Atomic Clusters on Surfaces:
Interaction, Structure, and Stability

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Surface relaxation and finite temperature properties of the (0001) Be surface are studied using many-body potentials and classical molecular dynamics method. The calculations show a large surface relaxation, in excellent agreement with experimental results. We obtain from the finite temperature simulations the melting point of bulk Be in good agreement with the experimental value. Thermal stability of a 55-atom Be cluster, both free and supported by a (0001) Be surface, have been studied. The melting point of the free cluster is significantly lower than that of the bulk. We observe a structural transition in the supported cluster at a temperature even lower than that of the free cluster. This transition, however, cannot be interpreted unambiguously as a melting transition.

I. Introduction

In recent years, after the advent of techniques to generate beams of atomic clusters and select them by size, the study of these systems has received a great deal of attention, mainly because of their potential application as building blocks of new materials[1]. Aside from their technological appeal, microclusters can be very useful tools for the understanding of basic properties of the condensed matter. For instance, how big a system must be to start exhibiting characteristics of the bulk phase, such as melting point, electrical and thermal conductivity, magnetic susceptibility, etc.? Answers to these questions can shed light on several open questions in condensed matter physics.

It is known theoretically that perfect and infinite crystalline substances have very high "melting point", much higher than the actual melting point of actual finite and imperfect solids. For those theoretical solids, "melting" only occurs when the atomic vibrations are so large that the crystal lattice collapses ("Born instability")[2]. Currently, there are experimental[3]

and theoretical[4] evidences that surfaces play a very important role in explaining the melting point of actual solids. Melting starts at the surface, at a temperature lower than the melting point of the bulk, propagating into the bulk as the temperature reaches the melting point of the solid. This phenomenon can be explained by the fact that the atoms at the surface layer have reduced coordination compared to those of the bulk. Since in particles and clusters, in the nanometer and subnanometer scales respectively, most of the atoms are surface atoms, their melting point is expected to be lower than the bulk melting point. Experiments seem to have confirmed this expectation[5,6]. However, the interpretation of these experiments is not straightforward. Most of the experimental studies on the melting of small particles are performed having the particles supported by a substrate. Therefore, a good understanding of the interaction between the particle and the substrate is crucial for the interpretation of the experimental observations. Another difficulty is related to the order parameter used to characterize melting. A change in the shape of the particle has been often

used to define melting. One can argue, however, that at a given temperature, the particle just changed to a more stable structure (a different local minimum of the energy surface) but it remains essentially "solid", with the atoms having a small mean square displacement and diffusivity.

A recent experiment[6] studied the thermal properties of Au and Ag clusters supported by a tungsten substrate. The melting point of the clusters is determined by a change in the shape of the cluster. The expected reduction of the melting point as the clusters become smaller is observed. However, for clusters with diameter smaller than 2 nm, the melting point becomes stable. This saturation of the melting point is completely unexpected, because in that size range their stability is mainly determined by their electronic structure. Indeed, calculations show that the melting point is a nonrnonotonic function of the cluster size[7,8]. This saturation behavior is likely to be caused by the presente of the substrate, since the energy of adsorption of Au and Ag on W is quite high.

Most of the theoretical work on the thermal stability of metal clusters has been done on clusters in the gas phase[9]. There have been studies on metal clusters supported by substrates[10]. However, they have been restricted to clusters containing very few atoms, and they were mainly concerned with the structure of the clusters at 0 K and the determination of energy barriers for the migration of clusters on the surface. To our knowledge, our work has been the first to address theoretically the question of the thermal stability of supported metal clusters[11]. We studied the thermal stability of a Be 55-atom cluster deposited on a Be (0001) substrate. We also studied, for sake of comparison, the same cluster in the gas phase. Sec. II describes the many-body potential used for the interactions between Be atoms and some technical details of the molecular dynamics method used in the simulations. In Sec. III, we discuss details of the thermal behavior of the clean substrate, which are relevant to show the accuracy of the many-body potential, as well as provide elements for our analysis of the effects arising from the interaction cluster-substrate. Sec. IV presents and discusses

Table 1 - Theoretical and experimental results for cohesive energy, lattice constants, and compressibility of bulk Be.

