Fragmentation of an energized cluster

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The fragmentation of a cluster with the liberation of an atom is investigated within the framework of two models: in the first case the cluster is modeled by a system of harmonic oscillators; in the second model its surface is considered to be macroscopic, and the evaporation time of an atom is expressed in terms of the saturated vapor parameters. The resulting expressions are compared with each other and with the results of numerical calculations. © *1996 American Institute of Physics.* [S1063-7761(96)00407-6]

1. INTRODUCTION

A large cluster, comprising a system of many bound atoms, exists in a metastable state even at fairly low temperatures, where the kinetic energy of the atoms is greater than the binding energy of a surface atom. However, the probability of fragmentation of a cluster with the liberation of an atom in this case is low, because the event would require an energy greatly exceeding the average to be concentrated in the corresponding degree of freedom. In the given situation, therefore, the cluster lifetime against fragmentation with the liberation of an atom is long on the time scale of energy transfer between individual degrees of freedom of the cluster. This parameter of an energized cluster will be calculated in simple models below.

2. STATISTICAL MODEL OF CLUSTER FRAGMENTATION

Since a large cluster of the kind discussed here has many degrees of freedom, statistical methods are well suited to its description. Based on the statistical approach, the probability of fragmentation of a cluster is proportional to the ratio of the density of states in the initial and final channels of the process. In the literature this approach is known as the Rice–Ramsperger–Kassel (RRK) method.[1–3] When it is used, the stated problem of fragmentation of an energized atomic cluster essentially coincides with the fragmentation problem for an energized molecular cluster, which has been studied in considerable detail. In this case the problem is formulated analytically for the case in which the motion of the atoms is modeled by a set of harmonic oscillators, which leads to simple expressions for the density of states of the system.[4–6] The problem then reduces to finding paths of the system in phase space that lead to transition from the initial to the final channel of the process.

The main conflict encountered in the given approach is that the harmonic oscillator approximation is not valid in the transition region, where the excitation of the system cannot be regarded as small. Consequently, the statistical treatment of the fragmentation of an energized molecular cluster in the harmonic oscillator approximation is a model approach. This assertion also applies to the atomic cluster discussed here, but now the fragmentation paths of the system are easily identified, because in ordinary space they correspond to the motion of surface atoms of the cluster in the direction of the outward normal to the surface.

We propose to apply the statistical approach to the fragmentation of an energized atomic cluster in the harmonic oscillator approximation as one of the models of cluster fragmentation. We have in mind clusters involving the pairwise interaction of atoms, so that an atom is a structural element of the cluster, and a certain cluster degree of freedom associated with the motion of the atom is responsible for the liberation of this atom. Consequently, treating the cluster as a set of harmonic oscillators, we assume that the given atom is liberated once the energy in the corresponding degree of freedom of the cluster exceeds the binding energy of the atom. Accordingly, our objective below will be to calculate the probability of the energy in a given degree of freedom exceeding a specified value.

The model of an atomic cluster as a system of harmonic oscillators is suitable for a solid cluster, where the atoms are localized at certain sites and execute harmonic oscillations about their equilibrium positions. In this case the cluster excitation energy ("excess" energy) E_{ex} bears a simple relation to the cluster temperature T:

$$E_{\mathrm{ex}}=sT, \tag{1}$$

where s is the number of degrees of freedom of the cluster (for an n-atom cluster we have $s=3n-6$), and the cluster temperature T is expressed in energy units. Introducing the binding energy ε of the atom to be liberated, we have $\varepsilon \gg T$ in the given situation, so that the temperature dependence of the cluster lifetime τ according to the Boltzmann law has the form

$$\tau \propto \exp(-\varepsilon/T). \tag{2}$$

Since this equation is also valid for the liberation of molecules of various sizes, and since the fragmentation of a molecule requires greater energy expenditures than an atom, it follows that the lifetime of the energized cluster with pairwise interaction between atoms is determined entirely by the liberation of atoms.[7] In particular, the successive evaporation (one-at-a-time ejection) of k atoms for a cluster with pairwise interaction of atoms is far more favorable than the fragmentation of a cluster with the formation of a k-atom fragment.[1)] For this reason we choose to consider only cluster fragmentations associated with the evaporation of single atoms.

