Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/0S132-05
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

SPONTANEOUS TRANSFORMATIONS OF NANOCLUSTERS

M. Rieth[a], W. Schommers[b], S. Baskoutas[c], and C. Politis[c]
[a] *AMA-SYSTEMS GmbH, Unterer Hardweg 9, 75181 Pforzheim, Germany*
[b] *Forschungszentrum Karlsruhe, Institut für Nanotechnologie, P.O.Box 3640, 76021 Karlsruhe, Germany*
[c] *Department of Engineering Science, University of Patras, 26110 Patras, Greece*

(Received 29 December 2000)

It is well-known that nano-systems can have properties which are distinctly different from macroscopic systems. In this study we point out the following specific behaviour: if the particle number is decreased so that the size of the system is in the nanometer-realm, new effects emerge which reflect certain features of biological systems although the system is inorganic in nature. This behaviour is shown by realistic molecular dynamics calculations in connection with aluminum-nanoclusters at various temperatures. The clusters can transform without external influence from a metastable into a stable state, and there can be more than one stable state, that is, we observe a bifurcation in the sense of chaos-theory. The stable states can differ in both the atomic structure and the outer shape.

Keywords: metastable states, chaos theory, molecular dynamics, biological systems
PACC: 6460Q, 0545, 7115Q

I. INTRODUCTION

It is well-known that nano-systems can have properties which are distinctly different from macroscopic systems. In this study we point out the following specific behaviour: if the particle number is decreased so that the size of the system is in the nanometer-region, new effects emerge which obviously reflect certain features of biological systems, although the system is inorganic in nature.

It is usually assumed that biological features (for example, those of alive systems) are strongly correlated with systems with sufficiently large complexity, in particular, in connection with complex molecules. It is generally assumed that a simple piece of inorganic material (for example, a mono-atomic system) cannot have specific properties in analogy to those of biological (alive) systems. That is certainly correct as far the size of the system is sufficiently large, for example, a piece of material with a size of approximately one centimeter. Such a system does definitely not behave biologically.

But do we really need complex systems and complex molecules for all phenomena which arise in connection with alive systems? The study given in this paper shows that this must obviously not be the case. A sufficiently small system consisting of aluminum atoms shows surprisingly new effects in analogy to those which are typical for biological systems. How far has such an Al-system to be reduced in order to show such features? In the micrometer-realm the system behaves completely non-biologically. However, if the size is of the order of a few nanometers, such new effects emerge, which are new in solid state physics and materials science.

What is the reason for that? In the nano-region the number of particles at the surface is relatively large, and this is obviously the cause that certain biological effects can come into play although the system is inorganic in nature. In other words, surface effects can be responsible for biological effects. We do not always need complex systems and complex molecules.

In the following we discuss the molecular dynamics results for simple nanometer-size systems made of Al, that is, nanoclusters consisting of an inorganic material.

II. MODEL

The properties of clusters are in general different from the corresponding bulk objects. This is mainly due to the fact that with decreasing number of atoms a relative increase of the number of surface atoms is accompanied. In the case of clusters of a few nanometers the structure and dynamics of the atoms is already dominated by the surface atoms.

These cluster-effects are essentially influenced by *anharmonicities*, which are distinctly larger at the surface than in the bulk. The surface particles are, in gen-

eral, less strongly bonded than the bulk particles and the mean-square amplitudes are significantly larger, leading to strong anharmonicities. Therefore, the harmonic approximation (see, for example, Refs.[1] and [2]) is not adequate for the description of such systems. Molecular dynamics (MD) calculations are important in studying classical many-particle systems with strong anharmonicities, since anharmonicity is treated without approximation[3].

Since the particles at the surface of clusters are less strongly bonded than bulk particles, we expect that the structure and dynamics at the cluster-surface are more sensitive to variations in temperature than in the bulk of the crystal[3].

In noble gases (for example, krypton[4]) the temperature-dependence of properties in the bulk as well as at the surface can be treated in a good approximatioin on the basis of temperature-independent pair potentials. However, this is obviously not possible in the case of metals where pseudopotentials are often used in the description of properties. Whereas the *core contribution* is in a very good approximation independent of temperature, the *longrange part* of such pseudopotentials critically depends on the electronic arrangement which is sensitive to variations in temperature and density. That implies that the interaction potential in metals is in general dependent on temperature.

