability of excitation of k atoms is

$$w_k = \frac{w_1^k}{(k!)^2} . \quad (29)$$

The denominator in this formula is determined by degeneration in transpositions of atoms on the cluster free shell ($k!$) and of vacancies on the cluster surface shell ($k!$). Because of the steep temperature dependence of the probability of single-atom excitation, the number of excited atoms increases steeply with rising temperature in a narrow temperature region. At still higher temperatures the number of excited atoms becomes saturated and is high for large clusters. It is then determined by the interaction of excited atoms with vacancies.

The most probable number of excited atoms of the Lennard-Jones cluster A_{147} was estimated in Refs [46, 47]. Within the framework of the cluster model with fixed lattice sites the expression for the partition function of a cluster with i excited atoms has the form:

$$Z = \sum_i a_i \left[g \exp\left(-\frac{\Delta\varepsilon}{T}\right) \right]^i , \quad (30)$$

where the factor a_i accounts for the degeneracy in configurations of several excited atoms, and g and $\Delta\varepsilon$ are the statistical weight and the excitation energy for an individual atom. This expression corresponds to the cluster model with fixed lattice sites where it is permissible to neglect the displacement of nonexcited atoms resulting from the excitation of neighbouring atoms. But, using the methods of molecular dynamics, we can drop this assumption. The change of the cluster free energy as a result of excitation of several atoms is given for this case in

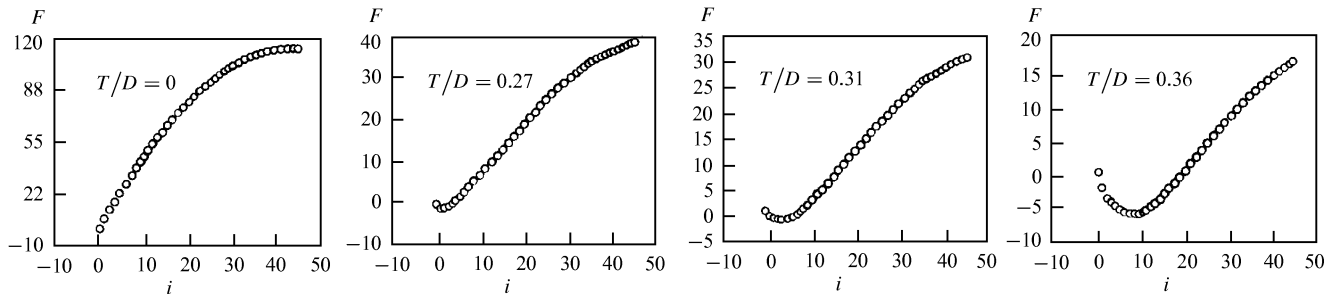


Figure 8. The difference of the free energies of the Lennard-Jones cluster A_{147} (in relative units) for a given number of atoms that migrate to a free shell and in the absence of transitions at different cluster temperatures [46, 47].

Fig. 8 for different temperatures [46, 47]. The most stable state corresponds to the minimum of the cluster free energy. Note that the transition of an atom from the surface shell to the free shell or the other way round brings about a change in the cluster temperature. It follows from data in Fig. 8 that in the liquid state of the cluster several atoms are on a free shell, and there is a distribution of the number of excited atoms for each excitation energy.

Let us construct a simple mathematical model of cluster melting by assuming that the liquid state includes only one excited state which can correspond to the excitation of several atoms. Then the probability for the cluster being in the solid or the liquid state is given by formulas (22), and each function, w_s and w_l , is a stepwise function of temperature because the statistical weight of the liquid state $g \gg 1$.

The average kinetic energy of cluster atoms on taking into account that the cluster can be both in the solid and the liquid state has the form

$$E_{\text{kin}} = \eta E_{\text{ex}} w_s + \eta(E_{\text{ex}} - \Delta E) w_l, \quad (31)$$

where ΔE is the excitation energy of the liquid state which must be entered in formulas (22) instead of $\Delta \epsilon$. Introducing the cluster heat capacity as $C_V = dE_{\text{ex}}/dT$ and taking into account that the kinetic energy of atoms is proportional to the cluster temperature, we have, on assuming $\eta(T) = \text{const}$:

$$C_V = C_V^{(0)} + \left(\frac{\Delta E}{T}\right)^2 g \exp\left(-\frac{\Delta E}{T}\right) \times \left[1 + g \exp\left(-\frac{\Delta E}{T}\right)\right]^{-2}. \quad (32)$$

where $C_V^{(0)}$ is a smooth function of temperature. From this it follows, in particular, that the maximum heat capacity, which the cluster has at the melting point, is:

$$C_V = C_V^{(0)} + \frac{\Delta E^2}{4T_m^2}, \quad (33)$$

where the melting point T_m is given by the relation (23):

$$g \exp\left(-\frac{\Delta E}{T_m}\right) = 1.$$

Let us treat the data in Fig. 9 for the Lennard-Jones cluster A_{55} on the basis of formulas (23) and (32). Assuming that all the cluster atoms are harmonic oscillators, we have $C_V^{(0)} = 80$, whereas the maximum cluster heat capacity is higher by an order of magnitude than this value. Therefore formula (23) allows us to determine reliably the excitation

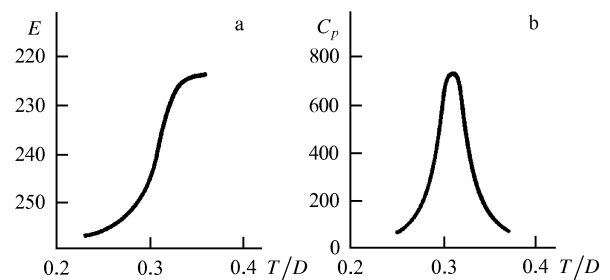


Figure 9. Parameters of the Lennard-Jones cluster A_{55} near the melting point [46, 47]: (a) the total binding energy of cluster atoms; (b) the cluster heat capacity at zero external pressure.

energy of the cluster liquid state as $\Delta E = 17D$. Then from formula (33) we find that the statistical weight of the excited state is $g \sim 10^{23}$. Note that the above excitation energy is consistent with the data in Fig. 9a, according to which the total binding energy of cluster atoms is around $250D$ before melting and $230D$ after melting, i.e. the excitation energy of the liquid state is approximately $\Delta E = 20D$. As follows from the analysis given in Ref. [52], the internal cluster shell becomes liquid at this phase transition, and the energy of this transition is $14D$ at zero temperature [Note added in Proof].

