Eur. Phys. J. D **9**, 437–440 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Core-melted clusters

D.V. Anghel[1,2,a] and M. Manninen[1]

[1] University of Jyväskylä, Department of Physics, P.O. Box 35, FIN-40351 Jyväskylä, Finland
[2] National Institute for Physics and Nuclear Engineering – "Horia Hulubei", P.O. Box MG-6,
R.O.-76900 Bucharest-Magurele, Romania

Received: 1 September 1998 / Received in final form: 5 October 1998

Abstract. The possibility of the existence of a core-melted cluster is investigated. To this end, a pair potential is introduced, with the property that the solid state of the cluster is less dense than the liquid state. With this kind of potential, the cluster exhibits a quite unusual behavior. In addition to the known states, solid, liquid, and surface-melted, it can also be found in a "dense-liquid" phase (a disordered state appearing at low temperatures), a "core-melted" phase, and a "core-surface-melted" phase. In the core-melted phase, the external part of the cluster consists of atoms that are vibrating around regular crystalline sites, while the core atoms have much bigger mobility, sometimes exhibiting a diffusive motion. The phase diagrams for different parameters that enter in the model potential are analyzed.

PACS. 36.40.Ei Phase transitions in clusters – 36.90.+f Other special atoms, molecules, ions, and clusters – 36.40.-c Atomic and molecular clusters

1 Introduction

In [1] R.S. Berry presents a list, the "menagerie", of phase-like forms of clusters. The list consists of solid, liquid, surface-melted, core-melted, soft solid, flexible planar, nonwetted, and slush forms. Among these, just the core-melted cluster (CMC) had not yet been identified in experiments or simulations. Our goal in the present paper is to prove that this form *can* exist. We will do this by simply constructing such a cluster. Moreover, it will appear that this is not just some kind of transient state, with a small lifetime, but a stable phase, which, at low enough temperature, does not transform into another phase. In order to obtain these properties, we will need to introduce a new pair potential. We want to stress, however, that we do not need any complicated many-particle interaction to obtain the core-melted cluster. Studying the properties of this cluster, we will find new phase-like forms to add to the menagerie mentioned above. The cluster can exhibit a core-surface-melted form (which will be defined later) and two different kinds of liquid forms, which are also a consequence of the potential that we are using.

The model potential

$$V(r)=\begin{cases}\infty & ,\ r\in[0,r_0]\\ \varepsilon_1\left(\frac{\sigma_1}{r-r_0}\right)^{12}+V_v-\int_{r_0}^{r} n_1(x-r_0)^7\times \\ (r_1-x+r_0)^{1/3}\mathrm{d}x & ,\ r\in(r_0,r_0+r_1]\\ 4V_w\left[\left(\frac{\sigma_2}{r-r_0-r_2}\right)^{12}-\left(\frac{\sigma_2}{r-r_0-r_2}\right)^{6}\right], \\ & r\in(r_0+r_1,\infty)\end{cases} \qquad (1)$$

is presented in Fig. 1. There is a lot of freedom in the choice of parameters that enter into the expression above. We shall present briefly the ones that we have used in our simulations. We fix from the beginning $\sigma_1=\sigma_2=1$ Å. In the simulations with $V_v<0$ we take $\varepsilon_1=-V_v$. For the calculations with $V_v\geq 0$, we use $\varepsilon_1=0.005\,\mathrm{eV}$. V_w is kept equal to $-0.02\,\mathrm{eV}$ in all simulations (about double the depth of the potential well used in the case of argon atoms). Once we fix the above mentioned-parameters, we calculate n_1 such that $\lim_{r\nearrow r_0+r_1}V(r)=V_w$ and r_2 such that $\lim_{r\searrow r_0+r_1}V'(r)=0$. It is easy to see now that $V\in C^1(r_0,\infty)$. The exponents 7 and 1/3, of $(x-r_0)$ and (r_1-x+r_0), respectively, in the second branch of (1), can also be changed so that different widths of the potential well can be obtained.

The parameters r_0, r_n, and V_v (and implicitly n_1) are varied in different simulations so that their influence on the properties of the cluster can be studied. We used standard molecular dynamics techniques to control the temperature and energy of the cluster (for details, see, e.g., [2]).

