

Elastic moduli of nanostructured carbon films

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(Received 31 May 2004; published 16 November 2004)

We have computed the elastic constants of nanostructured carbon films as obtained from classical molecular dynamics simulations of a cluster beam deposition process. The calculations show that the elastic constants of the deposited films are related to the average size of the clusters by a power law. This allows us to extrapolate the present theoretical data to the scale of the experimental results obtained by Brillouin scattering.

DOI: 10.1103/PhysRevB.70.195419

PACS number(s): 68.60.Bs, 61.46.+w, 81.05.Tp

Nanostructured carbon (ns-C) films grown by supersonic cluster beam deposition (SCBD) have been extensively investigated since their structural, mechanical, and tribological properties can in fact be tailored by tuning some relevant parameters of the SCBD growth process.¹ In particular, atomistic simulations have been exploited to characterize the growth of cluster-assembled carbon films² and to accurately reproduce several bulk and surface properties,^{2,3} such as the low density, high porosity, surface roughness, and self-affinity. In this framework virtual experiments based on molecular dynamics (MD) simulations have proved to be not only consistent with the available laboratory data, but also predictive as regards the leading atomic-scale mechanisms underlying cluster assembling. In particular MD simulations have been shown to predict how some of the properties of the deposited films depend upon the SCBD deposition protocol. In this work we further extend the computational modeling of SCBD ns-C films by investigating their elastic properties. The results of MD simulations are compared to the existing Brillouin scattering data.^{4,5} The present MD simulations have been performed using the Tersoff potential,⁶ whose reliability for modeling the structural properties of carbon-based materials has been extensively proved.^{2,7} In this work we have used an improved version of this empirical force field,⁸ which better models the effects of the local environment on the interatomic interaction. Further details about the simulation strategy adopted to model the growth of ns-C films by SCBD are reported in Ref. 2, while in Fig. 1 we show the final configuration of a typical computer-generated SCBD film.

The elastic properties of a material are fully determined by the elastic constants $C_{\alpha\beta\gamma\delta}$. The tensor $C_{\alpha\beta\gamma\delta}$ is equal to the second derivative of the Helmholtz free energy $\mathcal{F}(V, T)$ with respect to the strain tensor ϵ at a given temperature T :

$$C_{\alpha\beta\gamma\delta} = \frac{1}{V_0} \left(\frac{\partial^2 \mathcal{F}(V, T)}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_T, \quad (1)$$

where V_0 is the equilibrium volume. The indexes $\alpha, \beta, \gamma, \delta$ run over the Cartesian components x, y, z with the z axis taken along the growth direction of the film (Fig. 1).

The calculation of \mathcal{F} is prohibitively expensive for the typical system size we are interested in (about 10^4 particles). Furthermore, in order to compare theoretical predictions to experimental data, we need to restrict our investigation to room temperature only. At such a low temperature, we can assume that the contribution of the entropic term to \mathcal{F} is negligible, and therefore we replace the free energy with the total (internal) energy in Eq. (1), which is easily computed within a MD approach even for very large systems. For small strains the total energy change per unit volume (V_0) is then given by⁹

$$\frac{\Delta E}{V_0} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} C_{\alpha\beta\gamma\delta} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta}. \quad (2)$$

Accordingly, the elastic constants $C_{\alpha\beta\gamma\delta}$ can be easily obtained by a quadratic fit of the total internal energy variation upon suitable isothermal deformations of the simulation cell. We considered three kinds of deformations: (i) a tensile strain orthogonal to the growth direction (in-plane strain), represented by either ϵ_{xx} or ϵ_{yy} , (ii) a tensile strain along the growth direction (ϵ_{zz}), and (iii) a shear strain ϵ_{xz} or ϵ_{yz} . For each strain direction, four values of the total energy have been computed, corresponding to $\pm 2\%$ and $\pm 1\%$ strains, respectively.

