PHYSICAL REVIEW B VOLUME 54, NUMBER 23 15 DECEMBER 1996-I

Size dependence of the lattice parameter for Pd clusters: A molecular-dynamics study

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(Received 17 July 1996)

Small Pd clusters with diameters ranging from 14 to 30 Å have been studied using molecular dynamics with a many-body potential derived from first-principles calculations in bulk Pd. The results for the structural properties of these clusters are compared with recent experimental data obtained for Pd clusters embedded in an amorphous matrix. These calculated results for free clusters correlate rather well with the experiments. The main conclusions of the present study are that the amorphous matrix does not substantially affect the cluster structure, and that the many-body potential is appropriate for cluster calculations. [S0163-1829(96)05347-7]

INTRODUCTION

Structural properties of small metallic clusters is a subject of increasing interest, and theoretical and experimental efforts have been pursued in recent years to understand their unique features.[1] The understanding of how the properties of clusters evolve toward properties of the bulk material is rather important. Metallic clusters have lattice parameters that in general decrease as the diameter of these clusters decrease (reduction of the number of atoms in the cluster). The lattice contraction has been explained by Vermaak, Mays, and Kuhlmann- Wilsdorf,[2] who attributed it to surface stress.

Pd clusters, on the contrary, have been reported to show a dilatation of lattice parameter[3–5] with decrease of cluster size. This is a very unusual result, and a number of reasons have been put forward to explain this effect, namely, structural change,[3] pseudomorphism (perfect accommodation between the cluster and the substrate lattice),[5] and incorporation of other atoms such as oxygen,[6] hydrogen,[7] and carbon[8] into the Pd lattice.

Recently the size dependence of Pd clusters with diameters ranging between 14 and 50 Å have been measured by Lamber, Wetjen, and Jaeger.[9] Small clusters of Pd were prepared in a plasma polymer matrix. This technique for the production of clusters embedded in a plasma matrix provides clusters which are uniform in size and free from impurities. The lattice parameters of these clusters have been measured, and a contraction was found with decreasing size of the cluster. This result is in opposition to previous measurements of small Pd clusters.[2–5] To our knowledge the experiments reported in Ref. 9 are the first experimental instance in which Pd particles are produced as close as possible to the situation of free-standing clusters. Since the plasma polymer matrix is an amorphous structure, there is no crystalline lattice to provide pseudomorphism. Aside from that, this matrix has the advantage of protecting the clusters from contamination with others atoms such as H, O, C, etc.

The theoretical understanding of the above experimental results can be approached by the use of computer simulations (CS) for clusters of varying sizes. Of course, Pd clusters are transition-metal clusters (TMC's) and, therefore, the nature of the chemical bonding is more complex than in simple metals. An *ab initio* density-functional theory molecular-dynamics[10] study would be desirable in order to understand this kind of system. However, at this moment such calculations for large clusters ($n>20$) are computationally prohibitive. Most transition-metal cluster studies have used empirical potentials. Examples of these methods are the embedded atom,[11] the effective medium,[12] and the corrected effective medium.[13] A crucial aspect of any empirical potential for clusters is its ability to reproduce the size dependence of their properties. One potential that has been used to study TMC's is that proposed by Gupta,[14] which was used by Jelinek and Garzon.[15] The same potential, with a different parametrization, was used to study Na clusters.[16] A parametrization of such a potential appropriated for Pd was done by Zhong, Li, and Tomanek[17] to study the effect of H adsorbates on the surface-phonon modes of Pd. We consider this parametrization of Zhong, Li, and Tomanek[17] of Gupta's potential[14] to study Pd clusters. The present study considers the stability and lattice dependence of Pd clusters with the size of the cluster. In another publication we consider the stability of small Pd clusters and the absorption of H by these clusters.[18]

MANY-BODY POTENTIAL FOR CLUSTERS

The many-body potential (MBP) for clusters used in the present simulations goes back to the work of Gupta, who used it to study lattice relaxation at a metal surface.[14] This potential is suitable for metals which have a fcc structure in their bulk form. It is based on tight-binding arguments and has two terms, one corresponding to band energies and the other repulsive in nature. This type of potential has been successfully used in the study of surfaces, clusters, and bulk properties for transition and noble metals.

