Elasticity of nanometer-sized objects

D.E. Segall,¹ Sohrab Ismail-Beigi,² and T.A. Arias³

¹Department of Physics, Massachusetts Institute of Technology, Cambridge MA 02139

²Department of Physics, University of California at Berkeley, Berkeley, CA 94720

³Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

We initiate the development of a theory of the elasticity of nanoscale objects based upon new physical concepts which remain properly defined on the nanoscale. This theory provides a powerful way of understanding nanoscale elasticity in terms of local group contributions and gives insight into the breakdown of standard continuum relations. We also give two applications. In the first, we show how to use the theory to derive a new relation between the bending and stretching properties of nanomechanical resonators and to prove that it is much more accurate than the continuum-based relations currently employed in present experimental analyses. In the second, we use the new approach to link features of the underlining electronic structure to the elastic response of a silicon nanoresonator.

I INTRODUCTION

The recent development of artificial free-standing structures of nanometer dimensions has led to great interest in their mechanical properties. A wealth of experimental information is now available for nanowires¹⁻⁴ and nanotubes,^{1, 5, 6} and a computational literature is developing on the subject.⁷⁻¹³ Many of these works make use of results from the continuum theory of elasticity to analyze the behavior of nanometer structures. However, the applicability of continuum theories to nanoscale objects, where atomic-level inhomogeneities come to the fore, has yet to be explored in depth.

Rigorous understanding of the elastic properties of nanoscale systems is crucial in understanding their mechanical behavior and presents an intriguing theoretical challenge lying at the cross-over between the atomic level and the continuum. In the absence of an appropriate theoretical description at this cross-over, critical questions remain to be answered including the extent to which continuum theories can be pushed into the nanoregime, how to provide systematic corrections to continuum theory, what effects do different bonding arrangements have on elastic response, and what signatures in the electronic structure correlate with the mechanical properties of the overall structure?

Recently, there have been a number of theoretical explorations of the impact of nanoscale structure on mechanical properties.^{13–18} These studies fall under two broad approaches, either the addition of surface and edge corrections to bulk continuum theories^{13, 14} or the extraction of overall mechanical response from atomic scale interactions.^{15–18} The latter approach has the distinct advantage of allowing first principles understanding of how different chemical groups and bonding arrangements contribute to overall elastic response, thus opening the potential for the rational design of nanostructures with specific properties.

In coarse graining from interatomic interactions to me-

chanical response, some works rely upon the problematic decomposition of the total system energy into a direct sum of atomic energies,^{15,16} which is always arbitrary and particularly inconvenient for connection with *ab initio* electronic structure calculations. The remaining works which attempt to build up overall response from atomic level contributions^{17,18} fail to account properly for the Poisson effect. Below we show that failure to account for this effect leads to surprisingly unphysical results.

This manuscript presents the first theory for the analysis of overall mechanical response in terms of atomic-level observables which suffers from neither difficulty from the preceding paragraph. This analysis allows, for the first time, quantitative understanding of how continuum theory breaks down on the nanoscale, of how to make appropriate corrections, and of how to predict the effects of different bonding arrangements on overall elastic response. It is well known that the decomposition of overall elastic response into a sum of atomic level contributions is not unique. We show here, however, that with the additional constraint of dependence of moduli on local environment our definition of atomic level moduli becomes physically meaningful and essentially unique when coarse-grained over regions of extent comparable to the decay range of the force-constant matrix.

For concreteness, in this work we focus on nanowires. However, we will also describe briefly how this work can be extended to any system with nanometer dimensions. The manuscript proceeds as follows. Section II briefly overviews the present state of the field. Next, as the traditional concept of Young's modulus becomes ill-defined on the nanoscale, we begin by carefully defining continuum elastic constants appropriate for nanowires in Section III. We then show how to decompose these constants exactly into atomic-level contributions based on true physical observables (rather than individual atomic energies) using a straight-forward application of Born and Huang's method of long waves,¹⁹ resulting in a decomposition similar in spirit to those in References [17] and [18] (Section IV). Section V demonstrates the surprising, radical breakdown of this approach when applied to nanoresonators. Then, in Section VI, we identify the source of the difficulty as the Poisson effect and present the first analysis of mechanical response truly applicable to nanoresonators.

The manuscript then goes on to applications. Section VII verifies the physical meaningfulness of our newly defined quantities by verifying that they predict response to modes of strain for which they were not directly constructed. We then, in Section VIII, use our approach to generate a new, much more accurate, relationship between experimentally accessible observables describing response to flexural and extensional strain in nanomechanical resonators. Finally, Section IX uses this theory to explore possible links between underlying electronic structure and local elastic response.

II OVERVIEW

As the introduction mentions, the literature pursues two broad categories of approach to the study of mechanical properties on the nanoscale, either surface and edge corrections to continuum theory or extraction of overall response from the underlying atomic interactions. In the former category, Reference [13], through scaling arguments and numerical examples, notes that the Young's modulus for nanomechanical resonators scales as a bulk term plus surface and edge corrections. Although providing insight and motivation, this work leaves completely open how one should understand these corrections from first principles. Reference [14] provides a more rigorous study based on separating nanoscale systems into continuum surface and bulk regions. This latter approach allows prediction of changes in stiffness properties as one approaches nanometer length scales and has the appeal of generating physically motivated correction terms. However, it relies on the separation of a nanomechanical resonator into bulk and surface continua as an ansatz and therefore neither predicts when such a picture suffices to give an accurate description nor prescribes further corrections.

References [15-18], on the other hand, start from the more general atomic level description and then try to unveil physical properties from the underlying atomic description. It is important to note that these works do not deal directly with nanoscale systems but rather focus on the effects of nanoscale inhomogeneities in *bulk* systems.

