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Relaxation of pores in nanoclusters

M.A.Ratner[1], V.V.Yanovsky[1,2]

Institute for Single Crystals, NAS Ukraine,
60 Nauky Ave., Kharkiv, 61001, Ukraine
V. N. Karazin Kharkiv National University, 4 Svobody Sq.,
Kharkiv, 61022, Ukraine

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Relaxation of a solid nanocluster with an internal pore was invrstigated using the molecular dynamics method. The distribution function for the lifetime of a pore in a cluster is construted. According to the simulation data, it is close to an exponential distribution funtion. It was shown that clusters in which pore relaxation occurs during simulation demonstrate two relaxation mehanisms. An explanation based on interaction of three vibrational modes is proposed for an unusual explosive relaxation mehanism as a consequence of the resonant interaction of two surface vibration modes wit the pore vibrational mode. The simulation data are in good agreement with theoretical explanation.The features of pore relaxation in clusters are also disussed in detail.

Keywords: nanocluster, molecular dynamics method, pore, relaxation, explosive relaxation, metastable state, diffusion, wavelet transformation.

Релаксація пор у наносластерах. *М.А. Ратнер, В.В. Яновський*

Методом молекулярної динаміки досліджено релаксацію твердого нанокластера з внутрішньою порою. Побудовано функцію розподілу часу існування пори в кластері. Згідно з даними моделювання, вона близька до функції експоненційного розподілу. Було показано, що кластери, в яких відбувається релаксація пори під час моделювання, демонструють два механізми релаксації. Запропоновано пояснення для незвичайного механізму вибухової релаксації як наслідку резонансної взаємодії двох мод поверхневих коливань з модою коливань пори. Дані моделювання узгоджуються з теоретичним поясненням. Особливості релаксації пор у кластерах також детально обговорюються.

Introduction

Atomic clusters are intermediate particles between isolated atoms and macroscopic solids that can contain from a few to tens of thousands of atoms. Their unique size-dependent properties, in particular, thermal, optical, magnetic, and chemical ones are clearly different from both individual atoms and macroscopic bodies. It is known that atomic clusters can be used as catalysts that facilitate many industrial reactions. A variety of methods based on computer simulations have been adopted to generate their global minimum energy structures. Bond stretching isomerism, aromatic stabilization, Renner–Teller effect, enhanced superhalogen/superalkali properties, and electrical performance are some of the hallmarks of these clusters. Different all-metal and non-metal clusters exhibit a variety of aromatic characteristics. Some of these clusters are dynamically stable, whereby some or all of their atoms can exchange between symmetrically equivalent positions. It was established that some of these cluster structures have cavities that provide confinement effects that strongly affect diffusion, phase transformations, and catalytic properties when used as a catalyst. Atomic clusters have a potential to be good hydrogen storage materials as well as to activate small molecules for various purposes. Many atomic clusters exhibit exceptional optical-electronic and nonlinear-optical properties. Over the years, experimental and theoretical methods of studying clusters have undergone significant improvements, which allowed to discover various size-specific phenomena and physicochemical properties of clusters (see e.g. [1-2]). For small metal clusters (<100 atoms), the electronic structures are not continuous, as in bulk metals, but rather discretized, which is the main reason for different physicochemical properties and functional capabilities in small clusters and bulk metal . Studies have shown that atomic clusters of right size and composition can potentially mimic the chemistry of elementary atoms in the periodic table, and are thus known as superatoms (see e.g. [3]). Various experimental techniques, such as laser ablation combined with mass spectrometry, photoelectron spectroscopy, have been used to gain insight into atomic clusters. Along with experimental studies, theoretical studies are needed to better understand their geometrical arrangement and corresponding properties (see e.g. [4]). A large number of theoretical studies devoted to the search for minimal energy structures of atomic clusters using various optimization algorithms have been reported.

In the present work, clusters with pairwise interactions are considered. Clusters and three-dimensional systems of bonded atoms with pairwise interaction have two types of excitations: configurational, due to a change in the location of atoms in space, and thermal, associated with atomic vibrations. Configurational excitation is responsible for phase transitions in such systems and can be considered as a transition from the global minimum of the potential energy surface of an atom in the multidimensional space of atomic coordinates to some other higher energy local minima.