The cohesive energy of a cluster with n atoms is decomposed into binding energies of individual atoms,

$$E_{\mathrm{coh}}=\sum_{i=1}^{n} E_{\mathrm{coh}}(i). \tag{1}$$

The binding energy of atom i consists of an attractive part, due to the hybridization of its orbitals with their neighbors, and another one, which takes into account repulsive interactions,

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$$E_{\mathrm{coh}}=E^{A}(i)+E^{R}(i). \tag{2}$$

Over the years many different parametrizations have been proposed for the attractive part of the MBP. The embedded atom scheme takes $E^A(i)$ to be a unique functional of the total charge density of the unperturbed host at the site i. The Gupta expression is based on a tight-binding approach, where this part is taken to be proportional to the bandwidth of the solid and is written as the square root of the second moment of the local density of states.

The repulsive part $E^R(i)$ is parametrized by a pairwise Born-Mayer potential with an exponential dependence on the distance r_{ij} between atoms i and j. Therefore, the binding energy for an atom i is given by

$$E_{\mathrm{coh}}(i)=-\left\{\sum_{i\neq j}\xi_0^2\exp\left[-2q\left(\frac{r_{ij}}{r_0}-1\right)\right]\right\}^{1/2}+\sum_{i\neq j}\epsilon_0\exp\left[-2p\left(\frac{r_{ij}}{r_0}-1\right)\right]. \tag{3}$$

Here r_0 is the equilibrium distance in the bulk solid. The parameters p and q set the scale of the distance dependence of the hopping term and the Born-Mayer interactions, respectively. The terms ξ_0 and ϵ_0 are the energy scales for the attractive and repulsive energy terms.

The cohesive energy given by Eq. (3) for the MBP explains the essential physics governing cohesion in a wide class of solids. This expression takes into account many-body effects through the first term.

Several parametrizations for this MPB have been proposed over the years since the work of Gupta.[14] The present simulations shall use the parametrization due to Zhong, Li, and Tomanek,[17] which was obtained by fitting Eq. (3) to an *ab initio* total-energy band-structure calculation for bulk Pd and Pd-H. Their results reproduce well many features of surface phonons, and we expect that its transferability for the case of clusters to be a reasonable proposal. In the case of pure Pd clusters it has been used to study Pd$_n$ clusters with $n=4$–14.[19] We performed calculations for Pd$_n$ clusters with $n=4$–14, obtaining the same structure and similar cohesive energies as in Ref. 19. We shall not discuss such small clusters here, since in the present work we are concerned with clusters of larger sizes, ranging from 80 to 1500 atoms.

MOLECULAR-DYNAMICS SIMULATIONS

This work uses simulated annealing to obtain the equilibrium structures for Pd clusters as a function of their diameters. We use molecular dynamics to implement the simulated anealing. The equations of motion are solved using Verlet's algorithm.[20] The interaction between atoms was taken in the analytical form of Eq. (3), and used the parametrization of Zhong, Li and Tomanek,[17] which gave good results for Pd and Pd-H simulations for bulk and surface properties. The typical time step was taken as 2.5×10^{-16} s, and the typical rate of annealing was a 5% reduction in the magnitude of the velocities for every time step. The simulations started from a nonrelaxed fcc spherical cluster and the system evolved with the molecular-dynamics simulation to its equilibrium structure. Typically that was achieved for the smaller Pd$_n$ clusters within 15 000 time steps. The equilibrium for the clusters with $n>1000$ atoms was more difficult to achieve. As the size of the cluster increases, more and more local minima with small energy barriers seem to exist, and care is necessary in order to find the lowest-energy minimum. For those clusters smaller time steps and the choice of the starting point helps to find the proper minimum.

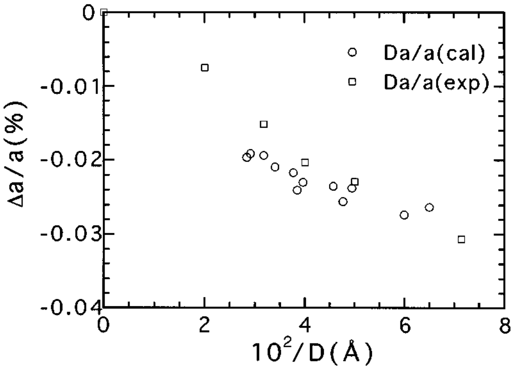

FIG. 1. Variation of the relative lattice parameter $\Delta a/a$ as function of the inverse diameter of Pd clusters.