References [15] and [16] concern the elastic properties of grain boundaries. These works define atomic-level elastic moduli as the second derivative of the energy associated with each atom with respect to strain and then go on to study the behavior of such moduli near grain boundaries. The difficulty with this approach is that it requires a breakdown into individual contributions from each atom of the total energy of any system. Such an atomic energy is neither observable nor uniquely defined and therefore cannot serve as an appropriate basis for theoretical understanding.

Although References [17] and [18] work from valid physical observables, the components of the forceconstant matrix, these works focus on bulk-like or mesoscopic scale systems and fail for nanoscale systems for the reasons which we describe in this work. Reference [17] investigates nonlocal elastic constants on the mesoscopic scale and links them to the underlying atomic interactions. It then proceeds to define an elastic constant for each atom and studies the behavior of these quantities near surfaces and grain boundaries. Reference [18] defines a bond frequency from the force-constant matrix from which it deduces the possibility of bond rupture during crack nucleation. Neither of the above works properly accounts for the Poisson effect, which we show in Sections IV, V and VI to play a critical role in the elasticity of nanoscale systems. Moreover, straightforward generalization of these works to include this effect fail for the the same reasons as does the related approach which we describe in Section IV.

III NANOWIRE RIGIDITIES

The prime difficulty in the application of continuum theory to objects of nanometer cross-section is the loss of the ratio of the inter-atomic spacing to the cross-sectional dimension as a small parameter. However, so long as the length of an object and the wavelength of the distortions considered both greatly exceed the inter-atomic spacing and the cross-sectional dimension, the object properly may be viewed as a one-dimensional continuum. Although we focus in this work on nanowires, the generalization of the discussion below to nanoscale systems of other dimensionality such as thin plates or nanoscopic objects is straightforward.

Viewed as a linear continuum, the free energy per unit length f of a nanowire is

$$f = (Eu^2 + FR^{-2} + T\tau^2)/2, \tag{1}$$

where u is the linear strain of extension, R is the radius of curvature and τ is the rate of twist of the torsion. The coupling constant E is the extensional rigidity, F is the flexural rigidity and T is the torsional rigidity. Unlike traditional bulk continuum concepts, the freeenergy function Eq. (1) is observable in principle and thus provides an unambiguous operational definition of the rigidities. We avoid the use of traditional continuum concepts, such as the Young's modulus and the cross-sectional area, because such concepts are neither uniquely nor well-defined for nanoscale systems. The rigidities in Eq. (1) are related to the phonon frequencies through

$$\omega_{LA} = \sqrt{E/(\lambda m)}q, \qquad (2)$$

$$\omega_{TA} = \sqrt{F/(\lambda m)}q^2, \qquad (3)$$

$$\omega_{BA} = \sqrt{T/(\lambda m I_r)}q, \qquad (4)$$

where ω is the frequency for either the longitudinal, transverse or rotational acoustic modes, respectively, λ is the linear atomic number density, q is the wave vector and m is the mass of a single atom. (This work focuses on single species systems for simplicity.) Finally, I_r is defined unambiguously as the mean rotational moment $I_r = (1/N_c) \sum_{\alpha} (x_{\alpha}^2 + y_{\alpha}^2)$, where the sum ranges over all atoms in the cell, N_c is the number of atoms per unit cell, the wire is assumed to run along the z-axis and the origin lies on the center line of the wire.

Finally we note that although the rigidities in Eq. (1) are well-defined, certain traditional continuum relations between them do not hold. Specifically, we will show below that the traditional continuum relationship between the extensional rigidity E and the flexural rigidity F fails on the nanoscale, similar to relations which have been recently used in the analysis of experiments.^{1,3,5,6}

IV METHOD OF LONG WAVES

One reason for breakdown of traditional continuum relations on the nanoscale is that the continuum perspective course grains away important fluctuations which occur over distances on the order of the inter-atomic spacing. To overcome this shortcoming, we propose to coarse grain only on distances over which the underlying interatomic interactions vary, the decay length of the forceconstant matrix. The straightforward approach to generate such a theory is the "method of long waves" developed by Born and Huang,¹⁹ which is somewhat similar to the approaches which have been used previously to defects in bulk systems.^{17,18} This section applies the method of long waves to nanoresonators. The next section shows how, surprisingly, this and related approaches fail in the study of systems with free surfaces and therefore, in general, cannot be used to describe nanoscale systems. In Section VI, we describe how to go beyond the straightforward application of the "method of long waves" in order to achieve a meaningful description.

We focus initially on longitudinal waves and, as noted in Section III, choose our origin to lie on the center line of the wire, which we let run along the z-axis. For nanowires, the presence of surfaces breaks periodicity in the transverse directions resulting in a one-dimensional crystal with an extremely large unit cell of length $L_c = N_c/\lambda$, where N_c and λ are as in Section III. In all expressions below, boldfaced quantities are $3N_c$ -dimensional and arrowed vector quantities are three-dimensional. Finally, sums with Greek indices range over atoms in the unit cell. To relate the rigidities to the dynamical matrix, we begin similarly to Born and Huang and choose to factor the Bloch phases (e^{iqz}) out of the representation of the phonon polarization vector **u**, incorporating them into the definition of the dynamical matrix **D**, so that the acoustic phonon polarization vectors are periodic across the cell boundaries. This ensures a uniform description of the distribution of elastic energy along the axis of the wire. To generate a scalar equation for the phonon frequency, Born and Huang project the secular equation for the dynamical matrix,

$$\mathbf{D}\mathbf{u} = -m\omega^2 \mathbf{u},\tag{5}$$

against the zeroth-order polarization vector $\mathbf{u}^{[0]}$. Here, however, to more symmetrically represent the distribution of elastic energy, we project against the full polarization vector \mathbf{u} . Equating the frequency ω in Eq. (5) with the longitudinal frequency in Eq. (2) gives

