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Ab initio determination of the phonon deformation potentials of graphene

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We calculated with *ab initio* methods the in-plane phonon deformation potentials of a graphite sheet. The two-dimensional Grüneisen parameter is found to be $\gamma = 2.0$ and the shear potential $(\mathrm{SDP}) = 0.66$. The two values agree well with experimental results on graphite and on carbon nanotubes.

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The elastic properties of graphene have become of renewed interest recently with the focus of research on carbon nanotubes. These tubes, being wrapped-up graphite sheets, have vibrational and elastic properties similar to those of graphite, and many analogies have been made. Experimentally, the vibrational in-plane frequencies are similar (e.g., 1592 cm^{-1} for nanotubes[1] and 1580 cm^{-1} for graphite[2]), and for the purposes of calculating many physical properties to first order the effect of curvature may be neglected.[3] On the other hand, there have been *ab initio* calculations of the vibrational eigenfrequencies,[4] which allowed the estimate of curvature-induced effects on the frequencies, and of the phonon eigenvectors which gave substantial new insight into the actual vibrations of chiral tubes.[5]

Recently, pressure-dependent Raman experiments gave rise to at first sight surprising results concerning the pressure derivatives. The low-energy radial-breathing mode around 200 cm^{-1} exhibited a many times larger logarithmic pressure derivative than the high-energy modes. This was understood in terms of a substantial contribution of van der Waals forces between neighboring tubes in a bundle.[6,7] The high-energy modes near 1600 cm^{-1} also exhibited unexpected behavior: In semiconducting tubes under hydrostatic pressure the pressure slopes of the three identified peaks were identical[6,7] to within experimental error 3.7 TPa^{-1} while slopes different by 0.56 TPa^{-1} were found in metallic tubes.[8] The absence of different pressure slopes in semiconducting nanotubes has recently been explained by a periodic variation of the eigenvector direction for E_1 and E_2 modes in chiral tubes when going around the circumference of a tube.[9] This effect is a property of chiral tubes and not present in armchair or zigzag tubes.

The situation in metallic tubes—different slopes for modes with different eigenvectors—is actually expected for a uniaxial system exposed to hydrostatic pressure. This can be nicely seen in Fig. 1 where we depicted an armchair (6,6) and a chiral (8,4) nanotube under exaggerated hydrostatic pressure; the original hexagons of the armchair tube deflate and become more similar to rectangles. This corresponds to applying shear strain and hydrostatic strain simultaneously to a graphene sheet. A similar picture holds for the chiral tube due to the larger strain in circumferential direction compared to the axial direction.[8] Under these circumstances the E_{2g} modes, which are degenerate in graphite and slightly split by the curvature of a tube at zero pressure, should shift at rates which depend on whether their eigenvector points along the axis or the circumference of the tube. The magnitude of the splitting, however, is not accessible from experiments on graphite, because of its brittleness when a uniaxial stress is applied in the basal plane. In this report we focus on the mode splitting in a graphite sheet and calculate with *ab initio* methods the volume and shear phonon deformation potentials. We show that the comparison of our results with experimental findings on graphite (Grüneisen parameter of graphene) and on nanotubes (shear potential of graphene) is favorable.

The elastic constants of solids determine how they deform under pressure and the deformation potentials give the corresponding change in vibrational frequencies. To first order in strain the frequencies of a hexagonal solid under pressure are given by only two independent constants $\tilde{K}_{11}$ and $\tilde{K}_{22}$. They are expressed in terms of the elements of a tensor with elements K_{ijkl}, which describe the change of the ij-th element of the force constant matrix with respect to the kl-th component of the strain tensor. $K_{1111} = K_{2222} = m\tilde{K}_{11}$, $K_{1122} = m\tilde{K}_{12}$, and $K_{1212} = m(\tilde{K}_{11} - \tilde{K}_{22})/2$, where m is the reduced mass of the vibrating atoms.[10] The Grüneisen parameter and shear phonon deformation potential (SDP) are then, respectively (ω_0 – eigenfrequency in equilibrium)

$$\gamma = -\frac{\tilde{K}_{11} + \tilde{K}_{22}}{4\omega_0^2} \quad \text{and} \quad \mathrm{SDP} = \frac{1}{2\omega_0^2}(\tilde{K}_{11} - \tilde{K}_{22}). \qquad (1)$$

A general strain in the two-dimensional graphene causes a frequency shift composed of a hydrostatic $(\Delta\omega_h)$ and a shear term $(\Delta\omega_s)$:[8,10]

