

Thermal stability of supported metal clusters

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Using *ab initio* many-body potentials and the molecular-dynamics method, we have studied the effect of temperature on the structural integrity of a 55-atom Be cluster in free space as well as when supported on a metal substrate. The melting point of the free cluster is found to be significantly lower than that of the bulk. The melting point of the supported cluster, however, is difficult to interpret due to the strong interaction between the cluster and the substrate. The structure of the cluster undergoes significant rearrangement even at 0 K. Thus the melting point of a supported cluster determined from its change of shape, as is usually done in experimental analysis, can provide misleading information.

The melting point of a crystalline substance is defined in terms of the temperature at which the solid, with long-range order, changes to a liquid with short-range order. It has been demonstrated both experimentally¹ and theoretically² that the melting process starts from the surface layer and propagates into the interior and that the surface melts at temperatures significantly lower than the bulk melting point. This phenomenon is well understood in terms of the reduced coordination of surface sites compared to the bulk atoms. In nanometer scale particles as well as in clusters in the subnanometer scale, most atoms are surface atoms. Thus, in analogy with the above discussion one would expect that the melting point of a nanometer scale particle would be smaller than that of the bulk and that the melting point will decrease as particle size decreases. This expectation seems to be borne out by recent experiments.³⁻⁵ However, there are two major difficulties that are associated with the interpretation of these experiments: First, the melting of a particle cannot be defined in an unambiguous manner since there is no long-range order. In experimental studies, melting is characterized by a change in the shape of a particle. This specification runs into difficulty because a particle can move from one local minimum to another as the temperature is raised. Thus the shape could change without the particle actually melting. Second, most of the melting studies of particles are performed on various kinds of substrates. One has to understand what role the substrate atoms play on the thermal stability of particles.

In a recent experiment³ involving Au and Ag particles supported on a tungsten tip, the melting point (characterized by changing shape) of the particle has been found to saturate to a constant value when the particle diameters are less than ~ 2 nm. This result is intriguing because it is well known that the stability of small clusters is characterized by electronic-shell structure⁶ which disappears in large clusters/particles due to competition with crystal-field effects.⁷ Thus, one would expect that in small clusters the melting point should be a nonmonotonic function of size.^{8,9} This would seem to contradict the experimental finding.³⁻⁶ However, the size of the clusters below 2-nm diam is not well characterized in terms of their atomic mass and the real size effects are expected to occur in

very small clusters consisting of less than ~ 100 atoms.

There have been a few theoretical studies¹⁰⁻¹⁶ on this subject. All of these have used the molecular-dynamics method and empirical potentials based on either pairwise Lennard-Jones form or embedded atom. The work by Liu and Adams¹⁰ and Erkoc, Halicioglu, and Tiller¹¹ deals with dynamics of particles at 0 K. Ercolessi, Andreoni, and Tosatti¹² and Hautman and Klein¹⁵ have studied the melting and wetting phenomenon in large clusters consisting of about 100 atoms. Jellinek and co-workers⁹ are the only authors who have studied the melting behavior of small free Ni clusters using an embedded atom potential. To our knowledge, no calculations of the thermal stability of small metal clusters supported on a metal substrate have yet been reported.

In this paper we present molecular-dynamics calculations of thermal stability of a 55-atom Be cluster supported on a Be (0001) surface using *ab initio* many-body interatomic potential.¹⁷ We study the geometry of the free cluster as well as the supported cluster at various temperatures. We demonstrate that the surface atoms undergo displacements as the cluster is deposited. Thus the change of the shape of a cluster cannot be entirely related to its thermal instability and that its interaction with the substrate atoms can play a significant role in the measured melting point.

Newton's equations of motion are integrated using Verlat's algorithm.¹⁸ The interaction between atoms were taken in an analytical form containing two- and three-body terms.¹⁷ The parameters for the potential were determined by a simultaneous fit to the total-energy hypersurfaces of Be₂, Be₃, Be₄, and Be₅ clusters based on *ab initio* local-spin-density calculations. This potential has been shown to predict the bulk properties at $T=0$ K, such as lattice constant, cohesive energy, and bulk modulus in quantitative agreement with experiment. Since we are using this potential to examine thermal stability of clusters, we also investigated its accuracy for predicting the finite temperature properties such as melting temperatures of bulk Be. This was done by considering a slab of Be with its exposed (0001) surface and containing 420 atoms in 12 layers. In order to simulate the presence of a semi-infinite crystal, the two bottom layers

