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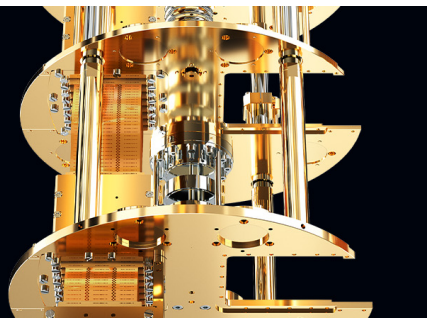

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# Lattice dynamics of ultrasmall silicon nanostructures

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A systematic study of the lattice dynamics of ultrasmall silicon nanostructures (nanoslabs, nanowires, and nanodots) is presented from the application of an adiabatic bond charge model. Characteristic features and trends unique to these structures are examined thoroughly. The smallest nanostructures are found to be characterized by the novel feature of gaps in the density of phonon states. Such gaps rapidly vanish with decreasing level of confinement of states as the size of the nanostructures increases. The results obtained for the highest confined mode for the three types of nanostructures have been fitted to analytic expressions following an extended Jusserand-type formulation. An expression has also been obtained for the size variation of the lowest nonzero zone-center mode. These expressions help explain and lend support to recently reported Raman scattering measurements. The present theoretical predictions for the variation of these modes will prove useful in accurate experimental determination of the confining size of the nanostructures. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2138790]

One of the key building blocks of future nanotechnology is the low-dimensional crystalline structure. Semiconductor nanostructures (NSs), such as those made from silicon, are particularly appealing alternatives to other NSs.[1] Silicon NSs are the focus of intense investigations because of their attractive electronic and optical properties, which depend on the interaction with confined phonon modes.[1,2] The ability to tailor such confined modes with size is very advantageous for possible technological applications. Raman scattering measurements have been made for confined zone-center optical phonons and nonzero acoustic phonons in NSs.[3–5] Theoretical investigations of such modes have been attempted, mainly with the continuum model[1] have been attempted. However, a simple analysis based upon the dominant phonon approximation[6] (i.e., the phonon mode defined as $\hbar\omega_{\mathrm{dom}} = h\bar{c}/\lambda = 1.6kT$, where $\bar{c}$ is average phonon speed) suggests that the continuum model would become inapplicable in silicon for phonon wavelengths $\lambda$ of less than 18 nm at 10 K so the nanocrystal must be much greater in size than 3 nm. A similar argument presented by Tanaka *et al.*[3] has also suggested that the continuum model may not be applied to structures smaller than 7.5 nm or less in width for CdS microcrystals. Other theoretical works have not thoroughly investigated the size dependence of confined modes in NSs.

In this letter we present a comprehensive lattice dynamical study of small and ultrasmall NSs characterized with different degrees of confinement, in particular, the effects of dimensionality and the effects of changes in size confinement. Interesting and new results are identified and explained, and analytic expressions have been obtained for the size variation of two key confined modes. These results, calculated from the lattice dynamics, and the analytic expressions thus derived, are used to lend support to available experimental observations and make further predictions.

Our theoretical investigations are based upon the application of the adiabatic bond charge model[7] to describe the lattice dynamical properties of silicon NSs. We applied this approach to the four different types of systems [three-dimensional bulk, and periodic supercells for quasitwo-dimensional slabs (2D), quasione-dimensional wires (1D), and quasizero-dimensional dots (0D)] without a change in methodology or introducing new variables or simplifications. Artificial periodicity was invoked to model the different types of reduced-dimensional systems. Neighboring NSs were separated by a vacuum region large enough to prevent interactions between them, but not oversized to maximize computational efficiency. The vacuum region consisted of an embedding material with the same atomic network as the NS, but with atomic mass equal $1/10^6$ of a single Si atom. This apporach produces a good description of the physics of atomic vibrations in NSs, but does not allow four acoustic branches expected for free standing nanowires.[8] We estimate a maximum inaccuracy of 3 $\mathrm{cm}^{-1}$ for mode energies, due to different considerations of the vacuum region, which is well within experimental error of measurements of such modes.