We can determine from this the width of the region of the phase transition introducing it as a temperature region in which the ratio w_s/w_l changes from 5 to 0.2, i.e. the two phases coexist only in this region. Then within the framework of our model we find from formulas (22) that this width amounts to $3T_m^2/\Delta E$, that is $0.02D$, for the Lennard-Jones cluster A_{55} , i.e. the temperature region of coexistence of the two phases changes from $0.31D$ to $0.33D$. For the Lennard-Jones cluster A_{13} the temperature interval of the coexistence of phases ranges, according to the data in Table 4, from $0.26D$ to $0.36D$. Because the excitation energy of the liquid state is $\Delta E = k \Delta \epsilon$, where k is the number of excited atoms, the width of the coexistence region $\Delta T \sim 1/k$, i.e. for a macroscopic system this region contracts to a point.

In our analysis of the transition of the cluster to the liquid state we have concentrated on clusters with filled shells, where the peculiarities of the phase transition stand out most sharply. Then considering the cluster liquid state as the first excited state, we obtained a large statistical weight for this state both because many atoms can take part in the transition and because many sites are available for excited atoms.

The situation is somewhat different for clusters with unfilled shells. The statistical weight of the ground state of these clusters is large because there are many sites for the atoms and vacancies in the partially filled shell. Therefore the ratio of statistical weights of the excited and nonexcited states is not as great in this case as for clusters with filled shells. But excitation energies for clusters with filled and unfilled shells are close to each other because the excitation energy of an individual atom is the same for both cases.

As a demonstration of this, Fig. 10 [42] gives structures of the excited states of the Lennard-Jones cluster A_{14} and the excitation energies of these structures at zero temperature. Single-atom excitations and excitations close to it are included in this figure. Of the collective excitations which are not included in Fig. 10 the most important one is the cubo-octahedral cluster structure with one atom above the filled shell. The excitation energy of this structure for the Lennard-Jones cluster A_{14} is $2.62D$ [96]. Excitation of the liquid state of the cluster may proceed via this structure.

Fig. 11 contains structures of saddle atom configurations and corresponding barrier energies at zero temperature. The first three structures involve transitions between sublevels of the cluster ground state with an excited atom migrating to a new site; in the fourth structure atoms of the filled shell participate in this transition. Therefore transitions through the barriers relate here to the liquid state of the cluster in which atoms can move from their sites to other sites. As seen from this example, the liquid state of a cluster with an unfilled shell is characterised by lower barrier heights than for clusters with filled shells. Hence the transition to the liquid state for such clusters takes place at lower temperatures and may proceed without a change of the cluster free energy. Furthermore, the statistical weights of the ground and the excited states for clusters with unfilled shells do not differ as much as for clusters with filled shells.

Let us return to the Lennard-Jones cluster A_{55} . The statistical weight of its liquid state is very large because several atoms take part in the transition. We can determine the number of these atoms by dividing the excitation energy ΔE of the transition by the excitation energy of one atom $\Delta \epsilon$

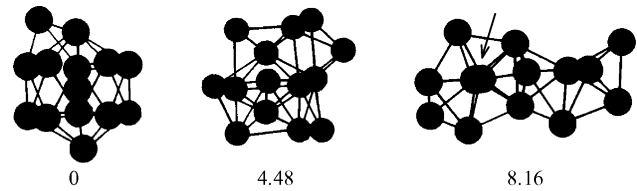


Figure 10. Structures of low excited states of the Lennard-Jones cluster A_{14} at zero temperature [42]. The excitation energy in units of D is given below each structure. The arrows mark atoms the projections of which in the plane of the figure coincide or almost coincide.

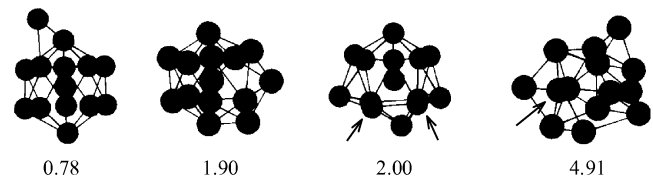


Figure 11. Saddle structures through which excitation of the Lennard-Jones cluster A_{14} takes place [42]. The values shown below each structure are the excitation energies of barriers (in units of D) through which transition to an excited state proceeds. The arrows mark atoms the projections of which in the plane of the figure coincide or almost coincide.

as a result of its transition to a free shell. Neglecting interaction between an excited atom and the vacancy, we find the atom excitation energy by analogy with formula (21) as $\Delta \epsilon = \epsilon_{55} - \epsilon_{56}$. Then using data in Ref. [91] we obtain $\Delta \epsilon = 2.64D$.

