Development of a First-Principles Many-Body Potential for Beryllium

Estela Blaisten-Barojas[a] and S. N. Khanna
Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284-2000
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An interatomic potential is developed for beryllium based on the simultaneous fit to the total energy of 2- to 5-atom clusters obtained in the local-spin-density approximation. The increasing *s-p* hybridization with cluster size is incorporated through a three-body term depending on the number of atoms. Results using the potential give an excellent description of the early stages of crystal growth and a correct prediction of the stability of the hcp lattice over bcc and fcc phases.

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The importance of accurate interatomic force fields in studies of the structural properties of materials is well documented.[1] Although it is common to construct empirical potentials by fitting bulk properties, it is not clear if these potentials can simulate the equilibrium structure of clusters and surfaces.[2] Recent molecular-dynamics studies of Si clusters[3] using empirical potentials[4] have predicted cluster structures in disagreement with quantum mechanical calculations.[5] An alternative is the Car and Parrinello[6] method where the electronic and nuclear relaxations are treated simultaneously.

In this Letter we propose another approach. We generate a class of potential functions that account for the orientational dependence of local quantities through a function containing two- and three-body terms built from a "simultaneous" fit to the local-spin-density (LSD) energy surface data of dimers up to pentamers. We have applied this technique to beryllium for the following reasons: (1) The beryllium dimer is very weakly bonded.[7,8] (2) The trimer is an equilateral triangle binded by the attractive three-body energy.[9] (3) As more atoms aggregate to form small clusters, the binding increases because of the increasing *s-p* hybridization.[8-11] Beryllium in bulk phase is metallic. Be_4 has a stable tetrahedral structure,[9,10] although the four-body term has been estimated to be repulsive.[12] Be_5 is a trigonal bipyramid where *s-p* hybridization has substantially evolved to the band values.[9,13] The *s-p* hybridization converges fast with cluster size to the bulk *sp* band overlap.[11,14] The model potential V_2+V_3 was fitted simultaneously to 119 points of the total-energy surfaces of Be_2 up to Be_5 obtained within the LSD approximation.[13] A nonlinear least-squares method was used to fit 23 points of the energy surface of Be_2, 76 points for Be_3, 19 points for Be_4, and 1 point for Be_5. By so doing, four- and five-body contributions are partially taken into account in terms of a "scaled" three-body term.

The binding energy of a system with N atoms is

$$E=\sum_{i<j} V_2(r_{ij})+\sum_{i<j<k} V_3(r_{ij},r_{ik},r_{jk};N). \tag{1}$$

The pairwise potential V_2 has the following form:

$$V_2(r)=A\exp(-\alpha r)-Cf_B(r)/r^5, \tag{2}$$

where $f_B(r)=\exp[-B(r_0/r-1)^5]$ if $r<r_0$ and $f_B(r)=1$ otherwise. The three-body term V_3 is of the ex-

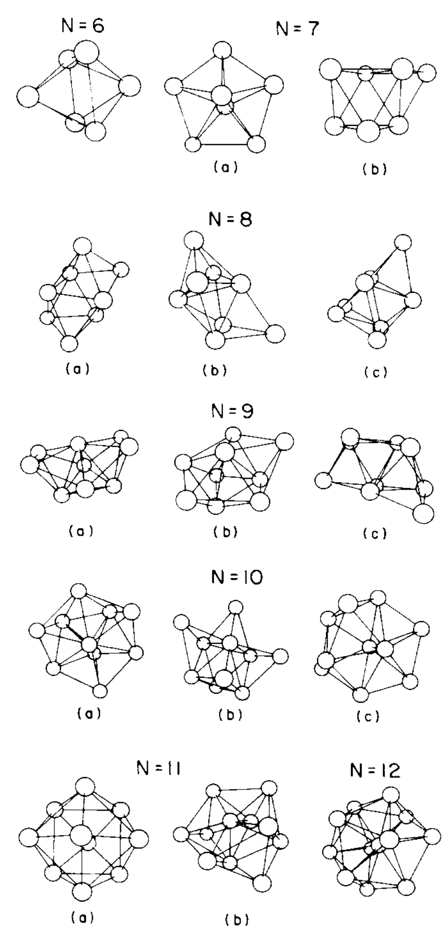

FIG. 1. Cluster configurations. Structures (a) correspond to the global minimum and bonds were taken as $1.25r_0$.

TABLE I. Coordination number C_N, mean bond length d, and binding energy per atom E_N (a.u.) for clusters in Fig. 1.