were kept rigid. Periodic boundary conditions were imposed on the directions parallel to the surface and no constraints were applied on the direction perpendicular to the surface. Since melting originates at the surface, and bulk characteristics are reached within the top five layers, the geometry used guarantees that the dynamics of the top layers is not affected by slab size. Melting was then monitored layer by layer by means of an order parameter defined for each layer. We chose to use as an order parameter the square of the structure factor, $S_1(G)$, where G is the reciprocal-lattice vector along the rows of atoms in each layer.² Starting from 0 K the system was heated up very slowly. At 1200 K vacancies started to appear in the surface layer. At 1500 K the surface layer was completely molten. The second and successive layers from the surface melted at 1600 and 1700 K, respectively. From these simulations we estimate the melting temperature to be 1600 ± 50 K, with error based on the fluctuations of temperature. This agrees very well with the experimental melting temperature¹⁹ of 1562 K.

We first start with the melting point of a free Be_{55} cluster. For this part of our work, we used a microcanonical molecular-dynamics simulation with a time step of 0.0015 psec. The total energy was conserved to five significant digits and the cluster temperature was determined from the average kinetic energy. The melting of the cluster was monitored through the root-mean-square fluctuation δ in the interatomic distance defined by

$$\delta = \frac{2}{N(N-1)} \sum_{i,j} [\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2], \quad (1)$$

where r_{ij} is the distance between the i th and the j th particle. In Fig. 1 we show our calculated values of the parameter δ as a function of temperature, T . One notices a \sqrt{T} behavior at low temperatures. At about 1000 K, the parameter δ begins to rise rapidly indicating a softening of the cluster, and around 1400 K, the cluster begins to

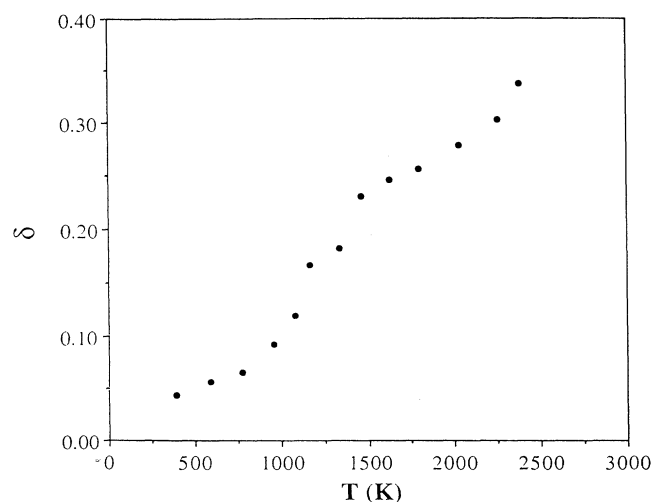


FIG. 1. Parameter δ [Eq. (1)] as a function of temperature T for a free Be_{55} cluster. ij are in atomic units.

have a liquidlike behavior. From these results we estimate the melting temperature of the free 55-atom cluster to be around 1200 K. We would like to add that this criterion for melting has also been used by various other authors.^{9,16}

We now consider the case of supported clusters. We modeled the substrate by a slab containing 504 Be atoms arranged in three layers forming (0001) surface. The bottom layer was kept rigid to simulate the presence of the semi-infinite solid. The atoms in the top two layers were allowed to move. Further, periodic boundary conditions were imposed in directions parallel to the surface. The finite temperature simulations were carried out by rescaling the velocities of the atoms in the second layer to the desired temperature. The top layer and the cluster atoms acquired this temperature via interatomic interactions with this layer. We adopted this procedure since it mimics the experimental conditions realistically.

We start by discussing the structure of Be_{55} placed on the surface at 0 K. The 55-atom icosahedric cluster (labeled by white atoms) was placed at rest in the vicinity of the surface (labeled by grey atoms) (Fig. 2) and the whole system was allowed to relax by minimizing energy using simulated annealing. The atoms were relaxed until the forces on each atom were reduced to around $1.0E-0.6$ eV/Å.

In Fig. 3 we show the equilibrium structure of the deposited cluster at 0 K. The cluster atoms are shown in white while the surface atoms are shown in grey. The black atoms are the initial surface atoms that leave the surface layer as the cluster approaches the surface. One notices several things. First, the cluster structure is dramatically influenced by the substrate. In fact the cluster acquires a layerlike structure on the surface. The landing surface is also modified and certain surface atoms leave the surface to marginally “wet” the oncoming cluster.

