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Structural properties of solid nuclei forming in Lennard–Jones clusters during simulated cooling

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ABSTRACT

Liquid Lennard–Jones clusters composed of $N = 923$ particles were frozen using Monte Carlo simulated cooling in order to analyse the process of nucleation of new phase. Among 100 final clusters obtained in independent simulations runs, 15 cases of creation of layered fcc/hcp structure were selected for detailed analysis. Formation of nuclei was carefully analysed to find their stability with respect to the number and composition of particles, geometric and structural properties as well as their position in the cluster. The analysis was carried out by extensive use of structural analysis, cluster detection procedure and visualisation. The investigated subcritical nuclei are very unstable regarding their size, shape, structure and composition. Larger nuclei are more stable keeping their layered structure, although migration of particles between the surfaces of solid nucleus and liquid cluster is large. Creation of nuclei occurs inside clusters, sometimes they overlap the cluster centre, but elongated or ramified nuclei tend to be contacted with cluster surface and grow toward the cluster centre.

1. Introduction

Nucleation is one of the less known processes in crystal growth from supercooled bulk liquid. Formation of nuclei of a new solid phase in homogeneous crystallisation is difficult to investigate experimentally mainly due to the probabilistic character of the process, the nanometre size of objects and the role of the surrounding liquid which, due to dominance of the number of atoms/molecules in the medium, determines signals in any possible experimental research.

Theoretical methods in the form of classical nucleation theory (CNT) are useful in modelling the homogenous nucleation process. It was postulated in the CNT that kinetic and energetic effects play a decisive role in the creation and growth of the nuclei. If randomly moving atoms form a temporary nucleus, its subsequent growth is possible only when more atoms are attached to it than those detached from it. When the nucleus size is smaller than the critical one, the probability of nucleus growth at every moment is lower than 0.5 due to an increase in the free energy of the system. After surpassing the critical size, which can occur in some attempts of nucleus formation, growth of the nucleus is privileged because it leads to a decrease in the free energy of the system. Free energy barrier for the formation of the critical nucleus determines the time necessary to form a stable seed of a crystal. Difficulty in the application of the CNT for quantitative predication of this nucleation time lag is mainly in calculation of the free energy barrier due to uncertain value of the interfacial tension of nanosized nuclei and unknown shape and internal structure of the nucleus [1,2]. For example, in recent paper Jungblut and Dellago [3] found that application of the CNT does not give accurately the free energy of the nuclei in undercooled Lennard–Jones (LJ) fluid, though qualitative results were correct.

Computer simulations were recently successfully applied to determine some structural properties of nuclei formed of relatively simple substances, where interatomic/intermolecular interactions can be described and used in effective computations. It was found in many systems composed of, for example, sodium atoms [4], fullerene molecules [5] or LJ particles [3,6,7] that the nucleus shape can be far from any regular form postulated by the CNT and also its internal structure can be different from that of the bulk crystals [3,6,7]. The main problem in simulations of bulk supercooled liquids is the necessity of using of unrealistically deep supercooling in the simulated system, because only in this situation one is able to observe the creation of a stable nucleus during reasonable computation time. Moreover, in order to mimic the real systems, the simulated system must be composed of thousands of atoms, which increases the computation time. The number of atoms should be much larger if the periodic boundary conditions are not applied in the computation model. The application of such conditions leads to a situation, where it is impossible to model a system characterised by a surface [8], though the liquid–vapour interface may play an important role in the homogenous nucleation.

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Simulations of freezing of liquid clusters of relatively large size give the possibility of investigating the role of the interface in the formation of a nucleus of the solid phase. Among a relatively small number of papers dedicated to nucleation in freezing clusters, papers reporting an important, if not a decisive, role of cluster surface dominate. Bartell et al. observed a strong tendency for the formation of a solid nucleus at or in the vicinity of the surface when they simulated clusters composed of SeF_6 molecules [8,9] or ions of salts like NaCl [8] or KI [10]. Later, in a quantitative analysis of nucleus site Bartell and Turner [11] found that nucleation frequently takes place in the interior of liquid clusters of SeF_6. Valkealahti and Manninen [12] observed crystallisation of a liquid copper cluster, composed of 4033 atoms, starting from the cluster surface. The present author [13] observed that unstable icosahedral units located near the surface of supercooled LJ cluster are able to induce solidification to regular polyicosahedral (r-PIC) structures. In the case of much larger systems, Tabazadeh et al. [14] found that ice nucleus formation at the air–liquid or oil–liquid interface can explain the results of many experiments with supercooled water microdroplets.

Nucleation occurring at the surface has not been explained satisfactorily until now. It is difficult to find reason why an ordered structure of the nucleus could be preferentially formed at or near the surface, where movement of atoms is the highest [15]. From an analysis of the freezing of KI clusters, Huang and Bartell [10] formulated earlier a similar opinion. A promising explanation was given by Tabazadeh et al. [14] who proposed a simple inequality condition, derived from a thermodynamics analysis, for surface tensions for three possible interfaces between liquid, solid and vapour. If this condition is satisfied, the work of nucleus formation at the surface is lower than that in the bulk, and, consequently, surface nucleation dominates over the nucleation in the bulk-volume. Another explanation based on kinetic effects was proposed by the author in the case of formation of a particular nucleus of the r-PIC structure in LJ clusters near the surface [13]. Since the region near a cluster surface is preferential for the existence of icosahedral units [15], they can induce frequent formation of r-PIC structure during the cooling of LJ clusters of various sizes [13].

