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1997 J. Phys.: Condens. Matter 9 4041

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# Molecular dynamics simulation of crystallization of liquid copper clusters

S Valkealahti and M Manninen

Department of Physics, University of Jyväskylä, PO Box 35, SF-40351 Jyväskylä, Finland

Received 6 September 1996, in final form 21 November 1996

**Abstract.** Crystallization of liquid copper clusters of 13 to 4033 atoms has been studied using the effective-medium theory and molecular dynamics simulation methods. Small clusters with 13, 55, and 147 atoms are observed to crystallize directly to icosahedral structure, which is the most stable structure for copper clusters with less than 2000 atoms. Larger clusters crystallize to twinned fcc structures having typically three to five grains of fcc structure but no regular geometry. The solidification transition of a cluster is a fast internal process and is independent of external conditions. Regardless of the cluster size, the time taken to achieve crystallization to a twinned structure was less than 100 ps, and only the core of the cluster crystallizes during the transition. One third of the atoms, mainly on the surface area, remain liquid, but no reordering due to diffusion of the crystallized core was observed after the transition on a timescale of several nanoseconds.

## 1. Introduction

Atomic clusters are grown in several different physical conditions, and the actual growing process is usually not known in detail. In a typical cluster beam experiment, the clusters are formed in the gas phase of atoms evaporated from a liquid or solid using heat, laser ablation, or ion bombardment [1]. Depending on the experimental conditions of the source, for example on the temperature and pressure of the carrier gas, the growing process can result in different cluster properties. The clusters can be liquid or solid and exhibiting electronic or geometric magic abundances, respectively [2]. The growing process can involve atom-by-atom adsorption or coagulation of clusters together. Certainly many of the basic principles involved are known, but what the detailed mechanisms are which produce different geometries, e.g. icosahedral [2, 3], decahedral [4] or octahedral [5, 6] clusters, and in what conditions the clusters would end up as Wulff polyhedra [7, 8], which is the macroscopic ground-state geometry, are not well known.

In experiments, the major difficulty in determining the geometry of a free cluster is the small size of the object. Diffraction experiments, which give direct information on the crystal structure, have only been made for a wide size distribution [4]. Clusters can be collected on a substrate surface, but the interaction with the substrate can change the geometry. It is thus very difficult to monitor small clusters directly by means of conventional materials science techniques. Therefore, most of the present experimental information on cluster growth and geometry comes from indirect measurements of the mass spectra.

Theoretically, ground-state geometries of large clusters have been studied extensively using several different interatomic interactions [9], and dynamical properties like melting [10, 11] and cluster collisions [12] have been studied by means of molecular dynamics

simulations. Also shape oscillations of small clusters in thermal equilibrium have been demonstrated in simulations [13], and clusters of the same size have been observed to have two different crystal structures [4]. Furthermore, theoretical considerations on minimum energies and experimental findings have shown that, for example, small noble-gas clusters [14, 15] and copper clusters [4, 16] are icosahedra, large clusters have polyhedral fcc structures, and medium-size clusters have some twinned, perhaps decahedral, structure.

Whether the cluster is in a liquid or in a solid phase during the growth can play an important role in the formation of the final structure. In the beginning of the growing process, clusters with only few atoms are expected to be liquid and, depending on the external conditions, they will grow as a liquid drop or fluctuate between solid and liquid phases up to a certain size. The structure after the last solidification depends on the cluster size, and will certainly influence the following growth. We have studied the solidification of copper clusters with 13 to 4033 atoms to understand better the dynamics of the crystallization transition, how it depends on the cluster size, what the crystal structure is as a function of cluster size, and how it influences the growth.

## 2. Simulations

We have used the molecular dynamics simulation method and the effective-medium theory to study the solidification of liquid copper clusters. Both of these are well established and documented in the literature, and we describe them only briefly. A general survey of the simulation set-up is given in our earlier work on the melting of copper clusters [10]. Briefly, the time evolution of the atoms is obtained from the velocity form of the Verlet algorithm [17], and forces between atoms are determined by the effective-medium theory extended beyond the nearest-neighbour interactions by Häkkinen and Manninen [18] from the original theory by Jacobsen *et al* [19].