RESULTS AND DISCUSSION

The aim of the present study is to obtain the dependence of the lattice parameter of Pd clusters with the size of the cluster. This was motivated by the experimental results of Lamber, Wetjen, and Jaeger[9] who produced small particles of Pd (embedded in a plasma polymer matrix) with sizes varying from 14 to 50 Å in diameter. Their results have shown the fcc lattice parameter of the cluster increasing with the size of the cluster. The present calculations show a trend similar to the experimental results: that is, the fcc lattice parameter of the clusters increases with the size of the cluster. Figure 1 shows a plot of $\Delta a/a$, where $\Delta a=(a_{\mathrm{cluster}}-a)$ with a_{cluster} and a the lattice parameter of the cluster and the lattice parameter of bulk Pd, respectively, as a function of the inverse of the cluster diameter $1/D$, where the present CS are compared with the experimental data.[9] Figure 2 shows the actual lattice parameters calculated along with the experimental results shown with an average error of 1%. The reported errors for the experimental results range from 1% to 2%; therefore the results of the present CS are all within the experimental error. Within the CS it is possible to perform

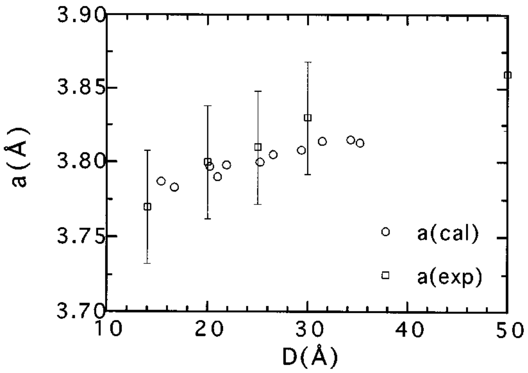

FIG. 2. Variation of the lattice parameter a as function of the inverse diameter of Pd clusters.

