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Monte Carlo modeling of atomic clusters in mesoscopic range

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A modification of the Monte Carlo method for atomic clusters in mesoscopic range is proposed thattakes into account the peculiarities of phase transitions in atomic clusters. The method was demonstrated as upplied to argon clusters of 2744 atoms in a broad temperature range. Thermodynamics fiunctions were calculated and equilibrium phase state found for these temperatures. It was shown that phase transition between solid and liquid states of an argon cluster of such size occurs abruptly at a temperature of about 75 K (for a macroscopic body the melting point is 84 K). The liquid and solid states practically do not coexist, in contrast to clusters of significantly smaller sizes where the phase transition is blurred. It wath shown that for the clusters of such size, melting begins from the outer shells of the cluster and in the liquid state, fluctuations of atoms increase as they approach the surface.
Keywords: cluster, mesoscopic range, Monte Carlo method, phase state.

Monte Carlo Modelling of Atomic Clusters in Mesoscopic Range. *M.A.Ratner, V.V.Yanovsky*

Запропоновано модифікацію методу Монте-Карло для атомарних кластерів у мезоскопічному діапазоні, яка враховує особливості фазових переходів в атомарних кластерах. Було продемонстровано застосування методу до кластерів аргону з 2744 атомів у широкому діапазоні температур. Для цих температур розраховано термодинамічні функції та знайдено рівноважний фазовий стан. Показано, що фазовий перехід між твердим та рідким станами для кластера аргону такого розміру відбувається різко при температурі близько 75 К (для макроскопічного тіла температура плавлення становить 84 К). Рідкий і твердий стани практично не співіснують, на відміну від кластерів значно менших розмірів, де фазовий перехід розмитий. Показано, що для кластерів такого розміру плавлення починається із зовнішніх оболонок кластера, а в рідкому стані флуктуації атомів посилюються в міру наближення до поверхні.

1. Introduction

Atomic clusters are aggregates of atoms in the size range from a few to thousands of the components. The structural and electronic properties of clusters bear resemblance neither to atoms they are composed of, nor to solidsof the same composition. Their physical and chemical properties depend on number of their atoms and change as cluster size increases. One of the main tasks of cluster studies is to understand how cluster structure and properties change with an increase of cluster size and how many atoms are required to form a solid (see e.g. [1]). Linking atomic and mesoscopic range become a challenging task, since the use of both traditional modelling methods for small

systems (Molecular Dynamics) and macroscopic statistical physics are restricted in this range of sizes.

In connection with the above said, Monte-Carlo algorithm comes to mind, that is a powerful method to study systems with a large number of degrees of freedom (see e.g.[2-11]). In the present work, this algorithm is used in order to model phase transitions in clusters in mesoscopic range.

Monte Carlo methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical results. As a rule, one experiment is repeated many times to obtain the probability distribution of the unknown quantity. These methods are often used to solve physical and mathematical problems and are the most useful, when it is difficult or impossible to obtain an exact solution. Monte Carlo methods is mainly used in three different classes of problems: optimization, numerical integration and distribution generation probabilities. To solve physical problems, Monte Carlo methods are very useful for modeling systems with many degrees of freedom, for example, liquids, disordered materials, strongly connected solids and lattice structures (see e,g. [2-14]).

Monte Carlo molecular modelling is the application of Monte Carlo methods to molecular problems. These problems can also be modelled by the molecular dynamics method. The difference is that this approach relies on equilibrium statistical mechanics rather than molecular dynamics. Instead of trying toreproduce the dynamics of a system, it generates states according to appropriate Boltzmann distribution. Thus, it is the application of the Metropolis Monte Carlo simulation to molecular systems. It is therefore also a particular subset of the more general Monte Carlo method in statistical physics. It employs a Markov chain procedure in order to determine a new state for a system from a previous one. According to its stochastic nature, this new state is accepted at random. Each trial usually counts as a move. The avoidance of dynamics restricts the method to studies of static quantities only, but the freedom to choose moves makes the method very flexible. These moves must only satisfy a basic condition of balance in order for the equilibrium to be properly described, but detailed balance, a stronger condition, is usually imposed when designing new algorithms. An additional advantage is that some systems, such as the Ising model, lack a dynamical description and are only defined by an energy prescription; for these the Monte Carlo approach is the only one feasible. The great success of this method in statistical mechanics has led to various generalizations such as the method of simulated annealing for optimization, in which a fictitious temperature is introduced and then gradually lowered (see e.g.[7]).