As a model we used a pseudopotential. The essential point is the consideration of interactions of *van der Waals-type* in the determination of the direct ion-ion potential and the ion-electron pseudopotential.[5] The pair potential for Al based on this kind of model describes various experimental data adequately.

III. CLUSTER-CALCULATION FOR Al

We performed molecular dynamics calculations for clusters consisting of $N = 500$ atoms.[6] For this system the classical Hamilton equations were solved by iteration. The time step in the calculation was 0.2×10^{-14} s. We did the calculations for 6000 time steps (1.2×10^{-11} s). The initial values for the positions were chosen to be the bulk structure. In the case of Al and $N = 500$ particles, the box size of the clusters is approximately 2.0 nm. The cutoff radius for the interaction potential was chosen as the six nearest neighbour distance.

The amplitude of the initial velocities of all particles was chosen to be equal, but Maxwell's distribution was reached after 100 time steps (2×10^{-13} s). The initial directions of the velocities were distributed randomly, so that the velocity averaged over all particles is zero and remains zero for all time steps. The amplitudes of the velocities determine the temperature of the system. Due to the finite number of particels the temperature fluctuates around a mean value. In the following, $t = 0$ refers to the time at which the systems reached their thermal equilibrium.

Figure 1 shows the temperature T as a function of time t. We observed two different regions: For times $0 \leq t \leq 3.5 \times 10^{-12}$ s the mean temperature is different from that for times $t \geq 4.5 \times 10^{-12}$ s. How can we understand this behaviour? There is thermal equilibrium within $0 \leq t \leq 3.5 \times 10^{-12}$ s, and there are stable temperature fluctuations within this region; the mean temperature is $T_{\mathrm{m}} = T_{\mathrm{m1}} = 59$ K. However, the system leaves this state without any external influence after $\sim 3.5 \times 10^{-12}$ s, and we obtain a new stable state for $t \geq 4.5 \times 10^{-12}$ s: Also here the system is in thermal equilibrium and there are also stable temperature fluctuations for $t \geq 4.5 \times 10^{-12}$ s; the mean temperature is here $T_{\mathrm{m}} = T_{\mathrm{m2}} = 146$ K.

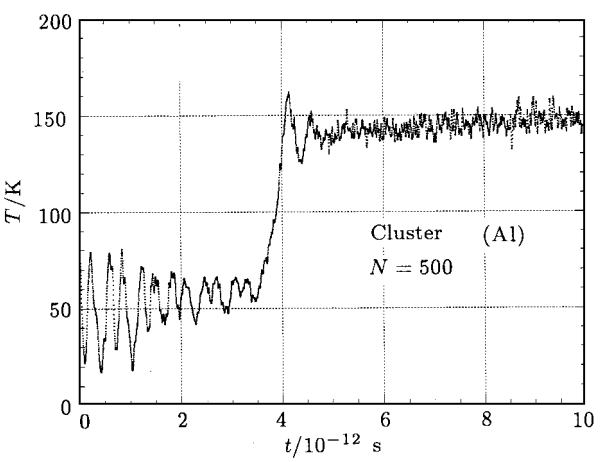


Fig.1. The temperature T of a nano-cluster as a function of time t. The mean temperatures are $T_{\mathrm{m1}} = 59$ K(metastable state) and $T_{\mathrm{m2}} = 146$ K (stable state).

The transition is interpreted as following: Within the region $0 \leq t \leq 3.5 \times 10^{-12}$ s ($T_{\mathrm{m1}} = 59$ K) the system is obviously in a *metastable state*. For $t \geq 4.5 \times 10^{-12}$ s the mean temperature is $T_{\mathrm{m2}} = 146$ K $> T_{\mathrm{m1}}$, and, because the energy of the system is conserved, the mean potential energy for $t \geq 4.5 \times 10^{-12}$ s must be smaller than for $0 \leq t \leq 3.5 \times 10^{-12}$ s. Since the potential energy depends on the relative distances between the particles, the structure in the metastable state ($0 \leq t \leq 3.5 \times 10^{-12}$ s) should be different from that in the stable state ($t \geq 4.5 \times 10^{-12}$ s). Also the dynamics of the system should be influenced by the

transition from $T_{m1} = 59$ K to $T_{m2} = 146$ K.

