

# NUMERICAL SIMULATIONS OF THE PHASE TRANSITIONS IN CLUSTERS

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## Abstract

We have studied the phase transitions in atomic clusters by molecular dynamics simulation, assuming Lennard-Jones interatomic pair potential. Calculations are performed by DAP parallel computer. The results are analyzed by simulating their orientational distribution plots (dot-plot), and neutron diffraction patterns. It is shown that all the main features of the bulk phase transitions are essentially exhibited by such a small sample. It is seen that by cooling the sample below the melting temperature, the atoms establish an icosahedral quasi-crystal structure with five fold symmetry. The Mackay predicted magic numbers are confirmed by our simulation. Finally, we conclude that in cooling the sample below the melting point, nucleation initiates from the central region and then propagates toward the surface.

## Introduction

In recent years, considerable interest, both theoretical and experimental, has been devoted to the study of atomic and molecular clusters [1,2,3]. One of the primary motivations for the study of small clusters is the desire to bridge the conceptual gap separating the common description of single molecules, or few-molecule systems, on the one side, and bulk materials on the other. Being larger than ordinary molecules but too small to be dealt with as bulk objects, clusters occupy a poorly understood area which is not well suited for the traditional experimental techniques [4].

A question which has particular interest is the nature of phase transition in rare gas clusters. Numerous studies have indicated that clusters undergo a transition from solid-like to liquid-like behavior and vice versa at temperatures well below the melting and freezing point of

bulk systems [5-9]. An understanding of nucleation in small systems is also very desirable.

Our purpose is to study the phase transition in clusters from a microscopic point of view with special stress on nucleation by molecular dynamics simulation. To the end, we shall consider the specific example of the Krypton cluster. Our aim is to answer such questions as: To what extent are the main features of the phase transitions observed in bulk systems also exhibited in small clusters? In which area and at what temperature do the first signs of nucleation appear? Is the order of the atomic distribution after nucleation similar to its initial symmetry before melting?

## Computational Method

As the most time-consuming part of a molecular dynamics calculation is the computation of the forces acting on the atoms, the problem is ideally suitable for using massively parallel computers. Parallel computers are machines in which thousands of simple processors

**Keywords:** Cluster; Computer simulation; Phase transition

work together on the same problem, speeding up the work almost in proportion to the number of processors. The computer used here is the DAP-600 consisting of 4096 single-bit processors connected in a square grid [10]. The interatomic potential  $V(r)$  was modelled by using a Lennard-Jones pair potential:

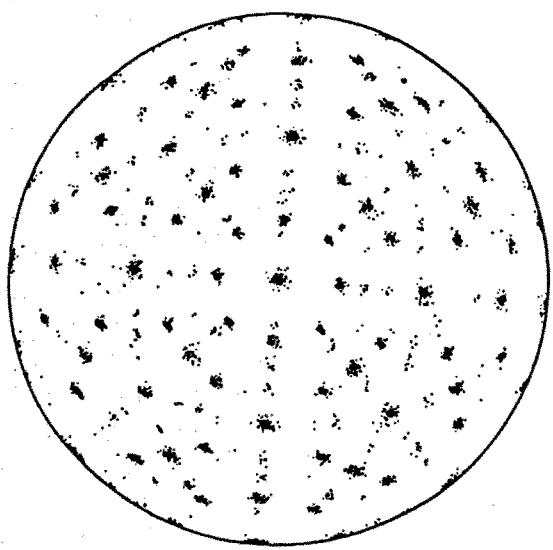
$$V(r) = -A/r^6 + B/r^{12}$$

with the two parameters chosen for Krypton from literature as follows:

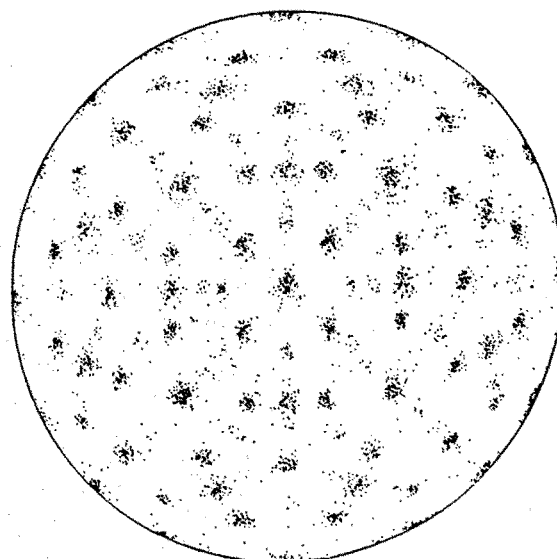
$$A = 2937 \text{ Kcal/mole} \cdot \text{\AA}^6$$
$$B = 6393392 \text{ Kcal/mole} \cdot \text{\AA}^{-12}$$

The first derivative of the potential gives the interatomic force interaction and Newton's equations of motion are solved using Beeman's algorithm [11], with a time step of 0.01 ps.