Since the investigated sample consists of a film deposited on a substrate and has a free surface,² the elastic constants are not uniform across the film. However, they are expected

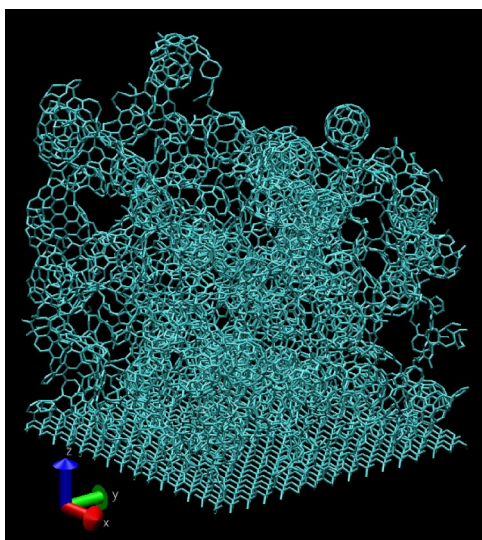


FIG. 1. Atomic structure of a ns-C model grown from a bimodal mass distribution in the supersonic beam with an average cluster size $\langle N \rangle \sim 20$ [sample (b)].

to be uniform in the region where the film density is constant. Thus for the evaluation of the total energy of the deformed systems we have computed the mass density along the growth axis for a sample resulting from a SCBD simulation—e.g., the sample shown in Fig. 1. The volume V_0 in Eq. (2) is then defined as the portion of the film where the density remains constant (within the numerical fluctuations due to the small size of the simulation cell). In the case shown in Fig. 2 this occurs for z between 5 \AA and 45 \AA . It should be noted that, in order either to enforce a strain along the growth direction or to avoid deformations along the z axis when an in-plane strain is applied, the positions of the atoms in the substrate ($z \leq 5 \text{ \AA}$ in Fig. 2) and in the surface layer (e.g., $z \geq 45 \text{ \AA}$ in Fig. 2) have been constrained as explained in the following: (i) when a strain is applied the coordinates of any atom are rescaled accordingly, and (ii) then, the positions of the atoms lying within the bulk portion are optimized by a room-temperature-simulated annealing as long as 50 ps, keeping surface and substrate atoms clamped at their deformed positions. Although unusual, this procedure

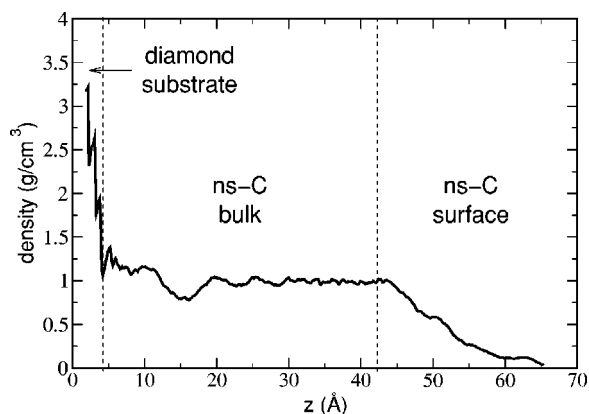


FIG. 2. The atomic density of sample (b) along the growth direction z .

TABLE I. Elastic constants of bulk diamond as obtained by a slab calculation as described in the text (present work), by a standard approach (bulk calculation), or by direct measurements (expt. data). Elastic constants are in units of GPa. η represents the anisotropy parameter as defined in the text.

	Present work	Bulk calculation ^a	Expt. data ^b
C_{11}	1038	1090	1076.4
C_{12}	119.4	120	125.2
C_{44}	628.5	640	577.4
η	0.730	0.758	0.824

^aReference 6.

^bReference 10.

is simple and effective in reproducing reliable deformation and border conditions, suitable to calculate the elastic constants. With this procedure we have computed the elastic constants of a slab specimen representing a perfectly crystalline diamond film, obtaining a good agreement with the data for bulk diamond. The calculated components of the elastic tensor, listed in Table I, are hereafter given in the compressed Voigt notation.¹⁰ The overall agreement with the experimental data¹¹ is within 5%, except for C_{44} which is known to be overestimated by about 10% by Tersoff's potential.⁶ Tersoff's potential for bulk diamond yields an anisotropy parameter $\eta = (C_{11} - C_{12})/2C_{44}$, which is about 8% smaller than the experimental value, and an even smaller value for the slab.