Both Classical Monte Carlo (MC) and Classical Molecular Dynamics (MD) simulations are used to perform simulations of ensembles of molecules. These MC calculations are calculating thermodynamic properties via an ensemble average, while the MD simulations are doing so via a time average. A computational review of molecular dynamics, Monte Carlo simulations, Langevin dynamics, and free energy calculation is presented in [4]. The exposition is made from first principles to promote a better understanding of the potentialities, limitations, applications, and interrelations of these computational methods.

The special type of Monte-Carlo method, the algorithm of Metropolis [12] lies in the following:

1) The energy of interaction between atoms in a cluster is calculated, i.e. energy of the "old" or initial configuration: E_1. After this, all atoms are given small shifts and the energy of the "new" configuration is calculated: E_2.

2) The energy of the "new" configuration is compared to that of the "old" one. The "new" configuration is accepted and becomes the initial one for the next step with probability

$$p\left(E_1 \to E_2\right) \sim e^{(E_1 - E_2)/T} \qquad (1)$$

However, the applicability of the method for atomic clusters is limited, since the time (number of modeling steps) required to observe a phase transition grows exponentially with the size of the cluster. This happens due to the fact that, if random displacements of all atoms occur in the same range, energy difference in the exponent (1) is proportional to the number of cluster atoms.

In connection with this, the present work proposes a modeling mechanism that is based on the nature of phase transitions in atomic clusters

1. Research idea

Until now, the Monte Carlo method in physics has been applied to systems with a relatively small number of degrees of freedom, such as

spin systems polymers (including dendrimers) with rigid bonds, etc. However, in an atomic cluster, the atoms are not rigidly connected, which leads to a large number of degrees of freedom of the system, and the number of possible microstates of the cluster grows exponentially with its size. Up to now, only clusters of small sizes (up to 100 atoms) were studied (see e.g. [13,14]).

However, in the present paper we are interested in studying clusters in mesoscopic range (thousands of atoms). In order to make the modeling timefeasible, the following approach is proposed, based on the fact that the melting process in real atomic clusters begins from the outer shells [15-19]. Thus, while modeling melting of the cluster, we look for "islands (nucleus) of new phase" forming on the cluster surface, deliberately choosing states with fluctuations of randomly chosen surface atoms. If, as a result of such approach, the outer shell of the cluster becomes less ordered, random fluctuation are given to the atoms in the next (closer to the center) shell. Thus, we mimic melting process in real cluster that starts from the outer cluster shell. Depending on cluster temperature, in the equilibrium cluster state either the entire cluster is heterogeneous (solid or liquid) or several outer shells can be melted while the core remains solid.

Thus, we are looking for the centrally symmetric macrostates, where the maximum possible displacement of an atom at one step is determined by the centrally symmetric function $\Delta(r)$, , and this function increases monotonically in towards the cluster surface, because the energy factor in formula (1) is less important for surface atoms.

It should be emphasized that displacement function $\Delta(r)$, obtained after averaging over N=10 initial random conformations, characterizes a new macrostate of the cluster, which corresponds to a large number of microscopic implementations, that is, microstates M. The set of microstates M under consideration must provide the macrostate $\Delta(r)$ can change during the evolution of the system via Monte Carlo method.

1a. Modified Metropolis algorithm.

It should be noted that such a function $\Delta(r)$ allows one to estimate entropy and free energy of the system. To do this, it is necessary that the algorithm allows estimating the number of microstates corresponding to the resulting macrostate of the system.

Let each of the atoms have an allowed range of displacements $\Delta(r_i)$ where i is atom number, ri where i is the number of the atom, ri is its distance from the cluster center. Let a certain number of modeling steps be performed using the Metropolis algorithm (1), and the displacement of each atom is chosen randomly in the range $\Delta(r_i)$. Moreover, in order for the estimate of the number of microstates to be correct, at each step the condition must be met that only a small fraction of nerr attempts to transition to a new microstate of the cluster, carried out according to algorithm (1), are unsuccessful. Otherwise, the range of allowed displacements must be narrowed. This guarantees that the newly obtained macrostate is realized by randomly chosen microstates in the characteristic range $\Delta(r_i)$.