The phonon dispersion curves of the thinnest Si NSs are shown in Fig. 1. These structures exhibit two unique features not observed in thick NSs. First of all, due to confinement effects, many branches show an almost flat dispersion in all directions, *including the direction of propagation.* This feature is much more pronounced for the nanowire and nanodot. Second, there are several gaps in the phonon spectrum both within and above the bulk acoustic range. The number and magnitude of the gaps increase as the number of degrees of confinement increases, i.e., from 2D to 0D. This is clearly seen in the density of states (DOS) plots in Fig. 2. Also, it is found that there is a gradual drop in the highest zone-center frequency as the number of degrees of confinement increases from the 2D towards 0D and the lowest nonzero mode increases from 2D towards 0D. To the best of our knowledge, the full and detailed results of the dispersions curves and the DOS presented here have not been available before for all three NSs using the same methodical technique, and should prove to be helpful in the interpretation of experimental investigations of such systems.

As the NS size increases, the number and magnitude of the gaps rapidly decrease and smaller peaks merge to produce broader peaks. A closer examination of Figs. 2(c), 2(d), and 2(e) shows that the DOS in the acoustic region follows the prediction of the continuum model [i.e., $g(\omega) \propto \omega$, $g(\omega)$

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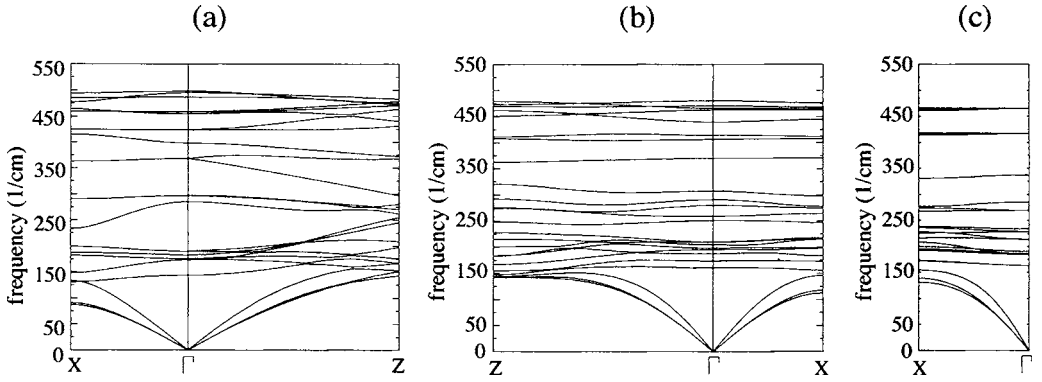


FIG. 1. Phonon dispersion of the smallest Si (a) nanoslab, (b) nanowire, and (c) nanodot. ΓX(ΓZ) is the direction of confinement (propagation).

$\propto \omega^0$, and $g(\omega) \propto \omega^{-1}$, for 2D, 1D, and 0D, respectively], before becoming bulk-like for much larger systems. This range becomes smaller with increase in the number of degrees of confinement, such that dots become characterized with bulk-like features even for a cubic length of 1.6 nm. These results clearly indicate that the lattice dynamics of ultrasmall NSs are quite different from those predicted by the continuum model. However, as expected, for thicker wires our results in the acoustic range tend to agree with continuum model.

Two zone-center phonon modes in NSs have received a great deal of attention, *viz.* the highest and the lowest nonzero mode. The confined highest optical mode $(\omega_o)$ has been examined by several experimental groups.[9–11] A few theoretical attempts have been made to understand the behaviour of this mode.[12,14] However, its variation with the NS size has not been examined in a systematic and consistent manner. Previously it has been shown[12,15,16] shown that for systems with confinement along one direction (such as heterostructures, quantum wells, superlattices, and nanoslabs)

$$\Delta\omega^2 \propto \frac{1}{d^2}, \tag{1}$$

where the magnitude of the wave vector $q$ is related inversely to the width $d$ of the NSs[12,16,17] and $\Delta\omega^2 = \omega^2_{\text{optical bulk}} - \omega^2_o$. Jusserand *et al.*[15] showed that the earlier result can be obtained from a simple consideration of the lattice dynamics of a diatomic linear chain using only nearest neighbor interaction. This is done by considering a single force constant $\Gamma_1$ for nearest nieghbour interactions within distances less than $2a$, where $a$ is interatomic distance. This model can be extended to simulate confinement effects in more than one direction. For confinement in two directions, we consider a diatomic two-dimensional grid and allow all interactions within distances less than $2a$. This involves consideration of two additional force constants $\Gamma_2$ and $\Gamma_3$ for second nearest neighbor interactions. This leads to an extension of Eq. (1) to