We calculated for both the metastable and the stable states, the structure and the dynamics of the cluster.[6] The structure by means of the structure function $S(\boldsymbol{q})$, where $\boldsymbol{q}$ is the wave vector; the dynamics with the help of the generalized phonon density of states $g(\nu)$, where ν is the frequency. We found that there are relatively large differences in the structure and dynamics when we compare the data of the metastable with those of the stable state.

The transition from a metastable to a stable state also takes place at higher temperatures. In Fig.2, the temperature T as a function of time t is shown. In this case the mean temperatures are T_{m1}=230 K (metastable state) and T_{m2} =340 K (stable state). Also here there are relatively large differences in the structure function $S(\boldsymbol{q})$; the differences in the generalized phonon density of states $g(\nu)$ are not so large as in the case of the transition shown in Fig.1. These data will be published elesewhere.

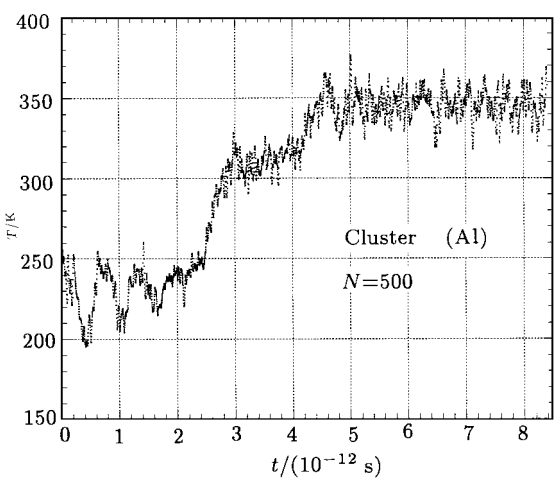


Fig.2. The temperature T of a nano-cluster as a function of time t. The mean temperatures are T_{m1}=230 K (metastable state) and T_{m2} =340 K (stable state).

IV. ANALOGIES

There is a certain analogy between metastable states of clusters and of atoms in an excited state:

The potential energy in the excited (metastable) state is larger than in the ground (stable) state.

The systems (atoms, clusters) leave their excited (metastable) state without external influence after a certain time interval, the atoms by emiting photons, the clusters by increasing their temperature (see also Fig.3).

The atoms stay 10^{-8} s in an excited state. The clusters discussed above stay approximately 10^{-11} s in a metastable state. The time interval of 10^{-11} s is much smaller than 10^{-8} s (excitation time of atoms). Nevertheless, the life-time of 10^{-11} s of the metastable state is relatively large; it is distinctly larger than the time interval (0.4×10^{-12} s) that a sound wave needs to propagate across the nano-system. The life-time of such metastable states is a function of the particle number and is also a function of the outer shape of the nano-system; this point will be discussed in a forthcoming paper.[7]

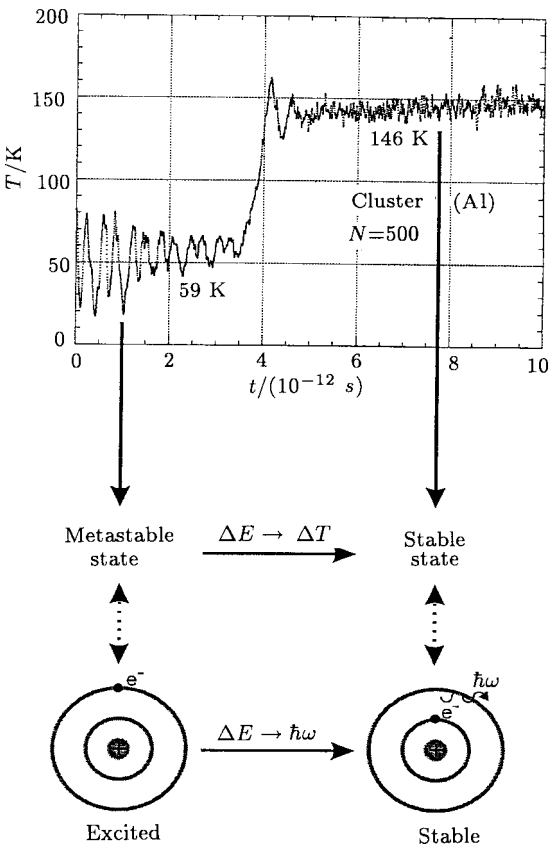


Fig.3. The systems (clusters, atoms) leave their metastable (excited) state without external influence after a certain time interval, the atom by emiting a photon, the cluster by increasing its temperature.