We now analyze the dependence of the elastic properties of cluster-assembled ns-C films upon the growth conditions. Three ns-C film models, deposited from a beam with different cluster mass distributions, have been investigated. The kinetic energy of the impinging clusters has been chosen in all cases to be 0.2 eV/atom, corresponding to the value reported in the experiments of Casari *et al.*⁵ This deposition energy is low enough to prevent the breaking of larger and more stable fullerene clusters, while small clusters in the form of rings or linear chains pack together, forming a porous amorphous network. Sample (a) has been obtained by the deposition of a unimodal distribution of small clusters (from 1 to 10 atoms per cluster), with an average size of 6 atoms/cluster. Samples (b) and (c) have been grown from bimodal mass distributions of precursors, containing either small chainlike or ringlike clusters, as well as large fullerene cages. The average size of the precursors of samples (b) and (c) is 20 and 60, respectively. In models (b) and (c) we selected a beam consisting of clusters of size 1–23 atoms (ringlike or chainlike shaped) and 46–120 atoms (cages) with a relative intensity of 5:1 and 1:10, respectively. All of computer-generated models contain about 10 000 atoms in a supercell with two-dimensional periodic boundary conditions in the plane orthogonal to the growth direction.

A first key issue is to establish whether the investigated systems are elastically isotropic. To this aim we independently computed the three diagonal components of the elastic tensor C_{11} , C_{22} , and C_{33} (Table II). Note that for a simulation cell infinitely extending in two dimensions C_{11} and C_{22} should be equal. Thus their difference may be taken as a measure of the numerical fluctuations due to the finite size of

TABLE II. Elastic properties of different ns-C models computed by MD simulations compared to the ones measured by Brillouin scattering reported in Ref. 5. Elastic constants are in units of GPa. $\langle N \rangle$ is the average number of carbon atoms in the molecular precursors of the supersonic beam.

	$\langle N \rangle$	C_{11}	C_{22}	C_{33}	C_{44}	B	ν
Model (a)	6	195.3	205.6	184.0	60.4	90.4	0.15
Model (b)	20	60.3	69.7	44.1	14.2	38.4	0.28
Model (c)	60	25.7	23.5	29.0	5.8	12.2	0.20
Experiment	500	5.4	-	-	2.5	2.1	0.08
Amorphous schwarzite	6	60.3	69.7	63.4	10.9	30.4	0.17

the simulation cell. However, the average in-plane component $(C_{11} + C_{22})/2$ is different from C_{33} by amounts which are significantly larger than numerical fluctuations and indicate an appreciable anisotropy: samples (a) and (b) are softer along the growth direction than in plane, while sample (c) is slightly stiffer along the z axis. The shear modulus has been calculated for a shear in the plane orthogonal to the growth direction (C_{44}), while the bulk modulus has been calculated by applying an isotropic strain and fitting on a Murnaghan function.¹²

Our simulations show that it is possible to tune the elastic properties of ns-C films within a given order of magnitude just by choosing an appropriate mass distribution of clusters in the beam. This conclusion is based on the fact that we have found a simple power-law relationship to link the elastic constants to the average size of the precursors $\langle N \rangle$:

$$C_{ij} = \beta \langle N \rangle^{-\alpha}, \quad (3)$$

where α and β are fitting parameters. These scaling laws are consistent with the fractal self-affine nature of the SCBD films.^{3,13} For C_{11} and B we obtained $\alpha = 0.87$, while for C_{44} , $\alpha = 1.15$. In Fig. 3 the above theoretical predictions for elastic constants are compared to the data of Casari *et al.* derived from Brillouin spectroscopy.⁵ The corresponding values for bulk diamond are also reported for the sake of comparison.

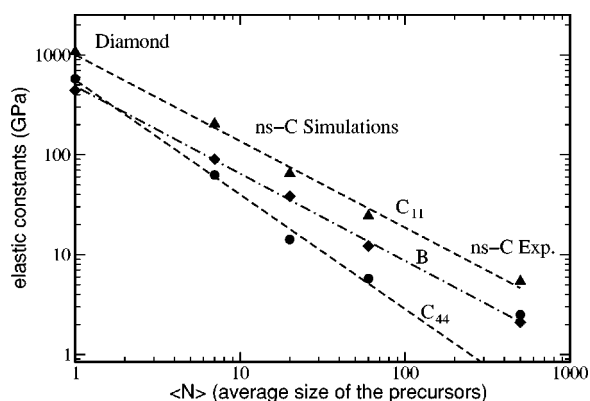


FIG. 3. Bilogarithmic plot of the bulk modulus B (diamonds) and of the elastic constants C_{11} (triangles) and C_{44} (circles) of diamond and ns-C samples from simulations and experiments, versus the average size of the clusters in the beam. Lines have been fitted to power laws (see text).