Thus, the modified Metropolis algorithm can be presented by the following equation set:

$$\begin{cases} p(\mathrm{E}_1 \to \mathrm{E}_2) \sim \mathrm{e}^{(\mathrm{E}_1-\mathrm{E}_2)/\mathrm{T}} & (2) \\ (\boldsymbol{r}_i' - \boldsymbol{r}_i)_k = Rand\left(-\frac{\Delta(r_i)}{2}, \frac{\Delta(r_i)}{2}\right), i = 1,2,\ldots Ncl \;\; , k = 1,2.3 & (3) \\ \left\langle \mathrm{p}(\mathrm{E}_1 \to \mathrm{E}_2) \right\rangle > 1 - n_{err}, \quad n_{err} & (4) \end{cases}$$

Here *Rand* function each time produces a new random number in the range determined by its arguments, $\mathrm{p}(\mathrm{E}_1 \to \mathrm{E}_2)$ — the probability of transition to a new microstate averaged over a large number (in this model 100) attempts. It should be noted that criterion (4) determines the form of the function $\Delta(r)$ and is essentially the only "fitting" parameter of the model. The independence of the result from n_{err} criterion (4) can be easily verified.

1b. Determining the entropy of the system.

Let, as a result of algorithm (2-4), a new macrostate of the cluster is obtained, with new macroscopic parameters, such as the radial density distribution and the degree of ordering of atoms as a function of the distance from the cluster center, as well as the internal energy of the cluster *E*. Then the number of microstates n, characterizing the new macrostate can be evaluate how

$$n = \prod_i \Delta(r_i) \qquad (5),$$

where the product is taken over all atoms of the cluster.

Accordingly, the entropy and free energy of the cluster can be estimated as

$$S = \sum_i \ln(\Delta(r_i)) \qquad (6)$$

$$F = E - T\sum_i \ln(\Delta(r_i)) \quad (7)$$

where the summation is performed over all atoms. Entropy, in turn, will make it possible to obtain the size and temperature dependences of the heat capacity and heat of melting of the cluster.

1c. Determining displacement function $\Delta(r)$

Of all the possible functions $\Delta(r)$ characterizing the new macroscopic state of the system in formula (1), one should choose the one that ensures the minimization of free energy. Without taking into account the surface, $\Delta(r)$ would be a constant, which can be taken as the zero approximation: $\Delta(r) =$ const. In order to account for the influence of the surface, cluster atoms, starting from the surface and moving towards the center, are given small additions to $\Delta(r)$, and the probability of transition to a new microstate is determined by formulas (2-4). The maximum of additives that satisfy criterion (4) is determined, and preference is given to small ranges of displacements for the maximum number of atoms, that is, the obtained function $\Delta(r)$ will be as "flat" as possible. Then the resulting conformation is taken as the initial one, and the process is repeated iteratively until the minimum free energy of the cluster is reached (7).

The implementation of such an algorithm is described in detail in Section 2. It should be noted that such an algorithm corresponds to the melting process in real atomic clusters, where melting begins from the outer shells.

In the case when there are 2 or more free energy minima, corresponding to macrostates with different degrees of cluster ordering, the probability of finding a cluster in each of these minima

$$P \sim \exp(-F / T) \quad (8)$$

where F is the free energy of the system, determined by formula (7)

In the next section, practical implementation of the modified Metropolis algorithm is described(2-4).

2.Model and Method.

The purpose of this work is to study the probability of a cluster transitioning from a solid state to a liquid one as a function of temperature and size.

As objects for modeling were chosen Ar clusters with number of atoms N=2744. Rare gas clusters are one of the simplest systems, in particular three-particle interactions can be neglected in this case [15]. 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: σ=3.405 Å, D=0.01032 eV. Here D is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero.

Moreover, the present simulation uses a discrete set of 100 possible ranges of random displacements with an upper bound on the range

$$d_k = k \cdot \frac{3r_{min}}{1000}, k = 1,\ldots,100\,. \quad (9)$$

Where $r_{\min}$ is the equilibrium distance between atoms. Within the k-th range, the displacement of each atom along each coordinate is chosen randomly in the range from $-d_k/2$ to $d_k/2$. Minimal range d1 is selected from considerations of the finite transition probability at which each cluster atom is given a minimum displacement from 0 to d_1:

$$e^{(E(r_{min}+d_1)-E(r_{min}))/T} \sim 1$$

The maximum range of displacements is chosen based on the fact that the transition of a substance from a solid to a liquid state occurs when fluctuations in the interatomic state reach 15%.

