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Evaluation of the elastic constants of nanoparticles from atomistic simulations ☆

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Abstract

We present an approach to estimate the elastic constants of molecules and nanoparticles, based on the analysis of thermal fluctuations from Monte Carlo (MC) or molecular-dynamics (MD) atomistic simulations. The method and the force-field used for these calculations have been tested by the calculation of Young's modulus of a graphite sample along the basal plane; the calculated value was found to be 1.07 TPa, in very good agreement with the experimentally determined one of 1.02 TPa.

The results on a carbon-based nanotube indicate that for the longitudinal direction of the particle, the value of the elastic constant is on the order of 400 GPa. The elastic constant of the considered nanotube in the radial direction is significantly lower, the predicted values being in the range 4–7 GPa.

The method was also applied to the elastic constants of a type of siloxane-based nanostructure, whose longitudinal elastic constant (30 GPa) is an order of magnitude lower than the corresponding value for the carbon-based nanotube. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Elastic constants; Thermal fluctuations; Monte Carlo or molecular-dynamics atomistic simulation

1. Introduction

Nanoscale materials have recently gained considerable interest since they are expected to provide unique properties on the account of their small size [1]. The expectations base on the facts that nanoparticles have dimensions bridging the quantum and the bulk scales, provide very high interfacial areas if embedded in a matrix, and assemblies with unique supramolecular architectures might be constructed by interconnected nanoparticles.

When dealing with different materials assemblies or composites, it is important to have knowledge of the properties of the individual phases in order to estimate the properties of the entire system. Here we explore the capability of simulations based on molecular modeling methods to evaluate some properties of particles with dimensions at the nanoscale level.

After Iajima's report in 1991 on the preparation of carbon nanotubes [2], these structural units have received a great deal of attention [3] as constituents of materials with potentially high mechanical strength. Indeed, experimentally, the reported values for the longitudinal Young's modulus of carbon nanotubes fall between 0.4 and 4.15 TPa [3]. Recently, a theoretical study [4] on carbon nanotubes invoked parameters derived from fitting available data for graphite to evaluate these mechanical properties, resulting in the conclusion that thin nanotubes are expected to have moduli in the upper part of the range mentioned above.

While, the carbon-based nanoparticles were recently discovered, time-honored sol–gel chemistry makes available a broad range of macromolecules with regular shape but different size [5]. Due to the special interest of one of the authors into this area, a siloxane-based ladder-type set of nanoparticles was also analyzed. Here, the main reason was to consider oblong nanoparticles with the same repeat unit, but different size. Starting with similar molecular structures, we look at the effect of the number of repeat units on the longitudinal elastic constant of the nanoparticles.

By putting high-performance nano-sized objects into polymers, one can produce advanced nanocomposite materials with improved stiffness and strength. Continuum theory of elasticity is known to be adequate for describing the mechanical behavior of traditional multi-phase materials — but what about nanocomposites? In particular, is it still possible to use the continuum-level elastic description to

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predict the overall elastic constants of nanocomposites, based on their morphology, elastic constants of the pure matrix, and some suitably defined elastic constants of the individual nano-objects?

In order to focus, let us consider a particular nanocomposite, e.g. a filled polymer comprised of relatively low-aspect-ratio carbon nanotubes dispersed in a polymer matrix. The elastic constants of both pure and filled polymer can be calculated from their atomistically detailed computer models. Alternatively, one can take the continuum perspective and approximate the carbon nanotubes by solid sphero-cylinders. One can build continuum-level models based on the positions and orientations of the nanotubes in the atomistic models of the filled polymer and use the theory of elasticity for predicting the overall elastic constants from those of the carbon nanotubes and the already calculated elastic constants of the pure polymer. Will the continuum and atomistic predictions for the elastic constants of the filled polymer be in harmony? If yes, then one can conclude that the continuum approach is applicable and employ quite effective and, in principle, accurate finite-element techniques for studying and understanding the mechanical properties of nanocomposites. If not, then one should rather consistently rely on expensive and not always very accurate full-scale atomistic simulations.