One of interesting properties of such systems is that at the same temperature such a cluster can be in different metastable states [5-8]. There can be a great number of such states with a different degree of ordering, and they can be quite close to each other. Thus, in the case of a small cluster, the definition of liquid and solid states is to a large degree a matter of agreement. The question also arises of how to distinguish a new metastable state from fluctuations of an existing one. Thus, in works [5-8], a small cluster with one atom that has left the volume to the surface is considered as a new metastable state. All these features follow directly from the smallness of the particle and the inapplicability of the statistical approach. Thus, the definition of the concept of the phase state of matter and phase transitions requires a new approach in the case of small particles. The above also applies to the determination of the activation energy of the diffusion of atoms and vacancies, the values of the surface energy and other energy parameters that depend on the phase state of the substance.

In this paper, we considered the relaxation of a solid nanocluster with an internal pore using the molecular dynamics method. The distribution function for the presence of a pore in a cluster over the observation time is constructed. According to the simulation data, it is close to an exponential distribution function. In other words, the pore in the cluster forms a metastable state and can persist for long periods of time. Some of the clusters in which relaxation occurs during simulation demonstrate two relaxation mechanisms. An explanation based on the interaction of three vibrational modes is proposed for an unusual explosive relaxation mechanism. These modes are two surface modes, surfaces of clusters and pores, as well as a shear mode of pore vibrations. The simulation data are in good agreement with these ideas. The features of pore relaxation in clusters are also discussed in detail.

2. Model and method

In the present work, modeling of pore relaxation in a nanoparticle was carried out by molecular dynamic method that allows to consider different phase states of the initial cluster and their influence on pore relaxation process. The object of the study were Ar clusters with number of atoms up to 10648. Rare gas clusters are one of the simplest systems, in particular three-particle interactions can be neglected in this case [8]. Up to the size of several thousand atoms, rare- gas clusters form icosahedral structure, that allows to minimize cluster surface, for larger clusters transfer to FCC structure occurs

Initially, cubic lattice of Ar atoms (atomic mass $m = 39.9$ a.u.) was constructed with the lattice period $a = 4.816$ Å (corresponding to solid Ar). Atoms are interacting via Lennard-Jones potential with the following parameters, taken for Argon atoms: $\sigma = 3.405$ Å, $D = 0.01032$ eV. Here D is the depth of the potential well, σ is the distance at which the particle-particle potential energy V is zero (often referred to as “size of the particle”). The Lennard-Jones potential has its minimum at a distance $r_{min} = 2^{1/6}\sigma$ where the potential energy has the value D. The inter-atomic force and its derivative was smoothed at the cut-off distance $R_{cutoff} = 3R_{min}$. Cluster temperature T is defined as mean kinetic energy per one atom. Below, the temperature is measured in the units of potential depth D while linear sizes are measured in the units of equilibrium inter-atomic distance r_{min}. The equations of motion are solved numerically via velocity Verlet algorithm with a time step $10^{-6} - 10^{-5}$ ps, dependently on cluster temperature.

The equations of motion are solved numerically via velocity Verlet algorithm [9, 10] with a time step ps, dependently on cluster temperature. Pore relaxation is described in a following way. The whole cluster is overlaid with a three-dimensional cubic lattice with a period . A pore is defined as any connected domain of cells, that are free from cluster atoms, with a minimal diameter no less then $2r_{min}$, and surrounded on all sides by occupied cells. If such domain has maximal diameter less than but greater then $1.5r_{min}$, it is defined as vacancy. Such criterion was obtained in empirical way in order to discern pore with single vacancies and avoid the influence of surface convolution. Cluster volume is found as summarized volume of occupied cells and free cells, belonging to pores or vacancies. In the present work, Ar clusters with number of atoms N, from 2744 to 10648, were investigated in the temperature range $0.36D - 0.80D$. Clusters in solid (the most ordered) state were considered. $Q = 50$ of random realizations of equilibrated clusters for each investigated pair (N, T) were obtained by the described in the previous works of authors method [11], over which the results were averaged. For each of obtained initial cluster realizations, a pore of the given initial radius was instantly cut off in the cluster center. Then MD run was conducted for up to 200 ps in order to investigated system relaxation. For all clusters investigated pore radii were taken $R_{pore}(0) = 3r_{min}$, $4r_{min}$.

