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Is There a Contraction of the Interatomic Distance in Small Metal Particles?

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A theoretical analysis is made of the bond lengths of small (100–1000 atoms) Cu particles at various temperatures. The interatomic interactions are calculated using the effective-medium theory and the finite-temperature properties obtained from a molecular-dynamics simulation. We find only very small changes in bond length with particle size, but the motion in the small particles is very anharmonic. We use this observation to resolve the current experimental controversy about the existence of bond contraction for small metal particles.

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Small metal particles attract a large amount of attention. By studying particles of various sizes one hopes to elucidate the transition from *molecular* to *solid-state* properties. Lately, the properties of very small metal particles with less than about 100 atoms have received special attention, due to the discovery of a *shell structure* like in the atom or the atomic nucleus as a function of the number of atoms in the cluster.¹ Small metal particles are also very important from a technical point of view. The active material in catalysts, for instance, often consists of very small metal particles.

One signature of the interatomic interactions in a material is the bond length. The dependence of the bond length on the particle size for small Cu particles has been studied using extended x-ray-absorption fine structure^{2,3} (EXAFS). Apai *et al.*² looked at small particles vapor deposited on a carbon substrate. The results suggested that the bond length decreases continuously with decreasing metal particle diameter. Montano *et al.*³ looked at particles isolated in a solid-argon matrix. These clusters showed hardly any change in the nearest-neighbor distances except for the very smallest particle diameters. This apparent discrepancy was attributed to interactions with impurities in the carbon support or to inhomogeneities in the particle-size distribution.³

We have studied this problem further by performing molecular-dynamics simulations of Cu particles with about 100–1000 atoms and for bulk Cu. In the present Letter we concentrate on two main findings of this work: First of all, we find that the average bond length is basically independent of the particle size in the whole range from particles with a diameter of 8 to bulk Cu crystals. Second, we show that the motion of the surface atoms is very anharmonic. We suggest that this is the main reason why two experiments on almost the same system can give rise to two different conclusions. The matrix-isolated Cu particles were studied at very low temperature, where the anharmonic effects are negligible, whereas the carbon-supported Cu particles were studied

at room temperature, where the anharmonicity gives rise to problems in the standard EXAFS analysis.⁴

The interatomic interactions in the small Cu particles studied have been described in the effective-medium theory.⁵ The form of the interaction potential is derived from density-functional theory, and it includes many-atom interactions in an approximate way. The method has been shown to give a good description of the cohesive and surface properties of metals.^{5,6} Still, the method is computationally efficient enough to be useful in molecular-dynamics and Monte Carlo simulations of bulk and surface properties of metals.⁷ For details of the potential calculation we refer to Refs. 5 and 8. It should be noted that we are ignoring the one-electron-energy corrections⁵ to the energy, which means that we do not include shell effects.⁹ This means that the stability of certain sizes of particles is not described in detail, but we do not expect that it influences effects studied here.

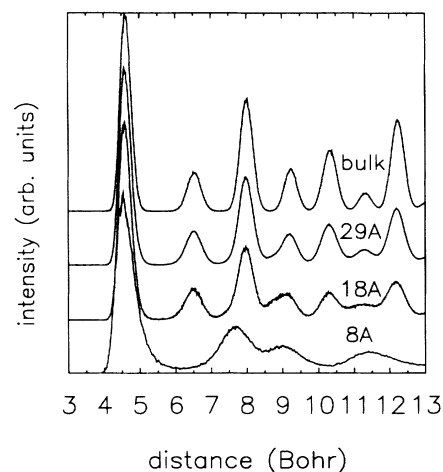


FIG. 1. The calculated pair-distribution functions at 300 K for a 78- (8-), 256- (18-), and 1072- (29-) atom Cu particle, as well as for bulk Cu.

The simulations were performed on particles with 72, 256, and 1078 Cu atoms, as well as for bulk Cu. The starting configuration for the atoms was an fcc arrangement. The propagation in time was made by the velocity-Verlet algorithm. During collection of averages, the system was propagated microcanonically, and collections of averages alternate with periods of stochastic temperature control. The clusters were initially run at a high temperature. The approach to equilibrium was monitored through the total energy of the cluster as well as through the fluctuations in atomic energies. The temperature was lowered in steps after the cluster had equilibrated at each temperature.¹⁰

The main output of the calculation for the present purpose is the pair-distribution function $g(r)$, which is the average number of atoms per unit volume found at a distance r from another atom. The calculated pair-distribution functions are shown in Fig. 1.

From $g(r)$, we define the nearest-neighbor distance as the average

$$r_{\text{nn}} = \frac{\int_0^{r_c} r g(r) 4\pi r^2 dr}{\int_0^{r_c} g(r) 4\pi r^2 dr}, \quad (1)$$

where the cutoff r_c is chosen to be half the way between the nearest- and next-nearest-neighbor distance for bulk Cu.

