Vibrational Properties of Metallic Nanocrystals

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Our calculated vibrational properties of Ag nanocrystals show three novel, size dependent features which have broad implications for their thermodynamic properties and stability. There is an enhancement in the vibrational density of states at low frequencies and an overall shift of the high frequency band beyond the top of the bulk phonons. Additionally, the vibrational projected density of states of the surface atoms scales linearly with frequency, at low frequencies. The generality of these results for systems with bond-order–bond-length correlation, low average coordination, and large ratio of surface to bulk atoms helps explain qualitatively several recent experimental observations. [S0031-9007(98)06877-X]

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For the last few decades, studies of surface structure and dynamics have yielded a wealth of information from which a detailed understanding of phenomena at and near the surface have been derived. An important aspect of this body of knowledge is information about structural and dynamical changes at surfaces. As a result of reduced coordination, most surfaces relax inward. The inward relaxation can be explained by the smoothing of the charge density at the surface known as the Smoluchowski [1] effect, as first presented by Finnis and Heine [2] for Al surfaces and put on a more comprehensive basis by Feibelman [3] based on the ideas of bond-order–bond-length correlation advanced by Pauling [4]. For an extended system with a surface, these structural changes will be localized at and near the surface, as the surface-to-volume ratio is vanishingly small. The presence of the surface thus does not affect the thermodynamic properties of the extended system in a noticeable way. But what will happen to the structure and dynamics of a system with a finite surface-to-volume ratio? How would the properties of these mesoscopic systems scale with the surface-to-volume ratio? These and related questions about novel characteristics resulting from the large surface-to-volume ratio surround the intense investigations pursued these days on the subject of nanostructures.

In this Letter we present results for the structure, dynamics, and thermodynamics of metallic nanocrystals with different sizes and show how the characteristics of the vibrational dynamics scale with size. For this purpose, we have investigated the structural properties of Ag, Cu, and Ni nanocrystals with diameters ranging between 2.0 and 5.0 nm. We find that in all cases there is a global shrinkage of the nearest neighbor distance which eventually leads to an overall shift of the high frequency band in the vibrational density of states (DOS) to beyond the top of the bulk phonons. We show that this shrinkage is a characteristic of metals which have a bond-order–bond-length correlation. Our calculated vibrational DOS for the nanocrystals also exhibits a higher population at low frequencies, as compared to that in the bulk. We show that this enhancement is due to the contribution of the surface atoms for which the DOS at low frequencies scales linearly with frequency instead of quadratically, as is typical for the bulk of a solid. As the surface-to-volume ratio decreases with increasing size of the nanocrystals, the total DOS converges to that for the bulk material.

To calculate interatomic distances and dynamics of nanocrystals, we use interaction potentials based on the embedded atom method (EAM) [5], which despite being empirical, have had success in predicting several surface properties like relaxations, reconstructions, and the dispersion of the surface phonons for Ag, Cu, and Ni [5–7]. We have used here the parametrization by Voter and Chen [8] in which experimental values of the bond length and binding energy of the diatomic molecule are also included in the fitting of the potential functions, in addition to several bulk properties. Nanocrystals with diameters 2.0, 2.5, and 3.5 nm containing 225, 459, and 1289 atoms, respectively, are first relaxed to their minimum energy configuration using a conjugate gradient algorithm, and their structure is examined. Next, with the atoms in the equilibrium configuration, the force constant matrix necessary to calculate the vibrational dynamics of the system is obtained from the partial second derivatives of the EAM potential. Since nanocrystalline materials have no long range order in any direction, a real space Green's function approach is employed to calculate the vibrational density of states. In previous work we have found this method to be very suitable for the calculation of vibrational dynamics and thermodynamics of systems with low symmetry [9,10], and also for those with no long range order [11]. Very briefly, from the trace of the Green's function, the vibrational density of states $N_n(\omega)$ is calculated using

$$\rho_n(\omega^2) = -\frac{1}{3n\pi}\lim_{\epsilon\to 0}(\mathrm{Im}\{\mathrm{Tr}[G_n(\omega^2 + i\epsilon)]\})$$

and

$$N_n(w) = 2w\rho_n(\omega^2),$$

where G_n is the Green's function matrix associated with the system containing n atoms.