In this paper we approach the problem of estimation of the elastic constants of nanoparticles and molecules. The computational avenue is based on the analysis of the shape-fluctuation of an isolated object, under molecular-dynamics (MD) or Monte Carlo (MC) atomistic simulation. To validate the current results, including the quality of the molecular-mechanics potentials employed, a standard deformational approach has also been used, and the calculated value of the elastic constants of graphite are compared with the experimentally determined ones.

2. Methods

The evaluation of the elastic constants by means of atomistic simulations for crystalline or amorphous materials has been previously described [7–9]. Here we tackle the problem of determining the elastic constants for an isolated molecule.

2.1. Strain of a molecule

The forces acting on a molecule can be readily estimated, but the calculation of stress and the assessment of strain for an object composed of a set of atoms requires the definition of an overall shape. To this end, one approximates the overall shape of the molecule by a set of points on its surface. In the case of a short molecular structure, all the atoms can be taken as 'shape atoms,' and their displacements by thermal motion or external action can be more or less accurately approximated by a single overall strain. In the case of longer molecules, such as nanotubes, it becomes impractical to consider all the atoms for the definition of an overall molecular shape. This is due to the fact that the surface atoms are subject to displacement modes that cannot be faithfully approximated by a single overall strain (e.g. bending).

Here we introduce a simple approximation, which is sufficient for the definition of simple extensions along the principal axes of the object. To this end, we define the size changes in a particular direction of the nanoparticle by two groups of atoms located at the opposite ends of the nanoparticle along the direction of interest. For example, to calculate the axial Young's modulus $E_{33} = 1/S_{3333}$ (the compliance tensor S_{ijkl} is the inverse of the tensor of elastic constants C_{ijkl}), the atoms belonging to the pentagonal rings at the tips of the nanotube (see Fig. 1) were averaged to define two mean end points of the molecule, the distance between which measures the size of the nanotube in that direction. The transversal dimensions of a nanotube were assessed by choosing two appropriate atoms at opposite sides of the cross-section in the middle of the object.

Alternatively, the dimensions of the particle can be defined by the dimensions of a triclinic box that includes the nanoparticle and that is minimized under periodic boundary conditions, thereby giving the dimensions of each particle in a crystal unit-cell arrangement. While such selections are admittedly somewhat arbitrary, the approach offers the means to evaluate the elastic constants in a straightforward manner. The results are expected to be influenced by the choice of the dimensions, because the evaluation of the modulus involves the ratio of the length of the sample to the surface area of the cross-section.

2.2. Fluctuation method

The starting point for calculation of the elastic constants by the fluctuation approach is a properly weighted set of uncorrelated configurations of the molecule that span the domain of configuration space occupied by the molecule at the temperature of interest. Such sets can be obtained from MD or MC simulations on a single molecule in vacuum or on the molecule in the crystal unit-cell obtained by employing periodic boundary conditions, at constant temperature, and it should contain a relatively large number of configurations that will assure proper statistics. The extent of the thermal fluctuations of the molecular shape is sufficient to estimate the elastic behavior of the molecule.

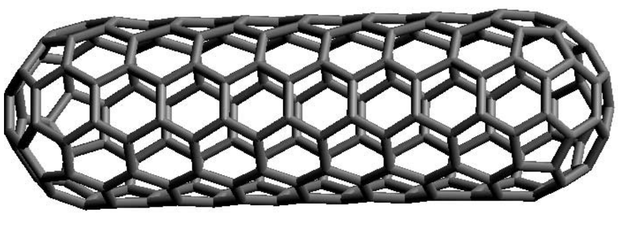

Fig. 1. The modeled carbon nanotube with 190 carbon atoms.

The state of zero strain is defined by the average shape of the molecule and an instantaneous strain in a particular direction is given by the change in length of the dimension in question, i.e. by $\epsilon_{ij} = \Delta l/l$.

The calculation is based on the Parrinello–Rahman [6] fluctuation formula for elastic constants:

$$C_{ijkl} = \frac{kT}{\langle V \rangle}\langle \epsilon_{ij}\epsilon_{kl}\rangle^{-1} \tag{1}$$

or

$$S_{ijkl} = \frac{\langle V \rangle}{kT}\langle \epsilon_{ij}\epsilon_{kl}\rangle \tag{2}$$

where S_{ijkl} are elastic compliances and ϵ_{ij} are the components of the strain tensor derived from the thermal shape fluctuations of the nanoparticle.