The relative change in r_{nn} is shown as a function of the particle diameter d in Fig. 2. Let us for a moment look apart from the smallest of the particles studied. The calculated nearest-neighbor distance is then basically constant, and as can be seen from Fig. 1 the equilibrium structure is fcc-like. This agrees well with the results of Montano *et al.*,³ whereas it is in apparent conflict with

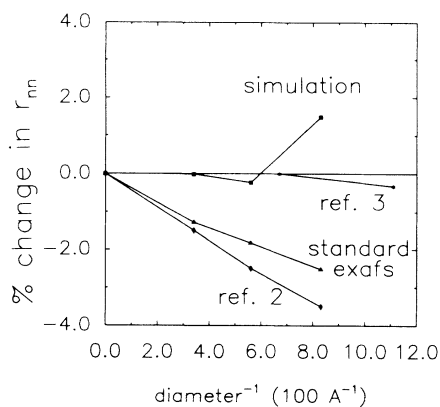


FIG. 2. The change in the average nearest-neighbor bond lengths relative to the bulk Cu value shown as a function of the inverse particle diameter. The result of the simulation [Eq. (1)] is shown along with the experimental EXAFS results of Apai *et al.* (Ref. 2) and Montano *et al.* (Ref. 3). Also shown is the result of a "standard EXAFS" analysis on the calculated pair-distribution functions.

those presented by Apai *et al.*² The smallest particle included in the simulation deviates in structure from the others, and shows a small *expansion*. We shall return to this question later.

It might have been suspected that the average bond length was affected by the large fraction of surface atoms in the small particles. The surroundings of the surface atoms are very different from those of the bulk atoms and hence their bond lengths could be different. This problem has been studied in great detail for metal surfaces.¹¹ It is found quite generally that there is a tendency for the distance between the first and the second layer to contract. The effect is very small (or even nonexistent) for the close-packed fcc (111) and (100) surfaces. For the open (110) surface of Cu, on the other hand, the experimental values for the contraction of the interlayer spacings range¹¹ from 5% to 9% (a calculation using the effective-medium potential gives 4%), corresponding to a contraction of the first- to second-layer bond length of 2.5%–4.5%.

The atoms at the surface of the small particles studied here show exactly the same tendency. The (111) and (100) "micro"-facets show hardly any contraction of the bond lengths whereas the (110) facets show a contraction comparable to the surface one. The reason this does not show up in the average bond length in Fig. 2 is simply that there are too few (110) and higher-order facets in the equilibrium structures for the particles studied. Figure 3 shows the distribution of coordination numbers for the 256-atom particle.¹² An atom in bulk fcc Cu has a coordination number of 12. As can be seen from Fig. 3 this is still the prevailing coordination number even for the 256-atom particle. The atoms at the surface have fewer neighbors and therefore smaller coordination numbers. The (111) and (100) surfaces have coordination numbers 9 and 8, respectively, whereas the atoms in the (110) surface have coordination number 7. Clearly the

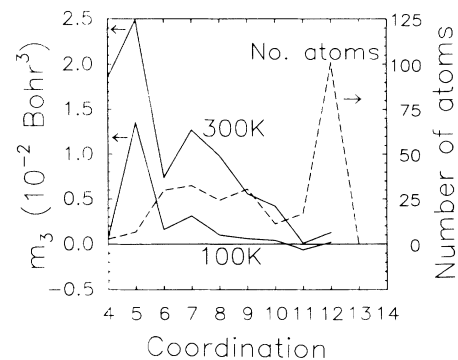


FIG. 3. The third moment [Eq. (2)] of the radial distribution function for the 256-atom particle calculated for atoms with different coordination numbers. The distribution of coordination numbers at 300 K is also shown. The distribution is very similar at 100 K.

fraction of the atoms in the small particles with coordination number 7 is small [about 15% of the total surface area for the 256-atom particle is (110)-like]. Add to this that it is only the first- to second-layer bonds that are contracted on the (110) facets, and one can understand why this does not show up in the averages in Fig. 2.

In order to study the effect of temperature on the bonding we have repeated the molecular-dynamics simulations at 100 K. It must be pointed out that at this temperature quantum effects will be important for the dynamics. The 100-K results are thus to be taken with some care. They will, however, include some of the effects of lowering the temperature of the sample. Lowering the temperature changes the nearest-neighbor distance [Eq. (1)] very little for all the clusters studied. If plotted as in Fig. 2, the 300- and 100-K curves are basically on top of each other.

To pinpoint the differences between the results at the two temperatures it is useful to look at the first few moments of the radial distribution function $g(r)$. The n th moment is defined for $n > 1$ as

$$m_n = \frac{\int_0^r (r - m_1)^n g(r) 4\pi r^2 dr}{\int_0^r g(r) 4\pi r^2 dr}, \quad (2)$$

where the first moment m_1 is equal to the average bond length r_{nn} in Eq. (1). The first moment is thus unchanged when the temperature is lowered except for a very small thermal contraction as seen in Table I. The second moment measures the width of the peaks in $g(r)$. As one could expect m_2 decreases with decreasing temperature. The most striking difference between the two temperatures is that the third moment, which measures the asymmetry of the peaks in $g(r)$, is a factor of 4 smaller at 100 than at 300 K. The asymmetry of $g(r)$ stems from the anharmonicity of the motion of the atoms. In Fig. 3 we show the third moment for the 256-atom particle as a function of the coordination number for the two temperatures. Clearly the relatively large m_3 at 300 K stems from the low-coordination-number atoms at the surface.