The calculated vibrational density of states for Ag nanocrystals together with those of atoms in the bulk are shown in Fig. 1a. Note that there are two features which distinguish the DOS of the nanocrystals from those for the bulk atoms: a higher population of low frequency modes and a high frequency tail that extends beyond the top of the bulk band. These two characteristics have been reported recently for the measured DOS of Fe and Ni_3Fe nanocrystals [12–14], but their origin has remained, by and large, unexplained. The observed enhancement of the DOS at low frequencies was initially attributed to the contribution from atoms in the grain boundaries. It was argued that these atoms had lower coordination [15] and hence softer force fields as compared to the atoms in the bulk. From the measured DOS of Ni_3Fe nanocrystals using inelastic neutron scattering [12] it was concluded that the force constants associated with atoms at the grain boundaries would have to soften by an order of magnitude from the values in the bulk to produce the observed effect. The argument that low frequency modes arise from grain boundary atoms becomes even more tenuous after x-ray absorption fine structure measurements by Stern *et al.* [16] showed that the grain boundaries in the Cu nanophase are similar in structure to Cu polycrystallines with a coordination number close to 12. There was thus no rationale for the drastic softening of the force constants for the grain boundary atoms.

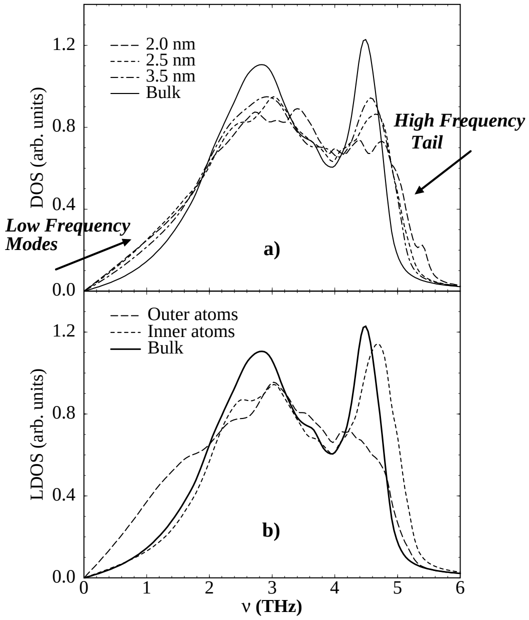

FIG. 1. Vibrational DOS for (a) Ag bulk (solid line) and Ag nanocrystals of diameter 2.0 nm (long-dashed line), 2.5 nm (dashed line), and 3.5 nm (dot-dashed line); (b) for Ag bulk (solid line) and for Ag nanocrystal of 2.5 nm diameter for the inner atoms (dashed line) and outer atoms (long-dashed line).

In our calculation, Ag nanocrystals are made of one single grain, i.e., no grain boundaries are present. Yet, we observe an enhancement of the DOS at low frequencies. Results of our calculations for Ag nanocrystal with a diameter of 2.5 nm, plotted in Fig. 1b, show that these low frequency modes come from the contribution of the surface atoms, i.e., those at the interface between the nanocrystals and the vacuum. These are labeled "outer" atoms and have a coordination number lower than 12, while the "inner" atoms have a coordination number 12. Note that the local density of states (LDOS) of the inner atoms is very close to the bulk DOS, at low frequencies. In previous studies of the vibrational dynamics of vicinal surfaces [9,10], we have found atoms with low coordination to present an enhancement of the DOS at low frequencies, as compared to that for an atom in the bulk. A loss of neighbors results in changes in the force field, which is partially reflected as softening of some force constants. For Ag nanocrystals, for example, we find softening of as much as 40% in several force constants for the outer atoms. It is this softening of force constants that strongly affects the LDOS of the surface atoms at low frequencies changing its dependency on frequency from quadratic to linear, in the case of nanocrystals. This linear dependence is in perfect accord with a recent experimental study of the vibrational properties of Pd nanocrystals, at low frequencies [17]. Figure 1b also points to a differential in the contribution of the inner and outer atoms at the other end of the spectrum. There is a major contribution to the high frequency modes from the inner atoms, while the outer atoms actually show a depletion in the number of such modes.