The use of larger displacement ranges expands the phase volume, however, the energy factor and time limitation will not allow a significant increase in the range of random displacements for all atoms simultaneously. It is logical to start expanding the range of displacements from surface atoms, where the binding energy is lower.

The algorithm is carried out in the following steps:

1. The cluster energy is minimized by the traditional Metropolis algorithm (1) at zero temperature. Then the initial state of the cluster is obtained by random small displacements of the cluster from 0.0001 rmin to 0.05 rmin for different initial conformations. 10 initial conformations are prepared for each such displace-

ment. Depending on the magnitude of these initial displacements, the evolution of the cluster can end up in either a solid or liquid state.

2. Then, all atoms in the cluster are given random displacements in the same range from $-d_1/2$ to $d_1/2$. One modeling step is made in accordance with algorithm (2-4), nerr in (4) is selected equal to 10%. If criterion (4) is met, the new conformation is taken as the original one, then one moves on to the next range of displacements from the list (9). Otherwise, one goes to point 3.

3. Let the kth range of displacements from the list (9) be reached in step 2. In the cluster conformation obtained in step 2, n random atoms of the cluster, starting with n=1, then n=2,3,..., are given a shift within k+1-th range and the modeling step is performed according to algorithm (2-4). First, atoms are selected randomly, but within the surface layer at a depth rmin, then, if n exceeds the number of atoms in the surface layer, algorithm moves on to the next layers. As soon as criterion (4) is no longer met, the conformation obtained at the previous step is taken as the initial one and modeling step described above in item 3, is repeated for the next range of displacements from the list (9).

4. Execution of the algorithm continues as long as criterion (4) is satisfied. Then the next iteration is carried out, that is, actions starting from item (2). This is necessary so that the inner shells can adapt to the disordering of the outer shells and actually simulates the melting process in real clusters.

5. Iterations in item (4) stop when the free energy of the cluster reaches a minimum. It is checked that the free energy minimum (7), local or global, has actually been achieved, that is, it does not change with small random displacements of atoms.

Since the displacement ranges change with a fairly small step compared to the equilibrium interatomic distance rmin, the radial dependence of the magnitude of "fluctuations" of atoms $\Delta(r)$ on the distance to the cluster center r turns out to be almost continuous.

It should be emphasized that the function $\Delta(r)$ itself evolves as it passes through the steps of the method, as illustrated in Fig. 1.

There are 3 possible simulation outcomes depending on the choice of the initial cluster conformation described in item 1: 1. The cluster remains completely ordered. 2. The cluster is completely disordered. 3. The outer shells are partially disordered.

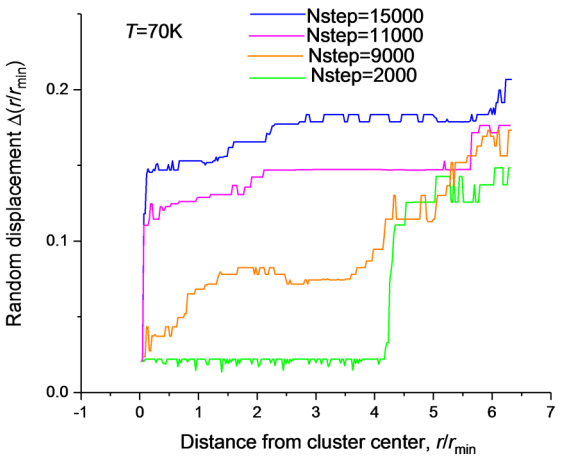

Fig.1. Displacement range $\Delta(r)$ as function of distance from the cluster center as function of number of Monte-Carlo steps. The "time-sequence" of the plots is shown in legend.

3. Results and discussion.

To illustrate the method, a simulation of an argon cluster of 2744 atoms was carried out in the range of 20-80K.

During the modeling process, two types free energy minima were found for all temperatures, which can be attributed to the liquid and solid states of the cluster. One of these minima is global and determines the phase state of the cluster at a given temperature.

Figure 2 shows the final (equilibrium) dependences $\Delta(r)$ for the liquid and solid phase states of the cluster at different temperatures. As expected, the closer the atom is to the cluster surface, the greater is its displacement range. As temperature lowers, solid and liquid states become indiscernible. Thus, at a temperature T=35K, $\Delta(r)$ in the liquid state differs slightly from that of the solid, and only for large distances from the center.

One can also see from Fig. 2 that melting begins from the outer shells of the cluster and in the liquid state, fluctuations of atoms increase as they approach the surface.