Fig. 12 shows the stages of formation of single-atom excitations for the Lennard-Jones cluster A_{55} at zero temperature [45]. Parameters of these transitions—the excitation energy $\Delta \epsilon$ and the barrier height ϵ_b —are given in Table 6 and Fig. 13. Comparison of the excitation energy of the liquid state for cluster A_{55} , $\Delta E = 17D$, with the excitation energy for an individual atom $\Delta \epsilon$ shows that approximately 6 atoms participate in this transition. This gives for the statistical weight of the excited state of an

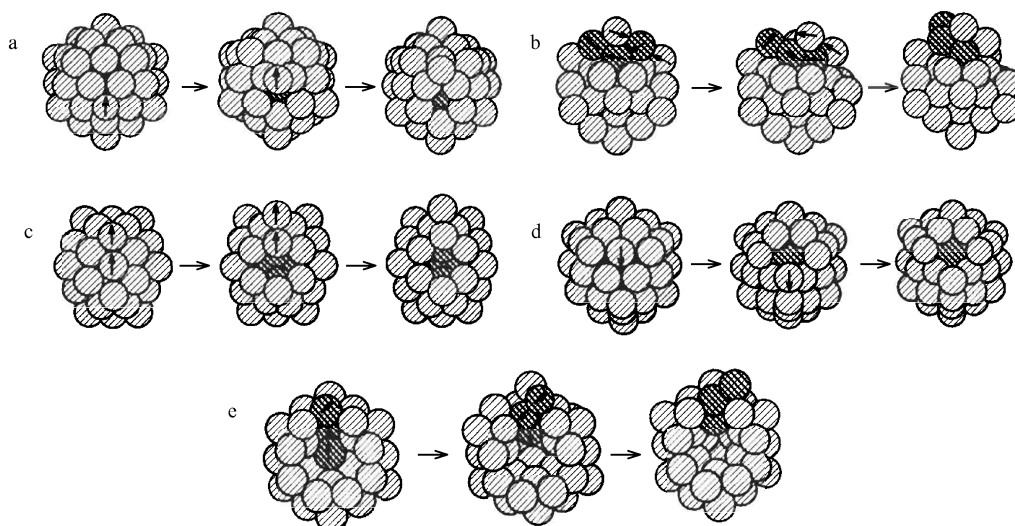


Figure 12. Stages of very simple excitations of the Lennard-Jones cluster A_{55} according to calculations reported in Ref. [45].

Table 6. Excitation energy and barrier height for the excited state of the Lennard-Jones cluster A_{55} with icosahedral structure [45]. The energies are expressed in units of D .

	Number of excitations				
	1	2	3	4	5
Excitation energy	2.87	2.63	5.51	5.75	7.06
Barrier height	1.14	5.87	0.65	0.47	6.88
Location of vacancy	vertex	vertex	side	side	cor

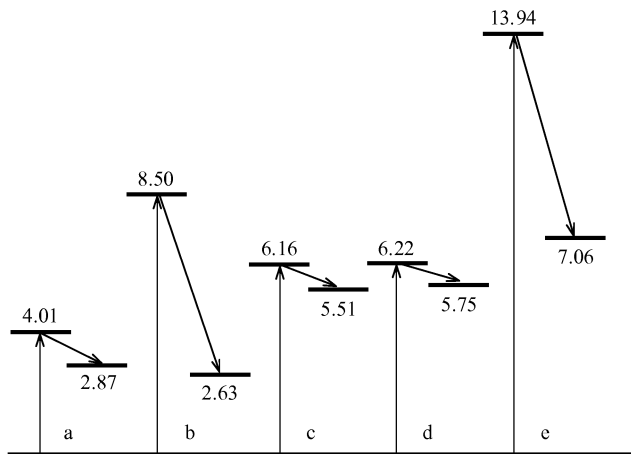


Figure 13. Energy diagram of excitation of the Lennard-Jones cluster A_{55} in accordance with Fig. 12.

individual atom the value $g_a \sim g^{1/k} \sim 10^4$, which is consistent with the data for cluster A_{13} and formula (26).

The aforementioned excitation energy of $17D$ for the Lennard-Jones cluster A_{55} , which is the transition energy

from the solid to the liquid state corresponds to migration of approximately 6 atoms from the outer cluster shell to the surface. It can be thought of as the result of excitation of atoms of the inner cluster shell. This energy is sufficient for forming two vacancies in the inner cluster shell. It appears that in reality an interaction of atomic configurations takes place that correspond to both transitions, and the inner cluster shell becomes liquid as a result of this transition.

Let us stress the principal feature of the liquid state of the cluster, which is brought out by Figs 12 and 13, namely the presence of a barrier on transition of clusters to the liquid state. It stems from the nature of the transition. Indeed, a migrating atom leaves a vacancy behind, and to form the maximum number of bonds on the surface it must be located to the side of the vacancy. In order to migrate to such a position it must overcome a barrier.

The presence of a barrier allows us to separate the solid and liquid states. When they coexist, the distribution function of atoms according to their kinetic energies (see Fig. 3) has two maxima. In the absence of a barrier this function can have only one maximum and a long tail, because in this case the typical time a cluster stays in a phase the probability of which is less than 0.5 is comparable to the time of its transition to the other phase.

Let us make one more comparison on the basis of the above analysis. In the liquid state of the Lennard-Jones cluster A_{13} there is one vacancy for 11 atoms of the surface shell which is initially filled. In the Lennard-Jones cluster A_{55} one vacancy corresponds to 6 outer shell atoms or 9 cluster atoms, whereas in a liquid inert gas one vacancy corresponds to 5.6 ± 0.2 atoms. This value is seen to grow with the increase in the number of bound atoms in the system.