Closer examination of the low frequency modes for nanocrystals shows that the enhancement of the DOS scales with the diameter of the nanocrystals. Since the density of states is an extensive quantity (it is the trace of a matrix), we expect the enhancement at low frequencies to be also related to the surface-to-volume ratio. Figure 2a shows the surface-to-volume ratio as a function of size for nanocrystalline, fcc and bcc, structures. Note that both structures display similar variations in the surface-to-volume ratio, as function of the size. On fitting the curves in Fig. 2a by the function $aD^{-\alpha}$, with D the diameter of the nanocrystals and a and α as parameters, we find $\alpha = 0.83$ and 0.81 for the fcc and bcc structures, respectively. This result indicates that, in general, the enhancement of the low frequency modes would scale approximately inversely with the size of the nanocrystal, in excellent agreement with the recent inelastic neutron scattering measurements of the Ni_3Fe nanocrystal DOS [14].

Now we turn to the high frequency tail in Fig. 1b, which is mostly the contribution from the inner atoms. In general, shifts of the phonon frequencies towards higher values are due to stiffening of the force constants resulting from a shortening of the nearest neighbor (NN) distances. These "impurity" modes at frequencies higher than the

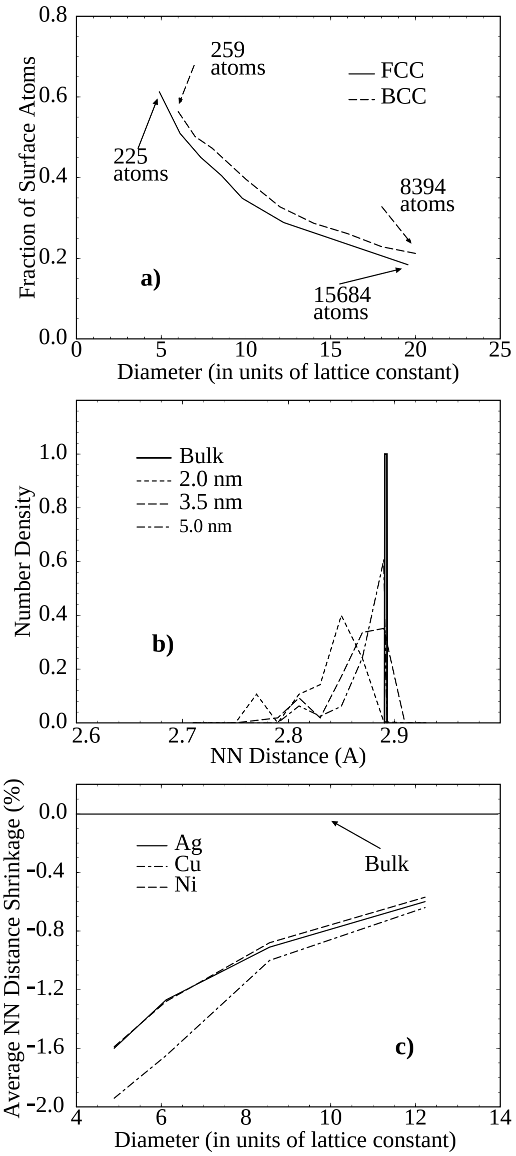

FIG. 2. (a) Surface-to-volume ratio for fcc and bcc nanocrystals as a function of the diameter, in units of the lattice constant. As a reference, the arrows show the number of atoms in small and large, fcc and bcc, nanocrystals; (b) distribution of nearest neighbor distance in relaxed Ag nanocrystals with diameters 2.0 (dashed line), 3.5 (long-dashed line), and 5.0 nm (dot-dashed line); the bold vertical line represents the NN distance in the bulk; (c) relative average NN distance as a function of the nanocrystalline diameter for Ag (solid line), Cu (dot-dashed line), and Ni (long-dashed line).