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We assume that the thermal energy of an atom in the cluster is much greater than the characteristic oscillatory quantum energy (i.e., the quantity $\hbar\omega_D$, where ω_D is the Debye frequency of the cluster) but much smaller than the binding energy of atoms in the cluster. The cluster then comprises a system of bound classical atoms, and the fragmentation of the cluster is determined by the motion of atoms along classical trajectories. It is therefore reasonable to expect the cluster fragmentation rate to be independent of the nature of the frequency distribution of the system oscillations. This assertion leads to major simplification of the problem, which can now be addressed on the assumption that the frequencies of all oscillations of the cluster are identical and equal to $\hbar\omega$. Setting the cluster excitation energy to E_{ex}, we obtain $p=E_{\text{ex}}/\hbar\omega$ for the number of excitations distributed among $s=3n-6$ harmonic oscillators (n is the number of atoms in the cluster). In our subsequent determination of the unknown probabilities we invoke methods of statistical mechanics as represented in Kompaneets' books.[9,10]

In the given situation we have s oscillators and p excitations. We construct a sequence of $s+p$ elements, including both oscillators and excitations. We then interpret the number of excitations for a given oscillator as the number of excitations occupying the given sequence after that oscillator and before the next one. On this basis we find the total number of alternative model distributions of p excitations among s oscillators, which is equal to

$$W_{ps}=\frac{(p+s-1)!}{p!(s-1)!}. \tag{3}$$

In generating each sequence of elements, we fill the first position with an oscillator, i.e., in reality we are working with a sequence of $p+s-1$ elements.

The number of model distributions for which the energy associated with a given degree of freedom exceeds the level $\varepsilon=k\hbar\omega$ is equal to

$$W_{ps}^k=\frac{(p-k+s-1)!}{(p-k)!(s-1)!}, \tag{4}$$

so that the probability of such a situation is

$$w_k=\frac{W_{ps}^k}{W_{ps}}=\frac{(p+s-k-1)!p!}{(p+s-1)!(p-k)!}. \tag{5}$$

Assuming that $k\ll p$ and $s\gg 1$, we obtain

$$w_k=[(p+s-1)/p]^k=(1-s/p)^k. \tag{6}$$

Introducing the average transition time τ_0 between states, i.e., the characteristic time of variation of the distribution of excitations among the oscillators, we obtain the following equation for the cluster lifetime against the liberation of an atom:

$$\tau=\frac{\tau_0}{n_{\text{sur}}w_k}=\frac{\tau_0}{n_{\text{sur}}(1-s/p)^k}. \tag{7}$$

Here n_{sur} is the number of atoms with binding energy ε, i.e., the number of surface atoms in identical states capable of being liberated with equal probability. Introducing the cluster temperature T according to Eq. (1), from (7) we obtain

TABLE I. Parameters of condensed inert gases in the vicinity of the melting point.

Parameter	Ne	Ar	Kr	Xe
a, Å	3.156	3.76	4.01	4.34
A	20.2	39.95	83.8	131.3
T_m, K	24.6	83.7	115.8	161.2
Q, K	220	819	1119	1561
p_0, 10^4 atm	0.34	1.15	1.14	1.28
N_0, 10^{24} cm^{-3}	1.01	1.01	0.721	0.58
N_0a^3	32	54	47	48
$\hbar\omega_D$, meV	5.2	6.7	4.9	4.3
τ_1/τ_2	0.67	0.97	0.87	0.89

Note. a denotes the equilibrium distance between atoms in a diatomic molecule, A is the atomic weight, T_m is the melting point, the saturated vapor pressure is approximated by the equation $p=p_0\exp(-Q/T)$, $N_0=p_0/T_m$, $\hbar\omega_D$ is the Debye temperature for an inert gas crystal at zero temperature, and τ_1/τ_2 is given by Eq. (20).

$$\tau=\tau_0\left[n_{\text{sur}}\left(1-\frac{\hbar\omega}{T}\right)^{\varepsilon/\hbar\omega}\right]^{-1}. \tag{8}$$

Passing to the stated limit $\varepsilon\gg\hbar\omega$ in Eq. (8), we obtain

$$\tau=\tau_0\exp(\varepsilon_n/T)/n_{\text{sur}}. \tag{9}$$

In Eq. (9) we have changed the symbol ε to ε_n to reflect the fact that the association of this parameter with an n-atom cluster. Clearly, the cluster lifetime does not depend on the frequency of the harmonic oscillators. This justifies the assumption of different oscillators having equal frequencies, which enormously simplifies the derivation of the expression for the lifetime of an energized cluster.