V. BIFURCATION PHENOMENA

In connection with metastable states the following effect is of particular interest. When the cluster passes during the calculation from the metastable to the stable state, it has obviously various possibilities for this transition, and it is principally not predictable which of the possible stable states the system will take. It is quite a matter of chance.

In other words, we have a bifurcation in the sense of chaos-theory. At the bifurcation point (see Fig.4) it is really playing dice (nature does it of course, not the observer; at the bifurcation point nature plays dice to get the branch (stable state) which the cluster will

occupy after it has left the metastable state). The stable states can differ in both the *atomic structure* and the *outer shape*. Concerning this point let us give the following additional remarks:

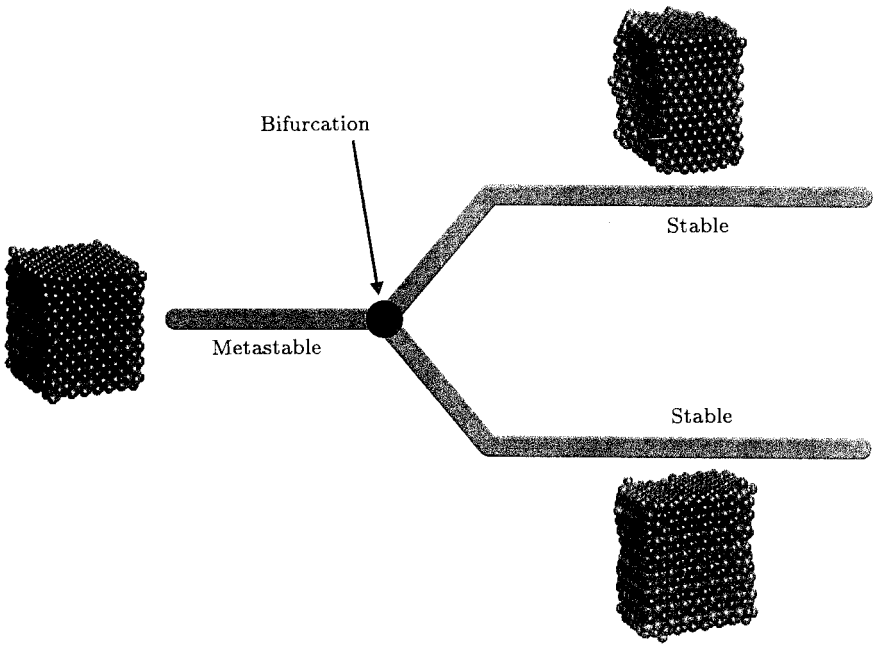


Fig.4. At the bifurcation point nature really plays dice to get one of the possible stable states.

The structure of the system in the metastable state is cubic face-centered (it is the structure in the bulk), and it transforms spontaneously after a certain time into a hexagonal structure which is, however, disturbed by inner surfaces which are formed randomly, and the various stable states (Fig.4) differ in the distribution of these inner surfaces. Furthermore, a certain distribution of the inner surfaces leads to a certain outer shape. In other words, the outer shape is a function of the distribution of the inner surfaces.

This is an interesting phenomenon, and there is no counterpart in micro- and macro-technique. In macro-technique, a system (for example, a machine) will always be destroyed after a certain time, if the mechanic does not keep the machine in good condition; this degredation of the system is due to its interaction with the systems sorrounding. There are no other transitions in micro- and macro-technique. As we have seen in Fig.4, the situation is different in connection with nano-systems. The transition at the bifurcation point is constructive; the system will not simply be destroyed but there emerges a new form, namely one of the possible stable states.

As said, in micro- and macro-technique we do not observe such phenomena, and this is because there are no such metastable states. If there were nevertheless metastable states also established in the macroscopic realm, in principle a screwdriver could transform spontaneously into a hammer or a parir nippers. Nature plays dice, a screwdriver becomes either a hammer or a parir nippers, and such transition wuold take place without any external influence. We know that such phenomena are not possible in micro- and macro-technique, but should be a real phenomena in nano-technology, in particular, within the frame of materials research at the nano-level.