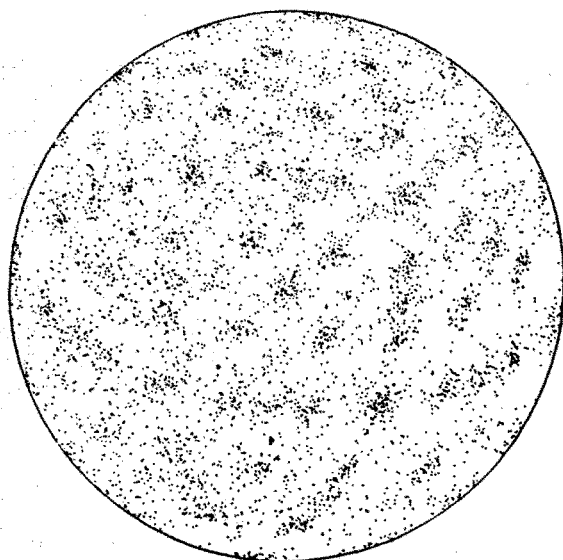
The simulation was performed with three different size clusters containing 64, 128, and 256 atoms. For each size, two clusters were initially prepared. One of them was made in a cubic shape with the atoms distributed in



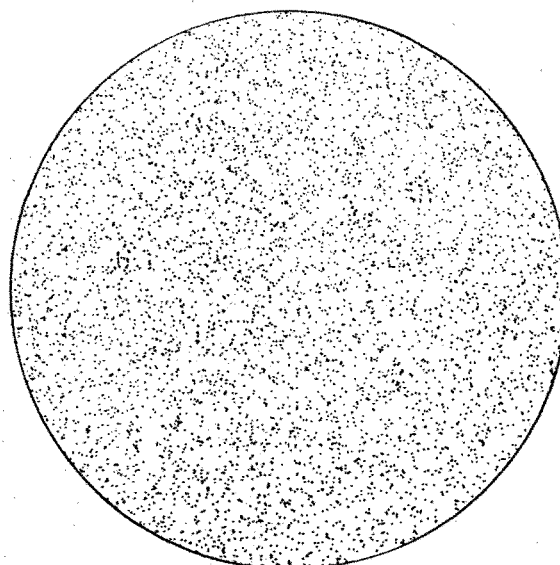
1a



1b



1c



1d

Figure 1. Dot-plots at different temperatures:  $T_a = 15\text{K}$ ,  $T_b = 35\text{K}$ ,  $T_c = 65\text{K}$ , and  $T_d = 80\text{K}$

fcc configuration. The second sample, which was intended to be similar to a droplet, was made by carving out a spherical cluster containing the required number of atoms at random positions. The atomic velocities were initially chosen at random and with values that the sample has at a temperature of 0.01K. Then, by rescaling the atomic velocities, it was heated in steps of 5K to above the melting point. The atomic velocities and displacements at each time step were constrained to give a net zero linear and angular momentum for the cluster so that the center of mass remains at the origin. The sample was then slowly cooled down to lower temperatures to investigate the nucleation process.

Finally, an explanation should be given regarding the reliability of the so-called "temperature" of the cluster: The temperature of an atomic ensemble containing  $N$  particles is determined using Boltzmann definition:

$$\langle E_{tran} \rangle = \left\langle \sum_{i=1}^N m_i (v_i)^2 / 2N \right\rangle = 3T / 2k_B$$

where  $\langle E_{tran} \rangle$  is the average translational kinetic energy of a particle,  $k_B$  the Boltzmann constant and  $T$  is considered as the temperature of the ensemble. Changing the temperature from  $T_1$  to  $T_2$  is done by rescaling all components of translational velocities by the factor  $\sqrt{(T_2 / T_1)}$ . The point that should be considered is that because of the small sample size, which is not really large enough for a statistically correct Maxwell-Boltzmann distribution of particle energies to be attained, comparing temperatures calculated in simulations to experimental values is rarely strictly valid. Strictly speaking, the use of a "temperature" in a simulation is only a method of expressing the average amount of kinetic energy in the ensemble. However, since we are concerned with the study of phase transitions induced by heating or cooling, the use of a temperature when presenting results is intuitively correct.

