Phase transitions in large atomic clusters. Computer modeling.

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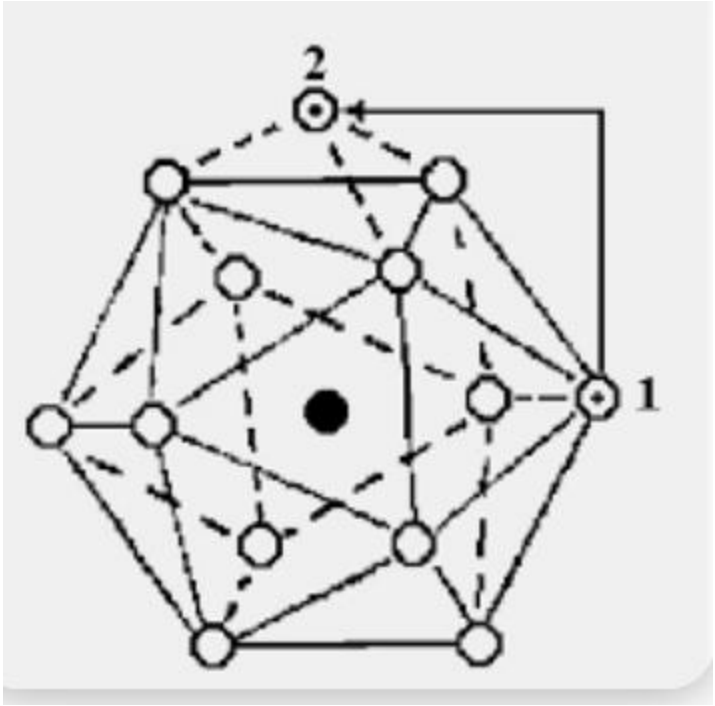
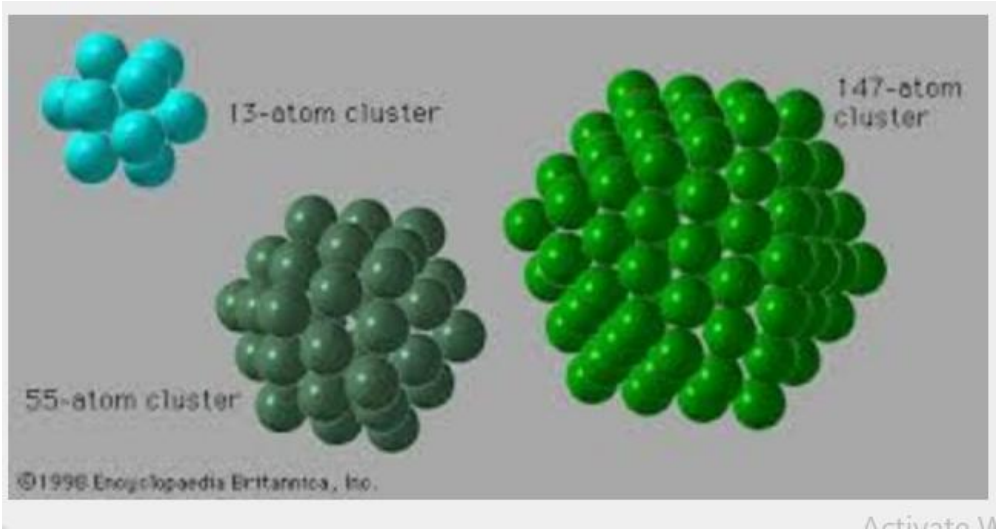
Atomic clusters

- Many properties of clusters are different from those of the bulk, like binding energies, thermodynamic functions, crystalline structure, optical, magnetic or chemical behavior
- One important property which is strongly size-dependent is the melting point.
- Small particles melt at significantly lower temperatures than bulk material, which is due to the fact that the surface energy of liquids is lower than that of solids - and small particles mainly consist of the surface.