In this framework one can regard diamond as the carbon form which would be ideally grown by deposition of single atoms ($\langle N \rangle = 1$) under the present SCBD conditions. On the other hand, the experimental average size of the cluster precursors of the film is estimated to be about 500 carbon atoms.⁵ The reported values for the bulk modulus and C_{11} for both crystalline diamond and the experimental ns-C films are in rather good agreement with the extrapolations of the present MD simulations. As regards the extrapolations of the shear modulus a good agreement is found for diamond, whereas the extrapolated C_{44} for $\langle N \rangle = 500$ is off with respect to experiment by a factor of about 4. In fact the shear modulus of the ns-C films as measured by Brillouin scattering is 2.5 GPa, while the extrapolated theoretical value is only 0.6 GPa. The nature of this discrepancy may be better understood by considering the Poisson ratio, which in experimental Brillouin data on SCBD films turns out to very small or, in some case, even negative.⁵ Under the assumption of isotropy, the scalar Poisson ratio ν can be estimated from the available values of the bulk modulus and the average C_{11} through the equation

$$\frac{1 + \nu}{1 - \nu} = \frac{3B}{C_{11}}. \quad (4)$$

This gives for the present model ns-C films a Poisson ratio in the range between 0.15 and 0.3 (see Table II), slightly smaller than what is found for most current materials.¹⁴ Since, according to the power laws given in Eq. (3), C_{44} decreases slightly faster than B for increasing $\langle N \rangle$, ν should be slowly increasing with the average size of cluster precursors. Thus the very small, or even negative, values of ν reported in Ref. 5 indicate some peculiar way of assembling large clusters through the formation of many more lateral intercluster bonds than occurring in our present simulations. This may be due to some fragmentation and rebinding of the large clusters occurring in experiments, which apparently do not occur for the smaller clusters used in simulations at the same energy of 0.2 eV/atom. It should be also noted that, whether fragmentation and rebinding does not occur, the interaction between the big molecular precursors (in our simulations we use cluster sizes up to 120 atoms) is in fact dominated by dispersion forces which the Tersoff potential does not account for. We attribute to both features the explanation

of why the calculated shear modulus is smaller than experiment.

In Ref. 2 it was suggested that cluster assembling under particular growth conditions (i.e., very low deposition energy and small precursors) is a viable route to the formation of random schwarzite structures. This goal has been achieved in a recent experiment,¹⁵ where a negatively curved spongy carbon network was grown by a pulsed plasma cluster source and the aid of metallorganic catalysts. Although the elastic properties of such materials have not been measured so far, there are a few theoretical predictions about the bulk modulus of crystalline carbon schwarzites.^{16,17} We have computed the elastic properties of a random schwarzite structure of about 1500 atoms, obtained by the deposition of small carbon clusters (chains or rings made of 2–10 atoms) at 0.1 eV/atom (see Ref. 2 for further details). Due to its relatively small size, the model is quite anisotropic. Its bulk modulus (30.4 GPa) is much smaller than the ones reported for the crystalline carbon schwarzites,^{16,17} which are between 75 and 192 GPa. This amorphous schwarzite film is also softer than sample (a) obtained by the deposition of cluster from the same mass distribution but with a twice as large kinetic energy per atom. It is interesting, however, to note

that the elastic constants of this schwarzite are about the same as for sample (b). This sheds some light on the role of the incident energy per atom, $\epsilon_a = \epsilon / \langle N \rangle$, in the elastic properties of cluster-assembled films. Apparently the same elastic properties are obtained if ϵ_a increases approximately as $(\langle N \rangle)^{1/2}$.

In summary, we have computed the elastic properties of a few models of ns-C films obtained by MD simulations of supersonic cluster beam depositions by different growth protocols. Particularly, we have shown that the elastic moduli of such materials are related to the size distribution of the clusters in the deposited beam by simple power laws, which, for the bulk modulus and C_{11} , allows us to extrapolate the calculated values to the values measured by Brillouin scattering on ns-C samples. The extrapolated isotropic and tensile elastic constants are in good agreement with the experimental data, thus providing a good level of confidence over three orders of magnitude in the cluster precursor size (from diamond to SCBD ns-C films). On the contrary the shear modulus and therefore the Poisson ratio are not well reproduced on the SCDB ns-C film scale, the extrapolated value corresponding to a much softer material against shear stress than actually measured with Brillouin scattering in ns-C films.

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