2.3. Deformational approach

An alternative approach to evaluate the elastic constants of a nanoparticle is to calculate the second derivative of the energy variation, when the molecular sample is minimized under specific constraints. This minimum-energy approach is exact (in the classical, strict harmonic approximation) at 0 K and appropriate for low temperatures. Again, the single-molecule-in-vacuum or the molecule-in-the-crystal-unit-cell approach can be chosen.

In the case of a nanotube, starting from the minimized structure in vacuum, the tips of the nanotube were fixed at a given distance and the energy of the structure was minimized with the displacements of all other atoms as degrees of freedom; the minimized energies ϕ as a function of preset distances then define the elastic constant through $C = 1/2(\delta^2\phi/\delta\epsilon^2)$. In the case of graphite, an external stress was applied to the sample under periodic boundary conditions, along an in-plane direction, and the structure was minimized, allowing the cell dimensions to change. The cell content was then minimized again with respect to its energy, the minimized energies as a function of cell dimensions defining the elastic constants.

3. Results and discussions

3.1. The molecular structure of the nanotube

A nanotube structure, as shown in Fig. 1, was energy-minimized using the PCFF-300-1.01 [10–14] force field provided with the Cerius2 software. The optimized structure was then used as input file for MD and MC simulations. The model was built as a single walled, zigzag symmetrical structure with a pentagonal ring at each tip, fused with 6-membered rings, and four other pentagons at the second level of cyclics from the ends of the nanotube. Overall, the structure comprised 190 carbon atoms. The central part of the structure consisted of stacks of five interconnected 6-membered rings. The nanotube could be included into an orthorhombic cell, which, after energy minimization under periodic boundary conditions, measured 25.82 × 9.82 × 9.82 Å, giving a density of 1.52 g ml^{-1}. The corresponding circular cross-section was chosen as reference area for calculating molecular volume and stress.

3.2. The structure of the graphite sample

The graphite sample was built using as a starting structure the crystallographic unit cell with hexagonal symmetry (P6 3/mmc) [15]. The simulation box was constructed comprising eight unit cells along the in-plane directions *a* and *b*, and three unit cells along direction *c*. The final, optimized structure consisted of six planar sheets of graphite, containing 768 carbon atoms with dimensions 19.37 × 19.37 × 20.54 Å.

3.3. Molecular-dynamics (MD) and Monte Carlo (MC) simulations

MD calculations were carried out with the single nanotube structure in vacuum, at several temperatures (see Table 1). The simulations were run for 5 ns at each temperature, saving the trajectories at intervals of 2 ps. The trajectory files generated in this way were then analyzed with self-built software to evaluate the fluctuations of distances between various groups of atoms, located at the ends of the principal axes of the nanotube. As previously mentioned, for the axial modulus, we considered the atoms belonging to the pentagonal rings at the tips of the nanotube and for the transversal direction, two connected atoms at the opposite sides of the cross-section in the middle of the structure.

MC calculations were performed with the same force field as the MD simulations, at the temperatures listed in Table 1, for 10^7 steps, saving the coordinates every 4000 steps.

3.4. Estimated properties from the deformational approach

The standard deformational approach based on

Table 1
The elastic constants (longitudinal and transversal) for the carbon-based nanotube, calculated from MC and MD simulations (in GPa)

T (K)	Longitudinal		Transversal	
	MC	MD	MC	MD
50	460	320	4.3	8.7
100	436	301	5.2	7.6
200	403	332	3.0	7.0
300	424	368	4.8	6.8
400		345		7.1
450	428		2.2	
600	415	395	6.7	6.9
1000	364	354	2.7	6.5
2000	391	368	3.6	6.4

energy-minimization with molecular mechanics calculations has been used to provide alternative values for testing and validation of the fluctuation results. The calculated values of the energy versus deformation were fitted with a quadratic form and the coefficient of this term (γ) yielded the Young's modulus (E) according to

$$E = 2\gamma L_0/S_0 \tag{3}$$

where L_0 is the length at zero-strain of the molecular sample in the direction of the deformation and S_0 is the initial cross-section.