Thus, at any given instant in the region of coexistence the cluster is either in the solid or in the liquid state. This is demonstrated in Fig. 14 for the argon Lennard-Jones

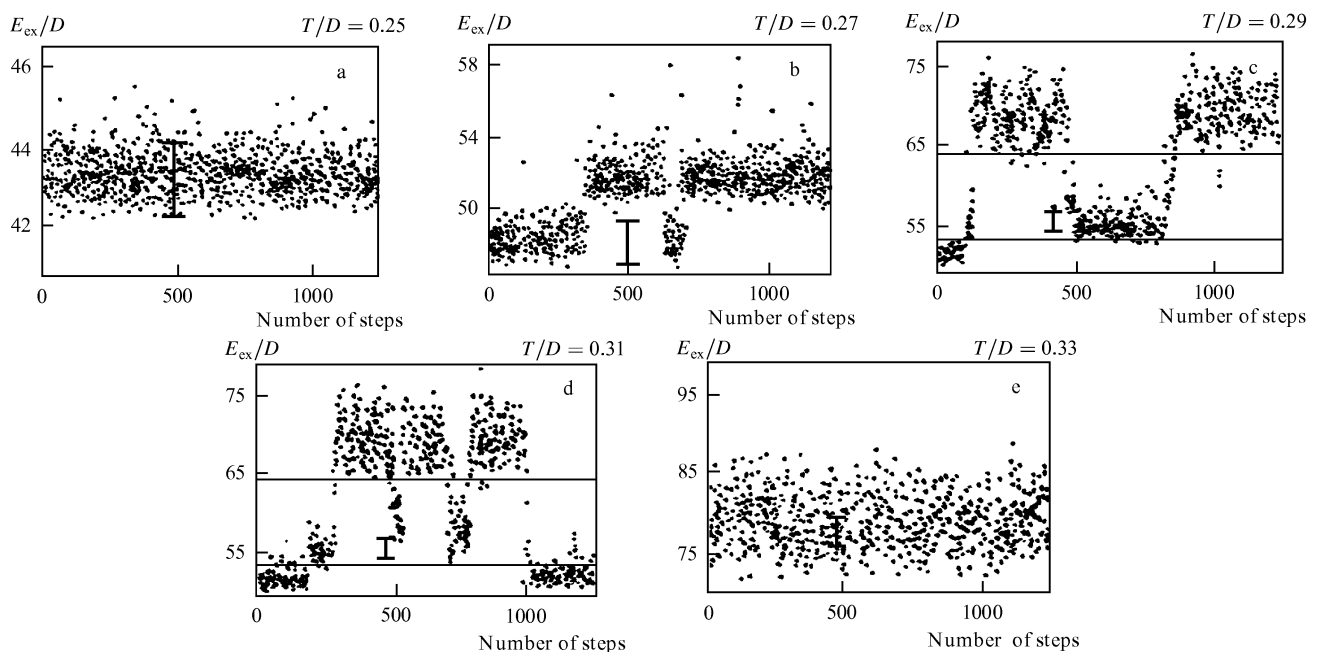


Figure 14. The total binding energy distribution of atoms in the argon Lennard-Jones cluster A_{55} at different temperatures [52]. Averaging is made over 1800 iteration time steps. The displayed fluctuation of the

mean binding energy has been obtained on the assumption that the motion of cluster atoms corresponds to the motion of a set of harmonic oscillators.

cluster A_{55} . This figure shows the total binding energy distribution of cluster atoms at different temperatures. In fact, this figure is equivalent to Fig. 3 for the Lennard-Jones cluster A_{13} , but here the problem is posed in another way. Cluster A_{13} to which Fig. 3 refers is isolated, whereas cluster A_{55} dealt with in Fig. 14 is placed in a thermostatically controlled bath that maintains a preselected constant temperature.†

Unlike cluster A_{13} , cluster A_{55} has two filled shells and there are three ranges of the total binding energy of atoms shown in Fig. 14. Range *I* corresponds to the solid state of the cluster, in range *II* the outer cluster shell is liquid and the inner shell is solid, and in range *III* both cluster shells are liquid. A similar dependence for the Lennard-Jones cluster A_{147} is depicted in Fig. 15. This figure shows the coexistence of four states: solid cluster with a liquid outer shell, with two liquid shells, and with three liquid shells. Figs 14 and 15 show also fluctuations of the total binding energy with the assumption that the cluster atoms can be treated as a set of harmonic oscillators. This value is equal to $(3n-6)^{1/2}T$ or $E_{\text{ex}}/(3n-6)^{1/2}$, where $3n-6$ is the number of harmonic oscillators (n is the number of cluster atoms), and E_{ex} is the excitation energy of cluster atoms. The energy fluctuation of cluster A_{55} at the melting point exceeds the excitation energy corresponding to the transition of one atom from the outer shell. Hence the excitation due to transition of one atom is not fixed by this dependence in contrast to the case of cluster A_{13} . Fig. 16 gives the calorimetric relationships for the states of the Lennard-

†Note that both statements of the problem may be valid. Under conditions of Fig. 3 the cluster is isolated, whilst under conditions of Fig. 14 it exchanges energy with the surrounding gas. Within our scheme of cluster studies the first statement is preferable because in the second case interaction of the cluster with the thermostat acts on its properties. If the cluster is in a gas, the first case corresponds to low gas densities and the second case to high ones. Assuming in accordance with data in Figs 14 and 15 a typical lifetime in the liquid or solid state to be approximately 100 iteration time steps ($\tau \sim 3 \times 10^{-13}$ s), we find that the transition from one case to the other takes place for the argon cluster A_{55} at atom number density $N \sim (v\sigma\tau)^{-1} \sim 1 \times 10^{22}$ cm $^{-3}$, where v is the thermal velocity of atoms, σ is the cross section of the collision of atoms with the cluster. It is seen that the first case applies better to our conditions.

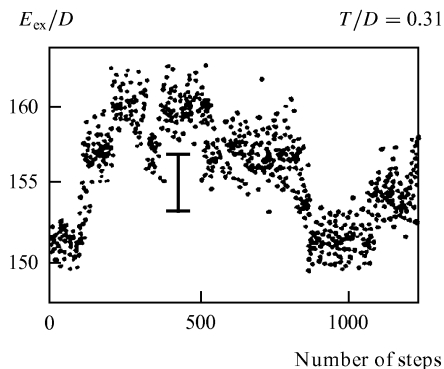


Figure 15. The total binding energy distribution of atoms in the argon Lennard-Jones cluster A_{147} at 38 K ($0.31D$) [52]. Averaging is made over 1800 iteration time steps. The fluctuation of the binding energy has been obtained on the assumption that the motion of cluster atoms corresponds to the motion of harmonic oscillators.