Configurational melting

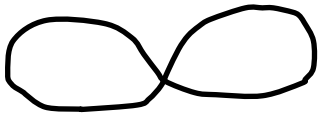
- Atomic clusters





Entropy and Phase Coexistence in Clusters: Metals *vs.* Nonmetals
by **Richard Stephen Berry**
and **Boris Michailovich Smirnov**

Computer modeling

- N<1000 – molecular dynamics
- N ⟶  Classical thermodynamics
- N~10000 – mesoscopic range-?

Metropolis -Hastings algorithm

$r_i - old\ coordinates$

$r_i' - new\ coordinates$

$$(r_i' - r_i)_k = Rand\left(-\frac{\Delta}{2}, \frac{\Delta}{2}\right)$$

$$p\left(\mathrm{E}_1 \rightarrow \mathrm{E}_2\right) \sim \mathrm{e}^{\left(\mathrm{E}_1 - \mathrm{E}_2\right)/\mathrm{T}}$$

Modified Metropolis -Hastings algorithm

$r_i - old\ coordinates$

$r_i' - new\ coordinates$

$$p\left(\mathrm{E}_1 \rightarrow \mathrm{E}_2\right) \sim \mathrm{e}^{\left(\mathrm{E}_1 - \mathrm{E}_2\right)/\mathrm{T}}$$

$$(r_i' - r_i)_k = Rand\left(-\frac{\Delta\left(r_i, N_{\text{step}}\right)}{2}, \frac{\Delta\left(r_i, N_{\text{step}}\right)}{2}\right)$$