---

[a] *Correspondence to*: D.V. Anghel, University of Jyväskylä, Department of Physics, P.O. Box 35, FIN-40351 Jyväskylä, Finland (e-mail: `dragos@ux.phys.jyu.fi`)

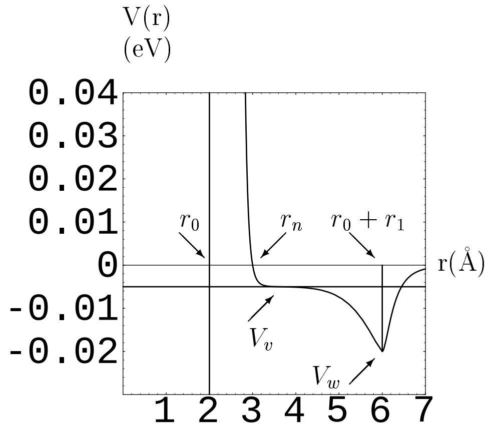

Fig. 1. Pairwise potential. The potential is 0 at $r=r_n$ and tends to ∞ as $r \rightarrow r_0$.

In the following sections, we will present the main properties of the cluster and describe the simulations.

2 New features

Because of the deep potential well V_w, the cluster presents solid phase-like forms, corresponding to local minima of the total potential energy. If the absolute minimum of the potential energy is reached or not in a solid phase-like form, depends also on the choice of other parameters, like r_0 and V_v, beside V_w.

The plateau V_v gives a possibility of the existence of closed packed configurations, which are denser than the solid phase. The stability of this phase is assured not by the nearest neighbour interaction, but by the interaction of distant atoms. The nearest neighbours will interact repulsively, in some cases very strongly. The atoms are pushed together by atoms further out. Consequently, we can say that we have a "dense-liquid" phase (DLP). Depending mainly on the ratio of r_0 and r_1 and on V_w and V_v, this phase-like form could be more stable or less stable than the solid phase-like form. The CMC can be formed in both situations, but it appears to be more natural in the case in which the solid is more stable than the dense liquid. For each fixed r_1, V_w, and V_v, there will be an r_0 at which the stability will change. At low r_0, the liquid phase is more stable.

At higher temperatures (i.e., higher than the temperatures at which the two phases mentioned above, DLP and CMC, are stable) we will see another, "liquid", phase (LP), which is much more disordered and less dense than the DLP. The qualitative difference between these two phases appears more obviously at bigger r_0, especially in the region where the energy of the solid state is lower than that of the DLP. In the LP, the minimum distance between two neighbouring atoms is larger than in the DLP. Usually, for normal substances, this distance decreases with the increase of temperature (as long as the liquid or solid phase is preserved), due to the increase in kinetic energy. When the cluster is in the liquid phase-like form, the surface atoms are evaporating.

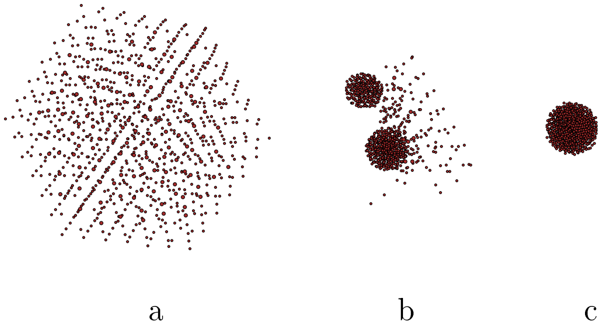

Fig. 2. (a) CMC ; (b) collapsing to DLC ; (c) DLC . $r_0 = 0$.

3 Simulations

In order to observe the behavior of the clusters for different values of the parameters, we performed numerous simulations. We will try to resume our observations in what follows.

If we start from icosahedral distributions, the CMC or dense-liquid cluster (DLC) can be found at low temperatures, depending on the nearest neighbour distance (NND) between the atoms in the initial configuration. If the atoms are packed at distances close to r_n (the range of distances depends on the other parameters also), we obtain the DLP. If the initial NND is close to r_0+r_1, we end up with CMC. From our simulations it appears that, with this kind of potential, it is not possible to obtain phases other than these two when we start from an icosahedral initial distribution at low temperatures (more specifically, the complete SP was never observed in this way).

The denomination "core-melted cluster" is justified by the following facts: (1) The NND of the atoms in the outer shell of atoms is close to r_0+r_1, as in the case of SP, while the NND between the atoms in the core is much smaller. (2) Measuring the mean square displacement (MSD) of the atoms in the outer shell and in the core, we obtain large differences (up to two orders of magnitude or more, depending, of course, on the temperature). For some choices of parameters, we can observe a clear diffusive motion of the atoms in the core.