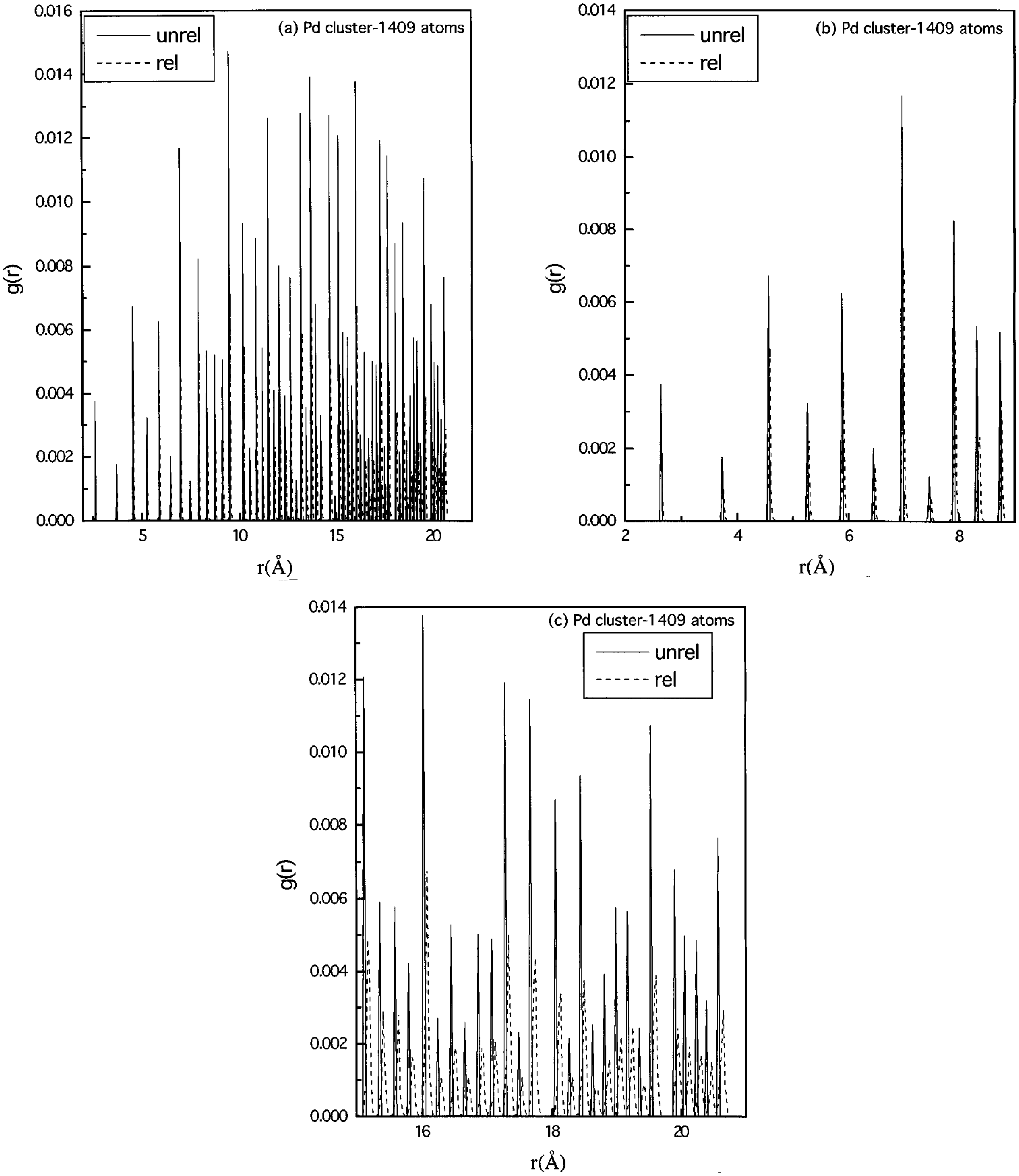

FIG. 3. Radial distribution function $g(r)$ for a Pd cluster of 1409 atoms. The full line displays $g(r)$ for a fcc undistorted cluster with lattice parameter a_u=3.798 Å, and the dashed line displays the same cluster relaxed under the simulation to a lattice parameter a_r=3.813 Å. (a) gives the full range of $g(r)$ for this cluster, (b) gives $g(r)$ for the first few closer neighbors, and (c) the same for the more distant neighbors.

calculations varying the number of atoms and consequently the size of the clusters on a finer scale than the experiments. Our results show an oscillation in the lattice parameter ratio with the cluster diameter. All the clusters we considered are fragments of a fcc lattice; however, the number of atoms in the outer shells can vary significantly, leading to very distinct relaxation. We have to emphasize that the structure of all the clusters we consider remained fcc after relaxation. We believe that the different relaxations, due to the different number of atoms in the outer shells, can explain the observed oscillations in the calculated lattice parameters.

In order to show that our relaxed cluster structures remain fcc in Fig. 3 we give the radial distribution function $g(r)$ for a typical cluster of 1409 atoms of Pd. The full line displays $g(r)$ for a undistorted cluster with a lattice parameter of a_u=3.798 Å, and the dashed line shows the same cluster after relaxation due to CS with a_r=3.813 Å. Figure 3(a) shows the whole range of $g(r)$ while, Fig. 3(b) shows the first few closer neighbors and Fig. 3(c) the more distant ones. One can see that the order is preserved at all distances. At large distances the effect of the relaxation can be seen more clearly, as well as the fact that the order is still preserved with well-defined peaks with a little distortion due to surface tension.

The present results correlate rather well with the experiments, and indicate that free clusters (calculated) are a reasonable proposition for a comparison with Pd clusters embedded in the plasma polymer matrix (which serve to protect the clusters from contamination with other atoms). The previous results that showed an expansion of lattice parameters with the reduction of the cluster size were probably caused by pseudomorphism induced by the substrate lattice used in experiments.[3–5] This is an effect that was ruled out in the experiments of Lamber, Wetjen, and Jaeger,[9] since the polymer matrix is an amorphous system.

We therefore have shown that, if not forced by a substrate lattice, Pd clusters have an increase in lattice parameter with the size of the cluster similar to other metals, as was shown by the experiments of Lamber, Wetjen, and Jaeger[9] and corroborated by the present computer simulations. The results also demonstrate that the many-body effective potential of Zhong, Li, and Tomanek[17] describes the trend of these clusters well, and can be used to study other questions concerning clusters of Pd.

ACKNOWLEDGMENTS

This work was partially supported by Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundo de A|poio ao Ensino e Pesquisa da Universidade Estadual de Campinas.

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