G ↘ G - Gibbs free energy

Thermodynamic functions are determined during modelling

- Number of microstates $n = \prod_i \Delta(r_i)$

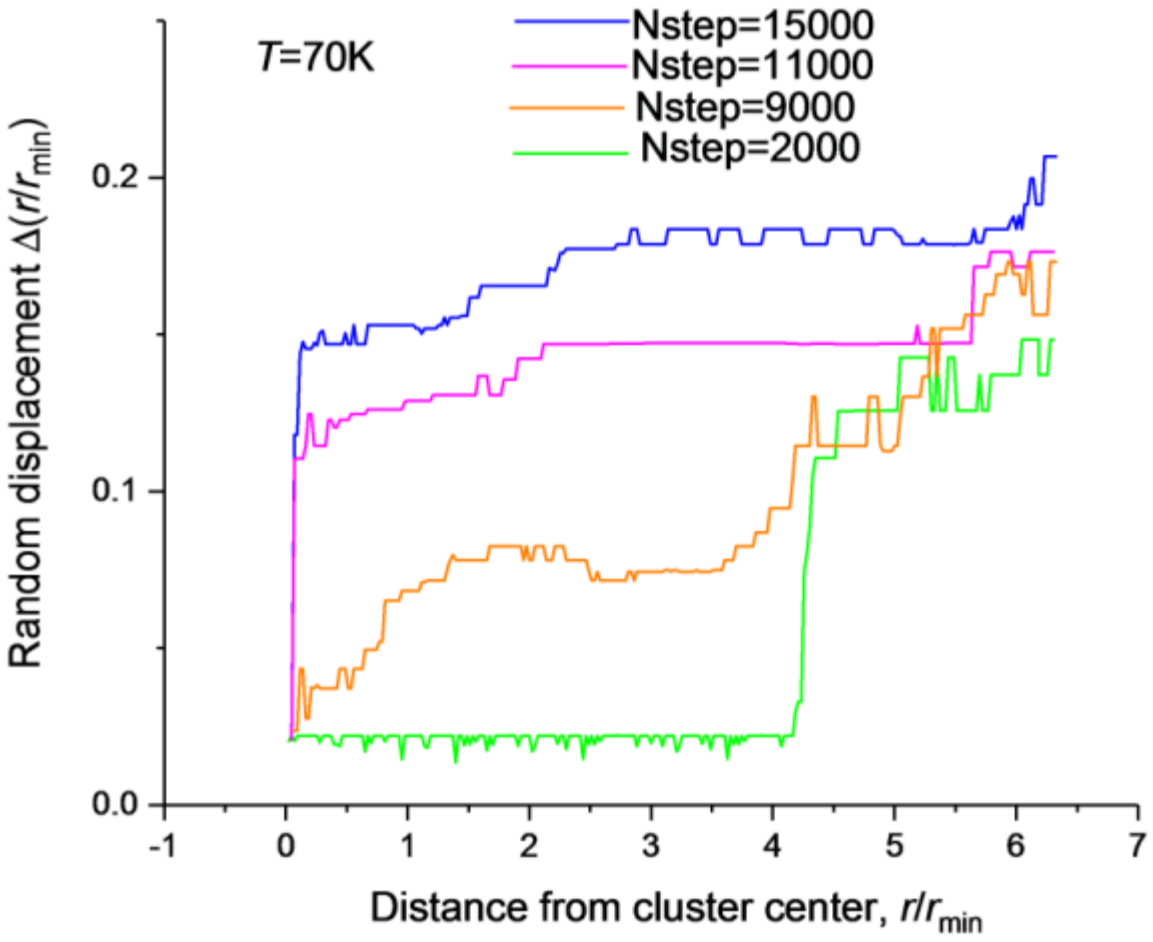
- Entropy $S = \sum_i \ln(\Delta(r_i))$

- Gibbs free energy

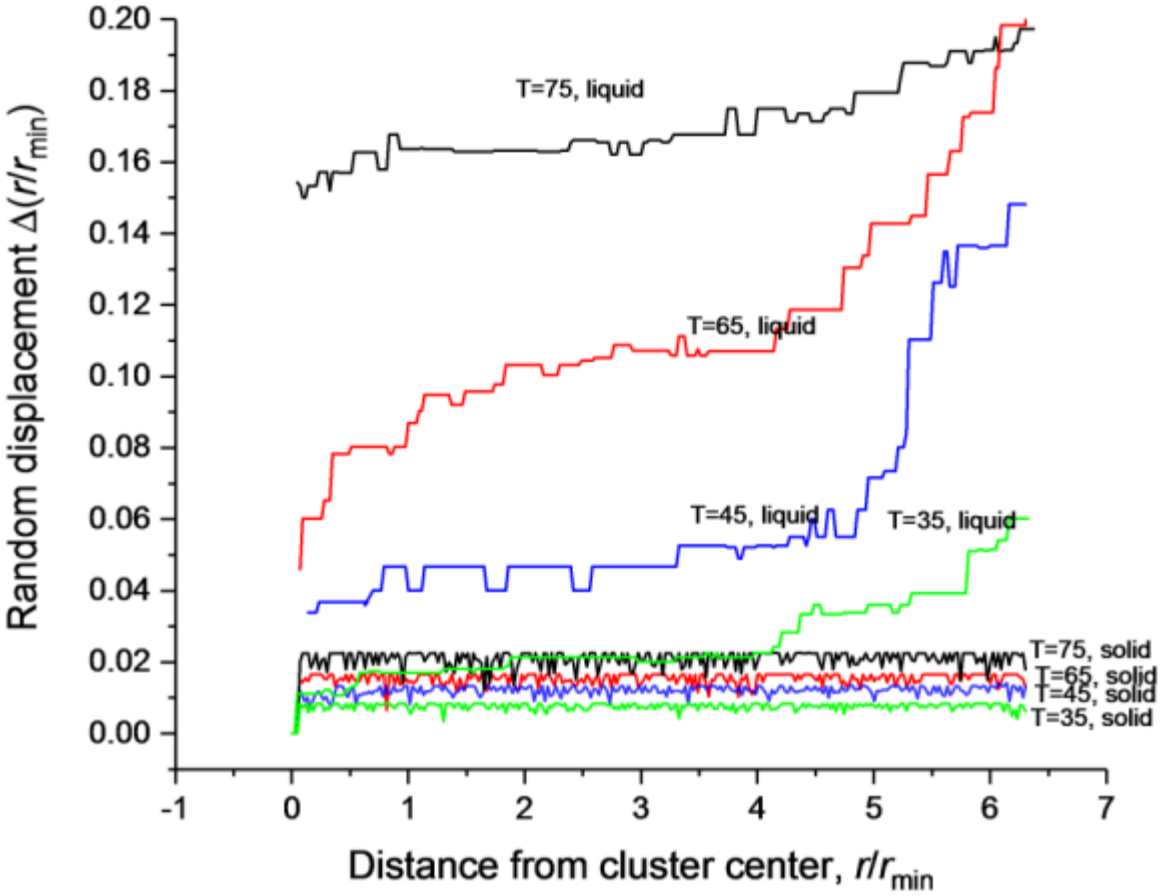
$$G = E + pV_{cl} - 3T \sum_i \ln \Delta(r_i, N_{step})$$