	Theory	Experiment
cohesive energy (eV)	3.57	3.35
lattice constants (Å)		
a	2.25	2.27
b	3.68	3.59
compressibility $(10^{12}$ cm^2/dyn)	1.001	0 997

our results for the thermal stability of the supported and the free cluster.

II. Interatomic potential and molecular dynamics

Until now, completely ab *initio*, e.g. Car-Parrinello method, molecular dynamics simulations of large systems at finite temperature are prohibitively expensive. To overcome these limitations several effective potentials have been proposed in order to describe the atomic interactions. The molecular dynamics simulations presented in this paper were performed using the many-body interatomic potential for Be proposed by Blaisten-Barojas and Khanna[12]. This potential was developed from parameter free LDA (local density approximation) calculations of Be small clusters. No experimental parameters are used in its derivation. The nature of the chemical bonding in Be depends crucially on the size of the system. For instance, the dimer Be_2 is very weakly bonded. As the number of atoms increase the binding energy also increases due to the increasing s-p hybridization. Beryllium in bulk phase is metallic. This potential, specially tailored for clusters, can reproduce quite well some parameters of bulk Be as shown in Table 1.

We use classical molecular dynamics in the simulations. Newton's equations of motion are integrated using Verlet's algorithm[13]. Simulated annealing and constant temperature simulations were done by rescaling the atomic velocities. Constant energy molecular dynamics (microcanonical) was used in the simulations

of the free cluster. Periodic boundary conditions in the directions parallel to the surface were imposed, following the minimum image convention, in the calculations involving the substrate. The typical time step used was around 5.0 x 10^{-15} s. More details of the simulations are provided in the following sections.

III. Substrate

A recent experiment shows that the (0001) surface of Be exhibits a large and anomalous relaxation of interplanar spacing of the top layers[14]. It is observed a large outward relaxation of the first and the second layers. This result is somehow unexpected, because for other metals a contraction of the spacing between these layers is observed. We study this relaxation using a slab containing 392 atoms in seven layers[15]. In order to mimic the presence of the semi-infinite crystal underneath, we kept the two layers at the bottom rigid and separated by the theoretical bulk interlayer distance $d_0 = 1.8$ Å. The remaining five layers are allowed to relax freely. The energy is then minimized using the simulated annealing technique until the forces acting on the atoms are of the order of 10^{-8} eV/Å. In order to make the calculation feasible, a cutoff in the potential was introduced. In order to assess the effect of the cutoff in the calculations it was varied from 9 a.u. to 13 a.u.. The effects on the relaxation of the first and second layers were negligible. We compare our results with the experimental findings in Table 2. The calculated outward relaxation of 5.9% in the first-second layers spacing is in excellent agreement with the experimental result of (5.8 ± 0.4)%. We calculated a small expansion in the second-third layers spacing of 0.9% in contrast with a small contraction observed experimentally of (-0.2 ± 0.5)%. However, since the experimental error is substantial, our result can be considered as quite good. According to our calculations, the spacing between the subsequent layers are not affected by the surface. We increased the number of layers to 11 in order to check the convergence of our results. In this case, the two bottom layers were kept fixed and the remaining nine were allowed to relax. Negligible differences were noticed. Our results show a better agree-

Table 2 - Relaxation in the interplanar distances given in percentage of the bulk Be interplanar distance d_0.

	Theory	Experiment[a]
Δd_{12}	+5.9%	$(+5.8 \pm 0.4)$%
Δd_{23}	+0.9%	(-0.2 ± 0.5)%
Δd_{34}	0 %	$(\$0.2 \pm 0.5)$%
Δd_{45}	0 %	

[a] See Ref. [14.]

ment with the experimental results than a recent calculation using the LAPW (linearized-augmented-plane-wave) method[16] .This large outward relaxation of the first layer is entirely consistent with the behavior of the interatomic distance in Be clusters. As the clusters increase in size the bonding evolves from a Van der Walls type of interaction, due to the closed shell of the Be atom, to a metallic bonding due to the s-p hybridization. As the atoms become more strongly bonded the interatomic distance decreases. The clusters of Na, for instance, have the opposite behavior, their interatomic distance increases with the number of atoms in the cluster.