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Clusters and three-dimensional systems of bonded atoms with pairwise interaction have two types of excitations: configurational, due to a change in the location of atoms in space, and thermal, associated with atomic vibrations. Configurational excitation is responsible for phase transitions in such systems and can be considered as a transition from the global minimum of the potential energy surface of an atom in the multidimensional space of atomic coordinates to some other higher energy local minima.

In order to disyinguish solid cluster phase state from the less ordered ones, the fluctuation δ of square root of mean sqare interatomic distance a was considered. According to [5], the conventional criterion of solid state is:

$$\delta < 0.15a \tag{1}$$

For the present investigation, cluster conformations in solid (most ordered) state were selected, that satisfy criterion (1) and have the lowest potential energy at given temperature (as at was mentioned above, at a fixed temperature, the cluster can be in different phase states with different potential energies). Such most ordered clusters, after appearing an intrinsic pore, can form a metastable state (see work of authors [11]).

Evidently, after equilibrating initial clusters at a finite temperature, obtained structures are far from global minimum of potental energy due to entropy factor, that is significan due to a large role of cluster surface. On the other hand, too low simulation temperature makes equilibration time too long. Thus, in order to obtain clusters, close to global potential energy minimum, the method, developed by authors in [11] was used. This method consists of slow cooling initially equilibrated cluster followed by relatively quick heating. The idea of this metod is, that cluster cooling rate can be ajusted in such a way that system, as a result of fluctuations, makes a number of consequent phase transitions to the closest more ordered phase states, but, due to temperature decrease, has no energy to return to the previous less ordered states. To stabilize the cluster and make the model realistic, the cluster is placed in an external central-symmetric field that simulates the atmospheric pressure.

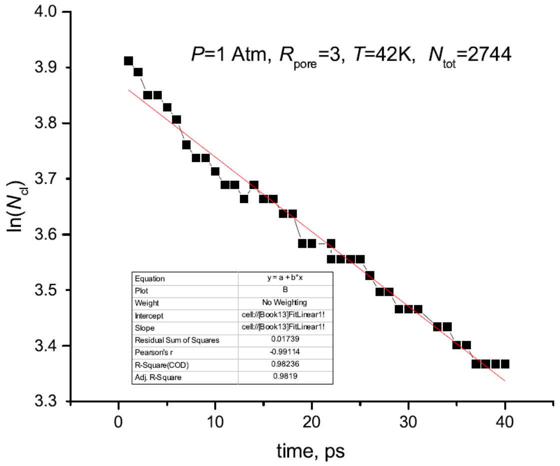

Fig. 1. Time dependence of the natural logarithm remaining number of cluster with stable (non relaxing) pore. Initial number of clusters $N_0 = 50$.

Thus, for each cluster-pore size ratio, $Q = 50$ of random initial conformations are obtained, which, on the one hand, makes the study statistically reliable, and on the other hand, allows to reveal rare events, such as unusual ways of system relaxation.

For each of obtained initial cluster realizations, a pore of the given initial radius was instantly cut off in the cluster center. Then MD run was conducted for up to 200 ps in order to investigated system relaxation. For all clusters investigated pore radii were taken $R_{pore}(0) = 3r_{min}$, $4r_{min}$.

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3. Scenarios for the disappearance of a pore from a cluster

Let us consider the mechanisms of relaxation of a pore from a solid cluster. A priori, two mechanisms for the disappearance of a pore can be imagined. Both of them are related to the fact that the vacancies forming the pore cannot disappear in the cluster. They must somehow be transferred through the material of the cluster to the outside. The most probable scenario seems to be gradual emission of vacancies, which, diffusing through the cluster, reach its boundary and leave the cluster. With slow "evaporation" of vacancies from the pore into the cluster material, one can expect that vacancies will leave the cluster, carrying away a volume equal to the sum vacancy volumes. In this case, one should expect a linear change in the volume of the pore and cluster. This scenario should be realized for clusters or particles of material of macro, meso, and nanosizes. Therefore, such a scenario can be called the usual mechanism for the disappearance of a pore.

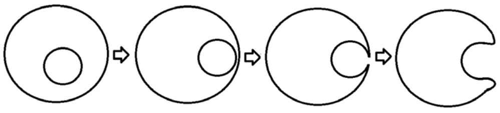

Fig. 2. Scheme of pore relaxation according to the "explosive" scenario. Then the cluster returns to a spherical shape.