¶

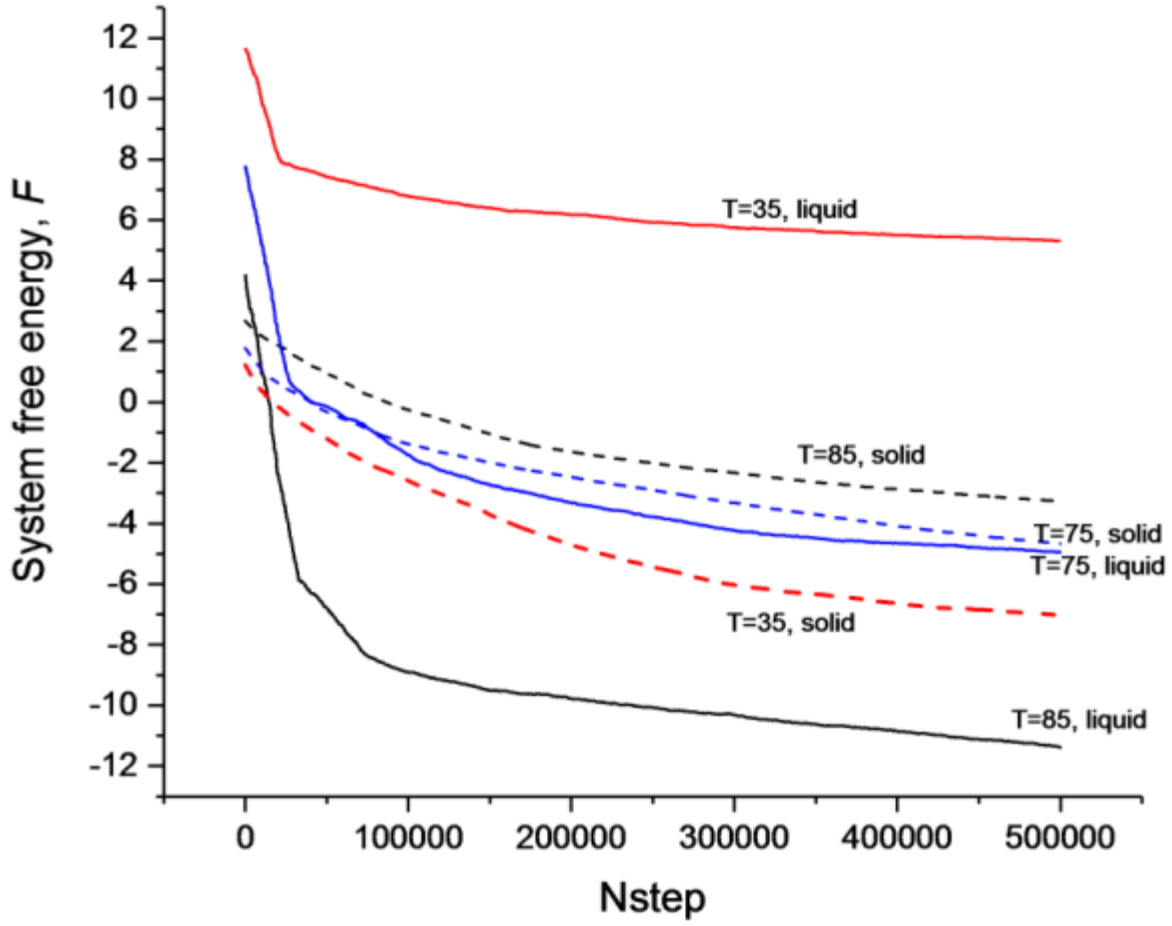
Evolution of random displacement function



