

Phase Change of Lennard-Jones Nano Clusters Containing Non Magic Numbers

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Phase changes of Lennard-Jones clusters containing $4N^3$ ($N = 1-20$) identical atoms in terms of solid and liquid phase-like forms have been studied by performing molecular dynamics (MD) simulation at sharply-bounded range of temperatures between freezing temperature (T_f) and melting temperature (T_m) and at constant pressure. The small differences between the free energies of clusters in different phase-like forms and also the non-rigidity of the cluster ($0 \leq \gamma \leq 1$) as an order-parameter, which characterizes the phase transition, have been calculated. Plots of the free energy of phase change *versus* the non-rigidity indicate that the free energy is a continuous function of the non-rigidity and also different crystalline-like cores with different free energies correspond to the same non-rigidity factor at any given temperature.

Keywords: Phase change, Solid like, Liquid-like, Nano-clusters, Non-rigidity factor, Molecular dynamics simulation

INTRODUCTION

Clusters constitute nanosystems made of a limited number of atoms or molecules which occupy an intermediate space size between atoms and bulk matters. Clusters, in addition to displaying similarities to bulk systems, possess also some unique properties. Clusters are different from bulk material since a large fraction of the particles comprising a cluster are on its surface. Their finite size also causes "rounding" of thermodynamic properties, so that extensive thermodynamic properties of clusters are non-extensive and their intensive thermodynamic properties are non-intensive [1].

An understanding of clusters and how their properties evolve with size will provide new insight into nanosystems. For example, the first-order phase transition in the bulk matter exhibits a melting transition at a single well-defined temperature. At this melting point, the free energies of the solid and the liquid phases are equal and coexistence of the

two phases takes place. Above the transition temperature the superheated solid would be metastable and is not generally observed and below it, the liquid would be metastable and can be sometimes observed as a super-cooled liquid. An important distinction between the phases of bulk matter and the phase-like forms of small clusters is that there are many varieties of the latter which do not exist in the limit of very large systems [1-3].

It has been indicated that small, finite, clusters exhibit both solid-like and liquid-like forms which are assumed to be thermodynamically stable in certain range of temperature and some kind of phase change occur between them [4]. Clusters may exhibit a sharp lower limit of temperature for the thermodynamic stability of the liquid form and a higher sharp upper limit for the thermodynamic stability of the solid form. The lower temperature is called the freezing point, T_f , and below T_f , the upper limit of thermodynamic stability of the solid is called the melting point, T_m [5,6].

The phase-like properties of clusters and nanoscale particles lend themselves to study by simulation and by

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analytic theory [2]. A few experimental studies have demonstrated specific phase-like forms of these species [7-9], but very little has come from the laboratory to elucidate the nature of the equilibrium or the transition between these forms [10].

The structures and properties of small clusters of Lennard-Jones atoms have been extensively studied by using a variety of both theoretical and experimental techniques over the past years [11,12]. It has been shown that clusters containing certain "magic numbers" such as 13, 55, 147 and 309 of identical atoms form icosahedra structures [13]. An extensive molecular dynamics study of melting and freezing of the Lennard-Jones clusters containing up to 5083 atoms have also been reported [5]. Theoretical studies have shown that phase change takes place in small Lennard-Jones clusters, but its nature is still in doubt due, in part, to the conflicting results that have been reported [13].

Although it has been reported [13,14] that the small clusters containing magic numbers of argon have icosahedra symmetry, bulk solid argon is known to have the face-centered-cubic (fcc) crystal structure [13]. A crossover from icosahedral to fcc ordering at a cluster size of about 750 atoms has also been reported [13]. Prediction of the fluid/solid phase boundary using Monte Carlo simulations and perturbation theory with the Yukawa potential have also indicated that the solid phase has a fcc microstructure [15]. It may also be emphasized that although the small solid phase clusters may have icosahedra symmetry, the structure deformation can be achieved by the molecular dynamics simulation process and icosahedra symmetry would not exist any more during the process. Also, the disordered phase appears at high temperatures and often has a simple structure, such as a face-centered cubic (fcc) or body-centered cubic structure. Therefore, the clusters which have been studied in this work have the fcc crystal structure by which the structure deformation does not occur by the molecular dynamics simulation, MDS, process. In this article, we report an MDS study of small Lennard-Jones clusters to examine the conditions for the validity of the assumption of coexistence for a number of clusters containing $4N^3$ ($N = 1-20$) identical particles (hereafter, non-magic numbers) which form fcc structures and do not form icosahedra structures as magic numbers do) and have not been previously investigated. We

present a systematic study of finite-size effects and the approach to the transition points for a class of Lennard-Jones potentials in three dimensions. All thermodynamic properties of solid clusters are determined by heating cluster from $T = 5$ to 50 K. The thermodynamic properties have been calculated while the clusters were equilibrated at a given temperature. MDS runs have been long enough for the cluster to equilibrate. We attempt to answer the two questions implicitly posed in the theory and method section, previously. The model supposes that the energy levels $E_j(\gamma)$ of the cluster are continuous functions of an order-parameter, γ , measuring the non-rigidity of the cluster [13,14]. This study has also undertaken to help resolve the following issues:

- What is the nature of the phase transition for small clusters containing non-magic numbers and possessing fcc ordering crystal structure?
- What is the effect of the crystal ordering on the structural change accompanying this phase change?
- How is the change of the free energy as a function of temperature and what is the equilibrium behavior in the phase transition region?
- Do the properties of the phase transition depend on the size of the cluster?

Theory and Method

Two useful questions have been put forwarded by Berry [15]: one about the nature of bulk melting and its relation to the theory or more precisely, why the melting point of bulk matter is so sharp and the same as the freezing temperature, and the other about the predictions of the theory regarding the stability of finite liquids and solids and how they are related to the behavior of bulk matter. The answer to the first question has emerged from the theory given by Berry *et al.* [6,14]. The answer to the second question emerges from the prediction that the freezing and melting temperatures T_f and T_m , interpreted as the limits of stability of the liquid and solid forms, respectively, are sharp but unequal, giving rise to two discontinuities in the equilibrium constant, one at T_f and one at T_m

$$K = \exp(-\Delta G / kT) = [\text{liquid}] / [\text{solid}] \quad (1)$$

where ΔG and k are the change in Gibbs free energy and the

Boltzmann constant, respectively. Now more precise questions are: What happens to the discontinuities in equilibrium constant, K , as N increases, and at what value of N does $\Delta T = T_m - T_f$ remain finite and non-zero?

These questions have been answered by using:

$$D = (K - 1)/(K + 1) = ([liquid] - [solid])/([liquid] + [solid]) \quad (2)$$

which ranges from -1 at very low temperature to +1 at high temperatures instead of K which changes from zero to infinity [5,16].

There is an equilibrium temperature, T_{eq} , between T_m and T_f at which the chemical potentials, $\bar{\mu}_i$, of the two phases are equal ($N\Delta\bar{\mu} = \Delta G = 0$) for clusters of a given N . Below this equilibrium temperature $\Delta\bar{\mu}$ is negative and above that is positive. This means that $\Delta\bar{\mu}$ changes from negative to positive and D changes from a number less than 1 to a number greater than 1, around T_{eq} [5]. This behavior has been illustrated for two values of N , one small enough to show a gradual change in D and the other, a steeper, more confined increase with N around T_{eq} [5].

Berry [15] has interpreted the behavior of $T_{eq}(N)$ and also has answered the questions of what happens to T_f and T_m as $N \rightarrow \infty$ and what is the N -dependence of the condition that the canonical partition function $Z_N(\gamma, T)$ has an interior minimum in the range $0 \leq \gamma \leq 1$. The order parameter γ is defined in a manner analogous to the quantity that characterizes the nonrigidity of a diatomic molecule, the ratio of the rotational constant B_e to the vibrational frequency ω_e . For a cluster it has been given as [17-19]:

$$\gamma = 2E_r / E_v \quad (3)$$

where E_r is the interval between the ground state and the excited state which becomes the first rigid-rotor excited state in the rigid limit and E_v is the excitation energy to that state which becomes the first vibrationally excited state in the rigid limit. In the most extreme rigid limit, E_v would become infinite, so $\gamma \rightarrow 0$ at that limit. As the system approaches the non-rigid limit, E_r approaches the energy of the first excited state of the $U(3N-3)$ harmonic ladder, and E_v approaches the energy of the second excited state of the same ladder, so $\gamma \rightarrow 1$ at the nonrigid limit [6]. This means that the energy of

states $E_j(\gamma)$ are continuous and smooth function of γ .

Molecular dynamic simulations can, in principle, provide accurate numerical results for a system but are *never exact*. Among the many possible pitfalls for simulators, especially those interested in phase transitions, are the effects of the finite extent of simulated systems on the observed results [20].