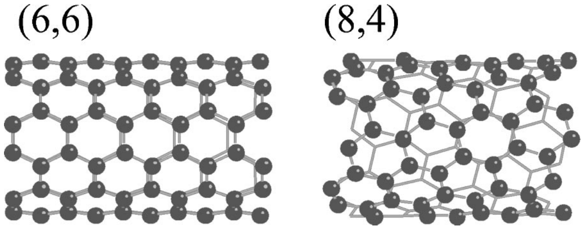

FIG. 1. Schematic shear deformation of a (6,6) and an (8,4) carbon nanotube under large hydrostatic pressure. The ratio of circumferential to axial strain was taken to be ≈2. See text for details.

$$\frac{\Delta\omega}{\omega_0}=\frac{\Delta\omega_h}{\omega_0}\pm\frac{1}{2}\,\frac{\Delta\omega_s}{\omega_0}=\gamma^{2\mathrm{D}}(\varepsilon_{xx}+\varepsilon_{yy})\pm\frac{1}{2}\mathrm{SDP}(\varepsilon_{xx}-\varepsilon_{yy}), \tag{2}$$

where ε_{xx} and ε_{yy} are the strains in x and y direction, respectively. We determined $\gamma^{2\mathrm{D}}$ and the SDP of graphene according to Eq. (2) by an *ab initio* calculation of the phonon frequencies in strained and unstrained graphene. We compare our results to hydrostatic pressure experiments on graphite[11] which yield the Grüneisen parameter of graphite and to hydrostatic pressure measurements on carbon nanotubes[8] which allowed an estimate of the shear deformation potential of graphene.

Ab initio calculations of graphene were performed using a numerical-atomic-orbital density-functional-theory method implemented in the *SIESTA* code.[12] We worked within the local-density-approximation as parametrized by Perdew and Zunger.[13] Core electrons were replaced by nonlocal, norm-conserving pseudopotentials,[14] the valence electrons were described by a linear combination of numerical pseudo-atomic orbitals. We used a double-ζ, singly polarized basis set[15] with cutoff radii for the s and p orbitals of 5.95 and 7.45 a.u., respectively. k-space integration was performed over 840 k points; we found it necessary to use a higher density in the k_x and k_y directions than for 3D graphite. Real space integrations were performed on a regular grid, the grid spacing corresponding to a plane wave cutoff around 350 Ry. Successful results with this method on carbon nanotubes have been reported elsewhere.[4] The reader is referred to Ref. 12 for details of the method of calculation.

We obtained an equilibrium lattice constant of $a_0=2.468$ Å compared to the x-ray value on graphite of 2.462 Å.[16] The dynamical matrix was found by a finite-difference approach, i.e., calculating the Hellman-Feynman forces for displaced atoms. The phonon deformation potentials were determined by calculating the vibrational frequencies under hydrostatic strain and under shear strain; a general strain can always be decomposed into these two components. Hydrostatic strain was applied by reducing the lattice constant; shear strain was introduced by multiplying the lattice vectors with the traceless tensor

$$\begin{pmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{pmatrix},$$

which to first order in strain leaves the volume of the unit cell constant. The so strained unit cell was relaxed until the remaining forces were below 0.02 eV/Å and the eigenfrequencies calculated.

In equilibrium the two degenerate E_{2g} modes where the carbon atoms vibrate out of phase in the graphene plane, lie at 1624 cm^{-1} and are equal to within 0.4 cm^{-1}. The third optical mode, an A_{1g} out-of-plane vibration, has a frequency of 837 cm^{-1} and will not be considered further. The E_{2g} equilibrium frequencies are about 3% higher than the experimental value[2] of 1580 cm^{-1} of graphite, a shift which was also found in *ab initio* calculations of carbon nanotubes[12] and which is not expected to influence the calculated deformation potentials noticeably. Figure 2 shows the dependence of the degenerate E_{2g} mode frequency under hydrostatic strain of the unit cell, i.e., as a function of $\Delta a/a_0$. We find that the frequency of the E_{2g} mode increases with pressure at a rate which compares excellently with the experimental values of Hanfland *et al.*, which are also shown in the figure. When comparing with experiment one has to make a choice of linear bulk modulus for which somewhat different values have been reported. The open circles in Fig. 2 were converted using $B_a=-p/(\Delta a/a_0)=(1580\pm200)$ GPa, as obtained from x-ray measurements of the lattice constant under hydrostatic pressure.[16] The value is larger than the one given by Ref. 11 [(1250 ± 70) GPa], but the errors in B_a are relatively large. From a full potential calculation Boettger[17] derived a value of 1270 GPa. The experimental Grüneisen constant was reported to be slightly pressure dependent with a tendency to decrease with increasing pressure, a result which we do not find in the calculation. Our value for the two-dimensional $\gamma^{2\mathrm{D}}=(1/2)d\ln\omega/d\ln a=2.0$ equals the experimental one ($\gamma^{2\mathrm{D}}_{\mathrm{exp}}=2.0\pm0.3$) (Ref. 11) if the latter is assumed to be linear, or otherwise corresponds to the average $\overline{\gamma}$ in the range 0 to 10 GPa (Fig. 2). The experimental Grüneisen parameter, of course, is affected by the choice of bulk modulus in the same way as Fig. 2.