In Fig.3. The dependence of the free energy of the cluster, calculated using formula (2) on the number of steps of the Monte Carlo method, is shown. It can be seen that with a sufficiently large number of steps, the free energy stabilizes and the system reaches a minimum free energy (global or local).

From Figure 3 it can be understood, which phase state is predominant for a given temperature. To clarify the results, the probability P of the cluster transition from solid to the liquid

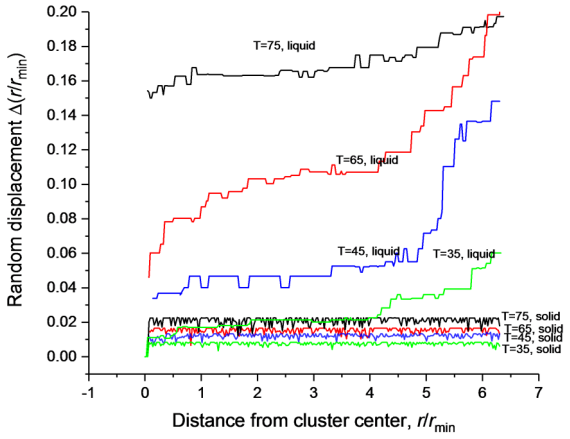

Fig.2. Displacement range $\Delta(r)$as function of distance from the cluster center for solid and liquid states at various temperatures.

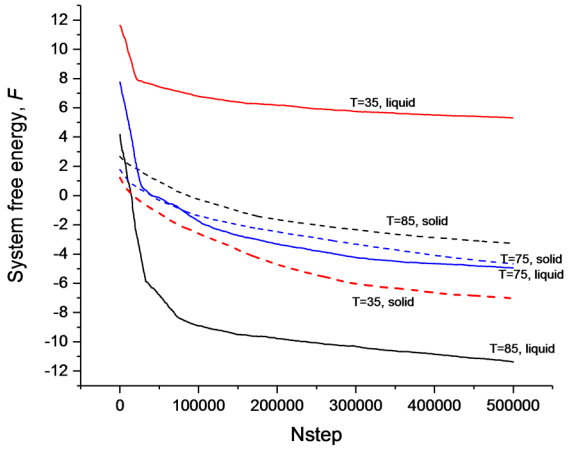

Fig.3. Free energy F for solid and liquid states of the cluster at various temperatures.

state, calculated using Eq. (8), is presented in Table (1). The table shows that the phase transition of an argon cluster of 2744 atoms occurs abruptly at a temperature of about 75 K (for a macroscopic body the melting point is 84 K). The liquid and solid states practically do not coexist, in contrast to clusters of significantly smaller sizes where, as is known from the literature [16,18], when the phase transition is blurred.

It can also be seen that proposed in the present work modelling method provides monotonous decreas of free energy for all studied initial conformations and provides reaching of stable conformation during feasible time (about $5{\cdot}10^6$ Monte Carlo steps for 2744 atoms cluster size).

4. Conclusions

This work proposes a modification of the Monte Carlo method for atomic clusters in mesoscopic range. The proposed modification takes into account the peculiarities of phase transitions in atomic clusters in which, as is known, melting begins from the outer shells and proceeds to the inner ones. At the same time, the randomness of the choice of atomic displacements at each step of the method is preserved, and the range of displacements is the same for centrally symmetric atoms, that is, the choice from all possible macrostates is made in favor to centrally symmetric ones. This is consistent with existing knowledge about the physics of clusters. We can say that from all possible macrostates we select those where islands of a new phase begin to form on the surface of the cluster.

Table 1. Ratio of probabilities to find cluster in liquid or solid state.

T,K	Ln(Pliquid/Psolid)
25	-75285
65	-36602
70	-2540
75	26
80	532

The proposed algorithm has the following advantages.

1. It takes into account the centrally symmetric structure of the cluster, allowing one to simulate surface effects (the evolution of cluster shells) and characterize phase states corresponding to different degrees of disorder.

2. Of all possible random conformations, it selects only a small part, that costitute spherically simmetrical 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, providing 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.

5. Proposed in the present work modelling method provides monotonous decreas of free energy for all studied initial conformations and

provides reaching of stable conformation during feasible time

Thus, new approach to computer modelling of atomic clusters in mesoscopic range is developed in the present work, that allows to obtain stable conformations of atomic clusters during feasible modelling time. This allows to study the dependendense of cluster thermodynamics and conformational properties on cluster size in mesoscopic size range.

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