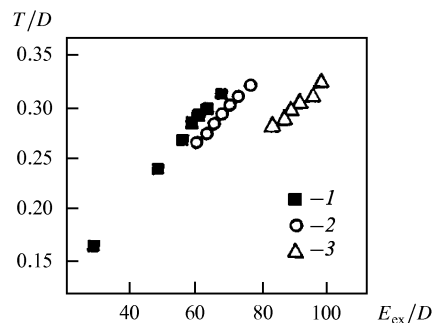


Figure 16. Calorimetric data for the argon Lennard-Jones cluster A_{55} [52]. Data are averaged over 1800 iteration time steps: *I* solid icosahedral cluster; *2* cluster with a liquid outer shell; *3* cluster with liquid outer and inner shells.

Jones cluster A_{55} in the range of coexistence of different phases. Melting of the outer and the inner shells proceeds practically at the same temperatures. But if the cluster is isolated and not thermostatically controlled, these values differ by the amount $\Delta T_m \sim \Delta E/(3n-6) \sim 0.1D-0.2D$, where ΔE is the excitation energy of an internal vacancy, and n is the number of cluster atoms.

From the data shown in Figs 14–16 it follows that the melting of outer and inner cluster shells takes place at close temperatures though the excitation energies of atoms belonging to the outer and the inner shells differ approximately by a factor of two, and therefore one would expect that the melting points for the outer and the inner shells would be different. We can explain this as a result of interaction of vacancies of the outer shell with atoms of the inner shells whereby vacancies in the outer shell become converted to vacancies in an inner shell. An indirect confirmation of this is provided by the difference in the melting points for clusters with filled shells and bulk systems with the same interaction potential of atoms. The surface layer of a bulk system contains relatively few atoms and does not influence the behaviour of inner atoms. Therefore the melting point of bulk systems is almost twice that of clusters.

Thus the cluster liquid state is a combination of low excited states and therefore has a large statistical weight. Excitation of a liquid state corresponds to the transition of some atoms from a filled shell to a free shell where excited atoms are attached to the cluster surface but can move on it. The transition of a cluster to the liquid state requires overcoming of the barrier which separates the solid and liquid states of a cluster. There are liquid states with different numbers of excited atoms, and the higher the temperature, the greater the number of excited atoms.

6. The nature of cluster melting

Studies of the melting of clusters by methods of molecular dynamics have improved our understanding of the nature of this transition. One would expect that with increasing temperature, atoms of the surface shell will leave their sites as a result of their random motion. This picture corresponds to amorphisation of the cluster surface and, ultimately, loss of its structure. This appears to take place for metallic clusters (see Fig. 17 [97]), but the physical picture of melting of the clusters with primary interaction

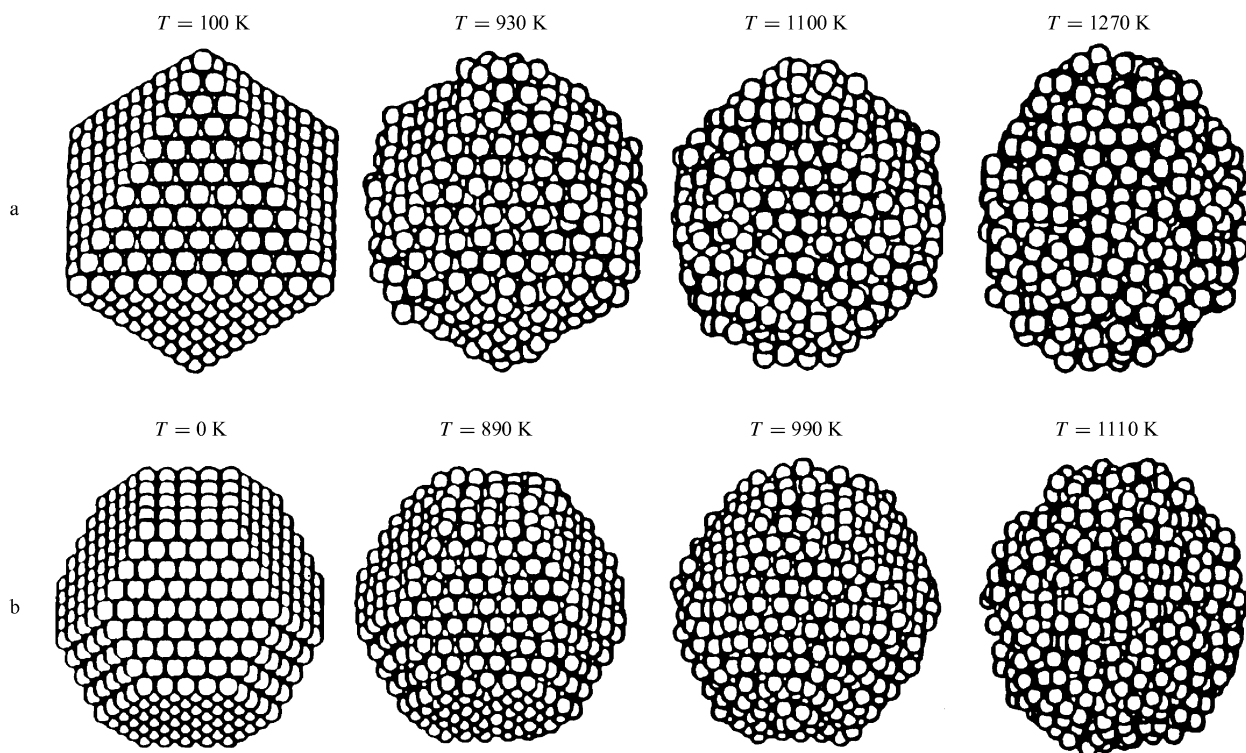


Figure 17. The character of change of the copper cluster structure on heating [97]. The initial cluster structure: (a) octahedron consisting of 891 atoms; (b) tetrakaidecahedron consisting of 1289 atoms.