The large third moments for $g(r)$ for surface atoms are a consequence of the nonsymmetrical surroundings the surface atoms feel. This gives rise to a potential, which is much more anharmonic than that felt by a bulk atom. The difference between the potential felt by a

TABLE I. The first three moments of the pair-distribution function for a 256-atom Cu particle at 100 and 300 K. The moments are in atomic units.

Temperature (K)	m_1	m_2	m_3
100	4.588	0.0124	0.0008
300	4.606	0.0346	0.0034

bulk and a surface atom is illustrated in Fig. 4.¹³

The difference between the low- and high-temperature results of the simulations holds a possible explanation of the difference between the conclusions of the two EXAFS experiments, which were performed on room-temperature² and low-temperature³ particles. To see this requires a little background on the standard EXAFS analysis.¹⁴ The measured EXAFS spectrum is basically the Fourier transform $g(k)$ of $g(r)$. The small- k part of the experimental signal is dominated by multiple scattering and therefore not included in the analysis. This means that the large- r part of $g(r)$ is lost. To solve this problem one assumes a form for $g(r)$. In the standard analysis the choice is simply a Gaussian. This means that m_3 is implicitly assumed zero. Figure 3 shows that this is a good approximation for bulklike (coordination number 12) atoms at both temperatures and for all atoms at the low temperature. At 300 K, on the other hand, the anharmonicity is important for all the surface (coordination number less than 10) atoms.

To illustrate the importance of the anharmonicity, we have Fourier transformed the calculated $g(r)$ at 300 K to get the EXAFS oscillations like those obtained experimentally. We have then performed a standard EXAFS analysis¹⁴ on these data, and extracted a nearest-neighbor distance, which can then be directly compared to the experimental one of Apai *et al.*² The result is included in Fig. 2. There is now a very nice agreement between experiment and simulation, in terms of both the absolute magnitude and the trend of the effect.

The smallest particle in the simulation shows a $g(r)$ with much broader and asymmetrical peaks than the other particles (cf. Fig. 1). Even at low temperature m_3 is large and it must be expected that a standard analysis of a low-temperature EXAFS experiment would run into problems. Such a situation has been discussed for ultrathin Co films.¹⁵ The difference between the simula-

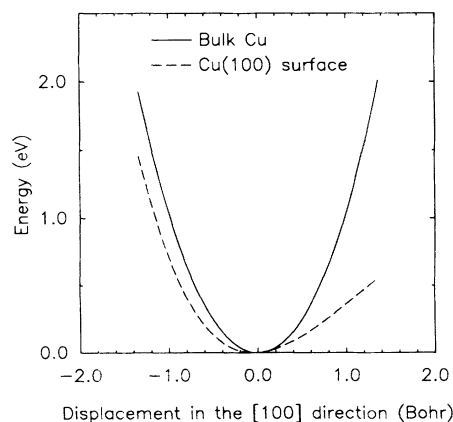


FIG. 4. The change in potential felt by a bulk Cu atom and a Cu atom in the first layer of a Cu(100) surface when the atom is displaced in the [100] direction.

tion and the low-temperature experiment for the smallest diameters in Fig. 2 may thus be due to a change in structure, but may, of course, also be due to the neglect of the one-electron-energy contribution, which becomes more and more important as the number of atoms per particle decreases.

The problem with the standard EXAFS analysis has been pointed out by several authors, and other forms have been suggested to describe EXAFS results from liquids, metallic glasses, and other disordered systems.^{15,16} The present results can be taken as strong support to this point of view.

In conclusion, we have shown that a molecular-dynamics simulation of the bonding properties of small Cu particles predicts only small changes in the average bond lengths when the size of the particles is varied. The surface atoms have very anharmonic vibrations and this gives rise to problems with the standard EXAFS analysis for the small particles at room temperature and above. We suggest that this is a general problem with EXAFS determinations of bond lengths at surfaces or for small particles where the surface atoms play an important role.

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the implications of the present analysis is that this is a smaller effect.

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¹⁰For the 1078-atom cluster, the cooling schedule was 1000 K for 118 ps, 600 K for 101 ps, and 300 K for 100 ps. The 256-atom cluster and the 72-atom cluster fragmented at 1000 K. For these clusters the schedule was 600 K for 118 ps and 300 K for 100 ps. Thermodynamic averages were calculated from 100 configurations collected over a period of 14 ps.

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¹²For all clusters a distinct minimum was found in the radial distribution function between the nearest-neighbor and the next-nearest-neighbor distances. The coordination number was determined as the average number of neighbors within the position of this minimum.

¹³The large anharmonicity of surface atoms show up as anomalously large thermal expansion surfaces. See, e.g., J. M. Frenken, F. Huussen, and J. F. van der Veen, *Phys. Rev. Lett.* **58**, 401 (1987).

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