$$-\frac{E}{\lambda} = \frac{[\mathbf{u}^{\dagger}\mathbf{D}\mathbf{u}]^{[2]}}{\mathbf{u}^{\dagger}\mathbf{u}} = \sum_{s,t=0}^{1} \frac{(-1)^{s}}{N_{c}} \mathbf{u}^{\dagger[s]} \mathbf{D}^{[2-s-t]} \mathbf{u}^{[t]}, \quad (6)$$

where we have expanded the numerator of the Rayleigh quotient to second-order in powers of (iq) and where the 3×3 sub-block of $\mathbf{D}^{[n]}$, which couples atoms α and β , is

$$[\mathbf{D}^{[n]}]_{\alpha\beta} = \frac{1}{n!} \sum_{\vec{R}} \Phi_{\alpha\beta}(\vec{R}) \left(\hat{z} \cdot (\vec{R} + \vec{\tau}_{\beta} - \vec{\tau}_{\alpha}) \right)^n.$$
(7)

Here, \vec{R} is a lattice vector along the z - axis, $\Phi_{\alpha\beta}(\vec{R})$ is the 3×3 sub-block of the force-constant matrix which couples atoms α and β located at positions $\vec{\tau}_{\alpha}$ and $\vec{R} + \vec{\tau}_{\beta}$, respectively, and

$$\Phi_{\alpha\beta}(\vec{R}) = -\frac{\partial^2 U}{\partial \vec{\tau}_{\alpha} \partial (\vec{R} + \vec{\tau}_{\beta})}$$

Finally, substituting Eq. (7) and $[\mathbf{u}^{[0]}]_{\alpha} = \hat{z}$ into Eq. (6), allows us to express E as a sum over atoms (α) in the unit cell and all atoms (β, \vec{R}) in the system,

$$E = \frac{1}{L_c} \sum_{\alpha} e_{\alpha} \tag{8}$$
$$e_{\alpha} = \sum \left\{ -\Delta \vec{Z}_{\alpha\beta} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \Delta \vec{Z}_{\alpha\beta}/2 + \vec{u}_{\alpha}^{[1]} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \vec{u}_{\beta}^{[1]} \right\}$$

$$\beta \vec{R} + \Delta \vec{Z}_{\alpha\beta} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \vec{u}_{\beta}^{[1]} - \vec{u}_{\alpha}^{[1]} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \Delta \vec{Z}_{\alpha\beta} \Big\}.$$
(9)

Here, $\Delta \vec{Z}_{\alpha\beta} \equiv \hat{z}\hat{z} \cdot (\vec{\tau}_{\alpha} - \vec{\tau}_{\beta} - \vec{R})$, $\vec{u}_{\alpha}^{[1]}$ is the first-order polarization vector and we refer to the e_{α} as the "atomic moduli".

The atomic moduli as currently defined in Eq. (9) provide a useful microscopic analysis of elastic response in bulk systems which is similar in spirit to the decompositions used previously in the study of bulk material systems.^{17,18} To see that Eq. (9) indeed decomposes the overall elastic response of bulk systems into atomic contributions coarse-grained over distances on the order of the decay-length of the force-constant matrix, we note first that for infinite bulk systems, elastic waves are planar. This implies that the first-order polarization vector $(\vec{u}_{\alpha}^{[1]})$ is uniform from primitive cell to primitive cell and thus depends only on the local environment of each atom. Next, we note that although the strain terms $(\Delta \vec{Z}_{\alpha\beta})$ scale linearly with distance between atoms, the terms which contribute to the final result are bounded in range by the inter-atomic interactions $(\Phi(\vec{R}))$. Thus, the atomic moduli depend only on the local atomic environment over distances which the decay of the force-constant matrix determines.

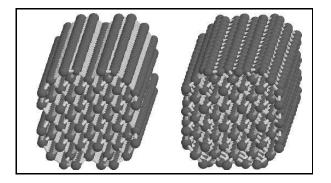


FIG. 1: Atomic structure of silicon nanowires with an approximate cross-sectional diameter of 1.5 nm. The wires are viewed along the longitudinal axis: $c(2 \times 2)$ structure (left), 2×1 structure (right).

V FAILURE OF STRAIGHTFORWARD APPROACH IN NANOWIRES

We now demonstrate through direct calculations that the approach outlined in the previous section gives unphysical results when applied to nanoresonators. Specifically, we study the behavior of [100]-oriented nanoresonators of silicon, which recent *ab initio* studies²⁰ predict to undergo a size-dependent structural phase transition between the two structures in Figure 1 at a cross-section of ~ 3 nm. (The interested reader may refer to Reference [21] for explicit details of the microscopic structure of these wires.) Initially, we work with the Stillinger-Weber inter-atomic potential,²¹ which suffices for the exploration of general nanoelastic phenomena and which allows study of cells with many thousands of atoms. Later in the manuscript (Section IX) we use the Sawada tight-binding model²² with modifications proposed by $Kohyama^{23}$ to explore the correlation between our local approach and the underlying electronic structure. For all calculations below, we fully relax the atomic coordinates, the periodicity of the wire and, need be, the electronic structure. Finally, we employ periodic boundary conditions along the z-direction.

Figure 2a shows that the atomic moduli e_{α} predicted for nanowires using the straightforward approach of Eq. (9) are unphysical in that they depend upon the macroscopic dimensions of the system and not simply on the local environment of each atom. In particular, the atomic moduli on the surface grow linearly with the diameter of the wire and the moduli in the center of the wire fail to approach the expected bulk limit, $e_b \equiv Y_b/\rho_b$, where Y_b is the Young's modulus in bulk and ρ_b is the number density in bulk. (Note that these two effects are interelated, as the moduli must sum to give the macroscopic value in the bulk limit.)