As an example, we will describe a simulation of a 6-shell icosahedral cluster ($N = 923$ atoms), with $r_1 = 4$ Å, $V_v = -0.005$ eV, and $V_w = -0.02$ eV (the other parameters are $\sigma_1 = \sigma_2 = 1$ Å, $\varepsilon_1 = 0.005$ eV, $r_2 \approx 2.88$ Å, and $n_1 = 1.31989 \times 10^{-8}$). After the equilibration of the cluster at $T_i = 10$ K, we increase the temperature slowly to $T_f = 100$ K. The following observations can be made:

1. For r_0 less than 4 Å the DLP is more stable than the SP. Therefore, the clusters that after the equilibration were in the DLP will stay like that until they start to evaporate. In these cases, the DLP and LP could be considered to be the same. The CMC clusters are unstable and will collapse below 100 K; the temperature of

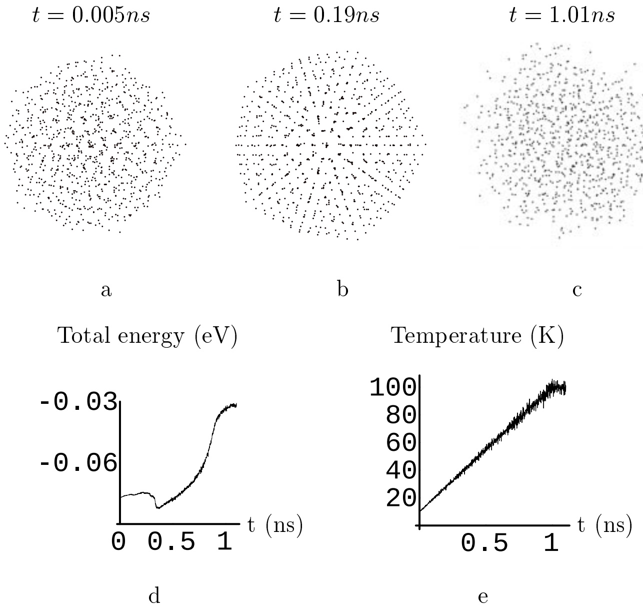

Fig. 3. Transition from DLP to LP through CMC, as the temperature increases. $r_0 = 6.88$ Å.

collapse depends on r_0 (in Fig. 2 the most violent collapse, $r_0 = 0$, is presented, during which, before the final cluster is formed, we can observe the formation of two small intermediate clusters).

2. For r_0 bigger than 4 Å the SP is more stable than the DLP. The CMC is still collapsing, but it is collapsing to the LP at the melting temperature, which is about 80 K for both core-melted and solid type of clusters.
3. When r_0 is bigger than about 6 Å, the DLC transforms to CMC at lower and lower temperatures as r_0 increases. (In Fig. 3 is presented the evolution of the cluster, with $r_0 = 6.9$ Å from DLC to LC passing through CMC.) In this range, the difference between DLP and LP becomes obvious, for they exist in disjoint temperature ranges.

In any situation, the passing from CMC to LC is made through the core-surface-melted cluster. This means that, before transition to the liquid phase-like form, the atoms belonging to the external shell of the core-melted cluster become *floaters* (see [1] for a definition). In this respect, the transition is very similar to the transition from the solid phase-like form to liquid phase-like form.

To illustrate the properties of the CMC mentioned above, we have plotted in Fig. 4a,b the average nearest neighbour distance and the maximum mean square displacement for each shell in an icosahedral core-melted cluster with 923 atoms and with $r_0 = 4.2$ Å. Of course, there exists a small mixing between different shells, especially for the inner shells.

It should also be noted that the diffusion of the core atoms is limited by the solid shell and by the fact that they have quite big dimensions (we could say that the radius of the atom is about r_n).