Basically two kinds of simulation are performed. In both, a cluster is first heated to a temperature well above the melting temperature of the cluster and is kept at the high temperature for some time to ensure the existence of a disordered liquid phase. The existence of a fully liquid phase is confirmed by conventional methods, i.e. methods based on root mean square displacements, radial distribution functions, and snapshots of the cluster. Then the liquid cluster is slowly cooled down for several nanoseconds, which is the timescale feasible for simulations.

The first cooling method, which is perhaps more realistic as regards real solidification of clusters, can be called a microcanonical ensemble calculation. In this method the velocities of all of the atoms are decreased very slowly by scaling them with a constant factor at each time-step. This corresponds quite well to the experimental situation, where clusters are cooled down via collisions with atoms of a surrounding gas. Scaling the velocities of atoms is done so slowly that during the solidification transition the simulation is in practice microcanonical, i.e. the total energy of the cluster is nearly constant during the short duration of the transition. This means that the potential energy released during the crystallization (latent heat) will increase the kinetic energy of the atoms and raise the temperature. The results presented in this paper are based on this kind of simulation. The second type of simulation is only used to give extra information on the crystallization process.

In the second method the temperature of the cluster was kept constant using a Nosé–Hoover thermostat [20] for canonical ensemble calculations, and the cluster was cooled down slowly by decreasing the reference temperature of the thermostat. In these simulations the extra heat delivered by the potential energy during the solidification transition was transferred to the heat bath via the thermostat. This means that the thermostat acts as a driving

force for all of the transitions, which is not necessarily the case in real transitions. However, these simulations provided a useful point of comparison for the more realistic simulations. For example, the change of the potential energy during the transition gives directly the heat of crystallization, to be compared with the heats of melting of known cluster structures.

The crystallization of copper clusters was analysed by means of total, potential, and kinetic energies as functions of time and temperature, root mean square displacements of atoms, and snapshots of clusters. These conventional analyses revealed the crystallization transition, its timescale, and average energetics, but gave very little information about the dynamics of the transition and of the final structure. Transition dynamics turned out to be difficult to monitor, and in several attempts [21], like calculation of local temperatures and corresponding variables, no useful method was found. The structure of a crystalline cluster is not straightforward to approach. However, the existence of an icosahedral structure can be revealed without doubt. Corner, edge, and facet atoms in the surface shell of an icosahedron have six, eight, and nine nearest neighbours, respectively. By using this information one can strip atoms from a cluster so that finally a complete icosahedron remains—if it exists—or all atoms are stripped. The stripped structure can be checked by comparing it with an ideal icosahedron.

The existence of a fcc order can be investigated via order parameters. Ordinary order parameters cannot be applied to clusters, because the position and direction of the possible lattice is unknown. Therefore, we have used an order parameter  $S$ , which is calculated with respect to the local order of each atom. We suppose that the possible order is fcc, and define the local order parameter as follows:

$$S = \left( \sum_i \sum_j \sum_k \sum_l \alpha(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l) \left\{ \sum_m \theta(\mathbf{r}_i, \mathbf{r}_m) e^{ik \cdot (\mathbf{r}_m - \mathbf{r}_i)} \right\} \right) \times \left( \sum_i \sum_j \sum_k \sum_l \alpha(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l) \sum_m \theta(\mathbf{r}_i, \mathbf{r}_m) \right)^{-1} \quad (1)$$

where  $\alpha(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l) = 1$  when the atoms  $i$ ,  $j$ ,  $k$ , and  $l$  are all nearest neighbours of each other, and 0 otherwise. The summations are over all bulk atoms, which we define as atoms with at least ten nearest neighbours. We have ignored surface atoms, because the surface layer relaxes considerably.  $k$  is the sum of primitive vectors of a reciprocal lattice corresponding to a direct lattice with primitive vectors  $\mathbf{r}_j - \mathbf{r}_i$ ,  $\mathbf{r}_k - \mathbf{r}_i$ , and  $\mathbf{r}_l - \mathbf{r}_i$ . The value of the order parameter is 1 for a perfect fcc lattice and 0 for an amorphous structure.