The structure in Fig. 3 may not be the most energetically favored structure. In this paper, our interest has been to simulate the experimental conditions where a cluster is brought onto a substrate. During this process the cluster could be confined to local minima. To insure

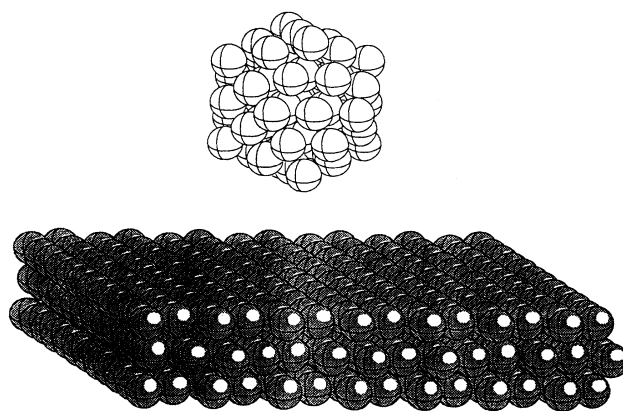


FIG. 2. Structure of a Be_{55} cluster in the vicinity of a surface.

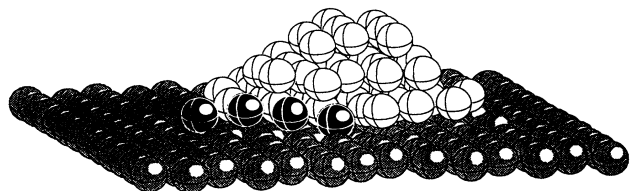


FIG. 3. Equilibrium structure of a Be_{55} cluster on the Be surface at 0 K. The cluster atoms are shown as white circles, the substrate atoms as grey atoms, and the initial surface atoms, which leave the surface to wet the cluster, are shown as black atoms.

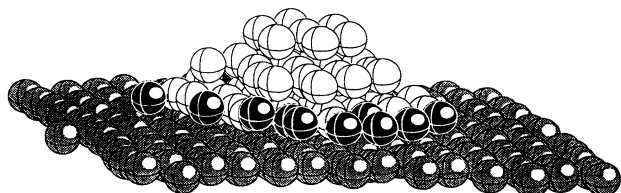


FIG. 4. A Be_{55} cluster on the Be surface at 300 K. The color code is the same as Fig. 3.

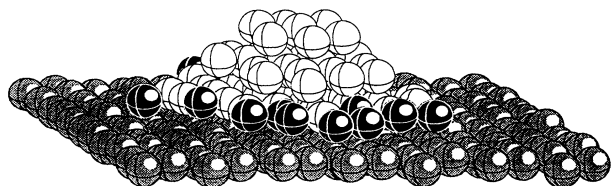


FIG. 5. A Be_{55} cluster on the Be surface at 500 K. The color code is the same as Fig. 3.

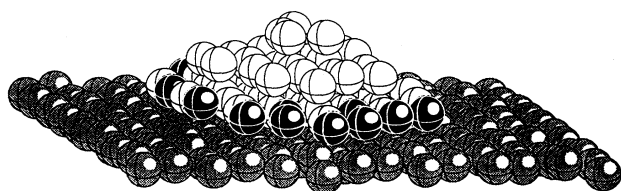


FIG. 6. A Be_{55} cluster on the Be surface at 600 K. The color code is the same as Fig. 3.

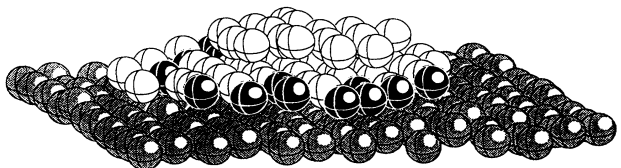


FIG. 7. A Be_{55} cluster on the Be surface at 700 K. The color code is the same as Fig. 3.

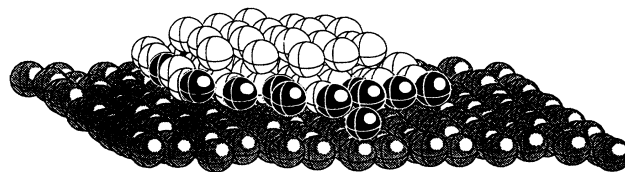


FIG. 8. A Be_{55} cluster on the Be surface at 800 K. The color code is the same as Fig. 3.