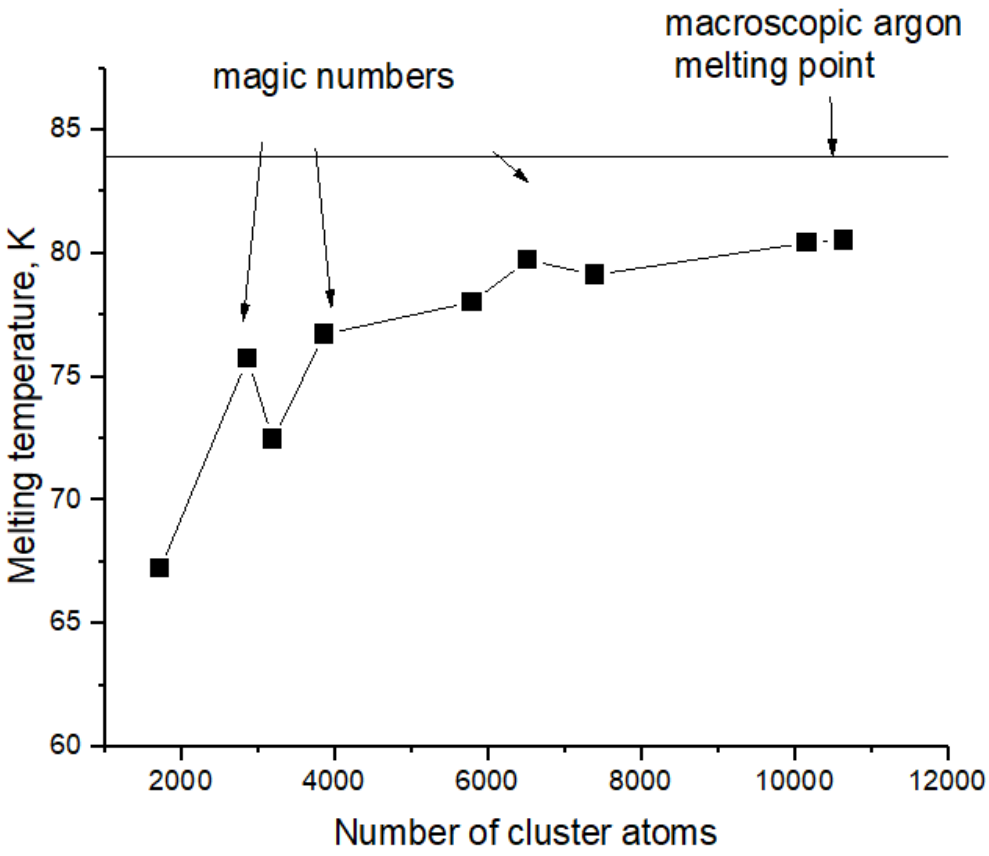
Random displacement function for various temperatures and cluster states



Free energy evolution for various temperatures and cluster states



Size dependence of melting temperature



Conclusions

- Modified Metropolis -Hastings algorithm

1. Shortens simulation time by 1-2 orders of magnitude
2. Takes into account the centrally symmetric structure of the cluster, allowing one to simulate surface.

3. Of all possible random conformations, it selects only a small part, that constitute spherically symmetrical macrostates. The displacement range of atoms starts from small values and grows gradually until free energy minimum is reached. Thus no “excessive” microstates are taken into account which saves substantially modelling time.

3. Gradual growth of allowed atom displacement range provides gradual system evolution from the most ordered to less ordered state, so that no free energy minima are missed.

4. During the calculation process, the thermodynamic functions of the cluster are calculated naturally without additional computer time.

Relaxation of pores in nanoclusters

- Relaxation of a solid nanocluster with an internal pore was investigated using the molecular dynamics method.
- It was shown that there exist “magic” sizes of pores similar to “magic” sizes of clusters with closed icosahedral shells.
- Like “magic” clusters, “magic” pores have special properties.
- 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.