top of the bulk band have been predicted for Cu vicinal surfaces [10] and recently observed experimentally [18]. Again, from previous work on the dynamics of low coordinated atoms at the surface [9–11], we expect the high frequency tail to be the result of the contribution from atoms with low coordination and shortened NN distance. For atoms in the nanocrystals of Ag, Cu, and Ni, in their relaxed configuration, with diameter ranging from 5 to 12 lattice constants, we find a persistent shortening of the NN distance. This global shrinking has been observed in Cu clusters by extended x-ray-absorption fine structure measurements [19,20] and also in Ni clusters [20]. Figure 2b shows the distribution of NN distances for relaxed Ag nanocrystals. We note that for the 2.0, 2.5, and 3.5 nm size crystals, most of the atoms present a NN distance shorter than the bulk one. For the 5.0 nm, 60% of the atoms have the bulk value but 40% have a shorter NN distance. Figure 2c shows the average NN distance for the relaxed Ag, Cu, and Ni nanocrystals. One can see that the average NN distance for the three elements, Ag, Cu, and Ni, is shortened by as much as 1.6%–2.0% for small nanocrystals and about 0.6% for relatively large ones, as compared to the bulk value [21]. The outer atoms experience both a shift towards low frequencies due to the softening and a shift towards high frequencies due to the global shrinking resulting in a net small contribution to the high frequency tail. For Ag nanocrystals, we find that some force constants experience a stiffening of up to 120% when compared to that for bulk Ag. We now turn to the question: what causes this global shortening and do Fe nanocrystals (with a bcc structure) behave like the above mentioned fcc metals?

By examining the bond length (NN distance) between neighboring atoms in Ag, Cu, Ni, and Fe in different structures with different coordination, we note that they belong to the class of elements showing a strong bond-order–bond-length correlation. Because of this correlation, the bond length between an atom and its neighbors would decrease with decreasing coordination. Thus the bond lengths of the dimer (2.53, 2.22, 2.15, and 2.02 Å for Ag, Cu, Ni, and Fe, respectively [3]), are shorter than the NN distance in their respective bulk values by 12.5% for Ag, 13.2% for Cu, 13.6% for Ni, and 18.6% for Fe. Note that Fe shows the strongest bond-order–bond-length correlation, as far as the dimer bond length is concerned. The pattern is similar for the surface relaxations of the top layer atoms for these elements, for several crystallographic orientations. Because of the low coordination at the surface, we expect these elements to show a contraction of the interlayer separation at the surface. Experiments and first principle calculations agree that the interlayer separation between the first and second layers contracts for these four elements. For Ag, Cu, and Ni, this contraction is in the range of 1%–2% for (111), 2%–3% for (100), and 6%–9% for the more open surface (110) [7,22]. For Fe(310), the surface is contracted by 16% and for Fe(210), the surface contraction is 22% [23]. From the above discussion, it is clear that Fe presents evidence for a strong bond-order–bond-length correlation, the same way as Ag, Cu, and Ni. Hence we expect Fe nanocrystals to experience the same global shrinking in the NN distance as we found for Ag, Cu, and Ni nanocrystals which would lead to modes above the bulk phonon band. Note that the vibrational DOS in the present calculations is for a harmonic system. Anharmonic effects may still lead to lifetime broadening as suggested by Frase *et al.* [12,14] and Fultz *et al.* [13]. The DOS presented here may then be used to obtain more realistic parameters for input in the damped oscillator model.

Since the vibrational DOS of the nanocrystals differs from the bulk one, at low and high frequencies, it is of interest to explore the deviation of the thermodynamic properties of these clusters from the bulk values. In this Letter we examine how the vibrational entropy of Ag nanocrystals with various sizes compares with the bulk one. The excess vibrational entropy (i.e., excess from the bulk entropy) is

$$\Delta S_{\mathrm{vib}} = 3k_BT \int_0^\infty \left[\frac{\hbar w}{2k_BT} \coth\left(\frac{\hbar w}{2k_BT}\right) - \ln\left(2\sinh\frac{\hbar w}{2k_BT}\right)\right] \Delta N(w)\, dw \,.$$

At temperatures higher than 100 K, we find that the excess vibrational entropy converges to 0.08, 0.1, and $0.07k_B$/atom for nanocrystals of diameter 2.0, 2.5, and 3.5 nm, respectively, which are comparable to the reported value of $0.18k_B$/atom for $\mathrm{Ni_3Fe}$ nanocrystals [12] but larger than $0.01k_B$/atom value reported for Fe nanocrystals [13]. The calculated heat capacities of the nanocrystals also do not exhibit the bulklike T^3 dependence at low temperatures. The exact power law depends on the surface-to-volume ratio for the atoms in the nanocrystal. These results call for a reexamination of the interpretation of the low temperature heat capacity data on Pd nanocrystals [24].