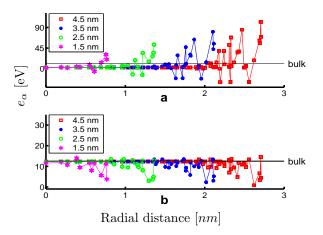


FIG. 2: Predictions of atomic moduli e_{α} for $c(2 \times 2)$ nanowires of varying diameter: (a) straightforward theory (Eq. (9)) and (b) new theory (Eq. (11)). The insets denote the approximate diameters of the wires. The value of the atomic modulus (Eq. (9) or Eq. (11)) is along the ordinate and radial distance of the atom from the center line is along the abscissa.

Although one has some freedom in choosing the terms used in the perturbation expansion Eqs. (5) and (6), for example to project Eq. (5) against $\mathbf{u}^{[0]}$ instead of \mathbf{u} , all such expansions will lead to similar linear scaling along the surface of the wire and approach an incorrect value at the center of the wire. Thus, straightforward application of the method of long waves fails to result in a local, and hence physically meaningful, description of elastic response in nanoscale systems, as will straightforward variations thereon such as those in References [17] and [18].

VI METHOD OF LONG WAVES IN NANOWIRES

To cure the difficulties uncovered in the previous section, we proceed by first identifying the cause of the pathological behavior and then exploiting the freedom in Eq. (9) to remove this pathology.

The failure of the straightforward approach arises from the fact that elastic waves in nanoresonators, or any system with free surfaces, are not strictly planar. In particular, the Poisson effect, which the first order polarization vector $\mathbf{u}^{[1]}$ contains, causes each atom to displace by an amount in direct proportion to its distance from the center line of the system. Eq. (9) then leads directly to linear scaling of the atomic moduli at the surfaces of the wire.

Defining an atomic elastic reponse dependent soley on the local enivornment requires separation of extensive elastic effects from intensive nanoscopic effects. To seperate the extensive motion in the first order polarization vector from that of its intensive motion, we define the atomic displacements (\vec{u}_{α}^{rl}) as the intensive nanoscopic motions,

$$\vec{u}_{\alpha}^{rl} \equiv \vec{u}_{\alpha}^{[1]} - (-\sigma_x \hat{x} \hat{x} \cdot -\sigma_y \hat{y} \hat{y} \cdot) \vec{\tau}_{\alpha}, \qquad (10)$$

where $\sigma_{x,y}$ are the Poisson ratios. There are three logical choices for the Poisson ratios: some sort of local atomic definition, an overall average for the wire, or the bulk values. We choose to use bulk Poisson ratios for a number of reasons. First, a locally varying definition makes it impossible to exploit the continuous rotational and translational symmetries in the dynamical matrix, which we find necessary to employ below in constructing atomic moduli with local behavior. Second, only by employing the bulk (rather than average) Poisson ratios do we find a definition which approaches the appropriate bulk value in the centers of wires of finite width. Finally, we note that we always have the freedom of working with bulk Poisson ratios because any motion along the surface in addition to that resulting from bulk Poisson effect will not scale extensively with the diameter of the wire and can therefore be incorporated into the intensive atomic displacements \vec{u}_{α}^{rl} .

After making the decomposition in Eq. (10), we next employ the continuous rotational and translational symmetries of the dynamical matrix to eliminate all extensive dependencies in Eq. (9). Appendix A outlines the procedure for doing this, which then transforms Eq. (9) into

$$e_{\alpha} = \sum_{\beta \vec{R}} \left\{ -\Delta \vec{r}_{\alpha\beta} \cdot \Psi_{\alpha\beta}(\vec{R}) \cdot \Delta \vec{r}_{\alpha\beta}/2 + \vec{u}_{\alpha}^{rl} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \vec{u}_{\beta}^{rl} + \Delta \vec{r}_{\alpha\beta} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \vec{u}_{\beta}^{rl} - \vec{u}_{\alpha}^{rl} \cdot \Phi_{\alpha\beta}(\vec{R}) \cdot \Delta \vec{r}_{\alpha\beta} \right\}, \quad (11)$$

where $\Delta \vec{r}_{\alpha\beta}$ represents the *total* strain between atoms α and β ,

$$\Delta \vec{r}_{\alpha\beta} \equiv (-\sigma_x \hat{\mathbf{x}} \hat{\mathbf{x}} - \sigma_y \hat{\mathbf{y}} \hat{\mathbf{y}} + \hat{\mathbf{z}} \hat{\mathbf{z}}) \cdot (\vec{\tau}_{\alpha} - \vec{\tau}_{\beta} - \vec{R}),$$

and $\Psi_{\alpha\beta}(\vec{R})$ renormalizes as

$$\Psi_{\alpha\beta}(\vec{R}) \equiv 2\Phi_{\alpha\beta}(\vec{R}) - \left(\operatorname{Tr}\Phi_{\alpha\beta}(\vec{R}) \cdot \Sigma\right)\Sigma^{-1},$$

where $\Sigma_{jk} \equiv \delta_{jk}\sigma_j$, is a diagonal 3×3 matrix with elements σ_x , σ_y and $\sigma_z \equiv -1$, respectively and δ_{jk} is the Kronecker delta.

This new construction ensures that the modulus of each atom depends only upon its local atomic environment because \vec{u}_{α}^{rl} no longer includes extensive motions and, although $\Delta \vec{r}_{\alpha\beta}$ still depends on relative atomic distances, the renormalized Ψ decays as Φ does. Thus, it is now the range of the force-constant matrix which controls the size of the neighborhood upon which each atomic modulus can depend. Therefore, the moduli of atoms in the interior now *must* correspond to the expected bulk value, the moduli of the atoms on the surface now *cannot* depend upon the extent of the system, and the resulting description is physically meaningful. Figure 2b illustrates the success of Eq. (11).