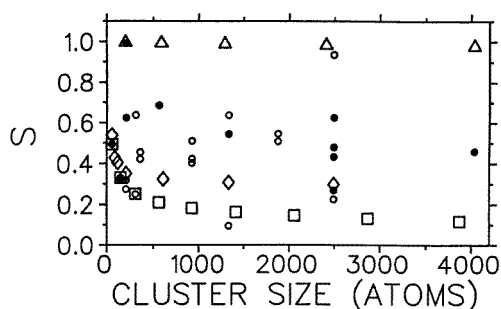
A cut-off function  $\theta(\mathbf{r}_i, \mathbf{r}_m)$  is used to control the range of the local order parameter, and is defined as

$$\theta(\mathbf{r}_i, \mathbf{r}_m) = \begin{cases} 1 & \text{if } |\mathbf{r}_m - \mathbf{r}_i| \leq \mathbf{R}_{cut} \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

where  $\mathbf{R}_{cut}$  is the cut-off distance. In large clusters the combined use of a small cut-off distance of the order of few lattice constants and a long distance (infinite) should reveal the average size of the grains and their order. However, we have studied clusters with only a few thousand atoms, and the cut-off distance is not a useful parameter. Therefore, all of the results presented in this paper are calculated using an infinite cut-off distance. The order parameter and the stripping of the clusters provide adequate information about the crystallized structures.

### 3. Results

In both the microcanonical and canonical simulations of crystallization, the cooling rate was varied between 1000 and 10 K ns<sup>-1</sup>. The dynamics of the crystallization was found to be independent of the cooling rate, and the final structure was also independent of the statistical ensemble used. Once the crystallization started, it proceeded quickly, and independently of external conditions. Small clusters with 13, 55, and 147 atoms crystallized to icosahedral structure, which is also the minimum-energy structure for them [16]. This is in agreement with recent molecular dynamics simulations [22] of the formation of small icosahedral Lennard-Jones clusters cooled down from liquid by direct evaporation of atoms. Small clusters, which do not have the number of atoms corresponding to closed-shell (magic) icosahedra, do not necessarily crystallize to the icosahedral structure, but crystallize to another twinned fcc structure. Also, larger clusters form twinned fcc structures, which usually contain from three to five grains of fcc structure. The number of grains seems to be independent of the cluster size.



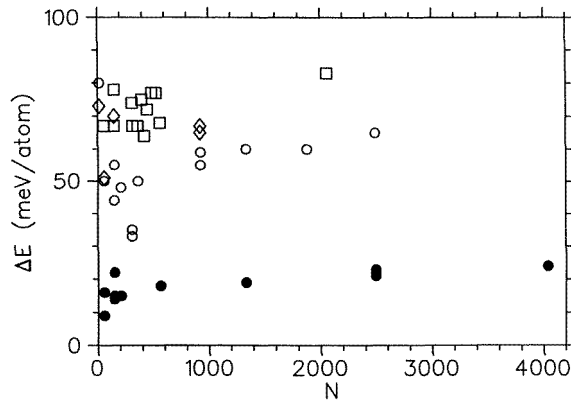
**Figure 1.** The order parameter as a function of the cluster size. Open triangles, diamonds, and squares correspond to relaxed ideal Wulff polyhedral, decahedral, and icosahedral clusters, respectively. Open circles correspond to clusters solidified using a Nosé–Hoover thermostat to decrease the temperature, and closed circles correspond to clusters cooled down by directly decreasing the velocities of all of the particles. All the order parameters are calculated using final configurations quenched to zero degrees Kelvin.