For small clusters with pores, a characteristic feature is the existence of magic pores[7], which have increased stability and can exist in a cluster for a long time. There are several such "magic" sizes of pores, which are a kind of analogue of magic clusters described earlier in the literature . In principle, the state of a pore in a cluster is a nonequilibrium state and, therefore, must be metastable. Modeling of clusters with magic pores makes it possible to determine the number of clusters with pores depending on the time of observation. Fig. 1 shows the dependence of the number of clusters with a stable pore on time on a logarithmic scale. The linearity of this dependence is noticeable and the approximation of the simulation data by the least squares method gives the dependence

$$N_{stable} = N_0 e^{-\frac{t}{t_l}}$$

where N_0 is initial number of clusters, t_l -mean lifetime of the pore. According to modelling data $t_l \approx 77$ ps. According to this, the magic pore can be found in the cluster after any time has passed. Random variables with such distributions have the absence "memory" property. This property can be explained if t_l is interpreted as pore disappearance time, then if it has not disappeared for some time of observation, then the probability of its disappearance in the next time interval remains the same as it was at the beginning [12].

It should be noted that if pore size does not correspond to the magic pore, then the pore relaxes according to the usual mechanism to the magic size and, after that, can persist for a long time in the metastable state.

Another important manifestation of the smallness of system size is the possibility of fluctuations of pore position in a cluster. This possibility leads to another scenario of magical pore disappearance from the cluster. In the presence of such fluctuations, the pore can spontaneously or due to external influences shift to the cluster boundary. Having touched

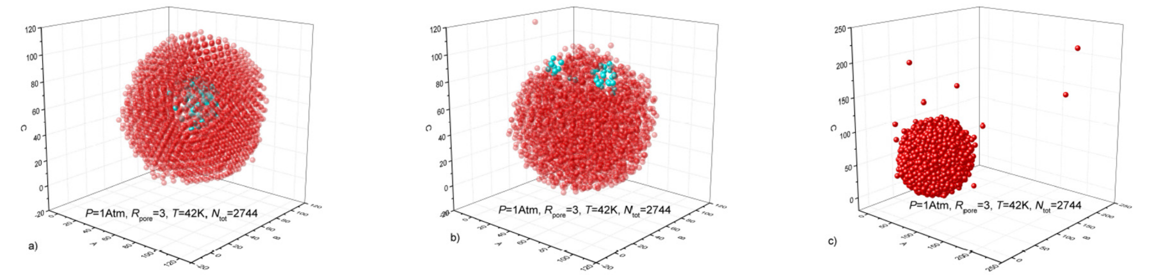

Fig. 3. The stages of pore relaxationare shown at successive time points that were observed in the simulation. a) - the initial position of the pore, b) - the advancement of the pore to the cluster boundary, c) - the pore completely disappeared with the violation of the order of atoms in the cluster and their partial evaporation.

this boundary, the vacancies will synchronously leave the cluster in an explosive manner. This scenario is shown schematically in Fig. 2. Further, this scenario will be referred to as explosive relaxation.

4. Results of MD simulation

Let us now discuss the results of modeling the relaxation of a pore in a cluster. A feature of small clusters is that at a fixed temperature they can be in different phase states corresponding to different degrees of ordering of atoms in the cluster. This issue for the model clusters used in this study is studied in more detail in the authors' article [11]. In this work, clusters in the solid (most ordered) state are chosen as the modeling object, the initial pore always has a centrally symmetrical position.

Simulation at each studied temperature demonstrated the existence of initial cluster conformations, which, after cutting out a magic pore in them, remain in a metastable state (a pore of a fixed size) throughout the entire simulation time (200 picoseconds). In other cases, relaxation according to the usual scenario of pore relaxation in a cluster prevailed. The explosive relaxation scenario was observed only for 5% of initial conformations.

4.1 Explosive pore relaxation

According to the modeling procedure, a magic pore of a certain size is placed in the center of the cluster. For some time, it retains a centrally symmetrical position, and then, spontaneously or as a result of an external influence, it relaxes in a jump or explosive manner, characteristic of overcoming an energy barrier.