The fact that decomposition of elastic response into atomic level contributions is not unique raises questions as to the physical meaning of such a decomposition. The new decomposition Eq. (11) is the first which remains dependent only upon local environment for systems with free surfaces. Any other definition which respects locality can only redistribute portions of each atom's modulus among other atoms within a region of extent comparable to the decay of the force-constant matrix. Any sum over such a region of the moduli will always be nearly the same. Therefore, coarse grained over such regions, properly localized atomic moduli become physically meaningful. Section VII and Appendix B demonstrate this explicitly by comparing the predictions for flexion from either properly localized moduli or straightforwardly defined moduli, respectively. To further demonstrate that alternate local definitions are equivalent in this coarsegrained sense, we have explored alternate local constructions. In particular, while our present construction takes care to employ the continuous symmetries of the dynamical matrix in such a way so as to respect symmetry among the x, y, z Cartesian coordinates, we have also repeated the construction while treating the x, y coordinates symmetrically but not the *z* coordinate and have found nearly identical results for all of the applications below.

We close this section with a brief description of how the above approach extends to any system of nanometer dimensions. To be considered small in this context, a dimension must be much smaller than the wavelength of the distortions considered. This manuscript focuses on nanowires, systems with two small dimensions. For a system with one small dimension, for instance a plate with nanometer thickness, the above approach develops in the same way with the one minor change that the definition of \vec{u}_{α}^{rl} (Eq. (10) involves the Poisson effect only in the one small dimension. For an object with three small dimensions, for instance adiabatic loading of a nano-object, the nature of the Poisson effect depends upon the mode of loading, and the system should treated as either of the above cases accordingly. Finally, objects of no small dimension, and hence no Poisson effect, can be described straightforwardly as bulk-like using Eq. (9).

VII TRANSFERABILITY

To establish that our new atomic moduli are not mere convenient mathematical constructions but are physically meaningful, we now consider their transferability to phenomena not considered in their original construction. In particular, we consider flexion, where the elastic distortion is no longer homogeneous throughout the cross-section.

If our atomic moduli are indeed a measure of the local elastic response, then under flexion the free energy per unit length will take the form

$$f = (1/L_c) \sum_{\alpha} e_{\alpha} u_{\alpha}^2 / 2, \qquad (12)$$

where u_{α} is a measure of the longitudinal strain which atom α experiences. For this form to be sensible, the diameter D of the wire must not become comparable to the range of the force-constant matrix so that the atoms which contribute to each e_{α} all experience similar strains u_{α} .

Within continuum theory, uniform flexion with radius of curvature R corresponds to a longitudinal strain which varies linearly across the wire, u = x/R. (This holds to better than to two parts in 10^3 for all wires in our study.) This would then predict a flexural rigidity of

$$F_{at} = \frac{1}{L_c} \sum_{\alpha} e_{\alpha} x_{\alpha}^{\ 2}.$$
 (13)

Figure 3a shows the fractional error (δF_{at})

$$\delta F_{at} \equiv (F_{at} - F)/F, \tag{14}$$

in predicting the flexural rigidity from Eq. (13), where F is determined directly through numerical calculations. The figure shows that these errors are indeed quite small. Note that use of the straightforward definition in Eq. (9) with its unusually scaling surface moduli leads to invalid predictions for flexion. (Appendix B shows this directly through scaling arguments.) As a result, to have *predictive* power, definitions of atomic moduli must properly account for the Poisson effect.

To demonstrate that our new approach has greater predictive power than traditional continuum approaches, the figure also shows the fractional error (δF_{tc}) in predicting the flexural rigidity when using the traditional continuum relation

$$F_{tc} = E(I/A), \tag{15}$$

$$\delta F_{tc} = (F_{tc} - F)/F \tag{16}$$

where I/A defines the mean bending moment, which we define unambiguously as

$$I/A = (1/N_c) \sum_{\alpha} x_{\alpha}^2.$$
 (17)

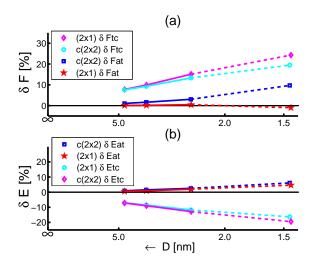


FIG. 3: Fractional error as a function of inverse diameter 1/D in predicting (a) flexural rigidity from extensional properties (δF_{at} , Eq. (14) and δF_{tc} , Eq.(16)) and (b) extensional rigidity from flexural properties (δE_{at} , Eq. (20) and δE_{tc} , Eq. (21)). Note, for convenience, the abscissa is labeled by D and not 1/D.

The linear behavior of the fractional error δF_{tc} as a function of 1/D indicates that continuum theory does not properly account for surface effects, a result of the fact that flexion places a larger emphasis on the surface than does extension. The dramatic improvement from the use of Eq. (13) arises because the atomic moduli place proper emphasis on the surface and on the interior, as they properly treat each atomic environment locally. The atomic moduli therefore properly account for elastic fluctuations along the cross-section of the wire which are on scales too small for traditional continuum theories to capture.

Finally, we note that the only appreciable error within the new framework occurs for the smallest wires (D \approx 1.5nm). At this point, the cross-sectional dimension becomes comparable to the range of the force-constant matrix, and Eq. (12) represents an improper use of the physical concept of atomic moduli. As described above (second from last paragraph in Section VI), only sums of atomic moduli over regions of extent comparable to the range of the force-constant matrix carry physical meaning. Any sum sensitive to variations over shorter scales, as is Eq. (12) when limited to wires narrower than the range of the force-constant matrix, cannot be depended upon to lead to meaningful results. This underscores the fact that properly construed atomic moduli are not truly atomic-level quantities but a concept coarse grained over the range of the force constant matrix. As we have seen, however, this coarse-graining is on scales significantly smaller than those captured by traditional continuum theory.