Figure 1 shows the order parameter  $S$  as a function of cluster size for clusters crystallized from liquid drops. For comparison, the order parameter has also been calculated for relaxed ideal Wulff polyhedra, decahedra, and icosahedra. The values of the order parameters of Wulff polyhedra are slightly smaller than one because of relaxation of surface layers. Icosahedra are combinations of twenty slightly tilted fcc tetrahedra, and for an ideal infinite icosahedron, the order parameter should approach the value  $1/20$ . A decahedron can be combined from five tilted fcc tetrahedra, and with increasing cluster size,  $S$  should approach the value  $1/5$ . In twinned structures the atomic order does not change sharply in the boundary of two neighbouring tetrahedra. Therefore, the order parameter is close to 0.5 for small twinned clusters, and decreases gradually with increasing cluster size, because the relative number of boundary atoms decreases with increasing cluster size.

There are no qualitative differences between the order parameters  $S$  of clusters cooled down by using microcanonical or canonical simulations. This means that the crystallization transition has to be a fast, internal process, which is independent of external conditions. The average value of  $S$  decreases only slightly with increasing cluster size, which suggests that the number of fcc grains in a solid cluster is on average constant. The value of  $S$

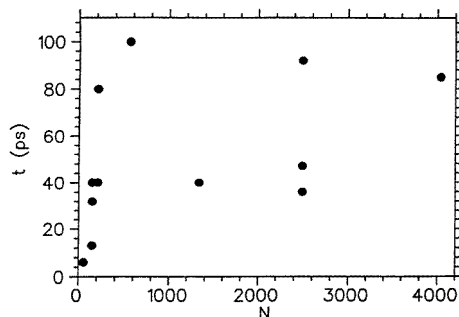
fluctuates considerably from one simulation to another, as can be seen, for example, from the crystallizations of 2491-atom clusters. These fluctuations describe the random nature of the crystallization process. The number of grains varies from one to over ten depending on how the crystallization happens to start. However, there are no indications that the clusters would 'prefer' any particular geometry, such as decahedra or Wulff polyhedra.

Only small clusters crystallize to the icosahedral structure, and in two cases the clusters happened to form a single-crystal fcc structure. The crystallization of small clusters directly to icosahedral structure is in agreement with our earlier work on melting of copper clusters [11], where small fcc clusters were observed to transform to icosahedral structure well below the melting temperature of the clusters.



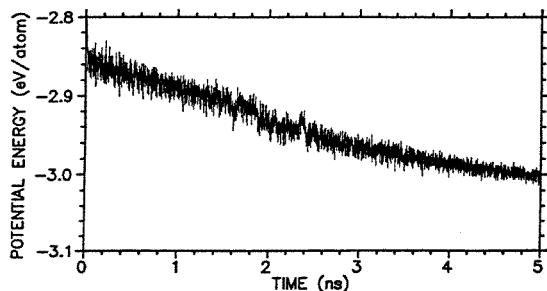
**Figure 2.** The heats of melting of icosahedral (squares) and decahedral (diamonds) clusters, the heat of crystallization of liquid clusters (open circles), and the decrease of the potential energy during the solidification transition of liquid clusters (closed circles). Heats of melting and heats of crystallization are the changes of total energies of clusters during the transitions when the clusters are heated or cooled down via the use of a Nosé–Hoover thermostat. The potential energy changes during the crystallization transitions are from simulations in which the temperature is decreased by gradually decreasing the velocities of the atoms.

The number of grains in the solid clusters seemed to be quite independent of the cluster size. The potential energy change per atom during the transition increases only slightly with increasing cluster size, as can be seen in figure 2. This is an expected result, because the average packing density of atoms in the surfaces of clusters is almost 9, which is close to the bulk value of 12. Also, relaxation of surface atoms increases their binding energies and, therefore, the surface-to-volume effect does not play an important role in crystallization energies. The potential energy change during the crystallization is roughly one third of the corresponding latent heat. This is in agreement with earlier simulations on the coexistence of solid and liquid phases in small Lennard-Jones clusters [23]. Argon clusters fluctuated spontaneously between solid- and liquid-like phases both in a microcanonical and in a canonical simulation, but the change in the potential energy in the microcanonical simulation was only one third of the one in the canonical simulation. When a free cluster suffers a crystallization transition, potential energy is released due to the increased order. The released potential energy is shared equally by the potential and kinetic energies. This means that the actual drop in the potential energy is only half of what it would be for constant temperature. However, one third of the heat of crystallization is missing. This indicates that roughly one third of the atoms are still in the liquid phase, or there are defects in the crystal.