$$\Delta\omega^2 = \frac{\alpha_1}{d^2} + \frac{\alpha_2}{d^3}, \tag{2}$$

with constants $\alpha_i$ as a, to linear combinations of $\Gamma_1$, $\Gamma_2$, and $\Gamma_3$. An appropriate extension to incorporate three-dimensional confinement, one further force constant $\Gamma_4$ (third nearest neighbor interaction) is required, leading to

$$\Delta\omega^2 = \frac{\beta_1}{d^2} + \frac{\beta_2}{d^3} + \frac{\beta_3}{d^4}, \tag{3}$$

with $\beta_i$ as constants, which are proportional to linear combinations of $\Gamma_1$, $\Gamma_2$, $\Gamma_3$, and $\Gamma_4$.

Our lattice dynamical results for the highest confined mode for the three kinds of Si NSs can be fitted to the Eqs. (1)–(3), as shown in Fig. 3. For a nanowire of width $d = 0.96$ nm, and less, the second term is dominant, though for thicker wires its importance drops as $1/d$. A similar behavior is obtained for nanodots. With a suitable choice of the constants $\alpha_i$ for wires, and $\beta_i$ for dots, these equations can also fit the results presented by Zi *et al.*[13] with reasonable accuracy. The size dependence of the energy of this mode, using both an extended Jusserand-type model and our full lattice dynamical calculations, is predicted to be different for different NSs, particularly for ultrasmall NSs. This characteristic feature will be very useful in explaining future experimental

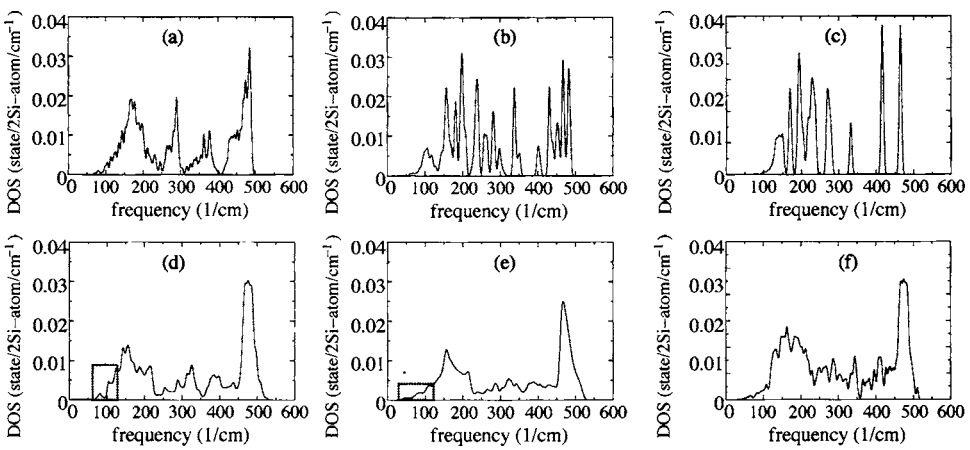


FIG. 2. The density of states for thin nanoslabs, square nanowires, and cubic nanodots of varying size: (a) nanoslab 0.543 nm thick, (b) nanowire 0.543 nm×0543 nm wide, (c) nanodot 0.543 nm×0.543 nm×0.543 nm in volume, (d) nanoslab 32.520 nm thick, (e) nanowire 3.801 nm×3.801 nm wide, (f) nanodot 1.629 nm×1.629 nm ×1.629 nm in volume. The results in the highlighted regions agree with the continuum model.

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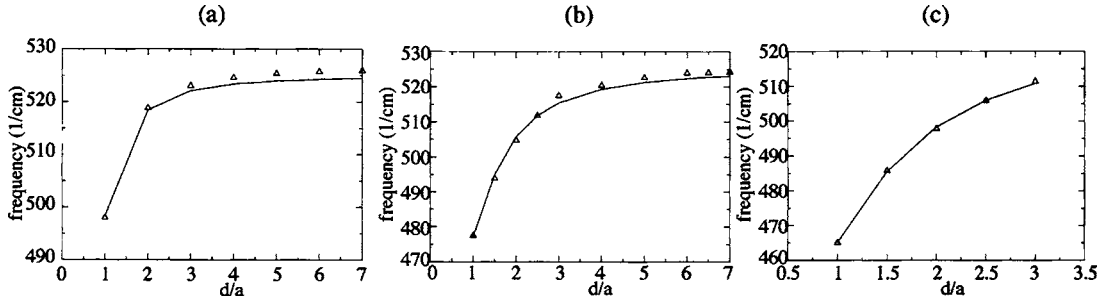


FIG. 3. The variation of the highest mode with the size of the nanostructure $d$: (a) nanoslab, (b) nanowire, and (c) nanodot. $a$ is the lattice parameter (0.543 nm). Symbols are the calculated values and curves are our theoretical fit.