Snapshots confirming the correctness of the scheme, shown in Fig.2, are given in Fig.3. In an explosive scenario of relaxation, when reaching the surface, the pore can break into two parts (see Fig.3). In this scenario, when the cluster surface is reached by the pore, a strong perturbation of the cluster shape occurs. Such a perturbation stimulates the evaporation of cluster atoms. Therefore, a decrease in the volume of the cluster occurs not only as a result of the disappearance of the pore, but due to the evaporation of some cluster atoms (see Fig.c). It should be noted that as a result of such explosive relaxation, the ordering of atoms in the cluster is disturbed, which can be visually seen in Fig.3.

A characteristic feature of the explosive scenario is a sharp jump-like change in the pore volume. An example of the change in pore volume obtained by modeling is shown in Fig.4. For a more visual demonstration of the structure of temporal behavior, the wavelet transform of the change in pore volume with time is shown on the right side. In this case, a well-known wavelet “Mexican hat” was used [13]. From the wavelet transform, several damped bursts of the pore volume are clearly visible at the initial times. Immediately before the onset of relaxation, there is an increase in pore volume followed by an explosive decrease. At this stage, small-scale oscillations are suppressed. The central figure shows the denoised behavior of the pore volume over time. It was obtained by inverse wavelet transform after removing the small scale component. The characteristic rough features of behavior preceding the disappearance of the pore are clearly visible. The nature of the volume change resembles the behavior during explosive instability. With such an instability, the amplitudes turn to infinity in a finite time [14].

Consider as a simple model a system of three oscillators interacting with each other. Let two of them model surface oscillations of a cluster and a pore , with frequencies ω_1 and ω_2

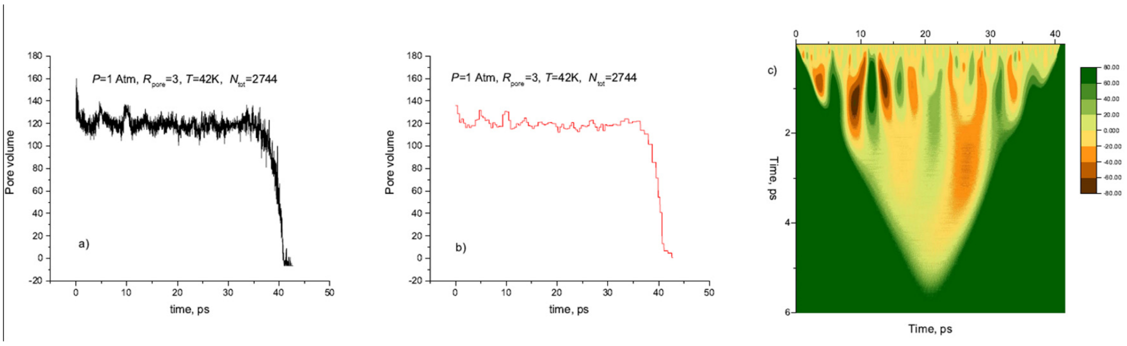

Fig. 4. An example of time dependence pore volume in the case of “jump” pore relaxation. b) Wavelet denoising of such dependence c) Wavelet transformation of such dependence.

correspondingly. The third one models oscillations of the pore as a whole or the center of the pore with frequency ω_3. Such a system is nonequilibrium, since placing a pore in a cluster increases its energy. Therefore, it is beneficial for the system to reduce its energy by getting rid of the pore. In such situation, the idea arises of negative energy waves, the excitation of which reduces the energy of the medium [14]. In our case, the disappearance of the pore, i.e., oscillations of the center of the pore, can be considered as reducing the nonequilibrium. Then we write the Lagrangian of these oscillations as

$$L = \frac{\dot{x}^2 - \omega_1^2 x^2}{2} + \frac{\dot{y}^2 - \omega_2^2 y^2}{2} - \frac{\dot{z}^2 - \omega_3^2 z^2}{2} + \varepsilon xyz$$