### Results and Discussion

In order to show the orientational ordering of the atoms, we have used the dot-plot representation [12] which is constructed as follows: First, every atom is connected by vectors to all other atoms. Then the unit vector in the direction from the position of atom  $i$  at  $(x_i, y_i, z_i)$  to the position of a neighboring atom  $j$  at  $(x_j, y_j, z_j)$  with radial separation  $R_{ij}$ , is calculated:

$$(x_{ij}, y_{ij}, z_{ij}) = (x_j - x_i, y_j - y_i, z_j - z_i) / R_{ij}$$

If this is done for all atoms and their neighbors, then what we have is a set of points,  $X_{ij}(x_{ij}, y_{ij}, z_{ij})$ , all of which

lie on the surface of a unit sphere. To represent these points as a two dimensional distribution function we use the procedure called "equal area projection". To project the three dimensional distributed point  $X_{ij}$  to point  $X_p(x_p, y_p)$  in the  $xy$  plane, we define  $r_1$  as the chord from the "north pole" of the unit sphere at  $(0,0,1)$  to  $X_{ij}$

$$r_1 = [(x_{ij})^2 + (y_{ij})^2 + (1-z_{ij})^2]^{0.5} = [2(1-z_{ij})]^{0.5}$$

and  $r_2$  as the "perpendicular" distance of  $X_{ij}$  from the  $z$ -axis:

$$r_2 = [(x_{ij})^2 + (y_{ij})^2]^{0.5}$$

The equal area projection of  $X_{ij}$  is defined as:

$$(x_p, y_p) = (x_{ij}, y_{ij}) * (r_1 / r_2)$$

The results for the  $N = 256$  cluster at different temperatures are shown in Figures 1a to 1d. Following the development of the dot-plot as a function of temperature it is seen that although the atoms are experiencing increased thermal motion, the order is persistent up to about 80K. At this temperature, the orientational ordering seems to have completely disappeared; hence it can be considered as the solid-liquid transition temperature. Similar plots (not presented) for the 64 and 128 atom clusters indicate the melting transition at about 55 and 65K respectively; while the corresponding experimental value for a truly macroscopic sample is about 120K. It is believed that the difference in the surface to volume ratio leads to the

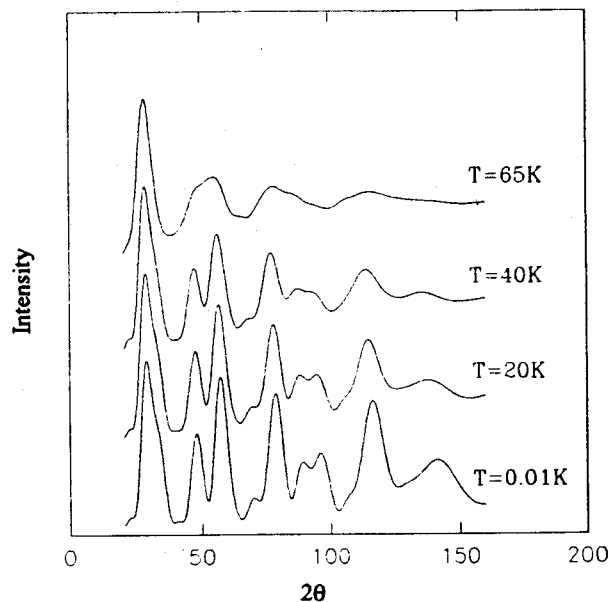


Figure 2. Diffraction patterns at different temperatures corresponding to the cluster with  $N = 128$

depression of the melting temperature in clusters as predicted by the Gibbs-Thompson relation [13].

In order to be comparable with experimental results, we have calculated the neutron diffraction pattern of the clusters at different temperatures as a function of Bragg angle. Radial distribution function (RDF) has been used to obtain the structure factor following the procedure outlined by Bartell [4]. As the diffraction results for the three different size clusters are essentially similar, we only show as a prototype the results of 128 cluster. In Figure 2, the diffraction patterns of a cluster with 128 atoms initially distributed in fcc structure are shown at different temperatures. The range of the total scattering angle  $2\theta$  is from 10 to 160 degrees. The neutron wavelength is assumed to be 1.6. It is clearly seen that although the low temperature patterns contain sharp peaks which indicate regular atomic arrangement, these peaks become more diffusive as the temperature is increased. This, of course, is characteristic behavior for liquids. Because the sharpness of the first peak, which persists even at high temperatures, arises from large interatomic separation, it contains information about the cluster size [4].