The much studied Lennard-Jones intermolecular potential model is the obvious choice for the present study. The potential, U_{LJ} , is of the form,

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (4)$$

where ϵ [$\text{J mol}^{-1} \text{K}^{-1}$] is the potential-well depth parameter, σ [m] is the hard core parameter, and r [m] is the distance between particles. In MD simulation it is often convenient to express quantities such as mass, distance, temperature, density, pressure in reduced (dimensionless) units that are indicated by a superscript asterisk “*”. This means that we choose convenient units for energy, length and mass and then express all quantities in terms of these basic units. Reduced quantities are defined so that distances are scaled by σ and temperature by ϵ/k , where k is the Boltzmann constant. In the example of a Lennard-Jones system, a pair potential that is used is of the form

$$u(r) = \epsilon f(r/\sigma) \quad (5)$$

A natural choice for our basic units is the following: unit of length; σ , unit of energy; ϵ , unit of mass; m (the mass of the atoms in the system) and from these basic units, all other units follow. For instance, our units of temperature is ϵ/k and the unit of time is $\sigma\sqrt{m/\epsilon}$. The reduced distance, energy, pressure, density and temperature can be defined as:

$$\text{The reduced distance: } r^* = r/\sigma \quad (6)$$

$$\text{The potential energy: } U^* = U/\epsilon \quad (7)$$

$$\text{The pressure: } P^* = P \sigma^3 \epsilon^{-1} \quad (8)$$

$$\text{The density: } \rho^* = \rho \sigma^3 \quad (9)$$

$$\text{The temperature: } T^* = k T \epsilon^{-1} \quad (10)$$

The experimental data $\varepsilon/k = 119.8$ [K], $\sigma = 0.3405 \times 10^{-9}$ [m], $M = 0.03994$ [kg mol⁻¹] which are available for argon were used in our calculations.

The velocity-Verlet algorithm was used with a time step of 0.05τ , where $\tau = \sigma(m/\varepsilon)^{1/2}$. The potential

$$U(r) = U_{LJ}(r) - U_{LJ}(r_c) \quad r < r_c \quad (11)$$

$$= 0 \quad r > r_c$$

is truncated at a cutoff distance, r_c , of 2.8σ for clusters containing of $N \geq 4$ atom. The following types of calculations on the Lennard-Jones clusters containing $4N^3$ ($N = 1-20$) atoms were then performed:

- Slow cooling runs using the constant temperature MDS to study the phase transition.
- Slow heating runs to examine the state of equilibrium at different temperatures in the transition region. The range of temperature between T_f and T_m is called transition region. To find whether the equilibrium exists at all temperatures, appropriate runs were also carried out in the same region and the same equilibrium diagrams were reproduced.
- Constant temperature calculations in the transition region to study coexistence of phases.

It should be noted that in contrast to Berry's work (-20-20 °C, [5]) the MD simulations were performed at temperatures low enough, $T = 5$ to 50 K, where evaporation of atoms from the clusters generally does not occur.

The Helmholtz free energy was calculated by using Eq. (12)

$$F(\gamma, T) = -T \ln Z(\gamma, T) \quad (12)$$

where Z is the partition function of the canonical ensemble and is, of course,

$$Z(\gamma, T) = \sum_j g_j e^{-E_j(\gamma)/T} \quad (13)$$

$$Z = \prod_{j=1}^{3N} (e^{-h\nu_j/2kT} / 1 - e^{-h\nu_j/kT}) e^{-U(0; \rho)/kT} \quad (14)$$

The information contained in $F(\gamma, T)$ has been given in detail [6]. The Helmholtz free energy has at least two minima as a

function of the order parameter that indicate two-phase like forms occur for the solid structures in the transition region.

The disordered phase appears at high temperatures and often has a simple structure, such as a face-centered or body-centered cubic structure. As the temperature of an orientationally disordered crystal is lowered, a phase transition to a more ordered phase takes place, and is characterized by a lower-symmetry crystal structure and the onset of long-range orientational order-structure. The transition may be continuous or weakly discontinuous. The fact that the crystalline structures are the only form observed of these molecular clusters indicates that they undergo a structural transformation during their growth to a final size of 1000 to 10000 particles. The performed experiments [21,22] have shown that argon clusters exhibit an amorphous, polytetrahedral, or polyicosahedral form when they are small, and only begin to adopt their bulk structures when they reach a size of at least 1000 atoms.

RESULTS AND DISCUSSION

To predict the freezing, T_f , and melting, T_m , temperatures, the internal energies (= kinetic energy + potential energy) were calculated at different temperatures ranging from 5 to 50 K. The values of energies are plotted *versus* temperature to find a loop-shaped part connecting two distinct branches of the curve, solid like branch of low energies extending to liquid like branch of higher energies. The results show that the similar s-bend shape plots would be obtained for all small clusters of different identical particles ($N = 32-32000$). However, as the N increases both T_f and T_m shift to higher values. In order to have a complete range of temperatures, we have taken T_f from simulating a small cluster with $N = 32$ and a small cluster with $N = 32000$. The melting and freezing temperatures were also found to be substantially below the bulk ones.