VIII EXTENSION FROM FLEXION

We now apply the above defined atomic moduli to derive a new relation for the extensional modulus in terms of the flexural modulus and other experimentally accessible observables, a relation often needed in experimental analyses.^{1,3,5,6} We then show that the new relation is much more accurate than the standard continuum-theory based relation currently employed in experimental analyses. Finally, we employ our concept of atomic moduli to provide quantitative insight into the improvement of our new relation over the traditional continuum relation.

The basis for the following analysis is the fact that Eq. (13) gives a very good estimate of the true flexural modulus, as Figure 3a confirms. Using the exact relation for E, Eqs. (8) and (11), and Eq. (13), one derives the following leading-order prediction E_{at} for the extensional modulus,

$$E_{at} = \frac{1}{2} \left(\frac{F}{I/A} + Y_b \frac{\lambda}{\rho_b} \right), \qquad (18)$$

with a predicted error $\delta E_{at}^{(p)}$ of

$$\delta E_{at}^{(p)} = \frac{N_s}{EL_c} \left\{ B_{at} \left[\langle e_s \rangle_{x^2} - e_b \right] + \left[\langle e_s \rangle_{x^2} - \langle e_s \rangle \right] \right\} (19)$$

Here, N_s is the number of "surface" atoms, defined as those for which e_{α} differs significantly from the limiting bulk value e_b , $\langle e_s \rangle_{x^2}$ is the inertia weighted average surface moduli

$$\langle e_s \rangle_{x^2} \equiv \frac{\sum_s e_s x_s^2}{\sum_s x_s^2},$$

with the sums (\sum_s) ranging over "surface" atoms, $\langle e_s \rangle$ is the average surface moduli

$$\langle e_s \rangle \equiv \frac{1}{N_s} \sum_s e_s$$

and

$$B_{at} \equiv (1/2) \frac{\frac{1}{N_s} \sum_s x_s^2}{\frac{1}{N_c} \sum_c x_c^2} - 1,$$

where \sum_{c} implies sums over all atoms in the unit cell. This result holds for any division of the atoms into "surface" and "bulk" to the extent that each "bulk" atom has atomic modulus e_b .

Figure 3b shows the relative error δE_{at} ,

$$\delta E_{at} = (E_{at} - E)/E, \qquad (20)$$

between the extensional modulus E determined directly from numerical calculation and as determined from our new relation, Eq. (18). (Note that $\delta E_{at}^{(p)} = \delta E_{at}$ exactly when the moduli prediction $F_{at} = F$ holds.) As the relevant point of comparison, the figure also shows the relative error δE_{tc} ,

$$\delta E_{tc} = (E_{tc} - E)/E, \qquad (21)$$

associated with the traditional continuum result

$$E_{tc} = F \frac{A}{I}.$$
 (22)

Hence, Eq. (18) is much more accurate than the standard continuum result Eq. (22).

To understand the improvement of the new relation, Eqs. (8) and (13) may also be combined to yield a prediction for the fractional error in the traditional continuum analysis,

$$\delta E_{tc}^{(p)} = \frac{N_s}{EL_c} \left\{ B_{tc} \left[\langle e_s \rangle_{x^2} - e_b \right] + \left[\langle e_s \rangle_{x^2} - \langle e_s \rangle \right] \right\}, \quad (23)$$

which takes *precisely* the same form as Eq. (19) except for the change in the prefactor in the first term from B_{at} to $B_{tc} \equiv 2B_{at} + 1$. For continuous wires of homogeneous circular or regular polygonal cross-section, we have exactly $B_{at} = 0$. Thus, generally we expect B_{at} to be close to zero and B_{tc} to be close to unity. We now note that the term in the first set of square brackets $([\langle e_s \rangle_{x^2} - e_b])$ in both Eq. (19) and Eq. (23) is an average difference between surface and bulk atoms and, therefore, is generally much larger than the term in the second set of square brackets $[\langle e_s \rangle_{x^2} - \langle e_s \rangle]$, which is the difference between two differently weighted averages over the surface atoms. Thus the larger term nearly vanishes in our new relation, Eq. (19), but not in the traditional continuum relation, Eq. (23). From this analysis, we see that the reason why the traditional continuum relation has larger errors is that it does not properly differentiate between the local surface and bulk environments.

The atomic moduli also lead to a quick, intuitive argument to understand the improvement of Eq. (18) over Eq. (22). From our results we know that the surface moduli can be quite different than those of the bulk. It is also known that flexion places larger emphasis on the surface than does extension. If the average surface modulus is less/more than that of the bulk then the first term in Eq. (18) $(F \cdot A/I)$ will underestimate/overestimate the extensional rigidity, while the second term will overestimate/underestimate it. Therefore, errors will tend to cancel in the average of the two.

IX CORRELATION BETWEEN LOCAL ATOMIC MODULI AND ELECTRONIC STRUCTURE

We now explore the local atomic moduli as a link between local elastic properties and the underlying electronic structure. To do this, we have calculated the atomic moduli, Eq. (11), for both the $c(2 \times 2)$ and (2×1) structures, using the Sawada²² tight-binding model with modifications proposed by Kohyama.²³ We have studied various wires, all of which give similar results. For brevity, we here only report on wires with cross-sectional diameter ≈ 2.4 nm. The supercell of our calculation is four bulk cubic lattice constants long in the periodic direction, and hence sampling the Brillouin zone at the Γ point in the electronic structure calculations is more than sufficient.

The left panels of Figures 4 and 5 show the resulting atomic moduli, with values color coded so that yellow corresponds to the bulk value (17.1 eV/atom). The figure shows that deviations from this value concentrate near the surface in patterns characteristic of the structure of the wire. Moduli near the surface fluctuate widely, ranging from 6-27 eV/atom for the $c(2 \times 2)$ structure and from 4-26 eV/atom for the 2 × 1 structure.