In case of the nanotube, the calculated value is 490 GPa; for graphite, the modulus along the basal plane was found to be 1.07 TPa, which agrees very well with the experimentally determined value of 1.02 TPa [16,17].

3.5. Estimated properties from the fluctuation approach

The axial and radial elastic constants have been evaluated from the MD and MC calculations, at different temperatures, using the fluctuation method described above. The calculated values at several temperatures are shown in Table 1.

The MC results provide for the axial elastic (longitudinal) constant an average value of 409 ± 25 GPa. The results derived from MD simulations are lower on average, 352 ± 30 GPa for the elastic constant in the longitudinal direction of the nanotube. MD seems to consistently yield lower values than MC. One would hope that the fluctuation method yielded the temperature dependence of the elastic constants when these are evaluated over a sufficiently wide temperature interval. The data shown in Table 1 do not reveal a clear tendency, however. At high temperatures, the values from MC and MD largely agree, but with decreasing temperature, the MC predictions increase in value, while those from MD for the considered carbon-based nanotube decrease.

Table 2
The average fluctuations $\langle \epsilon_{ij}\epsilon_{kl} \rangle$ (longitudinal and transversal) for the carbon-based nanotube, calculated from MC and MD simulations. Values have been multiplied by a factor 10^4

T (K)	Longitudinal		Transversal	
	MC	MD	MC	MD
50	3.8	5.6	6.1	17.6
100	8.0	12.0	12.7	61.0
200	16.9	22.0	27.0	79.4
300	24.2	32.6	39.2	118.2
400		39.2		157.6
450	34.8		60.8	
600	49.9	62.6	68.5	248.4
1000	85.6	91	143.7	439.2
2000	170.3	195.0	275.0	888.9

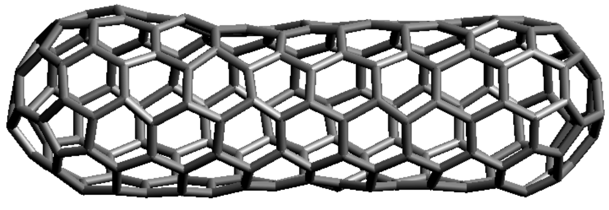

Fig. 2. Snap-shot from a MD run of the carbon nanotube shown in Fig. 1.

The elastic constant in the transversal (radial) direction for the carbon nanotube is consistently larger when evaluated by MD (average value over all temperature 6.9 ± 0.4 GPa) than by MC (4.0 ± 1.6 GPa). Here, the trend with temperature is unclear for the MC approach, while with MD there is a decrease with increasing temperature.

In principle, MC and MD are only different sampling methods that should yield the same results when applied to the same system. The differences observed here point to possible deficiencies in our implementations: One possibility is that MD is not capable of equitable sampling in the time allocated to the simulations (5 ns); a 'phase locking' might have taken place since, because of the harmonic nature of the thermal motion in nanotubes, the energy transfer between different normal modes of motion is very inefficient. This possibility was observed, as a trend, when the trajectories were saved after each MD step of 1 fs, but was not present under the currently reported conditions. Table 2 lists the average fluctuations that are consistent with the values reported for the elastic constants in Table 1. Nevertheless, because of the ready availability of standard software for MD simulations, this method will probably be preferred when many structures have to be compared.

Observing the dimensions of the nanotube as a function of temperature, it is evident that the average dimensions steadily decrease with increasing temperature. This indicates that in these materials a negative thermal expansion coefficient occurs along all directions. In the axial direction, MC simulations gave linear thermal expansion coefficients of $-1.4 \times 10^{-6}\ \mathrm{deg}^{-1}$, while MD simulations yielded

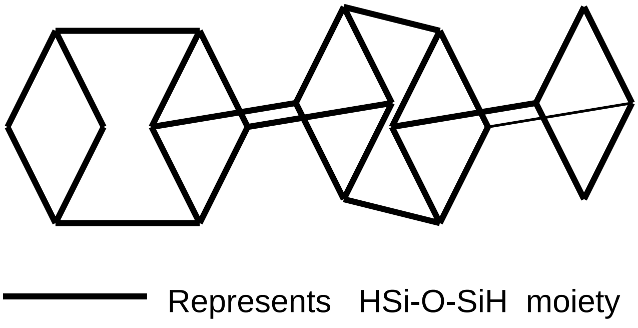

Fig. 3. Schematic of the 5-ring siloxane-based ladder structure, an example of the homologous series investigated here.