between nearest neighbours is different. Indeed, analysis of the Lennard-Jones cluster shows [46, 47] that a strong interaction between neighbouring atoms during their motion is conserved during the melting of the cluster. The amplitude of collective movements of the atoms increases at the phase transition and this leads to some atoms leaving their sites. These atoms attach themselves to the cluster surface and float on it until they collapse back to the vacant sites in the surface shell.

Such nature of this process implies that the mechanism of phase transition takes place through an interaction of structures [98]. Thus, at zero temperature a small cluster with pair interaction of atoms has the icosahedral structure where each inner atom has 12 nearest neighbours. This number of nearest neighbours for inner atoms is the same as in a cluster with close packing corresponding to fcc or hcp structures of the macroscopic system of bound atoms. Transition into these structures is energetically possible at temperatures below the melting point of the cluster. At the melting point an interaction of the icosahedral structure with close packed structures causes a strong interaction between collective movements, which leads to the phase transition.

Let us give values of the corresponding parameters for the Lennard-Jones cluster A_{55} [46, 47]. The total binding energy of atoms at zero temperature is equal to $279D$ for the cluster with icosahedral structure and $268D$ for the cubo-octahedral structure of the cluster, while the solid-liquid phase transition proceeds in the region of binding energies from $250D$ to $230D$. Thus, the cluster structure can change in the course of the phase transition, and the transition itself can result from the collective motion of atoms in the cluster.

We have demonstrated above that the probability of excitation of two atoms in an outer filled shell of a large

cluster is comparable with the probability of excitation of one atom. The same reasoning applies to the excitation of three, four, and more atoms. Therefore what limits the number of excited atoms is the interaction of the excited atoms with vacancies. Such considerations lay at the basis of the simple and popular model put forward by Stillinger and Weber [99] for the melting of a macroscopic system. The authors have arrived at this model from the analysis of computer modeling by methods of molecular dynamics of a system of bound atoms forming a body-centred-cubic (bcc) lattice. The model of Stillinger and Weber accounts for the interaction of vacancies and the influence of excitations on the energy of the system. The interaction energy of the two effects is assumed to be proportional to the square of the number of single vacancies inside the system. This approximation leads to an S-shaped dependence of the density of the system on temperature. This model describes both the phase transition in a bulk system [99] and the coexistence of phases in clusters [40].

The Stillinger-Weber model was subjected to serious criticism by the author of this review [98]. It is based on a single-atom character of formation of vacancies, i.e. a vacancy is formed as a result of release of an atom from a system of bound atoms in which the atoms are located at fixed points of the lattice. Such interaction of vacancies can be accounted for accurately in the case of short-range interaction of atoms. If one applies this to condensed inert gases one gets an unexpected result [79]. To comply with real parameters of melting of condensed inert gases we must assume that as a result of the phase transition bubbles containing approximately 50 single vacancies are formed inside the inert gas crystals. Such bubbles can be formed by the release of clusters consisting of 50 atoms from the crystal.

This result testifies that the Stillinger–Weber model [99] is not suitable for the quantitative description of the phase transition in a system with pair interaction of atoms. It reflects a general contradiction which we encounter in the analysis of melting of the systems under consideration. In trying to understand the physical nature of the processes and interactions in these systems, we use simple models of clusters and bulk systems where excitation is regarded to be the result of migration of individual atoms to the surface and the formation of single vacancies. But analysing the liquid state of the cluster we found that the primary role both in its statistics and in the character of melting is taken up by collective movements and interactions of atoms. For this reason computer modeling of this process is important and simple cluster models assuming single-atom migration with fixed lattice sites are suitable only for coarse, qualitative analysis of the process.

Thus considering excitation of the liquid state in a system of bound atoms with pair interaction as the formation of vacancies in the solid state, we conclude that formation of vacancies is accompanied by the displacement of neighbouring atoms. Hence the energetic parameters of vacancies and the interaction of vacancies with atoms or other vacancies cannot be described by simple cluster models with fixed lattice sites. Such a model can give only qualitative results, and this was the basis for the critique of the model by Stillinger and Weber for melting of condensed atomic systems. Quantitative results can be obtained by the methods of molecular dynamics. Thus even for a simple system of bound atoms such as a cluster with pair interaction, the microscopic picture of melting is quite complex.

Earlier we found that a cluster model with fixed lattice sites is not suitable for the evaluation of the statistical weight of the Lennard-Jones cluster A_{13} . This conclusion applies also to other clusters. Thus, within the framework of this model the average number of excited atoms of cluster A_{55} with close packing is equal to 0.1 at the melting point [89] whereas melting of this cluster corresponds to the excitation of several atoms.