The bifurcation phenomenon is the behaviour of single clusters, and this specific behaviour comes into play by the mutual influence of temperature and the interaction between the particles forming the cluster. There is a certain kind of independent creativity, and this creativity does not come from outside, that is, it is not forced by the observer or by other factors of the environment, but is an inherent characteristic of the system itself. Such a behaviour is also known in connection with biological systems which are, however, much more complex as the Al-clusters studied here. Since this specific behaviour (creativity) is essentially influenced by the temperature and the interaction potential between the particles, nano-systems at zero temperature have to be considered as "dead" systems without any creativity.

VI. CONCLUSION AND FINAL REMARKS

In conclusion, within the molecular dynamics cal-

culations discussed here the nano-clusters are in thermal equilibrium after a certain time. Nevertheless, such systems can be in a metastable state; they can be in a metastable state and are simultaneously in thermal equilibrium. We have to distinguish between three different regions: First, there is a short time interval, in which the system is not in thermal equilibrium. Secondly, there is a relatively large time interval in which the system is in a metastable state, but it is in thermal equilibrium here. Third, the clusters transform without external influence into one of the stable states; this behaviour reflects a certain creativity.

Although the Al-clusters represent inorganic systems there are certain analogies to biological systems:

a) A nano-system can be creative, that is, it can meet individual decisions which are influenced from outside; in this way the bifurcation phenomena (Fig.4) can be interpreted.

b) A nano-system can transform spontaneously; it can transform from a metastable state to a stable state without external influence. Spontaneous transformations are also typical phenomena in biology, in particular in connection with embryology.

c) New forms, new shapes emerge without external influence, which were not existent before. Also within biology (in embryology etc.) there emerge new forms which were not existent before.

d) The shape of such nano-systems transform to more complex forms. Also this behaviour is typical for biological systems and is a feature of biological evolution. The nano-systems transform from a cube to a cuboid (Fig.4), and a cuboid is more complex than a cube because one needs more description elements to characterize them.

In this connection also the following effect is interesting. In Fig.5 there are two nano-systems made of Al. The large cluster is at rest and the smaller one moves towards the larger system with a certain velocity (energy) and knocks it locally. Such an impact must not destroy the larger cluster. For example, the small system could knock out some of the surface atoms, which depends on the energy of the the small cluster. In the case of Fig.5, the larger cluster is not destroyed by the local impact but the response of the system is coherent: The larger cluster transforms globally; the face-centred Al transforms globally and we obtain a global hexagonal structure. Furthermore, the outer shape of the large cluster is transformed, too.

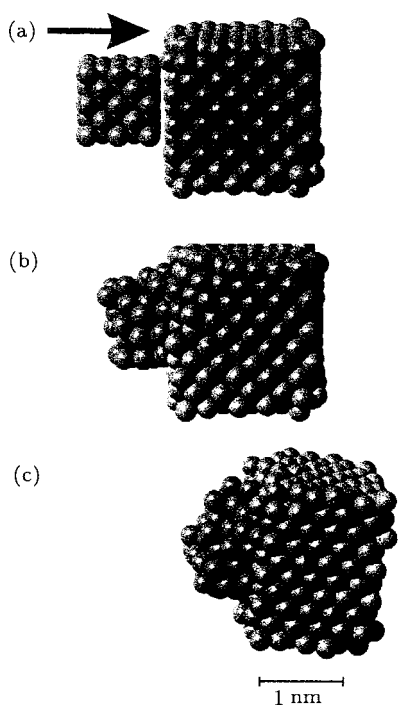


Fig.5. The atomic structure and the outer shape of the large Al-cluster are transformed globally by the local impact of the smaller Al-cluster. More details are given in the text.

References

[1] Allen R E and de Wette F W 1969 *J. Chem. Phys.* **51** 4820

[2] Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1967 *Theory of lattice dynamics in the harmonic* approximation *Solid State Physics* (Supp1.3) (New York: Academic)

[3] Schommers W Structure and dynamcis of surfaces I, *in Top. Curr. Physics Vol.41* ed by Schommers W and von Blanckenhagen P (Berlin, Heidelberg: Springer)

[4] Schommers W 1999 *Appl. Phys.* A **68** 187

[5] Schommers W, Mayer C, Göbel H and von Blanckenhagen P 1995 *J. Vac. Sci. Technol.* A **13** 1413

[6] Schommers W and Rieth M 1997 *J. Vac. Sci. Technol.* B **15** 1610

[7] Rieth M, Schommers W, Baskoutas S and Politis C to be published