We now turn to the finite temperature properties of the (0001) Be surface. Our interest is twofold. First, we need to know the thermal behavior of the clean substrate in order to understand the effects caused by a deposited cluster. Second, from simulations of the free surface at high temperature one can infer with reasonable accuracy the melting point of bulk Be. From what we have seen so far, the many-body potential is able to reproduce very well static properties ($T = 0$ K) of bulk Be, however, still remains the question whether or not it is able to reproduce dynamical (finite temperature) properties.

We considered in our calculations a slab of 420 atoms exposing the (0001) surface, arranged in 12 layers. The two bottom layers were kept fixed, in order to simulate the presence of the semi-infinite crystal underneath. The thermal effects on the structure were monitored layer by layer using as order parameter the absolute square of the structure factor $S(\mathbf{k})$, where k is the reciprocal lattice vector in the plane of the layers and along the row of atoms. Beginning at 0 K, the tem-

perature is slowly raised in intervals of 50 K, allowing the system to equilibrate at each new temperature for at least 10 picoseconds. Around 1200 K the first vacancies are thermally created. At 1500 K the first layer is completely molten. In Fig. 1, we show the order parameter for the seven layers. The order parameter is practically zero for the first layer only, indicating that the first layer is molten. Fig. 2 shows the order parameter layer by layer at 1600 K. One can see that at this temperature the second layer is also molten. This indicates that the liquid phase is propagating into the solid one, however, at a very low speed. Note that at the melting point, the boundary between the solid and liquid phases is stationary. In Fig. 3, we display the order parameter layer by layer at 1700 K. Now the first three layers are molten, indicating a faster propagation of the liquid phase. From these results one can estimate the melting temperature to be 1600 ± 50 K, where the error bar is taken to be standard deviation of the desired temperature. This estimate agrees quite well with the experimental melting point of Be of 1562 K. These results all together indicate that the many-body potential describes very well the atomic interactions in beryllium.
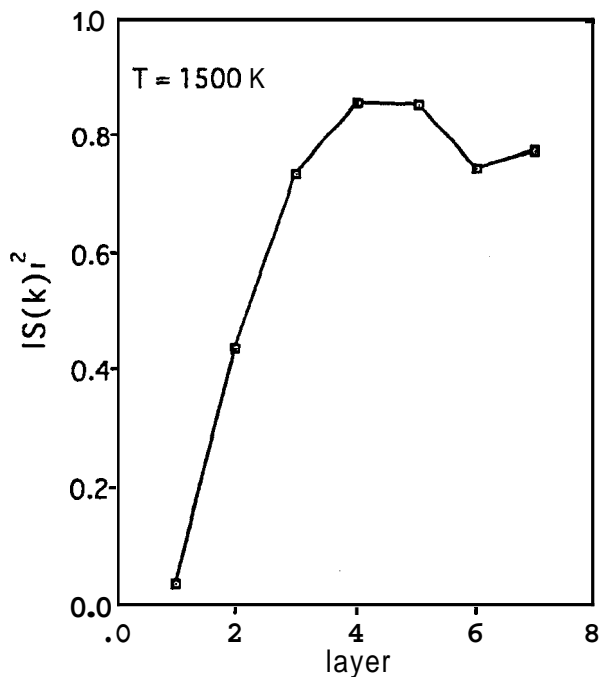
Figure 2: Absolute square of the structure factor of a in-layer reciprocal lattice vector for the top seven layers of a Be substrate at **1600** K.
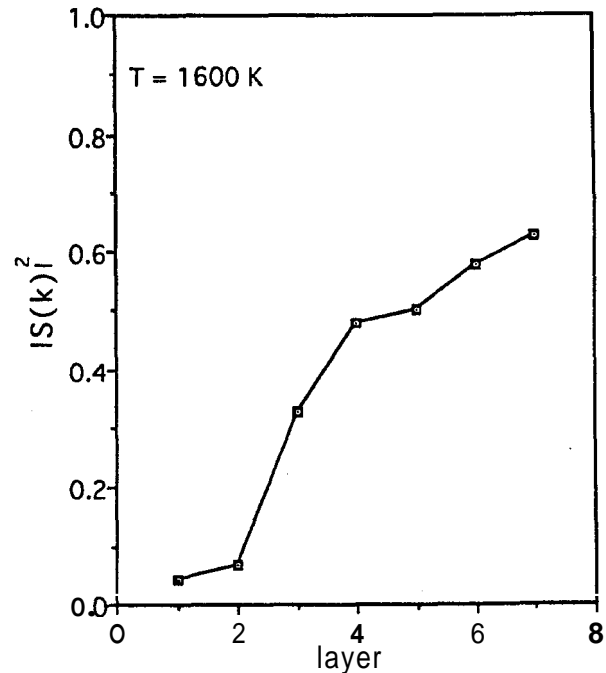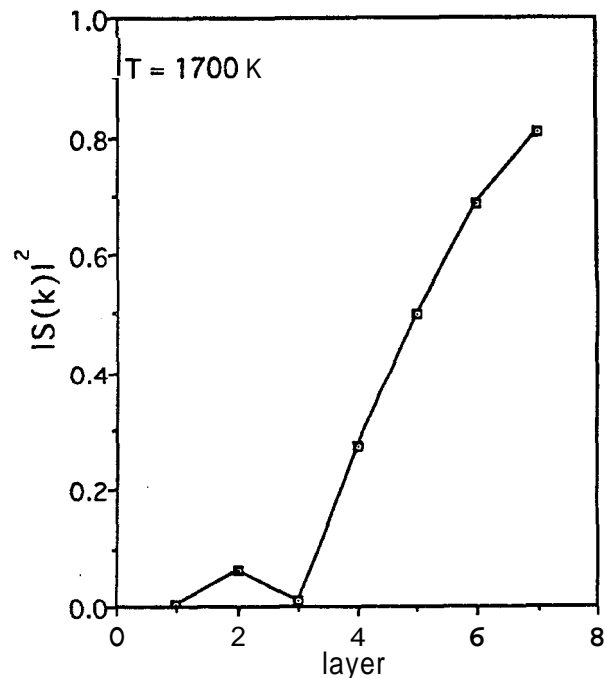
Figure 3: Absolute square of the structure factor of a in-layer reciprocal lattice vector for the top seven layers of a Be substrate at 1700 K.