In order to analyze the nucleation, we require all simulations to begin from an initial ensemble which is liquid-like, i.e. a random distribution of atoms so that there is no translational order. This state was achieved by first heating the sample to above the melting point, after which we gradually began to cool it down to 5K. The dot-plot representation of the supercooled cluster with 64 atoms at 5K is shown in Figure 3. It is clearly seen that by

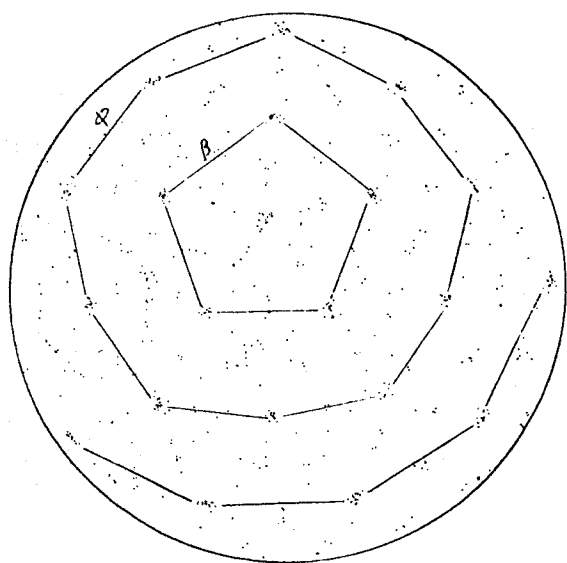


Figure 3. Dot-plot representation of the supercooled cluster with 64 atoms at 5K

cooling the sample to below the melting point, the atoms will redistribute on an icosahedral quasi-crystal structure with five-fold symmetry. Similar behavior was observed for 128 and 256 clusters. Hannes *et al.* [14] have simulated the cooling of Lennard-Jones fluids from liquid phase using periodic boundary conditions. They report an

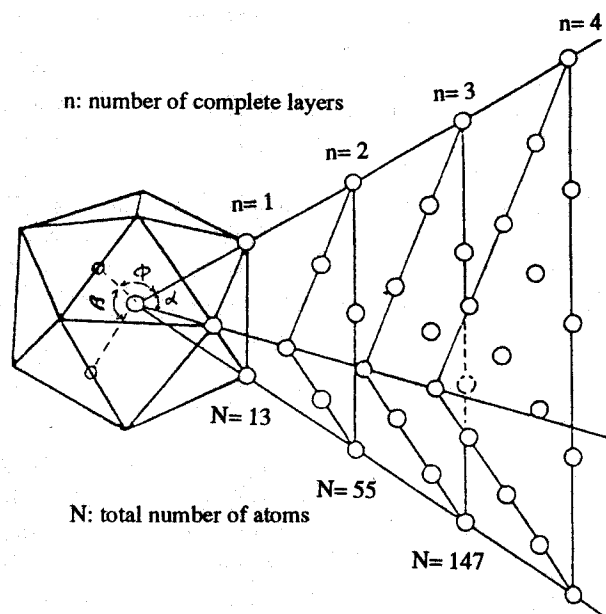


Figure 4. Successive icosahedral layers based on Mackay prediction;  $n$  is the layer index and  $N$  is the total number of atoms

icosahedral ordering as the liquid is supercooled to below the freezing temperature. It is interesting that in our simulation, which has a different boundary condition, similar behavior is observed. Additionally, Qi *et al.* [15], via performing molecular dynamics simulations for metallic liquids using an effective pair potential obtained from the generalized nonlocal pseudopotential theory, have observed an icosahedral order in the supercooled liquid. Thus, it can be concluded that the tendency for icosahedral structure in small supercooled clusters is a general trend independent of boundary conditions and even of the details of mutual interatomic interactions.

In 1962, Mackay [16] showed that clusters containing certain numbers of identical spherical atoms may form a family of icosahedral structures. In his arrangement, the atoms are located in successive icosahedral layers as shown in Figure 4. It is known that the layer of index  $n$  contains  $(10n^2+2)$  atoms [17], thus a sequence of well-known "magic" numbers for the total number of atoms  $N$  corresponding to a multilayer icosahedral with complete outer layer is found, namely 13-55-147-... . In order to compare our results with the Mackay predictions, we