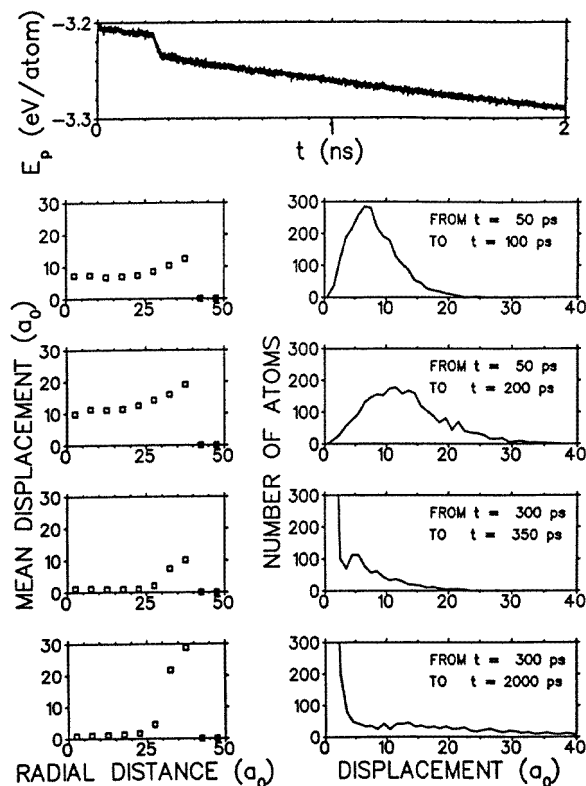
**Figure 3.** The liquid–solid transition time as a function of the cluster size in a microcanonical simulation.

One would expect the crystallization to start at a nucleation centre and proceed smoothly through the cluster. However, our results do not support this kind of idea. In the same way as the order parameter fluctuated considerably, but had no size dependence, the time of transition fluctuates, but also without any clear size dependence (figure 3). The exceptions are the small clusters, which transform to icosahedral structure faster than other clusters crystallize. It seems that the crystallization of clusters is a collective transition taking place almost simultaneously all over the cluster. Unfortunately, the transition is so fast and the thermal fluctuations of atoms are so large at the transition temperature that we were not able to monitor the dynamics of the transition in more detail.



**Figure 4.** The potential energy of a liquid 55-atom cluster cooled down gradually without the thermostat.

The smallest clusters fluctuated back and forth between solid and liquid phases within a small time (temperature) interval, as can be seen in figure 4. The first transition to a solid phase in a 55-atom cluster took place after  $t = 1.5$  ns, and at  $t = 2.4$  ns the solid cluster transformed to liquid phase for the last time and almost immediately back to the solid phase. This time interval corresponds to a temperature interval of about 100 K. These same phenomena have been demonstrated to take place in noble-gas clusters by several authors [23–28], and also in transition metal clusters [29]. It is obvious that with decreasing number of atoms in a cluster, a common melting and freezing temperature does not exist any more, and the transition temperatures are not defined accurately either. Instead, there is a temperature range within which solid and liquid clusters can coexist and transform dynamically between the two phases.

