Bond Stiffening in Small Nanoclusters and its Consequences

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Abstract

We have used density functional perturbation theory to investigate the stiffness of interatomic bonds in small clusters of Si, Sn and Pb. As the number of atoms in a cluster is decreased, there is a marked shortening and stiffening of bonds. The competing factors of fewer but stiffer bonds in clusters result in softer elastic moduli but higher (average) frequencies as size is decreased, with clear signatures of universal scaling relationships. A significant role in understanding trends is played by the coordination number of the bulk structure: the higher this is, the lesser is the relative softening of elastic constants, and the greater the relative damping of vibrational amplitudes, for clusters compared to the bulk. Our results could provide a framework for understanding recent reports that some clusters remain solid above the bulk melting temperature.

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With the emerging importance of nanotechnology, it has become vital to know how the mechanical strength, thermal stability and chemical properties of very small objects compare with those of macroscopic size. These properties depend crucially on the stiffness of interatomic bonds, which determines how difficult it is to move atoms from their equilibrium positions - either in thermally induced vibrations, or in response to external forces. In this paper, we suggest, using Si, Sn and Pb as examples, that the shortening and stiffening of bonds in small clusters may be significant enough to have a noticeable impact on elastic and thermal properties. We present evidence of some surprising scaling relations, and also suggest that our results could present a framework for understanding recent experimental [1, 2] and computational [3, 4, 5, 6] reports that some clusters remain solid above the bulk melting temperature, in contradiction to a long-held belief that small objects will melt at lower temperatures than the bulk [7].

Low-dimensional systems often display structures where the coordination number (CN) is less than in the bulk structures of the same element. From general chemical principles, one expects that such under-coordinated bonds should be shorter and stiffer; however, the extent of this stiffening is difficult to estimate accurately from simple arguments. An enhancement in the stiffness of interatomic bonds has previously been observed in some two- and one-dimensional systems, e.g., at the surfaces of metals [8, 9], in thin films [10] and in nanorods and nanotubes [11]. Here, we investigate trends in bond stiffness, as a function of size and element, in zero-dimensional clusters that are small enough that their properties do not obey continuum scaling relations of the bulk and surfaces. In order to study such effects theoretically, it is crucial to have a method that can reliably reproduce the effects of changes in coordination number. Pair potentials, being insensitive to atomic coordination, are obviously inadequate, while semi-empirical potentials have to be tailored carefully if they are to describe such many-body effects not merely qualitatively but also quantitatively. For these reasons, in this work we choose to perform quantum mechanical density functional theory (DFT) and density functional perturbation theory (DFPT) calculations, using pseudopotentials and a plane wave basis, as implemented in the Quantum-ESPRESSO distribution [12]. Exchange and correlation effects are treated within the local density approximation (LDA).

We have studied the bulk as well as small clusters (number of atoms $N \leq 20$) of Si, Sn and Pb. These three elements belong to the same column of the periodic table, but have different
FIG. 1: Smaller clusters have, on average, lower coordination, shorter and stiffer bonds, and higher frequencies. The dots show how the average (a) coordination number $\langle C \rangle$, (b) bond length $\langle L \rangle$, (c) vibrational frequency $\langle \omega \rangle$, and (d) radial force constant $\langle \beta \rangle$ vary with $N$, the number of atoms in the cluster. The dashed horizontal lines indicate the corresponding values for bulk Si, $\beta$-Sn and Pb; note that these lines are positioned differently, with respect to the dots, for the three elements.

The clusters we have studied are tiny enough that they do not resemble bulk fragments structurally. The equilibrium structures of clusters were obtained by starting from previously reported structures and/or regular polyhedral arrangements, and relaxing using an eigenvector-following technique that makes use of eigenvectors obtained using DFPT, and Hellmann-Feynman forces. On analyzing the clusters’ structures, we find that both $\langle C \rangle$, the average CN, and $\langle L \rangle$, the average bond length, indeed decrease as $N$ becomes smaller (see Figs. (a) and (b)). The shortening is particularly marked for such small clusters, where all atoms are essentially surface atoms, and bonds can contract freely, as there there is no need to need to maintain registry with
FIG. 2: DFPT results for the vibrational spectra of clusters and bulk. The thin vertical black lines indicate the vibrational density of states (VDOS) for ten-atom clusters of Si, Sn and Pb, while the thick curves (red online) indicate the phonon density of states for the corresponding bulk material. The highest frequency for the bulk is lower than that of the cluster for Sn and Pb, but not for Si.

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FIG. 3: Size-dependence of the elastic modulus for dilation, \( c_d \). \( N \) is the number of atoms in the cluster. The open circles, stars and filled triangles are the data for Si, Sn and Pb clusters respectively, while the dashed, dotted and dot-dashed lines represent the results for bulk Si, \( \beta \text{-Sn} \) and Pb respectively. Note that the clusters are softer than the bulk, and the data for clusters of the three elements appear to collapse onto a single curve.