A certain leeway in the choice of parameters of Eq. (9) exists within the framework of the statistical approach used here. As the characteristic transition time between cluster states we adopt the quantity $\tau_0=1/\omega_D$, where ω_D is the average Debye frequency for a macroscopic system of atoms, defined as $\omega_D=(\omega_1\omega_2^2)^{1/3}$; ω_1 and ω_2 are the longitudinal and transverse Debye frequencies. The values of this quantity[11] are given in Table I.

We introduce the number of surface atoms in such a way as to make the binding energy of atoms in the cluster equal to

$$E(n)=\varepsilon_\infty(n-n_{\text{sur}}),$$

where ε_∞ is the binding energy per atom in the macroscopic system, and n is the number of atoms in the cluster, so that the variation of the specific cluster energy relative to the macroscopic system is attributable to the developed surface of the cluster. For a large cluster with pairwise interaction between atoms and the symmetry of a cubic fcc structure, the binding energy of atoms in the cluster is[12,13]

$$E(n)=\varepsilon_\infty n(1-1.26n^{-1/3}), \tag{10}$$

so that the effective number of surface atoms is $n_{\text{sur}}=1.26n^{2/3}$. Accordingly, based on the given model, the cluster lifetime is obtained in the form

$$\tau_1=\frac{0.79}{\omega_D n}\exp\left(\frac{\varepsilon_n}{T}\right). \qquad (11)$$

3. EVAPORATION OF ATOMS FROM THE SURFACE OF A MACROSCOPIC CLUSTER

We now consider a second cluster model, according to which the evaporation of bound atoms from the surface of a cluster and attachment of atoms to it take place as in the case of a macroscopic surface. We assume that the cluster has a surface of area πr^2 (r is the radius of the cluster) and that equilibrium between the evaporation and attachment of atoms

$$A_n+A\rightleftarrows A_{n+1} \qquad (12)$$

has the same character as in the case of a macroscopic surface.

Let a cluster be situated in a gas with temperature T and density of atoms N. The flux of atoms attaching to its macroscopic surface is then

$$j_{\text{at}}=\sqrt{\frac{T}{2\pi m}}N\xi, \qquad (13)$$

where m is the mass of the atom, and ξ is the probability of an atom attaching to the cluster in collision with its surface. According to Eq. (2), the flux of evaporating atoms is given by

$$j_{\text{ev}}=C\exp(-\varepsilon_n/T), \qquad (14)$$

where ε_n is the energy to detach a surface atom from an n-atom cluster, and the parameter C depends weakly on the temperature and is determined by the properties of the surface. The same equations for the attachment and evaporation fluxes apply to the macroscopic surface, the two fluxes equalizing when the gas pressure corresponds to the saturated vapor pressure, i.e.,

$$j_{\text{at}}=j_{\text{ev}}=\sqrt{\frac{T}{2\pi m}}N_{\text{sat}}(T)\xi. \qquad (15)$$

Here N_{sat} is the density of gas atoms at the saturated vapor pressure, which is characterized by the temperature dependence

$$N_{\text{sat}}(T)=N_0\exp(-\varepsilon_\infty/T), \qquad (16)$$

where ε_∞ is the atom-to-surface binding energy. Invoking the analogy of the cluster surface with a macroscopic surface, we obtain the equation (14) for the flux of atoms evaporating from the cluster surface in the form

$$j_{\text{ev}}=C\exp\left(-\frac{\varepsilon_n}{T}\right)=\sqrt{\frac{T}{2\pi m}}N_{\text{sat}}(T)\xi\exp\left(-\frac{\varepsilon_n-\varepsilon_\infty}{T}\right). \qquad (17)$$

From this relation we obtain an expression for the cluster lifetime against evaporation of an atom:

$$\tau=\left[4\pi r^2\sqrt{\frac{T}{2\pi m}}N_{\text{sat}}(T)\xi\exp\left(-\frac{\varepsilon_n-\varepsilon_\infty}{T}\right)\right]^{-1}. \qquad (18)$$

We determine the cluster radius in this equation from the relation

$$n=4\pi r^3\sqrt{2}/3a^3,$$

in which the distance a between nearest neighbors is assumed identical for the cluster and the macroscopic system, and the cluster is endowed with the symmetry of a cubic fcc structure. Making use of this relation, along with the temperature dependence of the saturated vapor pressure of the atoms (16), we reduce Eq. (18) to the form

$$\tau=\left(\frac{2\pi}{81}\right)^{1/6}\frac{\sqrt{m}}{T^{1/2}n^{2/3}N_0a^2\xi}\exp\left(\frac{\varepsilon_n}{T}\right). \qquad (19)$$