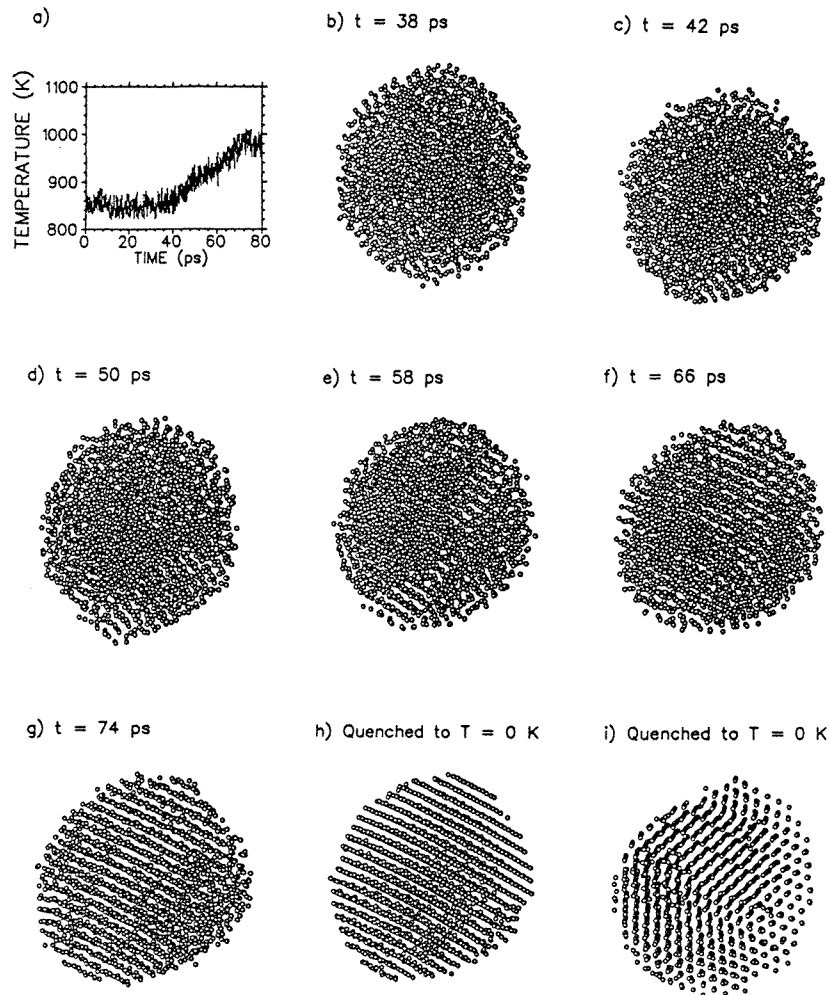


**Figure 5.** Crystallization of a liquid 2491-atom cluster. At the top is the potential energy as a function of time during the cooling down, and below are, side by side, the mean displacements of atoms as functions of the radial distance from the centre of mass of the cluster and the corresponding distributions of displacements of all of the atoms. The displacements of atoms from  $t = 50$  ps to  $t = 100$  and 200 ps correspond to clusters still in the liquid phase before the transition, and those from  $t = 300$  ps to  $t = 350$  and 2000 ps show how the atoms move after the transition.

The potential energy change during the crystallization transition in a microcanonical simulation was only one third of the corresponding heat of melting, indicating that only two thirds of atoms participated in the transition, and the rest stayed liquid. This can be confirmed by following the displacements of atoms before and after the transition as a function of radial distance from the mass centre of the cluster and the displacement distribution of all of the atoms. In figure 5 the mean displacement of atoms in a 2491-atom cluster is followed during the simulation before and after the transition. Before the transition, atoms all over the cluster are moving, and the displacement distribution is broad, corresponding to liquid clusters. After the transition, the mean displacement of atoms inside the cluster corresponds to thermal fluctuations, and atoms are not moving from their crystalline positions, whereas atoms on the surface area are moving as much as before. This is seen also in the displacement distribution, which has a huge peak close to the origin and a shallow tail due to moving surface atoms. This means that during the transition the core of the cluster crystallizes, and it stays solid after the transition. Surface atoms are liquid after the transition and solidify gradually with decreasing temperature of the cluster. For example, the temperature of a 2491-atom cluster after the crystallization transition was