Let us consider other features of melting of the clusters. Because of the higher excitation energy of clusters with filled shells, these clusters are characterised by a higher melting point than clusters with unfilled shells. This is demonstrated in Fig. 18 [36] where the melting points of Lennard-Jones argon clusters are given for numbers of atoms close to the first filled icosahedron shell. The dependence of the melting point on the number of atoms reveals clusters with magic numbers because magic numbers

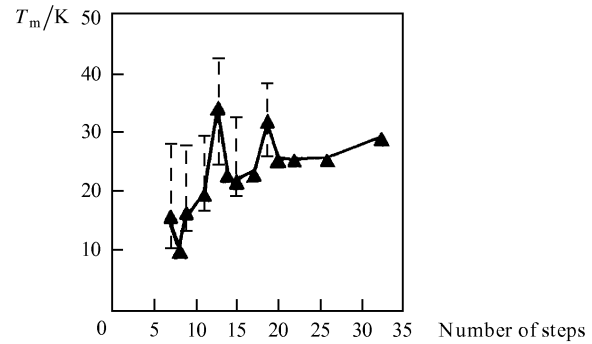


Figure 18. The melting points of Lennard-Jones argon clusters of different sizes [36]. Triangles correspond to the determination of the melting point from the position of the jump in the fluctuation of the bond length [formula (17)]; dotted lines show the limits of the region of coexistence of solid and liquid cluster phases.

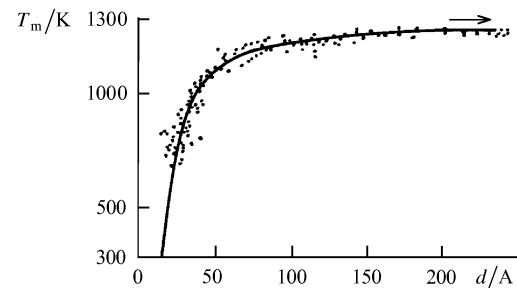


Figure 19. The melting point of large gold clusters as a function of their size [100]. The arrow shows the bulk melting point of gold.

correspond to stable cluster structures and hence to raised melting points.

Note that the melting point of the Lennard-Jones cluster A_{13} is $0.31D$, for cluster A_{55} it is $0.32D$, and the Lennard-Jones crystal melts at $0.61D$ [78]. The tendency for the melting point to increase with the increase of cluster size is demonstrated in Fig. 19 where this dependence is shown for large gold clusters [100].

Computer modeling of large clusters by methods of molecular dynamics has led to a significant progress in the understanding of the microscopic nature of melting both of clusters and of macroscopic systems with pair interaction of atoms. These methods are useful for the study of other phase transitions. One of these is the separation of phases in a system of bound atoms consisting of atoms of two types. The interaction between two atoms of different types is

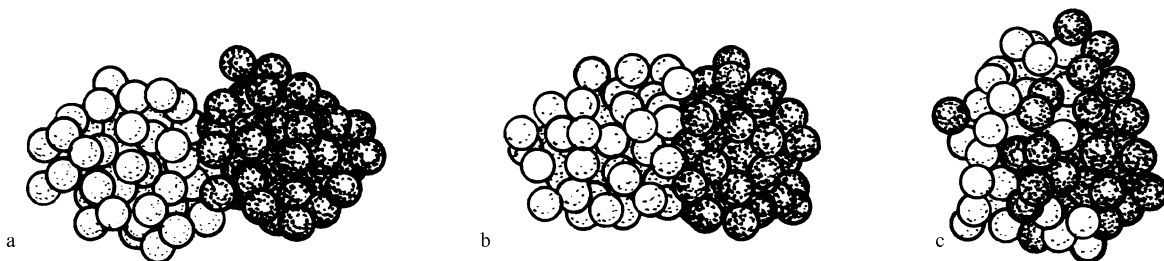


Figure 20. Structures of a liquid cluster consisting of 110 atoms of two types (55 atoms of each type) for different interaction potentials between atoms of different types [102]. The Lennard-Jones interaction

potential of two light atoms is the same as that of two dark atoms, and the interaction potential between light and dark atoms is a fraction α of these: (a) $\alpha = 0.3$; (b) $\alpha = 0.5$; (c) $\alpha = 0.9$.

weaker than the interaction between two atoms of the same type. At high temperatures the atoms of different types are mixed, whereas at low temperatures the cluster consists of two parts, each of which contains atoms of one type only.

Various aspects of this problem are considered in Refs [101, 102]. Fig. 20 demonstrates the phase separation in a cluster consisting of atoms of two sorts (A and B) with Lennard-Jones interaction between them. The interaction potentials for atoms A – A and B – B are the same, while the interaction potential for atoms A – B is equal to a fraction, α , of these potentials. Fig. 20 shows the phase separation as a function of α for a cluster in the liquid state.

7. Kinetics of melting and freezing of clusters

Let us derive qualitative expressions for the rates of transition between the solid and liquid states. Let us denote the typical time for the motion of an atom inside a cluster as:

$$\tau_0 = \frac{R_c}{v} = R_c \left(\frac{m}{2D} \right)^{1/2}. \quad (34)$$

Here R_c is the equilibrium distance between atoms of a diatomic molecule, v is the typical velocity of atoms, m is the atomic mass and D is the dissociation energy of the diatomic molecule. The values of τ_0 are 1.6 ps for Ne and Ar, 2.0 ps for Kr, and 2.3 ps for Xe. Let τ_{sl} be the typical time of transition from the solid state to the liquid state and τ_{ls} the typical time of the transition in the reverse direction. In the absence of a barrier we can estimate these values within the framework of the cluster model with fixed lattice sites on the basis of the formulae:

$$\tau_{sl} \sim \frac{\tau_0}{n_a} \exp \frac{\Delta \varepsilon}{T}, \quad \tau_{ls} \sim \frac{\tau_0}{n_v}, \quad (35)$$

where n_v is the number of vacancies, n_a is the number of sites of an excited atom on the cluster surface. Within the framework of the aforementioned cluster model the cluster statistical weight for the liquid state is equal to $g = n_a n_v$. For simplicity, we consider here the cluster liquid state as an excited state of one atom, which applies to cluster A_{13} .

Let the height of the barrier between the solid and liquid states be ε_b . Then expressions (35) are transformed into:

$$\tau_{sl} \sim \frac{\tau_0}{n_a} \exp \left(\frac{\varepsilon_b + \Delta \varepsilon}{T} \right), \quad \tau_{ls} = \tau_{sl} g \exp \left(-\frac{\Delta \varepsilon}{T} \right), \quad (36)$$

where T is the temperature of the solid state of the cluster, and g is the ratio of the statistical weights of the liquid and solid states.