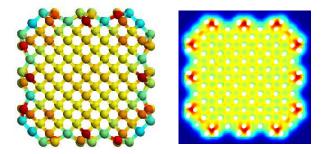


FIG. 4: $c(2 \times 2)$ wire, with cross-section ≈ 2.4 nm. Results are from the tight-binding model described in the text. Left: atomic moduli color coded from small to large: blue-green-yellow-red. Right: valence electronic density projected (integrated along the wire axis) onto the cross-section color coded from low to high: blue-green-yellow-red. White dots in the right figure indicate the location of atom cores. Note the correlation of large atomic moduli with large charge density along the surface.

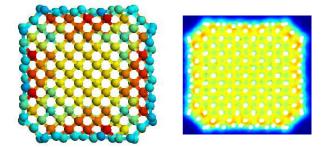


FIG. 5: 2×1 wire, with cross-section ≈ 2.4 nm: same conventions as Figure 4.

To allow comparison with the underlying electronic structure, the right panels in the figures display the valence charge densities from the tight-binding calculation projected (integrated along the wire axis) onto the crosssection of the wire. (To compute the electron density from the tight-binding coefficients, we employed orbitals from a density functional calculation of the silicon atom.) The figures display the electron densities using a color map similar to that employed for the atomic moduli. Intriguingly, there is an apparent correlation between the values of the atomic moduli and the underlying electron density. In particular, large/small atomic moduli correlate with regions of large/small electron density in Figure 4, indicating that charge distribution along the surface of these wires greatly affects the local elastic properties and thereby the overall elastic response, particularly to flexion which emphasizes surface effects. Figure 5 exhibits a similar correlation, but not as pronounced. Note that, in this figure, coincidence of red atomic moduli just under the surfaces of the first layer of atoms correlates with red charge densities in the same location.

Unlike in the classical potential case, where properly defined surface moduli are systematically lower or equal to the bulk value due to decrease in the number of bonds (Figure 2b), we find that in a quantum model, surface moduli may even greatly exceed the bulk value due to changes in local charge density which can enhance the mechanical strength of bonds (Figures 4 and 5.) This contrast underscores both the importance of considering contributions of the electronic structure to mechanical response and the need for a definition of atomic moduli which can be computed from physical observables obtainable from electronic structure calculations.

The ultimate use of atomic level moduli is to understand mechanical response. Table I compares the errors from both continuum theory and the use of atomic-level moduli in predicting mechanical response for the two wires under consideration in this section. The quantities compared exactly parallel those of the previous section. The first two columns of the table consider prediction of flexural response from continuum theory and our atomic moduli, respectively, and the second two columns consider prediction of extensional response from flexural response using either the traditional continuum relation or our new relation, respectively. The table shows that the new relations, Eqs. (13) and (18) are again very accurate. The table also shows that these predictions are superior to the corresponding continuum results, Eqs. (15) and (22), respectively.

ĺ	Structure	δF_{tc}	δF_{at}	δE_{tc}	δE_{at}
	2×1	13.1%	2.86%	-11.6%	1.78%
	$c(2 \times 2)$	4.91%	1.79%	-4.68%	2.02%

TABLE I: Comparison of errors between the traditional continuum theory and the atomic moduli description when predicting flexural response through Eqs (15) and (13) (first and second columns, respectively) and when inferring extensional response from flexural response through Eqs. (22) and (18) (third and fourth columns, respectively).

Interestingly, the continuum predictions for the $c(2 \times 2)$ wire are fairly reliable. The atomic moduli provide an av-

enue for understanding this as well. Fluctuations in the moduli in the $c(2 \times 2)$ wires are localized and hence average out over regions of extent comparable to the decay of the force-constant matrix. Moreover, in this particular case they tend to average to values close to that expected of the bulk. Without meaningful fluctuations on the length scales of the decay of the force-constant matrix, we expect continuum theory to perform well for this wire. In contrast, the 2×1 wire exhibits much more systematic variations in the moduli. The outermost surface atoms have a consistent and significantly reduced modulus, and there is also a clear significant and systematic variation in the moduli throughout the cross-section of the wire. Because this second wire does exhibit meaningful fluctuation over distances comparable to the decay range of the force constant matrix, we expect traditional continuum relations to give particularly poor results, underscoring the importance of the local atomic-level moduli description.

X CONCLUSIONS

This manuscript presents the first definition of atomiclevel elastic moduli for nanoscale systems which are defined in terms of physical observables, correctly sum to give the exact overall elastic response and depend only on the local environment of each atom. Although these moduli are not necessarily uniquely defined, their sum over regions of extent comparable to the range of the force constant matrix is physically meaningful and may be used to make accurate predictions of mechanical response. The moduli resulting from our formulation transfer to different modes of strain and correctly account for elastic fluctuations on the nanoscale. They also lead to a quantitative understanding of when traditional continuum relations breakdown and how to properly correct them properly. Specifically, we demonstrated a more accurate method for relating extensional and flexural properties. These moduli provide a clear and natural method for distinguishing *mechanically* between "surface" atoms and "bulk" atoms and give insight into the correlation between the local mechanical response and the underlying electronic structure. Finally, these moduli allow the identification of which atomic arrangements lead to more pliant or stiffer response opening the possibility of their use as a tool to aid in the rational design of nanostructures with specific mechanical properties.

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A USE OF CONTINUOUS SYMMETRIES TO PRODUCE LOCAL MODULI

This appendix outlines the use of rotational and translation symmetries of the force constant matrix to reformulate the ill-defined atomic moduli in Eq. (9) into the well-defined form in Eq. (11).