4. LIFETIME OF AN ENERGIZED CLUSTER

We now analyze the results. The ratio between the cluster lifetimes against evaporation of an atom for the statistical model (τ_1) and for the macroscopic surface model (τ_2) has the form

$$\frac{\tau_1}{\tau_2}=\frac{0.52N_0a^2\sqrt{T}\xi}{\sqrt{m}\,\omega_D}. \qquad (20)$$

We set the parameter ξ equal to unity from now on. Clearly, the ratio of the lifetimes for the given models does not depend on the size of the cluster, but does depend on its temperature.

These models have different domains of validity. The statistical model of evaporation of an atom from the surface of a cluster in the harmonic oscillator approximation is calculated for low-temperature solid clusters, whereas the model of a cluster with a macroscopic surface is geared more to large liquid clusters, since the saturated vapor pressure above liquid surfaces has been accurately measured. Consequently, it is more practical to compare Eqs. (11) and (19) at the melting point of the macroscopic system. Table I gives the corresponding parameters of the clusters, including relation (20) for inert gas clusters at the melting point of the macroscopic system. The data on the saturated vapor pressure above a liquid surface are taken from Ref. 14.

The stated comparison provides a useful tool for refining equations (9) and (11) obtained for the statistical model of cluster evaporation, which only allowed us to estimate the characteristic transition time between cluster states. Now, using data on the saturated vapor pressure, which give the evaporation rate of atoms from the macroscopic surface, we can normalize Eq. (9). For real inert gas clusters it assumes the form

$$\tau=\frac{0.8}{\omega_D n_{\text{sur}}}\exp\left(\frac{\varepsilon_n}{T}\right). \qquad (21)$$

We note that molecular-dynamics methods are ideally suited to the analysis of the behavior of the investigated clusters in that the motion of the atoms obeys classical laws. This method provides a means for surmounting the abovementioned difficulty of applying the statistical model to the analysis of cluster fragmentation, i.e., the invalidity of perturbation theory on the fragmentation channels of atoms in phase space. Molecular-dynamics methods have therefore been used on many occasions not only for the analysis of fragmentation of an energized cluster, as in the pairwise interaction of atoms in a cluster consistent with the Lennard–Jones potential,[16–20] but also for a more complex interaction potential[8] modeling transition metals.

However, despite the capabilities of molecular-dynamics methods, the analytic methods discussed here hold their own in the analysis of the fragmentation of energized clusters. In fact, the molecular-dynamics solution of the given problem has complications of its own insofar as this process is rare and therefore requires long computation times. For this reason, as a rule, the calculations are carried out for highly energized clusters and not for clusters of real inert gases. Below, we compare the derived equations with calculations for the model cluster A_{13}, whose atoms have the mass of the argon atom and in which pairwise interaction between atoms corresponds to the Lennard–Jones potential.

Next we discuss the general properties of the investigated clusters and the laws governing their fragmentation. The Lennard–Jones cluster A_{13} has icosahedral structure, with one central and $n_{\mathrm{sur}}=12$ surface atoms. The energy to detach one atom at zero temperature ε_n is approximately[21,22] $6.36D$, where D is the energy to break the bond in a diatomic molecule. The energy to excite a cluster with the transfer of an atom to its surface is approximately $2.9D$ (Ref. 22). Such excitation takes the cluster into the liquid state, where the excitation energy of the liquid state at the cluster melting point is approximately $2.5D$ (Refs. 23 and 24), which is slightly lower than the previously indicated excitation energy at zero temperature. Moreover, the statistical weight of the liquid state at the cluster melting point is approximately an order of magnitude greater than the value corresponding to the cluster model with pinned sites. All this attests to the differences in the parameters of the cluster in the solid and liquid states.

Unfortunately, data are not available on the saturated vapor pressure above the macroscopic surface of a condensed system of atoms with a Lennard–Jones interatomic interaction potential. Without this input, Eq. (21) is a crude estimate. Indeed, a comparison with molecular-dynamics calculations for clusters having a Lennard–Jones interatomic interaction potential, illustrated in Fig. 1, shows that calculations using Eq. (21) normalized to the saturated vapor pressure of real inert gases yield considerably shorter cluster lifetimes.