Explosive scenario of pore relaxation

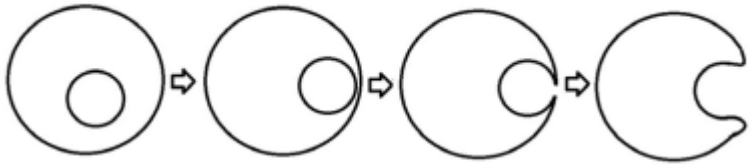


Fig. 2. Scheme of pore relaxation according to the "explosive" scenario. Then the cluster returns to a spherical shape.

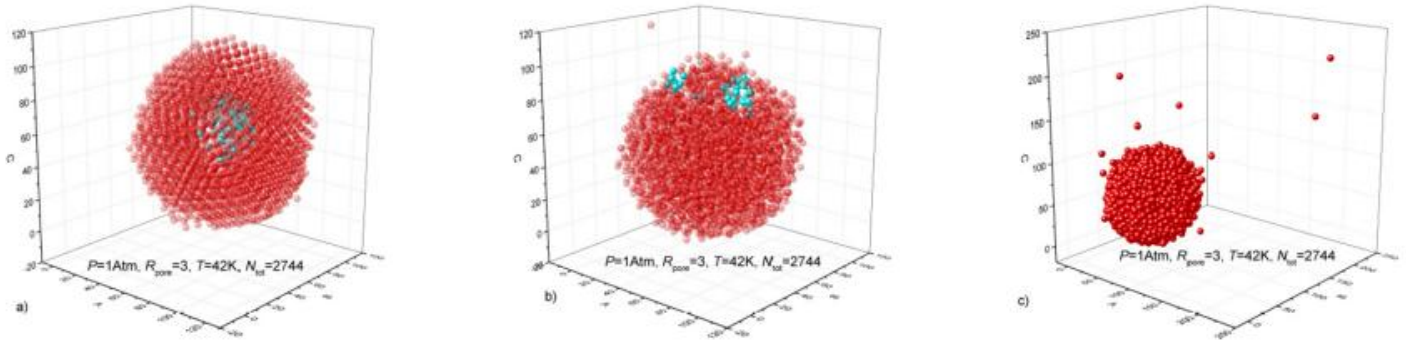


Fig. 3. The stages of pore relaxationare shown at successive time points that were observed in the simulation. a) - the initial position of the pore, b) - the advancement of the pore to the cluster boundary, c) - the pore completely disappeared with the violation of the order of atoms in the cluster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