\( \omega_{b\text{max}} \), the highest phonon frequency of the bulk; however, this is not true for Si clusters (with the exception of \( N=3 \) and \( N=20 \)). As an example, we present the vibrational spectrum for ten-atom clusters of Si, Sn and Pb in Fig. 2 as well as the corresponding bulk phonon density of states. Note that the highest frequency mode for Sn\textsubscript{10} and Pb\textsubscript{10} exceeds \( \omega_{b\text{max}} \) by 32% and 73% respectively, whereas for Si\textsubscript{10} it is lower by 7%.

In order to display trends more clearly, we fit the (exact) IFCTs to a sum of pairwise radial and tangential terms. By assembling the results for all pairs of atoms for all sizes of clusters, we have in this way obtained a very large number of results for radial force constants \( \beta \) as a function of bond lengths \( L \). We find that \( \beta \) varies surprisingly smoothly as the inverse eleventh power of \( L \), for all three elements. In Figs. 1c and 1d, we show that the average vibrational frequency \( \langle \omega \rangle \) and average radial force constant \( \langle \beta \rangle \) increase as \( N \) is decreased. Note again the three different kinds of behavior relative to the bulk: in this size range, clusters of Sn and Pb, but not Si, have stiffer bonds and higher vibrational frequencies (on average) than the corresponding bulk. It is also clear, on examining the panels of Fig. 1, that the size of cluster below which bonds become stiffer in the cluster than in the bulk is effectively determined by the coordination number of the bulk structure.

Though the Sn and Pb clusters have stiffer bonds than the corresponding bulk, there are
fewer such bonds per atom. These two effects compete in determining elastic and thermal properties. We find that the latter effect dominates when we compute the elastic modulus for dilation, which serves as a measure of hardness and is defined as $c_d = \frac{1}{N} \partial^2 E / \partial \delta^2$, where $E$ is the total energy of the system consisting of $N$ atoms, which has been dilated or compressed by a factor $(1+\delta)$; for the clusters, the dilation was carried out about the centre of mass. A striking feature of the graph of $c_d$ vs. $N$ (Fig. 3) is the unexpected data collapse for all but the smallest cluster sizes; we find that this results from a scaling relation such that, for a given $CN$, the bond stiffness multiplied by the square of the bond length is approximately the same for all three elements. Note also that while all the clusters are softer than the corresponding bulk, Pb clusters are hardest relative to the bulk and Si softest, in agreement with the trends observed above.

The enhanced bond stiffness competes with the lesser number of bonds also in determining the mean squared displacements (MSDs) of atoms; however, in this case, it is the former and not the latter that wins out. Within the harmonic approximation, the MSD of the $i^{th}$ atom in the cluster/bulk, at temperature $T$, is given by [22]:

$$\langle u_i^2(T) \rangle = \frac{1}{N_k} \sum_{k,\lambda,\alpha} \frac{\hbar}{M \omega_{k\lambda}} |e_{k\lambda}^{i\alpha}|^2 (n_{k\lambda} + \frac{1}{2}),$$

where the vibrational frequencies $\omega_{k\lambda}$ and eigenvectors $e_{k\lambda}^{i\alpha}$ are known from DFPT; $k$ denotes the phonon wavevector ($k=0$ for all cluster modes), $N_k$ is the number of wavevectors in the Brillouin zone, $\lambda$ runs over all modes at a given $k$, $\alpha$ specifies Cartesian directions, $M$ is the atomic mass, $\hbar$ is Planck’s constant, and $n_{k\lambda}$ is the temperature-dependent Bose-Einstein occupation factor. We find that, for a given temperature $T$, (i) though there is some variation in the MSDs amongst different atoms in a cluster, there is an overall trend toward smaller MSDs as the cluster size decreases (see Fig. 4a); (ii) this variation is however non-monotonic; (iii) the MSDs for most Sn and Pb (but not Si) clusters are smaller than for the bulk. This is in contrast to what is observed at the low-index surfaces of single crystals, where, though the undercoordination of surface atoms leads to an enhancement in some force constants [8, 9], the MSDs at the surface are still larger than in the bulk [9, 23].

Finally, we investigate the possible implications of our results for the melting behavior of clusters. The conventional argument has been that surface atoms have fewer neighbours than bulk-like atoms, and are therefore less constrained, resulting in greater amplitudes of
thermal vibration, and lower melting temperatures. This is in accordance with the frequently observed phenomenon of premelting at flat surfaces of single crystals [24], and would suggest that clusters (with their large surface-to-volume ratio) should melt at lower temperatures than the bulk. This view was supported by early experiments and molecular-dynamics simulations on the melting of clusters [25]. However, the majority of these simulations used pair potentials, e.g., Morse or Lennard-Jones [25, 26] and thus cannot incorporate any effects of bond stiffening. Moreover, recent experiments on size-selected clusters of Sn and Ga suggested that some clusters melt at temperatures above the bulk melting temperature [1, 2]. These experiments were initially motivated [3], and later confirmed [4, 5, 6], by *ab initio* molecular dynamics simulations, which showed that certain clusters of Sn and Ga are solid above the bulk melting temperature $T_b^m$. However, it has not been clear whether such results hold only for sizes corresponding to particularly stable atomic arrangements, or whether they can be extended to other elements.