From continuous translational symmetry, all force-constant matrices obey

$$\sum_{\beta,\vec{R}} \Phi_{\alpha,\beta}(\vec{R}) \cdot \vec{c}_{\beta} = 0, \qquad (1)$$

for any vector $\vec{c}_{\beta} = \vec{c}$ that is the constant vector for all atoms in the unit cell. Moreover, the SO(3) rotational symmetries imply

$$\sum_{\beta,\vec{R}} \Phi_{\alpha q,\beta s}(\vec{R}) r_{\beta t} = \sum_{\beta,\vec{R}} \Phi_{\alpha q,\beta t}(\vec{R}) r_{\beta s}, \qquad (2)$$

where the q, s, t correspond to one of the x, y, z Cartesian coordinates, $\Phi_{\alpha q,\beta s}(\vec{R})$ is the q, s component of $\Phi_{\alpha,\beta}(\vec{R})$ and $r_{\beta s}$ corresponds to the s component of the position vector \vec{r}_{β} .

The ill-defined atomic moduli, Eqs. (8)-(9), contain divergent terms which are in one of the following two forms:

$$\sum_{\alpha,\beta\vec{R}} \sigma_s r_{\alpha s} \Phi_{\alpha s,\beta t}(\vec{R}) u_{\beta t}^{rl},\tag{3}$$

or

$$\sum_{\alpha,\beta\vec{R}} \sigma_s r_{\alpha s} \Phi_{\alpha s,\beta t}(\vec{R}) r_{\beta t} \sigma_t.$$
(4)

All of these terms scale linearly along the surface of the wire and give rise to the linear scaling of the surface moduli with system size evident in Figure 2a.

From Eq. (1), one can set Eq. (3) equal to

$$\sum_{\alpha,\beta\vec{R}} \sigma_s (r_{\alpha s} - r_{\beta s}) \Phi_{\alpha s,\beta t}(\vec{R}) u_{\beta t}^{rl}.$$
 (5)

Using both Eqs. (1) and (2), one can set Eq. (4) equal to

$$-\sum_{\alpha,\beta\vec{R}} \sigma_{s} \left[(r_{\alpha s} - r_{\beta s}) \Phi_{\alpha s,\beta t}(\vec{R})(r_{\alpha t} - r_{\beta t}) - \frac{1}{4}(r_{\alpha s} - r_{\beta s}) \Phi_{\alpha t,\beta t}(\vec{R})(r_{\alpha s} - r_{\beta s}) - \frac{1}{4}(r_{\alpha t} - r_{\beta t}) \Phi_{\alpha s,\beta s}(\vec{R})(r_{\alpha t} - r_{\beta t}) \right] \sigma_{t}. (6)$$

The above terms now only depend on relative distances over a range controlled by the decay of the force-constant matrix and therefore no longer scale linearly with the size of the system. Combining the above transformations with the separation of the extensive motion from the intensive motion in the first-order polarization vector, Eq. (10), then results in the well defined form Eq. (11).

B FAILURE OF STRAIGHTFORWARD APPROCHES TO PREDICT FLEXION

We now demonstrate that although the moduli defined in Eq. (9) indeed sum to give the correct overall extensional response, their unphysical scaling properties lead to invalid physical predictions when used in other contexts and, therefore, that they are ill-defined. In particular, we use simple scaling arguments to prove that these ill-defined moduli give a nonnegligible error in predicting the flexural rigidity in the continuum limit.

Consider a circular wire whose radius R is sufficiently large such that continuum theory applies. From Figure 2a we see that the surface moduli defined by Eq. (9) scale linearly with R. Because of this, and in order to arrive at an analytic result for the error in predicting the flexural rigidity, we can assume, to a good approximation, that all surface moduli e_s are proportional to their radial distance r from the center of the wire,

 $e_s = \bar{e}_s r.$

Here, \bar{e}_s is the same for all surface atoms. Next, we define R_i as the inner radius such that all atoms at position $r < R_i$ are in the bulk and all atoms with positions $r > R_i$ are on the surface. Finally, we define $\Delta R \equiv R - R_i$.

Because of the facts that the surface moduli scale linearly with the system and that the sum of all atomic moduli must equal the extensional rigidity, we conclude that the moduli in the bulk region of the wire, derived from Eq. (9), e'_b cannot equal the average value of the bulk material e_b . (Figure 2a also evidences this behavior.) The two above facts imply that the following equality must hold,

$$\int_{R_i}^{R} e_s r \, dr + \int_0^{R_i} e_b' r \, dr = \int_0^{R} e_b r \, dr,$$

or to leading order in $\Delta R/R_i$,

$$\bar{e}_s \Delta R(1 + \Delta R/R_i) + e'_b/2 = e_b(1/2 + \Delta R/R_i).$$
 (1)

In the continuum limit, the traditional continuum relation Eq. (15) holds, and therefore the fractional error in predicting the flexural rigidity from the ill-defined atomic moduli Eq. (9) is equal to

$$\delta F_{ill-at} = \frac{\int_0^{2\pi} d\theta \left(\int_{R_i}^R dr \, x^2 e_s r + \int_0^{R_i} dr \, x^2 e_b' r \right)}{\int_0^{2\pi} d\theta \, \int_0^R dr \, x^2 e_b r} - 1$$

or to leading order in $\Delta R/R_i$,

$$\delta F_{ill-at} = \frac{\bar{e}_s \Delta R (1 + 2\Delta R/R_i) + e_b'/4 - e_b' \Delta R/R_i}{e_b/4}$$
(2)

Using Eq. (1) to solve for $\bar{e}_s \Delta R$, Eq. (2) becomes

$$\delta F_{ill-at} = 1 - \frac{e'_b}{e_b} + \frac{2(e_b - e'_b)}{e_b} \Delta R/R.$$

Therefore, in the continuum limit, the ill-defined moduli do not approach the correct result and thus give a prediction which is even worse than that of traditional continuum theory.

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