In summary, we have shown that the vibrational properties of metallic nanocrystals are affected strongly by their high surface-to-volume ratio. At high frequencies, the DOS is shifted beyond the top of the bulk band creating a high frequency tail which we trace to a global shrinking of the nanocrystal. We suggest that this global shrinking is a general characteristic of elements obeying bond-order–bond-length correlation. In agreement with recent experimental data, at low frequencies, the atoms at the surface of these nanocrystals present a linear dependency on frequency and a significant enhancement of the vibrational DOS. Since the enhancement is solely due to the contribution of the surface atoms, it scales with the inverse of the nanocrystal size. The contributions, to the excess vibrational entropy, of the low frequency enhancement and the high frequency tail almost cancel each other and result in a small value which is also in agreement with observations.

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[1] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[2] M. W. Finnis and V. Heine, J. Phys. F **4**, L37 (1974).
[3] P. J. Feibelman, Phys. Rev. B **53**, 13 740 (1996).
[4] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, NY, 1960), 3rd ed.
[5] For a review about the embedded atom method, see M. S. Daw, S. M. Foiles, and M. I. Baskes, Mater. Sci. Rep. **9**, 251 (1993).
[6] T. S. Rahman, in *Condensed Matter Theories,* edited by J. Clark, K. Shoaib, and A. Sadiq (Nova, New York, 1994), Vol. 9, p. 299.
[7] K. P. Bohnen and K. M. Ho, Surf. Sci. Rep. **19**, 99 (1993).
[8] A. F. Voter and S. P. Chen, Proc. Mater. Res. Soc. **82**, 175 (1986).
[9] A. Kara, S. Durukanoglu, and T. S. Rahman, J. Chem. Phys. **106**, 2031 (1997).
[10] S. Durukanoglu, A. Kara, and T. S. Rahman, Phys. Rev. B **55**, 13 894 (1997).
[11] U. Kürpick, A. Kara, and T. S. Rahman, Phys. Rev. Lett. **78**, 1086 (1997).
[12] H. N. Frase, L. J. Nagel, J. L. Robertson, and B. Fultz, Philos. Mag. B **75**, 335 (1997).
[13] B. Fultz, C. C. Ahn, E. E. Alp, W. Sturhahn, and T. S. Toellner, Phys. Rev. Lett. **79**, 937 (1997).
[14] H. Frase, B. Fultz, and J. L. Robertson, Phys. Rev. B **57**, 898 (1998).
[15] S. Trapp, C. T. Limbach, U. Gonser, S. J. Campbell, and H. Gleiter, Phys. Rev. Lett. **75**, 3760 (1995).
[16] E. A. Stern, R. W. Siegel, M. Newville, P. G. Sanders, and D. Haskel, Phys. Rev. Lett. **75**, 3874 (1995).
[17] U. Stuhr, H. Wipf, K. Andersen, and H. Hahn, preceding Letter, Phys. Rev. Lett. **81**, 1449 (1998).
[18] H. J. Ernst (private communication).
[19] P. A. Montano, G. K. Shenoy, E. E. Alp, W. Schulze, and J. Urban, Phys. Rev. Lett. **56**, 2076 (1986).
[20] G. Apai, J. F. Hamilton, J. Stohr, and A. Thomson, Phys. Rev. Lett. **43**, 165 (1979).
[21] In L. B. Hansen *et al.*, Phys. Rev. Lett. **64**, 3155 (1990), calculations based on the effective medium theory have produced smaller changes in the bond lengths in Cu clusters than those reported here.
[22] A. M. Ridriguez, G. Bozzolo, and J. Ferrante, Surf. Sci. **307–309**, 625 (1994).
[23] J. Sokolov, F. Jona, and P. M. Marcus, Phys. Rev. B **29**, 5402 (1984); **31**, 1929 (1985).
[24] Y. Volokitin, J. Sinzig, L. J. de Jongh, G. Schmid, M. N. Vargaftik, and I. I. Moiseev, Nature (London) **384**, 621 (1996).