As a rough indicator of the consequences of bond stiffening on melting behaviour, we have computed the Lindemann melting temperature $T_L^m$, using a generalized form [26] of the Lindemann criterion, which states that objects melt when vibrational amplitudes become equal to a critical fraction $\Delta$ of interatomic distances:

$$\Delta = \frac{1}{N_b} \sum_{|r_{ij}| < R_c} \frac{\{\langle u_i^2 \rangle + \langle u_j^2 \rangle - 2\langle u_i u_j \rangle\}}{\langle r_{ij} \rangle}^{1/2},$$  \hspace{1cm} (2)

Here, $\langle r_{ij} \rangle$ is the mean value of the distance between atoms $i$ and $j$, and $N_b$ is the number of bonds shorter than the cutoff distance $R_c$. We have chosen $\Delta = 0.13$ and $R_c = 1.15$ times the bulk NN distance [30]. We first computed $T_L^m$ for the bulk phases (dashed lines in Fig. 4b) obtaining values of 1350, 537 and 588 K for Si, $\beta$-Sn and Pb respectively, in fairly good agreement with the experimental melting temperatures of 1680, 505 and 600 K. The underestimation of $T_b^m$ for Si is a well-known feature of the LDA, and our estimate is in excellent agreement with the result obtained using a more sophisticated treatment [27].

The dots in Fig. 4b show our results for $T_L^m$ for clusters, as a function of $N$. (This is only an approximate indicator of melting temperature, both because of the empirical nature of the Lindemann criterion, and because of the broad nature of the melting transition in finite-sized systems. Moreover, in some clusters, the melting temperature may be preempted by fragmentation [28].) From Fig. 4b, we see that huge oscillations are superposed on an
FIG. 4: Trends and oscillations in vibrational amplitudes and melting temperatures: \( \langle u_{r_{rms}} \rangle \) is the root-mean-squared displacement at 300 K, averaged over all the \( N \) atoms of the cluster, and \( T_m^L \) is the Lindemann estimate of the melting temperature. The dots and dashed lines are the calculated values for the clusters and bulk respectively. Note that for Sn and Pb, but not Si, the dots lie below (above) the dashed line in the upper (lower) panel.

The overall trend where \( T_m^L \) increases as \( N \) decreases. We find that these oscillations in \( T_m^L \) result primarily from oscillations in the value of the lowest vibrational frequency \( \omega_{min} \). Unlike \( \langle \omega \rangle \), \( \omega_{min} \) varies non-monotonically with \( N \), is very sensitive to the exact structure, and reflects variations in tangential force constants. These oscillations are reminiscent of those observed in the size-dependence of the melting temperature of Na clusters \[7\], which could not be explained by either geometric or electronic shell closing arguments.

The trends we have observed for the clusters relative to the bulk are maintained here too (compare dots and dashed lines in Fig. 4b); i.e., for Sn (Pb), most (all) clusters in this size regime have \( T_m^L \) above that of the bulk, whereas for Si, the majority of clusters have \( T_m^L \) below the bulk. For Sn, this is in qualitative agreement with experimental and computational findings \[1, 2, 3, 4, 5, 6\], while we offer our results of enhanced melting temperatures for Pb clusters as a prediction awaiting experimental validation.

Interestingly, we find that if the comparison for Sn clusters were to be made not with \( \beta \)-Sn but with the low-temperature phase of diamond-structure \( \alpha \)-Sn (which, in reality, transforms to \( \beta \)-Sn before it melts), the behaviour of Sn would be similar to that of Si, i.e., the clusters would have lower vibrational frequencies and softer bonds, and melt at lower temperatures, than the bulk.
In summary, we have computed the structure and vibrational properties of clusters and
bulk of Si, Sn and Pb, and shown the presence of clear size-dependent trends. The results
and analysis presented above suggest persuasively that the differences (in the comparative
behaviour of clusters and bulk) between Si, Sn and Pb can be attributed to differences
in bulk structure; our arguments are general enough that we believe they should be valid
for a variety of elements. Our results lead to the following rules-of-thumb: the larger the
coordination number in the bulk, the less the relative softening in the elastic moduli of
small clusters, and the more likely it is that such small clusters are stable at temperatures
above that where the bulk melts. In accordance with this understanding, we note that a
very recent molecular dynamics simulation \cite{29} suggests that Au clusters have a melting
temperature above that of bulk (fcc) gold.

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