It is possible that much more examples of nucleation events near the cluster surface are presented in the literature because it is easy to observe visually ordered small nucleus near the surface than that immersed in the cluster interior/core. Unstable nuclei formed inside entire LJ clusters are generally seen frequently before the phenomenon of cluster solidification (see Fig. 3c in paper [13]). This was also observed by Saika-Voivod et al. [16] in medium-sized LJ clusters, where they observed the formation of fcc tetrahedral subunits in the cluster core. The above observations suggest that it is necessary to develop some tools for a more precise and quantitative analysis of the formation of nuclei than a simple visual observation of ordered rows of atoms.

The aim of the present simulations is to describe quantitatively the formation of solid nucleus inside LJ clusters composed of 923 particles and answer the question where and how a stable nucleus of solid phase is formed in a solidifying LJ cluster. Detailed analysis is limited here to the formation of nuclei during freezing, leading to the layered structure [13] in the final cluster. One reason for this structure selection is the ease in the visual observation of layers, which enables one to uncover initial stage of their formation. Secondly, the author expects that this structure can be formed in the interior of these relatively large liquid clusters, since it was found that density layers around the centre of mass of the large LJ clusters of $N = 923$ are practically absent [15]. The aim of the analysis of geometric and structural properties of the nuclei will be realised by extensive use of structural analysis, cluster detection procedure and visualisation.

2. The method

Nucleation of the new solid phase in liquid LJ clusters occurs when initially liquid clusters are cooled sufficiently long in simulations with reasonable (not to fast) rate. Here, a sequence of canonical Monte Carlo (MC) simulations characterised by constant number of particles in the system $N_{sys} = 923$, volume of simulation cell V (with periodic boundary conditions), and system temperature T was applied during selected number of MC cycles. To obtain the freezing of clusters, the temperature was gradually decreased by an abrupt change after selected number of MC cycles. As was proved before [17], it is sufficient to use 200,000 MC cycles after each change of the temperature by $\Delta T^* = 0.01$ in the temperatures range $\langle 0.43; 0.49\rangle$ near the freezing temperature at $T_f^* = 0.45$ [17] in order to effectively solidify the cluster (asterisk denotes usage of reduced LJ units when giving value of a variable). Below $T^* = 0.43$, all simulated clusters are already solid; therefore faster cooling is applied using $\Delta T^* = 0.05$ to reach finally $T^* = 0.05$, where the cluster structure is stable and in most cases well ordered.

In this work results of 100 simulation runs of cluster cooling were analysed: 20 of them were taken from previous simulation data [17], while 80 simulations runs were realised additionally to obtain more examples of formation of the defected crystalline cluster. The simulation method and the applied parameters were the same as described in the previous paper [17].

In order to detect structural changes during the freezing, the internal structure of simulated clusters was inspected every 10th MC cycle using the Coordination Polyhedron (CP) method [18]. For this purpose, all particles [17] were found, which had coordination polyhedra, built on their first neighbours, regular and characteristic for the structure type: face-centred cubic (fcc), hexagonal close-packed (hcp), icosahedral (ic), decahedral (dh), and bulk-centred cubic (bcc). Each such particle is called a centre of structural unit. When a large increase in the number of structural units for any value of T was detected, it was understood that at this simulation stage the analysed cluster freezes/solidifies. When the obtained final cluster at $T^* = 0.05$ had the layered fcc/hcp structure, simulations were repeated for this temperature to write coordinates of all particles in the system to data files every 200th MC cycle during entire simulation stage (200,000 MC cycles). This enabled precise observation of structure evolution. The final cluster and the 1000 data files recorded during the process of freezing were investigated using structural analysis based on the CP method. It starts from a search of all particles, possible centres of structural units, each characterised by a completed shell of 12 first neighbours (8 in the case of bcc structure) in the distance range $1.15 \leqslant R^* \leqslant 1.40$. All particles characterised by the number of neighbours up to the maximum distance $R^*_{max} = 1.40$ lower than 12, are located at the cluster surface.

Method for the nucleus detection in a cluster is illustrated in Fig. 1. In order to find all particles composing the cluster, a cluster detection procedure was applied. This procedure is based on a geometrical criterion such that all particles separated at a distance R not larger than $R^*_{max} = 1.40$ are treated to be in the same cluster. For the analysed temperatures, this leads to the detection of one cluster and sometimes of one or, at the maximum, two vapour particles. The next stage is detection, with use of the structural analysis, of all particles in the cluster, which are centres of structural units (Fig. 1b). Coordinates of these particles and of all of their first neighbours are recorded, because they are necessary for visualisation of location in the cluster of all particles forming nuclei shown in Fig. 1c, where the cluster surface is illustrated by thin lines connecting all neighbouring surface particles. The particles of the nuclei can be divided into several groups (two in Fig. 1d) using