Let us look at the cluster as it melts or freezes, taking into account the rate of its heating or cooling. Because of the strong temperature dependence of the transition times, the difference in the behaviour of the cluster on heating and cooling can manifest itself in a wide temperature region of the transition. This is shown schematically in Fig. 21.

Equations giving us the balance of probabilities of the cluster being in the solid w_s or the liquid w_l state have the form ($w_s + w_l = 1$):

$$\frac{dw_s}{dt} = -v_{sl} w_s + v_{ls} w_l, \quad \frac{dw_l}{dt} = v_{sl} w_s - v_{ls} w_l, \quad (37)$$

where $v_{sl} = 1/\tau_{sl}$ is the frequency of transitions from the liquid to the solid state, and $v_{ls} = 1/\tau_{ls}$ is the frequency of the reverse transitions. If the cluster temperature changes

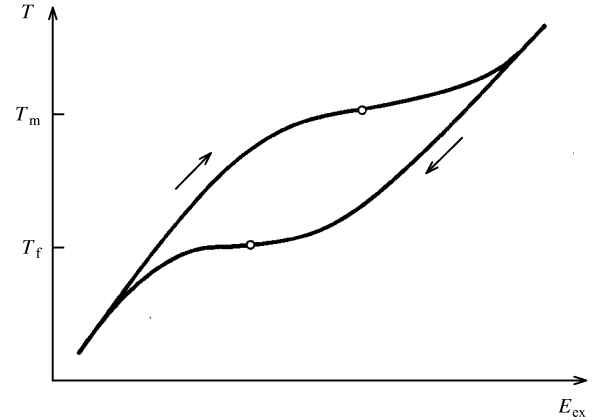


Figure 21. Schematic dependence of the cluster temperature on the excitation energy on melting and freezing. Arrows mark the directions of change of the cluster internal energy.

slowly, i.e. the left part of the equations equals zero, the probabilities for the cluster being in the solid and liquid states are given by formulas (22).

Let us define temperature T_0 by the relation:

$$v_{sl}(T_0) = v_{ls}(T_0) = v_0. \quad (38)$$

In particular, for the Lennard-Jones argon cluster $v_0 \sim 4 \times 10^8 \text{ s}^{-1}$. Let us write down the melting point of the cluster when it is heated as:

$$w_s(T_m) = w_l(T_m) = \frac{1}{2}. \quad (39)$$

Then at the beginning at temperature T' we have $w_s(T') = 1$, $w_l(T') = 0$ and the rate of temperature change dT/dt is given. In the same way we introduce the freezing point T_f according to the relation $w_s(T_f) = w_l(T_f)$, and at the initial time we have $w_s = 0$, $w_l = 1$. As the zero approximation for the solution of equation (37) we shall choose expressions (22), i.e. we shall use an expansion in terms of the small parameter dT/dt . Then, according to the perturbation theory, the first of the two equations (37) has the form ($w_s = w_s^{(0)} + w_s^{(1)}$):

$$\frac{dw_s^{(0)}}{dt} = -(v_{ls} + v_{sl}) w_s^{(1)}.$$

From this we obtain for the melting and freezing points due to a rapid change of the cluster temperature:

$$T_m - T_0 = T_0 - T_f = (v_{ls} + v_{sl})^{-1} \frac{dT}{dt}. \quad (40)$$

Thus the different behaviour of the cluster on melting and freezing is determined by the rate of temperature change. In particular, from this we have that a 10% difference between the melting and freezing points for the Lennard-Jones argon cluster A_{13} corresponds to the rate of temperature change $dT/dt \sim 3 \times 10^9 \text{ s}^{-1}$. Though this is a large value, from the viewpoint of computer operations it is not very large. For example, the range of the coexistence of phases is traversed in this case in $10^5 - 10^6$ iteration time steps.

8. Conclusion

The analysis of the solid-liquid phase transition for clusters with pair interaction of atoms throws light on the microscopic nature of this phenomenon, the main

contribution to the understanding of this phenomenon coming from computer modeling of clusters by the methods of molecular dynamics. The liquid state, which makes it possible for atoms to move from site to site, is an excited cluster state with a large statistical weight. Therefore the melting occurs at temperatures which are much lower than the excitation energy, and the region of coexistence of solid and liquid phases is relatively narrow. Its value is inversely proportional to the number of atoms that undergo a transition, i.e. the coexistence region becomes narrower with increasing cluster size, and shrinks to a point for a bulk system where the phase transition is stepwise. Collective movements and interactions play the principal role in the phase transition in clusters. This is reflected both in the statistics of the liquid state and in the nature of the transition which results from collective movements of atoms caused by the interaction between different cluster structures.

Though there has been a remarkable progress in the understanding of the nature of cluster melting, the physical picture of this phenomenon is based on studies of a small number of systems. The main conclusions of this review are based on data for the Lennard-Jones argon clusters A_{13} , A_{55} , A_{147} . We need to increase the range of analysed clusters and ascertain the dependence of melting parameters on the mass of the cluster atoms.

The aim of this review is the analysis of data on melting of clusters with pair interaction of atoms and a classical character of their motion. These results have been obtained by methods of molecular dynamics, but the attempt to construct simple and reliable models for this process has only been partly successful. It is convenient to consider the set of liquid cluster states as one degenerate state with a large statistical weight. But the cluster model with fixed lattice sites provides only a qualitative description of the liquid state. One can expect that simple and realistic models will be devised in the near future in which the phase transitions in clusters and crystals will be described by the interaction of the collective movements of atoms. This will also lead to better understanding of the melting of bulk systems of atoms.

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