Here x, y are surface mode variables, while z – characterizes porecenter position and ε is characteristic value of mode interaction. It is natural to supode from physical considerstions, that vibration frequency of the pore center is the largst one $\omega_3 > \omega_2 > \omega_1$. Interesting effects can beexpected in resonance case, when the condition $\omega_3 = \omega_2 + \omega_1$ is fulfilled. Using the Lagrangian, we obtain a system of nonlinear equations of motion

$$\ddot{x} + \omega_1^2 x = \varepsilon yz$$

$$\ddot{y} + \omega_2^2 y = \varepsilon xz$$

$$\ddot{z} + \omega_3^2 z = -\varepsilon xy \qquad (2)$$

In order to analyze it, the assumption is used of a slow change in the amplitudes. For problems of interacting oscillators, it is convenient to use complex variables. So let’s change the variables

$$n_1 = \frac{1}{\sqrt{\omega_1}}(\dot{x} - i\omega_1 x)e^{i\omega_1 t}$$

$$n_2 = \frac{1}{\sqrt{\omega_2}}(\dot{y} - i\omega_2 y)e^{i\omega_2 t}$$

$$n_3 = \frac{1}{\sqrt{\omega_3}}(\dot{z} - i\omega_3 z)e^{i\omega_3 t} \qquad (3)$$

and after retaining resonant terms only (see Appendix A), the system of equations is obtained

$$\dot{n}_1 = V n_2^* n_3$$

$$\dot{n}_2 = V n_1 n_3^*$$

$$\dot{n}_3 = V n_1 n_2$$

Where $V = \frac{\varepsilon}{4}\sqrt{\omega_1\omega_2\omega_3}$ is interaction element, and the asterisk denotes complex conjugation. The system of equations for a particular case $n = n_1 = n_2 = n_3$ is reduced to the equation

$$\dot{n} = V n^2$$

whose solution can be found easily

$$n = \frac{n_0}{1 - tVn_0} \qquad (4)$$

It is just this solution that corresponds to the regime of explosive instability. Oscillation amplitude for a finite time $t_c = 1/Vn_0$ turns to infinity. In our case, this means the occurrence of a large displacement of the pore center and its contact with the cluster surface. The latter leads to the disappearance of the pore. Let us pay attention to the increase in the surface vibration modes of the pore, which can also lead to its splitting into parts. disn.eps de-.eps An example of the dependence of the distance between the center of the cluster and the pore on time during the explosive relaxation of the pore. Shown on the left is an inverse relationship that exhibits linearity consistent with explosive instability. Thus, when the resonance condition $\omega_3 = \omega_2 + \omega_1$ is satisfied, explosive instability should arise. The fulfillment of this condition is determined by certain conformations of the cluster surface, and, for other con-

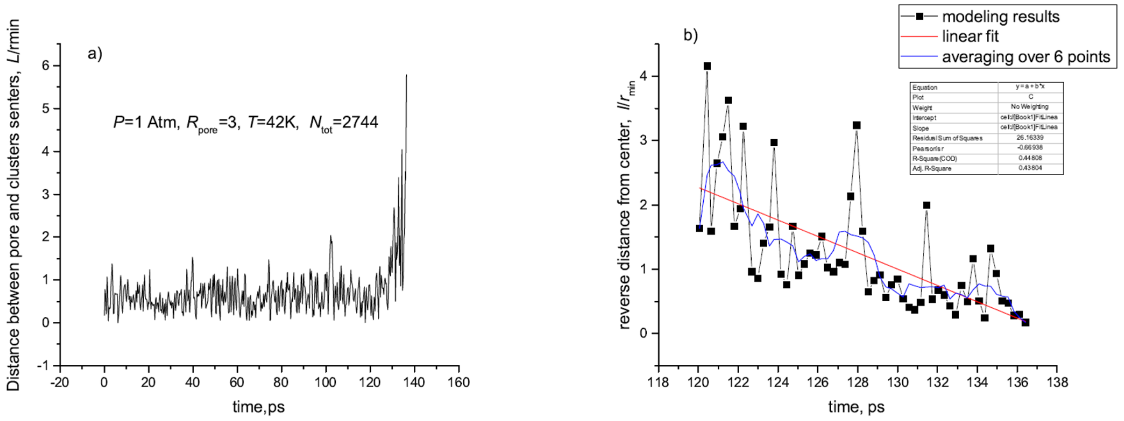

Fig. 5. An example of the dependence of the distance between the center of the cluster and the pore on time during the explosive relaxation of the pore. Shown on the right is an inverse relationship that exhibits linearity consistent with explosive instability.