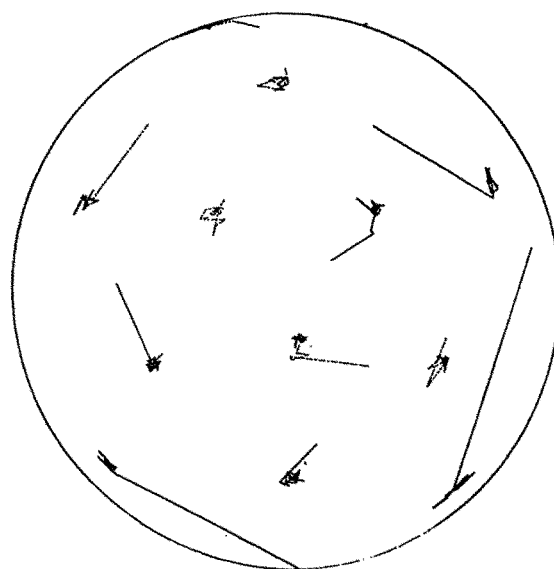
**Table I.** Our calculated results for the icosahedral characteristic angles (as shown in Fig. 4) compared with the ideal values

	$\alpha$	$\beta$	$\phi$
Our results	63°	35°	32°
Ideal values	63°26'	34°20'	31°43'

have shown the atomic distributions for the first two layers of our supercooled cluster in Figures 5a and 5b containing, respectively, 13 and 55 atoms. The coincidence with Mackay icosahedral is excellent. Finally, we calculated the three characteristic angles  $\alpha$ ,  $\beta$  and  $\phi$ , as shown in Figure 4, using our dot-plot representation. The results are compared with the values for an ideal icosahedral in Table I; the agreement being excellent.

It is interesting to find out the temperature at which the first signs of nucleation appear. This is done in Figure 6, where the atomic displacements in dot-plot representation for the 64-atom cluster are shown from 45K to below 30K in steps of 2K for the 13 central atoms. The substantial value obtained for the first step compared to the others clearly indicates that nucleation starts at around 43-45K which is lower than the melting temperature for the same sample.

In order to find the area in which the first signs of nucleation appear, the experiment was repeated for 13 noncentral atoms. It was observed that the nucleation temperature drops to around 41-43K. Hence, we conclude that in cooling, the cluster nucleation initiates from the

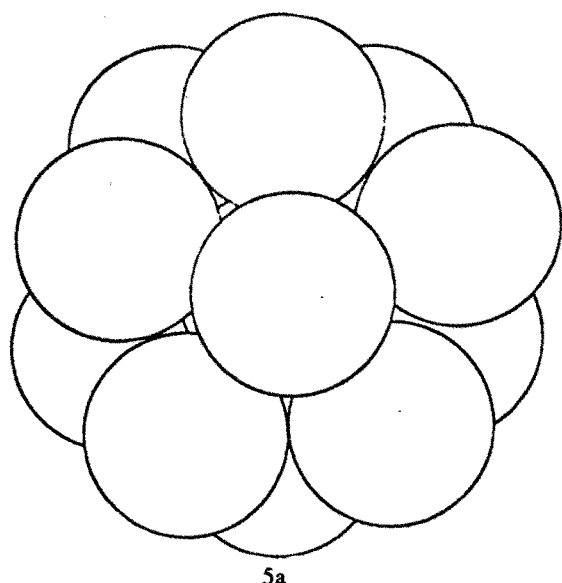


**Figure 6.** Atomic displacements in dot-plot representation for the 13 central atoms in steps of 2K ( $N = 64$ )

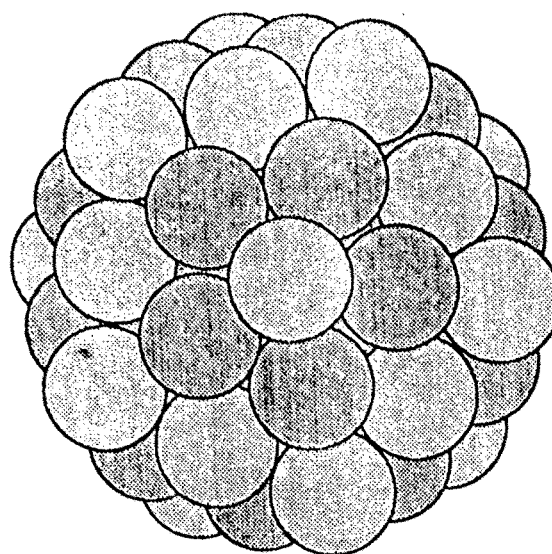
inner regions and then propagates toward the surface. This is confirmed by Fuchs *et al.* [12] who, in studying the plastic to triclinic phase transition in clusters of SF<sub>6</sub>, have shown that the growth of the crystallization starts from the central region of the sample.

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5a



5b

**Figure 5.** (a) The atomic distribution for the first layer of our supercooled cluster (13 central atoms); (b) The atomic distribution for the second layer of our supercooled cluster (55 central atoms)

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