			Model potential		*ab initio*	
N	Structure	C_N	d/r_0	E_N	d/r_0	$10^2\ E_N$
2	Diatomic	1.0	1.25	−0.0067	1.15	−0.175[a]
3	Eq. triangle	2.0	1.08	−0.0184	1.04 ± 0.02	−1.274[a]
4	Tetrahedron	3.0	1.00	−0.0404	0.97 ± 0.02	−2.987[a]
5	Trig. bipyr.	3.0	1.004	−0.0479	1.07	−2.907[b]
6	Octahedron	4.0	0.982	−0.0585	0.98	−3.023[b]
7(a)	Pent. pyr.	4.6	1.013	−0.0595	1.18	−1.831[c]
(b)		4.3	1.008	−0.0574		
8(a)		4.5	1.009	−0.0614		
(b)		4.7	1.027	−0.0591		
(c)		4.5	1.028	−0.0565		
9(a)		5.1	1.032	−0.0624		
(b)		5.1	1.035	−0.0622		
(c)		4.9	1.036	−0.0598		
10(a)		5.4	1.038	−0.0653		
(b)		4.8	1.027	−0.0634		
(c)		5.0	1.034	−0.0622		
11(a)	Bioctahedron	6.2	1.068	−0.0684		
(b)		5.5	1.051	−0.0646		
12(a)		6.0	1.044	−0.0717		
13(a)	Icosahedron	6.5	1.043	−0.0777		
(b)	hcp	5.5	1.031	−0.0707	1.00	−5.094[d]
(c)	fcc	5.5	1.033	−0.0703	0.99	−5.451[d]

[a]Harrison and Handy, Ref. 10.
[b]Marino and Ermler, Ref. 9, MP4/6-31G*.
[c]Marino and Ermler, Ref. 9, MP4/6-31G.
[d]Rohlfing and Binkley, Ref. 11.

change overlap form[15] added to the triple dipole term,[16]

$$V_3(r,s,t;N)=\{-D(N)\exp[-\beta(r+s+t)]+C'/(rst)^3\}h(r,s,t)f_{B'}(r)f_{B'}(t)f_{B'}(s), \tag{3}$$

where

$$h(r,s,t)=3\cos\theta_1\cos\theta_2\cos\theta_3+1$$

depends upon distances r,s,t and angles θ_i substended by any triplet of atoms. Variations of the s-p binding with N are scaled by the parameter $D(N)=D-G(0.25-N^{-1})$ if $N\geq 4$ and $D(N)=D$ otherwise. V_3 gives a local picture of the bonding since the s-p directional bonding builds up by the addition of triplets of atoms.

The ten parameters in Eqs. (1)-(3) are in a.u. (hartrees for energy): $A=77.27716$, $\alpha=1.71169$, $B=0.6961$, $C=87.39774$, $D=9.65426$, $\beta=0.485767$, $G=35.945$, $C'=673.4099$, $B'=\frac{1}{3}$, $r_0=4.04$. This fit led to a sum of squares of 0.0022 using the Levenberg-Marquardt algorithm.

With this potential we have generated clusters with up to 13 Be atoms by repetitive steepest-descent minimization of Eqs. (1)-(3) from a set of initial geometries obtained by an unbiased Monte Carlo technique.[17] The resulting lowest-energy structures are drawn in Fig. 1 for clusters with 6 up to 12 atoms. Pertaining quantities are listed in Table I. The LSD binding energies for Be_2 to Be_5 are −0.00667, −0.01974, −0.03989, and −0.04473 a.u. As seen from Table I they compare well with values based on the model potential. In addition, we tested the performance of the potential by calculating 15 Be_5 distorted trigonal bipyramids using the LSD and po-

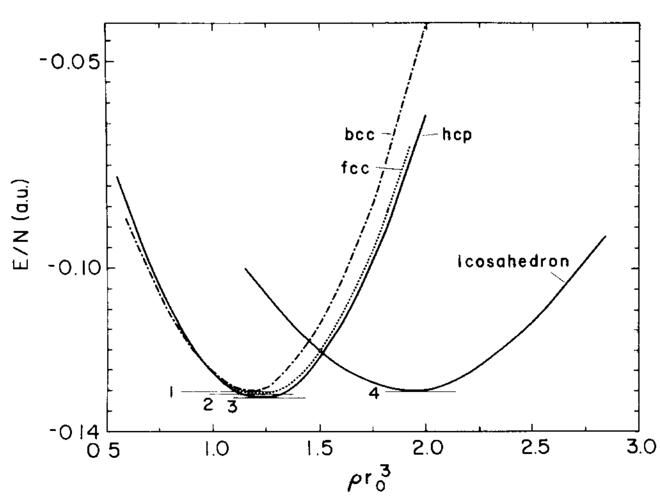

FIG. 2. Lattice energy as a function of atomic density.

tential. The agreement is within 5%. We also compared the binding energies of Be_5 in the square pyramid triplet configuration. The potential leads to -0.0436 a.u., while LSD gives -0.0404 a.u. This geometry was found stable by other authors[9] as well. Furthermore, the structures of Be_3 up to Be_7 based on the potential are the same as those predicted by *ab initio* studies[9,10] (see Table I). Inspection of Fig. 1 shows that two 6-atom units, the octahedron and the pentagonal pyramid, are the basic building blocks in the aggregation of the larger clusters. Be_{11} is made up of two octahedrons sharing one atom and rotated 45° with respect to one other. This cluster is the smallest to have one internal atom (not drawn in the figure). Be_{12} is an icosahedron with one missing atom. Be_{13} has three symmetries—icosahedron, hcp, and fcc polyhedra in decreasing order of stability. *Ab initio* results[11] without geometry optimization predict the fcc structure to be more stable than the hcp cluster. However, no quantum mechanical calculation exists for the icosahedron. Be_{13} binding energies obtained from the potential for geometries as in Ref. 11 are fcc $=-0.897$ a. u. and hcp (singlet) $=-0.8887$ a.u., showing a reversal in the energy ordering when structures are not optimized. From the binding energy values and from the relations $\delta E = E_N - (E_{N-x} + E_x)$, $x < N$, the 4-, 6-, and 13-atom clusters appear as energetically preferred.