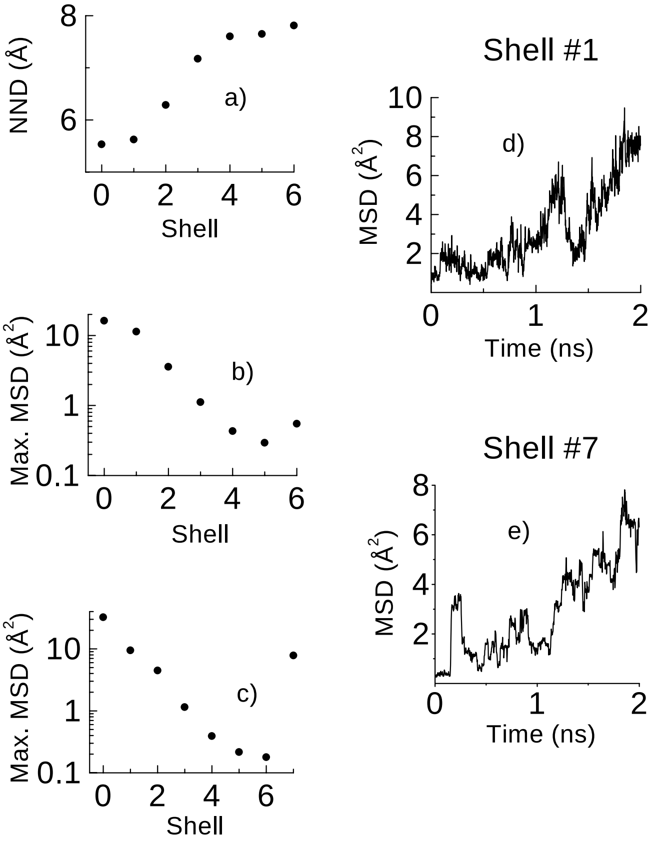

Fig. 4. In figures (a) and (b), we plot the average NND and, respectively, the maximum mean square displacement (MMSD) in each shell for an icosahedral core-melted cluster consisting of 923 atoms ($V_v = -0.005$ and $V_w = -0.02$ eV). For an icosahedral core-surface-melted cluster consisting of 1415 atoms, we show the MMSD in each shell (c), and the MSD vs. time in shell 1 (d) and in shell 7 (e) ($V_v = -0.002$ eV and $V_w = -0.02$ eV). Both clusters were simulated for 2 ns.

Modifying the parameters of the potential, one can change the mobility of the core atoms and the stability of the solid phase (or of the solid shell). As an example, we have plotted in Fig. 4c the MMSD for each shell of an icosahedral core-surface melted cluster ($N = 1415$ atoms, $r_0 = 3.7$ Å, $-V_v = \varepsilon_1 = 0.002$ eV, $V_w = -0.02$ eV, and $n_1 = 1.58386 \times 10^{-8}$, the rest of the parameters being the same as before). In the same figure (Fig. 4d,e) we show the mean square displacement versus time of the atoms for shells 1 and 7, to emphasize the diffusive motion. The simulation is carried out at constant energy, with the average kinetic energy corresponding to a temperature of 60 K. It can be seen that the outermost shell is not stable, and some diffusive motion over the surface is present. This case would be in the category of the core-surface-melted clusters. Bigger displacements of the core or surface atoms can be obtained by an increase in the temperature. In these cases, the cluster might stay in this state for a shorter time.

It is interesting that even when $V_v = 0$, the cluster can be found in all the above-mentioned phase-like forms. There exists a value $V_v > 0$ above which the DLP and CMC disappear.

We performed similar simulations also by starting from a Wulff polihedron based on an fcc lattice. In these simulations we obtained the solid, liquid, and dense-liquid phases, but not the core-melted phase. It seems that the open (100) facets prevent the formation of the solid shell around the melted core.

The transitions among DLC, LC and SC are very similar to those described for CMC.

4 Conclusions

Introducing a new type of pair interaction, we were able to obtain a phase-like form of clusters (the core-melted clusters) in which the shell is solid, while the core atoms are very mobile. For proper choice of the parameters of the potential, at a certain temperature range, we can observe diffusive motion of the inside atoms. Besides this, another new phase was found: the core-surface-melted phase.

The atoms interacting with this type of potential can have, besides the "pure" solid and liquid phases, another phase, which we call the *dense-liquid* phase.

When the cluster cools down from the liquid phase, the cluster solidifies with difficulty. Usually, in the case when the solid phase is more stable than the dense liquid, the cluster stays super-cooled for long time, but evolves mainly towards the core-melted cluster (depending on the size of the cluster and on the potential parameters).

The stability of the different phases depends mainly on the ratios of the parameters, such as $r_0/(r_0+r_1)$ and V_v/V_w. Of course, the dynamics of the atoms in the cluster changes when the parameters are modified, but the potential energy of different configurations, and the relative potential energies, which determines the stability of the phase-like forms, depends in principle on these quantities.

The authors thank the Academy of Finland for financial support. We are grateful to A. Rytkönen and H. Häkkinen for advice on molecular dynamics.

References

1. R.S. Berry: *Phases and Phase Changes of Clusters*, in *Large Clusters of Atoms and Molecules*, ed. by T.P. Martin (Kluwer, Dordrecht 1996) pp. 281–295
2. M.P. Allen, D.J. Tildesley: *Computer simulations of liquids* (Oxford University Press, New York 1990)