Figure 1: Absolute square of the structure factor of a in-layer reciprocal lattice vector for the top seven layers of a Be substrate at **1500** K.

IV. Supported cluster

We now turn our attention to the case of the cluster deposited on a substrate. We consider a 55-atom Be cluster deposited on a (0001) Be surface. Since we are

not interested in the process of collision itself, only the case of extreme soft-landing was considered. The 55-atom icosahedric Be cluster, as shown in Fig. 4,
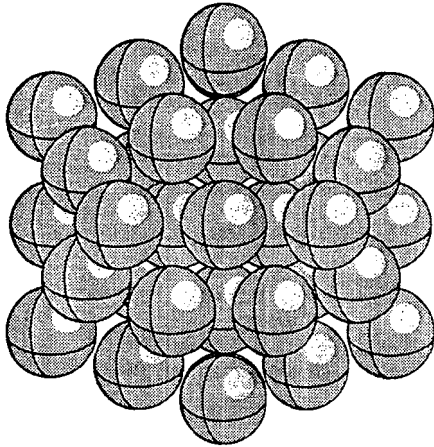

Figure 4: Atomic structure of the free Be_{55} cluster.

is placed nearby the substrate at T = 0 K. In this case, the substrate was simulated by a slab containing 504 Be atoms arranged in three layers. The bottom layer was kept rigid. The second layer had its temperature controlled by rescaling the atomic velocities. In order to mimic the experimental conditions, the atoms in the top layer and in the deposited cluster were not submitted to any external force or constraint, their motion determined only by the interatomic forces. The energy is then minimized using the simulated annealing technique. The whole system, except the bottom layer, is allowed to relax until the interatomic forces are about 10^{-6} eV/Å. Fig 5 shows the final atomic structure. The atoms represented by black balls belong to the cluster, the "white" atoms belong to the substrate top layer, and the "gray" atoms belonged to the substrate and have been removed from it. From the figure one can see that the atomic structure of the deposited cluster has now a layered structure, bearing no resemblance with the original icosahedral cluster. This dramatic change is caused by the strong interaction between cluster and substrate.
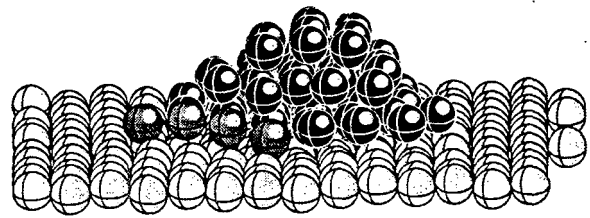