In order to examine how the potential reproduces bulk structural properties, we have calculated the cohesive energy of the hcp, bcc, and fcc lattices of beryllium as a function of atomic density (Fig. 2). We also report the changes in the binding energy of icosahedral clusters with 309 atoms. Binding energies, densities, and lattice constants calculated from the minimum of the curves in Fig. 2 are given in Table II and compared with experimental values.[18] Several conclusions can be drawn. First, the most stable phase of Be has the hcp structure (3 in the figure). Second, as density gets lower, the bcc (1) structure is more stable than both fcc (2) and hcp (3) as observed experimentally. Icosahedral packings (4) are stable only at high densities. Third, the calculated cohesive energy is in quantitative agreement with experiment. Finally, the predicted lattice constants and the compressibility agree with experiment to within 2% and 1%, respectively.

Also relevant is the relative effect of the two- and three-body terms of the potential in the aggregation of hcp clusters as they grow in size. Figure 3 shows the two- and three-body contributions to the energy of the central site. It is clearly shown that the energy of larger clusters "seems" to be dominated by the two-body terms because the long-range contribution to V_3 averages out with size. However, three-body terms have a dominant role locally since they build up the orientational bonding. Consequently, an effective potential fitted exclusively to bulk data will underscore the importance of the local binding and will not give a correct description of clusters. In the same vein, potentials obtained from trimers alone will overestimate the three-body term and may not lead to the correct extended behavior of the bulk. These shortcomings are avoided when the fitting procedure takes into account additional points obtained from the energy surface of clusters larger than trimers.

It is extremely satisfactory to obtain these results for bulk Be from a potential obtained exclusively from the description of the electronic structure of clusters. We are presently investigating the meltinglike transition in alkaline-earth clusters in a molecular-dynamics simulation using this new potential.

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TABLE II. Cohesive energies E/N, atomic density ρ, lattice constants a and c, and compressibility K.

		E/N (a.u.)	ρr_0^3	a,c (a.u.)	$10^{12}K$ (cm^2/dyn)
This work	hcp	−0.1322	1.23	4.26,6.96	1.001
	bcc	−0.1292	1.19	4.76	
	fcc	−0.1313	1.15	4.33	
	Icosahedron	−0.1313	2.03		
Expt.	hcp	−0.1230	1.2	4.3,6.8	0.997
	bcc	high T		4.7	

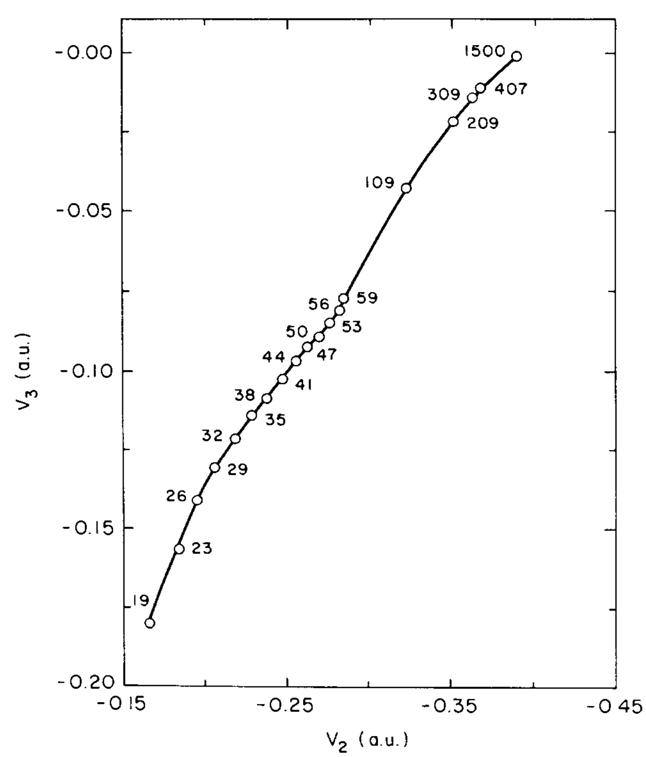

FIG. 3. Two-body and three-body contributions to the binding energy of the central site in aggregates with hcp symmetry.

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[a]On sabbatical leave from Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Apartado Postal 20-364, 01000 Mexico, D.F., Mexico.

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