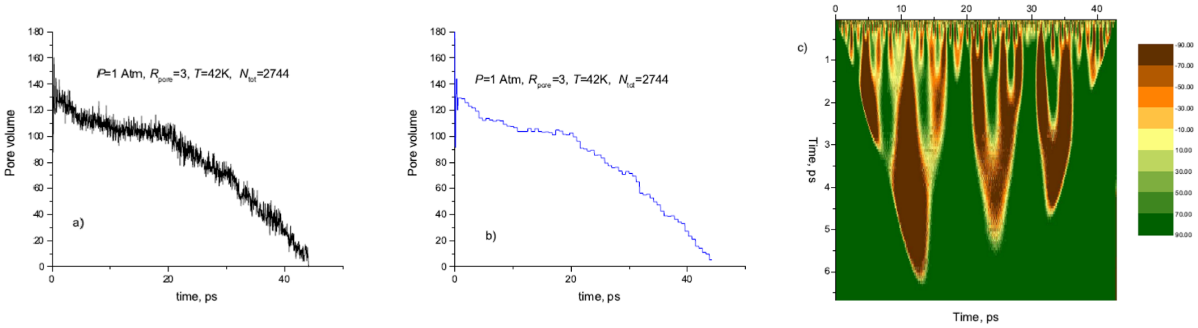

Fig. 6, a) An example of time dependence pore volume in the case of “usual” pore relaxation. b) Wavelet denoising of such dependence c) Wavelet transformation of such dependence.

formations, the resonance condition is violated and such a regime does not arise.

Direct simulation of pore relaxation makes it possible to follow the behavior of the pore position. When observing the explosive relaxation of a pore, a characteristic change in its position with time is shown in Fig. 5. One can see the displacement of the pore as a whole, which is characteristic of the explosive scenario of relaxation. It is easy to notice the existence of a period of rest or small fluctuations when the pore is in the center of the cluster. The displacement is accompanied by an increase in the oscillation amplitudes before a sharp change in the volume of the pore and its disappearance. In Fig.5, on the left, the dependence of the inverse distance on time is also shown. In accordance with the concept of explosive instability, this dependence demonstrates a linear dependence on time (see relation (4)). It can be seen that the simulation results are in good agreement with such ideas.

4.2 “Normal” pore relaxation

A more typical mode of pore relaxation is characterized by a linear decrease in the pore volume, and the rate of such a decrease is determined only by the temperature and the initial geometric parameters of the system. Since a linear decrease in the pore size is not typical for the system to overcome the energy barrier, as occurs during explosive relaxation, it can be assumed that in this case the pore emits vacancies that alternately pass through the cluster bulk, reach its boundary and “evaporate” from the cluster. The additivity of such a process explains the linearity in time of the decrease in the pore volume. Then the cluster surface oscillates with a small amplitude, but for a long time during relaxation (until most of the vacancies leave the cluster).

An example of such relaxation is shown in Fig.6. The figure shows the time dependence of the pore volume, as well as its continuous wavelet transform (Mex Hat). Based on the wavelet transform, three large-scale regimes observed during pore relaxation can be distinguished. If small-scale noises are removed with the help of an inverse transformation, then these regimes become clearly visible (see Fig.6b). Thus, it begins with a regime lasting up to 20 ps, when the decrease in the pore volume reaches a plateau, then a linear decrease begins with a small decrease rate up to 30 ps, and then a linear decrease begins with a slightly higher rate.

It is natural to assume that the first stage is explained by the evaporation of vacancies into the bulk of the cluster and its saturation with vacancies. It stops when the first vacancies reach the cluster surface. Then the vacancies leave cluster bulk. At the second stage, the balance between the rate of evaporation of vacancies from the pore and the rate of their leaving the cluster has not yet been established. The third stage corresponds to the mode when such a balance is maintained with a decrease in the pore volume.

Of course, such stages can also be detected during the relaxation of a pore from large clusters . However, the quantitative values of the characteristic quantities in this case may differ significantly from the analogous values for the nanocluster.

5. Conclusions

Scenarios for the relaxation of magic pores from nanoclusters that are in the solid state are considered.The absence of relaxation of some of the magic pores was demonstrated, for which the distribution function of the observation time is obtained. In other cases, two relaxation scenarios were found: explosive and “normal”. For explosive relaxation, a mechanism for its implementation is proposed as a consequence of the resonant interaction of two surface vibration modes (cluster surface and pore) and oscillations of the position of the pore center in the cluster. In the resonant case, explosive mode instability arises, which leads to displacement of the pore and its reaching the cluster surface. In this case, the pore leaves the cluster in an abrupt or explosive manner. If the resonance conditions are not met, the amplitudes perform small chaotic oscillations and relaxation occurs according to a different scenario. This scenario is called “normal” relaxation, in which the pore volume decreases linearly with time. At “normal” relaxation of pores, the existence of three stages of relaxation is shown and a physical explanation of their nature is proposed.