Table 3
The dimensions (in Å) of the bounding box containing the siloxane-based ladder structures with various lengths

	6 rings	8 rings	10 rings	12 rings
A	25.85	34.57	43.15	51.73
B	6.78	6.73	6.74	6.76
C	7.99	8.03	8.09	8.00

-2.3×10^{-6} deg^{-1}. Along the radial direction, MC provides a value of -5.9×10^{-6} deg^{-1}, while MD gives -3.7×10^{-6} deg^{-1}. The negative values for all thermal coefficients are due to an increasing 'crumpling' of the nanotube's surface. The vertices of the fused rings are moving inward from the envelope of the low-temperature surface of the nanotube, and the angular deformations lead to a decrease in the overall dimensions. An illustrative image is given in Fig. 2.

In addition to the carbon nanotube, a set of siloxane-based nanoparticles was also studied. The objective was to have a set of structures that are similar but have different size. It would be expected that, if molecular features are similar, so would be the values of the elastic constants. A generic structure consisting of five inter-connected siloxane rings is shown in Fig. 3 and the corresponding molecular sizes are listed in Table 3. The considered structure is believed to occur in sol–gel products resulting from the hydrolysis and condensation of trichloro, or trialkoxysilanes [5]. Contrary to the case of carbon nanotubes, the more box-like outer shape of these objects suggests that for the estimation of molecular volume and stress, the rectangular cross-section given by *a* and *b* is chosen. Table 4 lists the values of the elastic constants in the longitudinal direction of the ladder structures at several temperatures. With the exception of the values at 50 K, which are significantly higher than the others, the estimates fall into a narrow range with an average value of 30 GPa. The same value calculated from MC simulation at 300 K was 26 GPa for the structure consisting of 12 rings. Overall, the ladder structures containing a siloxane framework have significantly lower longitudinal elastic constant than the carbon nanotube, and the MD results are providing consistent results with a narrow standard deviation.

Table 4
The longitudinal elastic constants (in GPa) for siloxane-based ladder structures with various lengths at several temperatures

T (K)	6 rings	8 rings	10 rings	12 rings
50	37	38	34	35
200	25	28	32	30
300	28	29	29	29
400	30	30	32	30
600	32	31	33	31

4. Conclusions

We have shown that it is possible to evaluate the elastic properties of nanostructures and rigid molecules based on the analysis of thermal fluctuations of the atomic positions in a particular molecular environment. Simple approximations have been proposed and been found to be practical and to give credible results. The fluctuation method can be used to determine the elastic constants at a given temperature. The presented method allows for the determination of the extensional elastic constants in any direction by selecting the appropriate atoms or groups of atoms in the structure. The precision of the simulated results for these nanostructures seems to be limited by sampling problems, probably in the MD method.

The carbon nanotube characterized here has a value for the axial (longitudinal) elastic constant that is considerably lower than the often expected value of 1 TPa; our simulated results agree with the lowest reported experimental values for such constants (400 GPa [3]). Our calculations include the hollow part of the nanotube as integral component of the structure. Excluding this part would obviously increase the reported value that would then correspond exclusively to the walls of the nanotube. The radial elastic constants are even smaller, by about two orders of magnitude.

The linear thermal expansion coefficients of the studied nanotube are all negative. This can be explained in terms of out-of-surface displacements of the sp^2 carbon atoms that make up the nanostructure.

Finally, the estimation of the longitudinal elastic constants for siloxane-based ladder structures of different lengths at several temperatures showed consistent and precise agreement between the values computed for different object lengths as well as agreement between MD and MC methods. We conclude that the methods presented here allow for a straightforward and correct estimation of the elastic constants of nanoparticles.

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