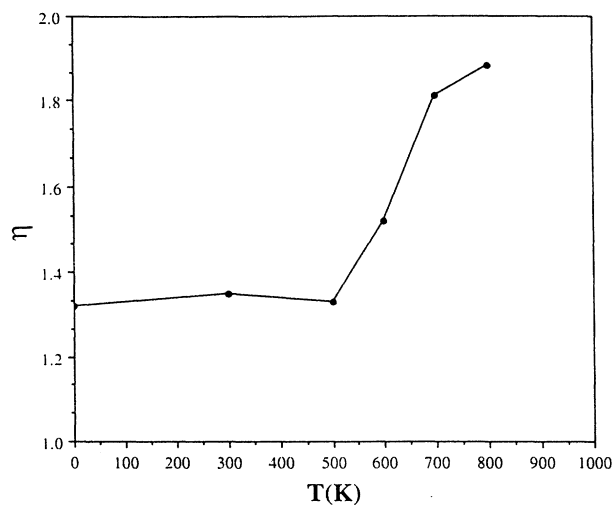


FIG. 9. Parameter η [Eq. (2)] as a function of temperature calculated by including only the atoms belonging to the original cluster.

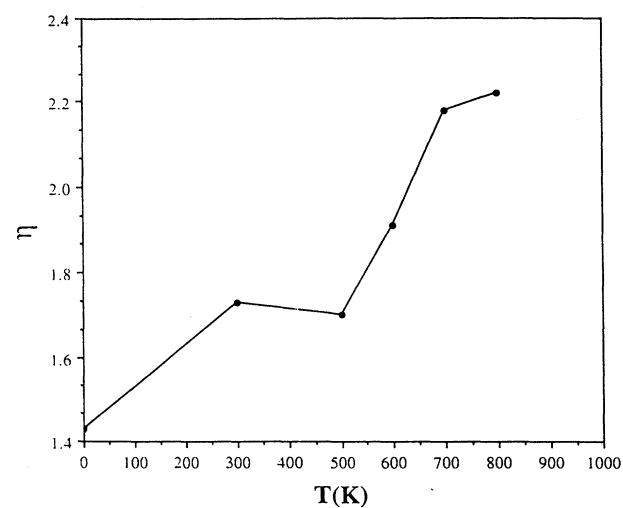


FIG. 10. Parameter η [Eq. (2)] as a function of temperature calculated by using atoms belonging to the original cluster as well as those surface atoms which leave the surface and wet the clusters.

that the structure in Fig. 3 does not correspond to a shallow local minimum which could undergo further structural changes with a marginal change in temperature, we allowed the surface temperature to rise to 50 K and annealed back to 0 K. The structure remained intact implying that it is trapped in a deep minimum. Since the Be(0001) structure does not reconstruct to the topology in Fig. 3, it is safe to assume that the supported 55-atom cluster represents a metastable state.

To investigate the thermal stability of the supported cluster, we gradually increased the substrate temperature. About 4 psec were allowed for attaining equilibrium at each new temperature. In Figs. 4 and 5 we show the snapshots at 300 and 500 K, respectively. At both these temperatures, the topmost layer has eight atoms. This situation changes as the cluster is heated to 600 K (shown in Fig. 6) when the cluster spreads and the top layer now has only four atoms. The process continues and the top layer disappears as the temperature is increased to 700 (Fig. 7) and 800 K (Fig. 8).

In order to quantify the qualitative changes we use an order parameter η defined by

$$\eta = R/h, \quad (2)$$

where R is the mean cluster radius and h is the height of the center of mass from the substrate. This parameter has been used by experimentalists³ to establish the melting point. The mean radius R was obtained by averaging the distance of atoms from a vertical axis passing through the center of mass. In Fig. 9 we show this parameter calculated by including only the atoms belonging to the

original cluster. As is clear, η remains constant as the temperature changes from 0 to 500 K. After this temperature η begins to rise abruptly indicating a transition. We have also calculated η by including surface atoms which wet the cluster and this is shown in Fig. 10. Note that η increases in the range 0–300 K due to the “wetting” of the cluster. It remains constant from 300 to 500 K indicating that the wetting saturates. At 600 K it shows a very similar sharp increase, as in the case of the “dry” cluster.

Regarding the wetting process, it is important to mention that separate simulations of the bare surface show that vacancies are thermally created at much higher temperature, about 1100–1200 K. Therefore, this process is not due to a thermal instability of the surface, but it is caused by the presence of the cluster.

From the above discussion we conclude that a Be₅₅ atom cluster deposited on a Be(0001) substrate would exhibit a marked departure from its original shape at 550±50 K. This departure marked by a sharp rise in η [Eq. (2)] cannot be identified as melting since the cluster substrate interaction is quite strong and the wetting phenomenon would mask the real effect of temperature. Thus one should be careful in analyzing the experimental data that identify shape changes with the melting point of a cluster. This analysis may be less severe in cases where the substrate interacts rather weakly with the cluster.

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