The values of free energies which were obtained by simulating a small cluster with 32 particles are plotted *versus* the values of non-rigidity parameter, γ , are shown in Fig. 1. This figure illustrates that the results of a long simulation can be separated into the solid-like, liquid-like and the intermediate regions at any given temperature. It should be mentioned that the performed simulations of all small clusters

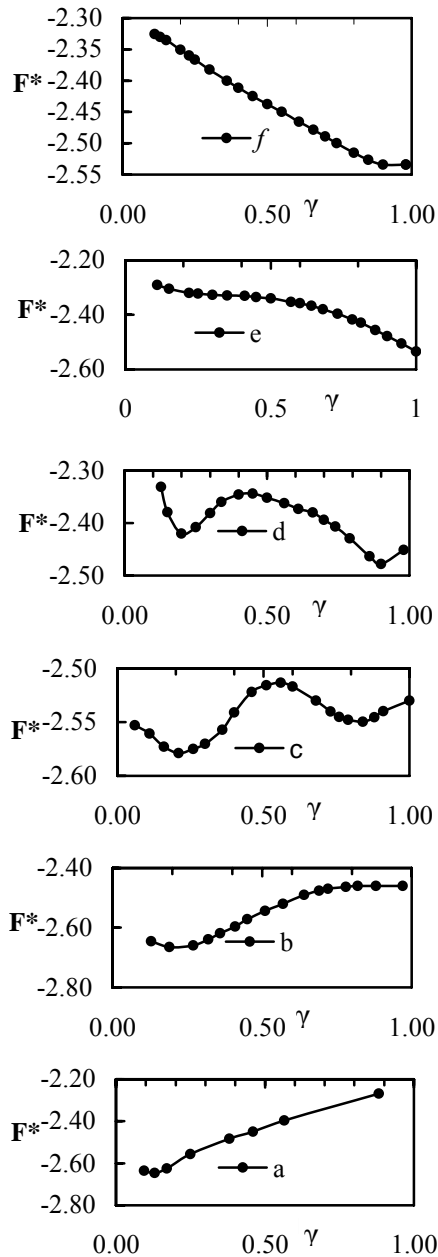


Fig. 1. The variation of free energy of a small cluster with 32 identical particles with the values of non-rigidity parameter, γ , at given temperatures.

with $4N^3$ particles gave the same results, except for $N = 1$ for which the values of free energies and γ remain constant during the MDS run. Dynamic coexistence of phase like forms, solid, surface melted and a homogeneously melted phase could be

found in isothermal MDS. Different plots of Fig. 1a-f can be interpreted as follows:

- The free energy has only one minimum in the solid like end of the scale, *i.e.* near $\gamma = 0$.
- The free energy develops a point of zero slope near the non-rigid limit, *i.e.* near $\gamma = 1$.
- The free energy has two minima, one for lower γ corresponding to locally stable solid like form and another for the higher γ corresponding to a locally stable liquid. The maximum shows the transition state.
- Here the behavior is similar to c.
- The free energy has one minimum and one other point of zero slope and zero second derivative, as a function of γ .
- The free energy has only one minimum in the liquid-like end of the scale, *i.e.* near $\gamma = 1$.

It was mentioned above in the introduction that this study was undertaken to resolve four issues. Now the results show that:

- MDS reveals that small clusters undergo equilibrium structures from the low-energy solid-like to a set of higher energy liquid-like structures, much like a melting transition of bulk material at the transition temperatures.
- The transition is not a sharp one in that the solid-like and liquid-like structures and typically one or more intermediate structures coexist over a range of temperatures.
- The energy as a function of temperature rises from a lower value characteristic of the solid-like structure to a higher value characteristic of the liquid-like structures over the range of temperature.
- The properties of the transition depend on the size of the cluster. The s-bend shape of the plot of the internal energy *versus* temperature depends on the size of the cluster. Thus, as the number of particles increases the value of ΔT decreases.

CONCLUSIONS

MDS showed that small Lennard-Jones clusters of non-magic number of identical particles (Ar) undergo equilibrium structures from the low-energy solid-like to a set of higher energy liquid-like structures at any temperature ranging from T_f^* to T_m^* . Our results do not accord with what has been reported previously by Berry *et al.* [2]. We have found different plots of the free energy *versus* non-rigidity for any

Lennard-Jones cluster containing $4N^3$ ($N = 2-20$, non-magnetic numbers and fcc structure) identical particles at any temperature between its T_f and T_m (T_f and T_m are included), whereas Berry *et al.* have reported them for six temperatures increasing from $T_1 < T_f$ through $T_6 > T_m$.

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