Appendix A

Let us perform the substitution of variables () in the equation system (). Differentiating () with respect to time, one obtains

$$\dot{n}_1 = \frac{1}{\sqrt{\omega_1}}(\ddot{x} + \omega_1^2 x)e^{i\omega_1 t}$$

$$\dot{n}_2 = \frac{1}{\sqrt{\omega_2}}(\ddot{y} + \omega_2^2 y)e^{i\omega_2 t}$$

$$\dot{n}_3 = \frac{1}{\sqrt{\omega_3}}(\ddot{z} + \omega_1^2 z)e^{i\omega_3 t}$$

Using these relations, and replacimg the left parts of the system of equations () one obt

$$\dot{n}_1 = \frac{\varepsilon}{\sqrt{\omega_1}} yze^{i\omega_1 t}$$

$$\dot{n}_2 = \frac{\varepsilon}{\sqrt{\omega_2}} xze^{i\omega_2 t}$$

$$\dot{n}_3 = -\frac{\varepsilon}{\sqrt{\omega_3}} xye^{i\omega_3 t}$$

It remains to replace the right parts. Note that the change of variables can be written as

$$\dot{x} = \frac{\sqrt{\omega_1}}{2}(n_1 e^{-i\omega_1 t} + n_1^\star e^{i\omega_1 t})$$

$$-i\sqrt{\omega_1}x = \frac{1}{2}(n_1 e^{-i\omega_1 t} - n_1^* e^{i\omega_1 t})$$

$$\dot{y} = \frac{\sqrt{\omega_2}}{2}(n_2 e^{-i\omega_2 t} + n_2^* e^{i\omega_2 t})$$

$$-i\sqrt{\omega_2}y = \frac{1}{2}(n_2 e^{-i\omega_2 t} - n_2^* e^{i\omega_2 t})$$

$$\dot{z} = \frac{\sqrt{\omega_3}}{2}(n_3 e^{-i\omega_3 t} + n_3^\star e^{i\omega_3 t})$$

$$-i\sqrt{\omega_3}z = \frac{1}{2}(n_3 e^{-i\omega_3 t} - n_3^* e^{i\omega_3 t})$$

Then, using these relations, one can perform the change of right-hand sides

$$\dot{n}_1 = -\frac{\varepsilon}{4\sqrt{\omega_1\omega_2\omega_3}}(n_2 e^{-i\omega_2 t} - n_2^* e^{i\omega_2 t})(n_3 e^{-i\omega_3 t} - n_3^* e^{i\omega_3 t})e^{i\omega_1 t} =$$
$$= -\frac{\varepsilon}{4\sqrt{\omega_1\omega_2\omega_3}}\Big\{-n_2 n_3^* e^{i(\omega_3+\omega_1-\omega_2)t} +$$
$$+ n_2 n_3 e^{i(-\omega_3+\omega_1-\omega_2)t} - n_2^* n_3 e^{i(-\omega_3+\omega_1+\omega_2)t} +$$
$$+ n_2^* n_3^* e^{i(\omega_3+\omega_1+\omega_2)t}\Big\}$$

Now, assuming that the amplitudes change slowly, we average over the fast time. All oscillating contributions turn to 0 and only the third term remains. This is a non-oscillating term, taking into account the resonant condition $\omega_3 = \omega_1 + \omega_2$. TThus the first equation becomes

$$\dot{n}_1 = \frac{\varepsilon}{4\sqrt{\omega_1\omega_2\omega_3}} n_2^* n_3$$

The rest of equations is transformed in the same way:

$$\dot{n}_2 = \frac{\varepsilon}{4\sqrt{\omega_1\omega_2\omega_3}} n_1^* n_3$$

$$\dot{n}_3 = \frac{\varepsilon}{4\sqrt{\omega_1\omega_2\omega_3}} n_1 n_2$$

Thus, approximate equations are obtained that describe the growth of the amplitudes of the corresponding modes. It should be noted that allowance for damping does not stabilize the explosive instability, but leads to the appearance of an instability threshold.

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