Figure 5: Equilibrium structure of a Be_{55} cluster deposited on a (0001) Be surface at T = O K. The "white" atoms are substrate atoms, the "gray" atoms also belong to the substrate but have been removed from it "wetting" the cluster, and the "black" atoms belong to the cluster. Only the first layer of the substrate is shown.

In order to investigate the thermal stability of the supported cluster the temperature of the substrate is raised very slowly. Figs. 6 and 7 show the snapshots of the system at 300 K and 500 K, respectively. These two figures are very similar and also very close to the structure at 0 K, except for the larger number of atoms removed from the substrate. As the temperature continues increasing the system undergoes a structural transition. In Fig. 8 we display a snapshot of the system at 700 K. The cluster spreads out and its top layer disappears at this temperature. In order to quantify these structural changes we used as order parameter the ratio given by

$$\eta = \frac{R}{h} \, , \qquad (1)$$

where R is the mean cluster radius and h is the height of the center of mass of the cluster from the substrate. This parameter has been used in the experimental determination of the melting point of supported clusters[6]. In Fig. 9 we display the order parameter η as a function of temperature considering only the atoms in the original cluster. One can see that η remains practically constant from 0 K up to 500 K. Above 500 K it rises abruptly indicating a transition. In Fig. 10 we include the atoms that were pulled out of the substrate ("black" atoms) in the determination of η. In this case, η rises between 0 K and 300 K because of the atoms coming from the substrate to "wet" the original cluster. It remains constant from 300 K to 500 K. At 600 K it rises abruptly as in the case of the "dry" cluster. From these results it is clear that the atoms that are pulled out from the substrate "wetting" the cluster do

not affect the transition temperature. We also have to emphasize that the "wetting" process is not an artifact of our simulation, because, as we mentioned in our analysis of the free surface, the vacancies are only created at temperatures around 1200 K. Thus, the "wetting" process is caused by the presence of the cluster.
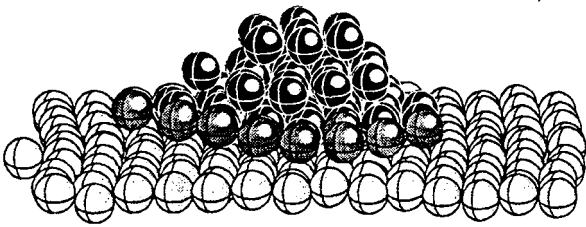

Figure 6: A snapshot of the atomic structure of a Be_{55} cluster deposited on a (0001) Be surface at $T = 300$ K. The color code is the same as in Fig. 5.
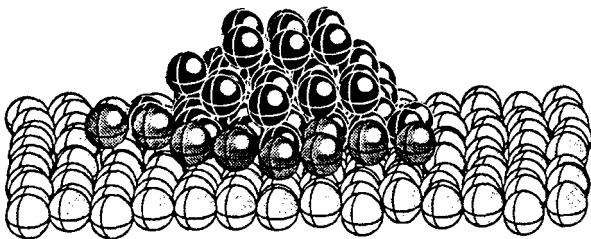

Figure 7: A snapshot of the atomic structure of a Be_{55} cluster deposited on a (0001) Be surface at $T = 500$ K. The color code is the same as in Fig. 5
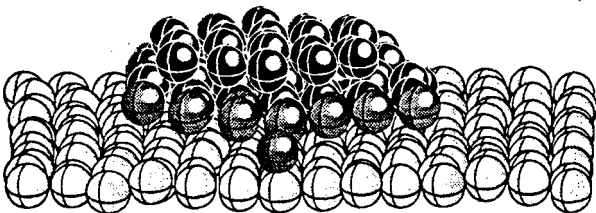