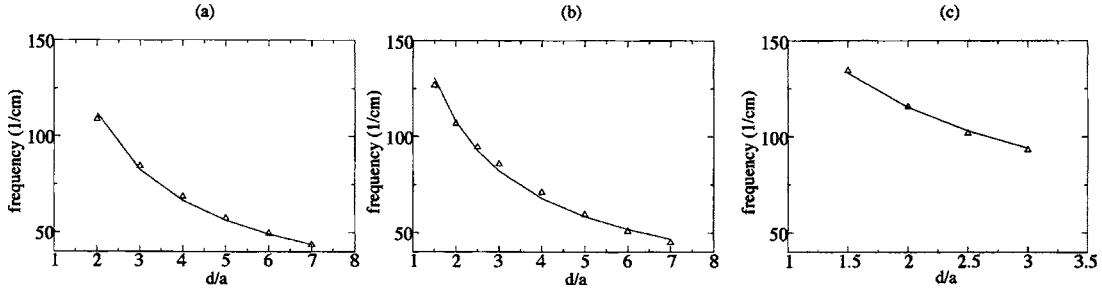


FIG. 4. The variation of the lowest nonzero mode with the size of confinement, $d$, of the nanostructure in the form of $d/a$ [$a$ is the lattice parameter (0.543 nm)]: (a) nanoslab, (b) nanowire, and (c) nanodot. Symbols are the calculated values and curves are our theoretical fit.

works, and also in explaining differences between grain-like and wire-like behavior observed in Raman measurements in nanowires.[18]

Our lattice dynamical results also allow us to show that the lowest nonzero zone-center mode ($\omega_\sigma$) varies as

$$\omega_\sigma \propto \frac{1}{d^\alpha}, \tag{4}$$

irrespective of whether the ultrasmall NSs is a slab, or a wire, or a dot. The best fit of our simulated data to Eq. (4), shown in Fig. 4, suggests that for 2D, 1D, and 0D, $\alpha$ is $\frac{3}{4}\pm0.04$, $\frac{2}{3}\pm0.06$, and $\frac{1}{2}\pm0.08$, respectively. Furthermore, the proportionality constant in Eq. (4) is 3.57 $\text{nm}^{3/4}$ THz, 3.41 $\text{nm}^{2/3}$ THz, and 3.60 $\text{nm}^{1/2}$ THz, for 2D, 1D, and 0D, respectively, with $d$ measured in nanometers. An extrapolation of the calculated results for the nanodots to the thickness of 5.5 nm, and by taking into consideration appropriate lowering of frequency due to the embedding material, agrees with the experimental Raman measurements carried out by Fujii *et al.*[4] Using the relationship between $\omega_\sigma$ and $d$ in Eq. (4) it is straightforward to determine the confining size of a NSs from Raman scattering measurements. Conversely, if the size of the NS is known, then this mode can be obtained directly without the need for any measurements. We suggest that this simple equation will prove useful in determining the confining size of both ultrasmall as well as relatively thick NSs of 2D, 1D, and 0D types. In particular, the predicted size dependence of dot- or grain-like behavior can easily be identified in a given NSs.

In summary, we have carried out systematic lattice dynamical calculations for Si NSs based upon the adiabatic bond charge model. For ultrasmall dimensions these structures are characterized by the novel feature of gaps in the DOS. These gaps rapidly close with an increase in the size of the structures. Such behavior cannot be observed by the application of the continuum theory. The results obtained in this work for the highest confined mode have been fitted to analytic expressions following an extended Jusserand-type formulation. An expression has also been obtained for the size variation of the lowest nonzero zone-center mode. The theoretically calculated trends are consistent with observed Raman measurements, and can provide useful guidance for measurements of these modes for all such NS. In particular, we believe that the present theoretical predictions for the variation of both these modes can help Raman scattering and high resolution electron micrograph studies determine confinement size, or conversely the modes if the confinement size is known, more accurately.

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