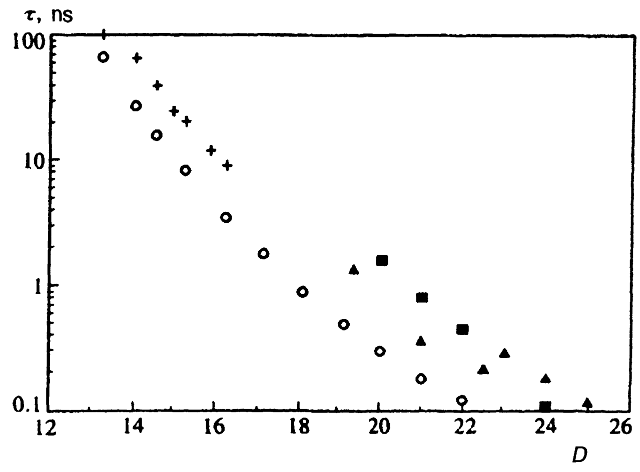

FIG. 1. Lifetime of an A_{13} cluster with a Lennard–Jones interatomic interaction potential. Molecular-dynamics calculations from: Ref. 15 (+), Ref. 16 (■), and Ref. 17 (▲); calculations according to Eq. (21) (○).

5. CONCLUSION

The final result of the foregoing analysis based on the dynamics of atoms moving in a heated cluster and the character of evaporation from the macroscopic surface is an expression for the cluster lifetime. The accuracy of this expression depends on the parameters of the cluster and the accuracy of the information used in the expression. The method set forth in this paper can be used to estimate the lifetimes of different types of clusters within certain error limits.

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[1] In this case the pairwise interaction potential does not depend on the interaction of either atom in the pair with other atoms. Accordingly, the detachment of a molecule from the cluster requires higher energy than does an atom. This is not necessarily true for a different type of interaction between atoms in the cluster (see, e.g., Ref. 8).

[1] O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1928).
[2] S. L. Kassel, J. Chem. Phys. **32**, 1065 (1928).
[3] R. A Marcus, J. Chem. Phys. **43**, 2058 (1965).
[4] E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases*, Clarendon Press, Oxford (1974).
[5] W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York (1973).
[6] E. E. Nikitin and B. M. Smirnov, *Atomic and Molecular Processes* [in Russian], Nauka, Moscow (1988).
[7] B. M. Smirnov, Usp. Fiz. Nauk **164**, 665 (1994) [Phys. Usp. **37**, 621 (1994)].
[8] M. A. Lopez and J. Jellinek, Phys. Rev. A **50**, 1445 (1994).
[9] A. S. Kompaneets, *Theoretical Physics* [in Russian], Gostekhizdat, Moscow (1958).
[10] A. S. Kompaneyets, *Theoretical Physics*, Dover, New York (1961).
[11] N. Schwentner, E. E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases*, Springer-Verlag, Berlin–New York (1985).
[12] B. M. Smirnov, Usp. Fiz. Nauk **162**(12), 97 (1992) [Sov. Phys. Usp. **35**, 1052 (1992)].
[13] B. M. Smirnov, Zh. Éksp. Teor. Fiz. **107**, 2080 (1995) [JETP **80**, 1151 (1995)].
[14] *Handbook of Chemistry and Physics*, D. R. Lide (ed.), CRC Press, London (1993), pp. 6–74.
[15] C. E. Roman and I. L. Garzon, Z. Phys. D. **20**, 163 (1991).
[16] S. Weerasinghe and F. G. Amar, Z. Phys. D. **20**, 167 (1991).
[17] R. W. Smith, Z. Phys. D. **21**, 57 (1991).
[18] C. Rey, L. J. Gallego, M. P. Iniguez, and J. A. Alonso, Physica B **179**, 273 (1992).
[19] S. Weerasinghe and F. G. Amar, J. Chem. Phys. **98**, 497 (1993).
[20] M. R. Hoare and P. Pal, Adv. Phys. **32**, 161 (1971); **24**, 645 (1975).
[21] J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).
[22] T. L. Beck and R. S. Berry, J. Chem. Phys. **88**, 3910 (1989).
[23] J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986).
[24] B. M. Smirnov, Usp. Fiz. Nauk **164**, 1165 (1994) [Phys. Usp. **37**, 1079 (1994)].

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