Figure 8: A snapshot of the atomic structure of a Be_{55} cluster deposited on a (0001) Be surface at $T = 700$ K. The color code is the same as in Fig 5.
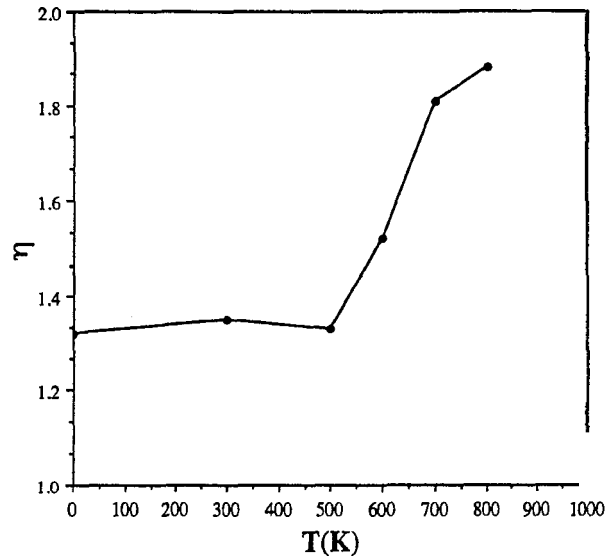

Figure 9: Parameter η [Eq. (1)] as a function of temperature, considering only atoms of the original cluster.
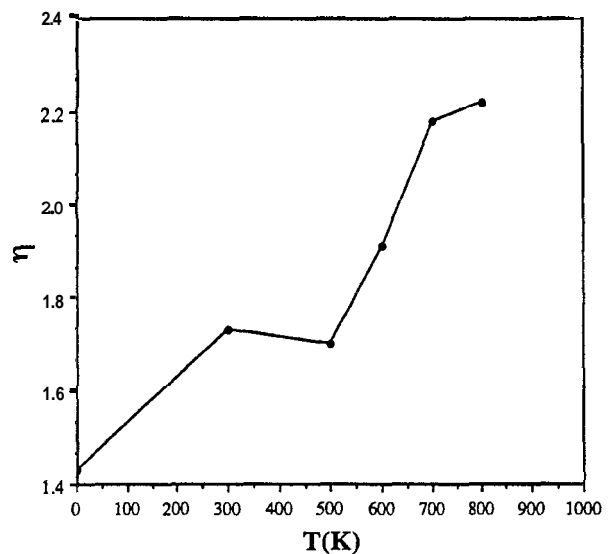

Figure 10: Parameter η [Eq. (1)] as a function of temperature, considering atoms of the original cluster plus those removed from the substrate.

We now consider the case of the thermal stability of the free 55-atom Be cluster. The root-mean-square fluctuation of the interatomic distance given by

$$\delta = \frac{2}{N(N-1)} \sum_{i,j} \frac{\sqrt{< r_{ij}^2 > - < r_{ij} >^2}}{< r_{ij} >}, \quad (2)$$

where r_{ij} is the distance between the ith and j^{th} atoms, has been used as a order parameter to investigate the thermal stability of free clusters. We performed molecular dynamics simulations at constant energy (microcanonical) for a 55-atom Be cluster at several energies.

The order parameter 6 is obtained from the simulations and the results are shown in Fig. 11 as a function of temperature, which in this case is obtained from the mean kinetic energy of the particles. At low temperatures the order parameter 6 has a $\sqrt{T}$ behavior. Around $T = 1000$ K it rises very rapidly indicating the softening of the cluster[8]. Above 1400 K the liquid behavior is very clear. From these results we estimate the melting temperature to be around 1200 K. This estimate for the free cluster is about twice the transition temperature of the supported cluster. From our simulations it is clear that the substrate can play an important role in the thermal stability of the cluster. The simulations indicate that, when there is a strong interaction between cluster and substrate, the structure of the deposited cluster bears no resemblance with the free cluster. This dramatic structural change may be a clue for the constant transition temperature behavior observed experimentally for clusters with diameter below 2 nm[6].
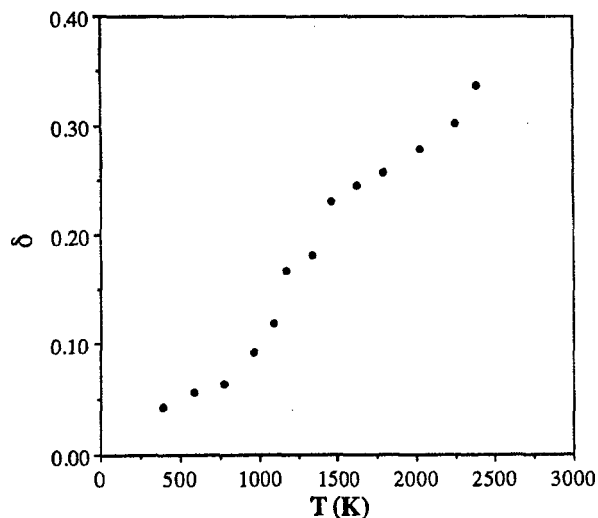