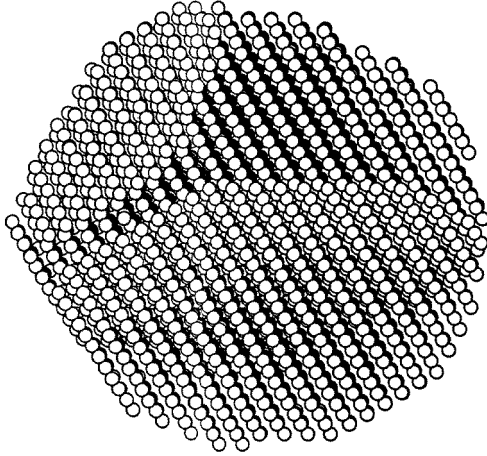


around 1000 K, and 700 to 800 atoms were mobile (liquid). After cooling down to 800 K, about 200 atoms were still mobile, and even at 600 K, about 30 atoms were mobile—the longest displacement being two lattice constants in 100 ps. All solidification transitions, except those to icosahedral structure, behaved in the same way. A similar kind of partial crystallization has been observed also in molecular dynamics studies of small rare-gas clusters [25].



**Figure 6.** The crystallization transition in a liquid 2491-atom cluster: (a) temperature as a function of time during the transition; (b)–(g) snapshots of the cluster during the transition; (h) a snapshot of the cluster quenched to 0 K at the end of the simulation, taken from the same direction as figures (b) to (g); and (i) a snapshot of the cluster quenched to 0 K, taken from another direction.

The dynamics of the transition was difficult to monitor, and all of our attempts gave barely qualitative results. Actually, snapshots of the clusters turned out to be most informative. Therefore, we only present, in figure 6, a series of snapshots for a 2491-atom cluster during the transition. By looking at figures 6(c) and 6(d), one can imagine that crystallization



**Figure 7.** A snapshot of the 4033-atom clusters crystallized from a liquid phase and finally quenched to 0 K.

starts from the surface, which is consistent with the fact that close-packed order often exists on liquid surfaces, but in the middle of the transition (figure 6(e)), order already appears through the whole cluster. After the transition (figure 6(g)) the whole cluster seems to be in a crystal structure, but actually the surface atoms are very mobile. They just stay most of the time in lattice sites, and jump from one to another. The cluster seems to solidify to a layered structure, but a snapshot taken from another direction reveals that the final structure is not a perfect fcc one. Atoms are organized in rows, but the rows are twisted with respect to each other. In a perfect fcc lattice, the atoms would be in parallel rows. In the clusters crystallized from the melt, the atomic rows have areas of different directions, as can be seen in figure 6(i) and in figure 7, which shows the final structure of a 4033-atom cluster.

#### 4. Summary

Microcanonical and canonical molecular dynamics simulations of the crystallization of liquid copper clusters with 13 to 4033 atoms have been performed using the effective-medium theory to describe the atomic interactions. Liquid–solid transitions have been analysed by conventional methods, by stripping the final clusters, and by calculating a local order parameter. Total, kinetic, and potential energy changes, transition times, final structures, and corresponding properties were quite straightforward to find, but we were not able to monitor the actual dynamics of the transition, because the short time of the process and the small number of atoms prevent an accurate determination of any order parameter.

The transition time and the final structure did not depend on the statistical ensemble used in the simulation. Once the crystallization started it proceeded independently of external conditions. Small clusters with 13, 55, and 147 atoms formed their minimum-energy structure, an icosahedron. Small clusters with other sizes and larger clusters crystallized to twinned fcc structures, which usually contained from three to five grains of fcc structure. The number of grains, transition time, potential energy change per atom, and crystallization dynamics seem to be independent of the cluster size. The number of fcc grains varied from one to over ten depending on how the solidification happened to start. However, there were

no indications that crystallization would 'prefer' any particular geometry, like decahedra or Wulff polyhedra, for any size range.

The potential energy change during a crystallization transition was roughly one third of the corresponding heat of melting. The potential energy released due to the increased order was shared by the potential and kinetic energies, which means that roughly one third of the atoms stayed liquid during the transition. The core of the cluster was solid after the transition, and the surface atoms were liquid.

The dynamical coexistence of liquid and solid clusters was observed in small closed-shell icosahedra in accordance with earlier results for small rare-gas and transition metal clusters. The width of the coexistence region was for a 55-atom cluster about 100 K.

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