“Explosive” pore relaxation

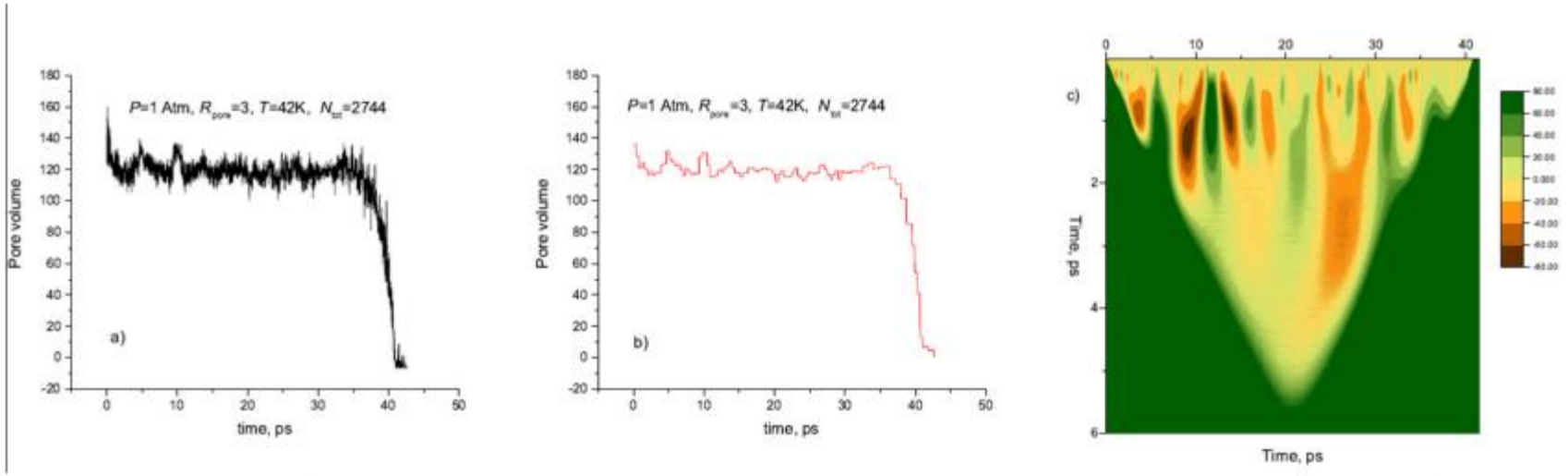


Fig. 4. An example of time dependence pore volume in the case of “jump” pore relaxation. b) Wavelet de-noising of such dependence c) Wavelet transformation of such dependence.

Continuous pore relaxation

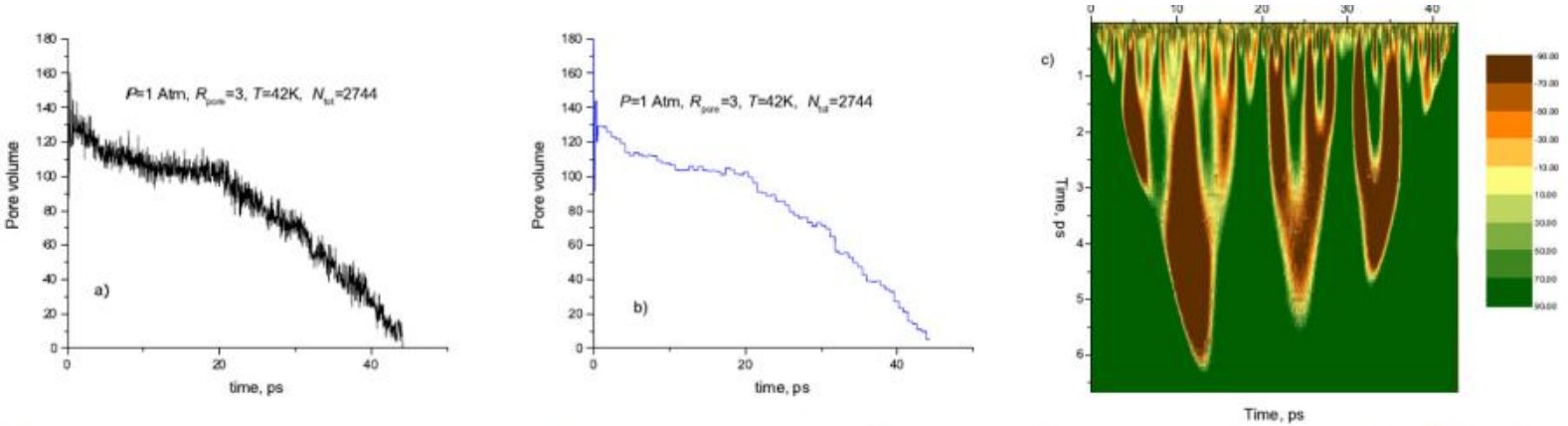


Fig. 6, a) An example of time dependence pore volume in the case of "usual" pore relaxation. b) Wavelet denoising of such dependence c) Wavelet transformation of such dependence.

“Explosive” pore relaxation

ω_1 and ω_2 -Oscillation frequencies of cluster and pore surfaces

ω_3 Oscillations of pore center

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.

“Explosive” pore relaxation

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

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

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

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

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

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

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

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

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

Where $V = \frac{\varepsilon}{4}\sqrt{\omega_1\omega_2\omega_3}$ is interaction element, and the asterisk denotes complex conjugation.

“Explosive” pore relaxation

The system of equations for a particular case $n = n_1 = n_2 = n_3$ is reduced to the equation

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

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.

Conclusions

- Scenarios for the relaxation of nanoclusters with intrinsic pore 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.