Figure 11: Parameter 6 [Eq. (2)] as a function of temperature.

V. Summary

The many-body potential for Be proposed by Blaisten-Barojas and Khanna[12] derived from LDA calculations describes very well both zero and finite temperature properties of the free (0001) Be surface. The large and unexpected expansion of the first-second layer spacing determined theoretically agrees very well with recent experimental findings. The melting point estimate of 1600 ± 50 K for the melting point of bulk Be obtained monitoring the propagation of the liquid the phase into a thick slab of Be is also in good agreement with the experimental melting point of 1562 K.

Our simulations show that the supported cluster has a layered structure which is very different from the icosahedral structure of the free Be 55-atom cluster, due to the strong coupling between cluster and substrate. As the temperature of the substrate is raised, the supported cluster undergoes a sharp structural transition around 550 K, which is much smaller than the transition temperature for the free cluster of 1200 K. These results show that comparisons between experiments performed on supported clusters and calculations involving free cluster have to be done very cautiously, specially when there is a strong interaction between cluster and substrate.

References

1. *Physics and Chemistry of Finite Systems: from Clusters to Crystals*, edited by P. Jena, S. N. Khanna and B. K. Rao (Kluwer, Dordrecht, The Netherlands, 1992).

2. S. R. Phillpot, S. Yip and D. Wolf, Computers in Physics, Nov/Dec, 20 (1989).

3. J. W. Frenken and J. F. Van der Veen, Phys. Rev. Lett. 54, 134 (1985).

4. P. Stolze, J. K. Norskov and U. Landman, Phys. Rev. Lett. 64,440 (1988); C. T. Chen, N. Barnen and U. Landman, Phys. Rev. B 41, 439 (1990); E. Carnevali. F. Ercolessi and E. Tosatti, ibid. 36, 6701 (1987).

5. Ph. Buffat and J. P. Borel, Phys. Rev. A **13,** 2287 (1976).

6. T. Castro, R. Reifenberger, E. Choi and R. P. Andres, Phys. Rev. B 42, 8548 (1990).

7. W. A. de Heer, W. D. Knight, M. Y. Chou and M. L. Cohen, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 94.

8. Z. X. Cai, S. D. Mahanti, A. Antonelli, S. N. Khanna and P. Jena, Phys. Rev. B 46, 7841 (1992).

9. J. Jellinek and J. L. Garzon, Z. Phys. D 20, 235 (1991); J. Jellinek and J. L. Garzon, ibid. 20, 239 (1991); F. Ercolessi, W. Andreoni and E. Tosatti, Phys. Rev. Lett. 66, 911 (1991); A. Bulgac and D. Kusnezov, ibid.' 68, 1335 (1992).

10. C. L. Liu and J. B. Adams, Surf. Sci. 268, 763 (1992); S. Erkoc, T. Halicioglu and W. A. Tiller, ibid. 274, 359 (1992).

11. A. Antonelli, S. N. Khanna and P. Jena, Phys. Rev. B 48, 8263 (1993).

12. E. Blastein-Barojas and S. N. Khanna, Phys. Rev. Lett. 61, 1477 (1988).

13. L. Verlet, Phys. Rev. 159, 98 (1967).

14. H. L. Davis, J. B. Hannon, K. B. Ray and E. W. Plummer, Phys. Rev. Lett. 68, 2632 (1992).

15. A. Antonelli, S. N. Khanna and P. Jena, Surf. Sci. Lett. 289, L614 (1993).

16. P. J. Feibelman, Phys. Rev. B46, 2532 (1992).