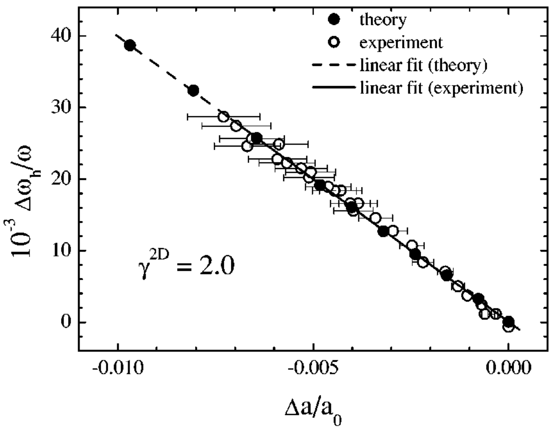

FIG. 2. Dependence of the degenerate high-energy E_{2g} eigenfrequency of graphene under hydrostatic pressure and the theoretical Grüneisen parameter $\gamma^{2\mathrm{D}}$. The experimental points of Hanfland *et al.* (Ref. 11) on graphite were converted using a bulk modulus of $B_a=(1580\pm200)$ GPa, the horizontal error bars reflecting the error in B_a.

Having shown that our volume deformation potential γ agrees well with experiment we now turn to the shear deformation potential. In Fig. 3 we show the results for negative and positive shear strains. It can be seen that the doubly degenerate E_{2g} mode splits into two with mutually perpendicular eigenvectors. The frequency splitting from Fig. 3 amounts to

$$\frac{\Delta\omega_s}{\omega_0}=1.32\frac{(\varepsilon_{xx}-\varepsilon_{yy})}{2}, \tag{3}$$

where we have ignored a small constant term resulting from numerical inaccuracies. By comparison with Eq. (2) we find SDP$=0.66$ for the shear phonon deformation potential.

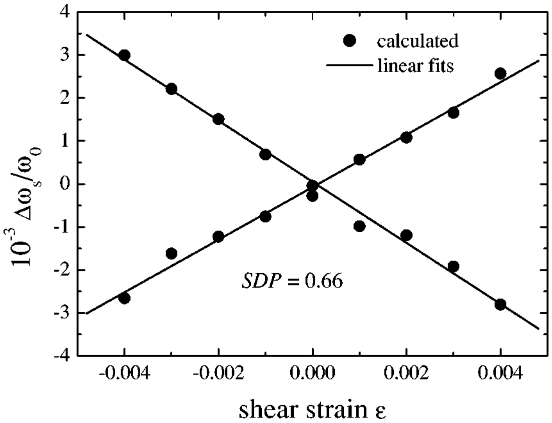

FIG. 3. Splitting of the E_{2g} eigenmode of graphene under pure shear strain and the shear deformation potential (SDP).

Experimentally the shear deformation potential is usually determined in unaxial stress measurements.[10,18] Because such measurement is unavailable for graphite in the lateral direction, a direct comparison with our calculation is not possible. Carbon nanotubes, however, in principle, offer such a possibility. The graphene sheet wrapped up to form a nanotube, deforms with different strain along the tube axis as compared to in the direction of the circumference. The ratio of circumferential to axial strain under hydrostatic pressure (≈ 2 in Fig. 1) has been estimated by various authors with different models (I–III) and ranges from 1.9 to 3.7; see Table II in Ref. 8 for a compilation of results. In all cases, the strain along the circumference is much larger than the axial strain, and hence hydrostatic pressure on a nanotube corresponds to a combination of volume and shear deformation of a graphite sheet. The measurements of Reich *et al.*, together with model I in Ref. 8 (based on elastic constants) yields a deformation potential of 0.45, model II (elasticity theory) 0.50, and model III, a molecular dynamics calculation results in 0.22 for the shear deformation potential of graphene. Since none of these models are preferred *a priori* the experimental value for the shear deformation potential of graphene is 0.4 ± 0.2, which agrees well with our value of 0.66.

In conclusion, we have calculated the volume and shear phonon deformation potential of a graphite sheet and compared them to experimental values. Hydrostatic pressure measurements on graphite are in excellent agreement with our calculation of the Grüneisen constant ($\gamma^{2D}=2.0$). The calculated shear deformation potential (SDP=0.66) was compared to values derived from hydrostatic measurements on carbon nanotubes and agreed as well. Our approach, calculating the deformation potentials for graphene and applying them to the phonons of carbon nanotubes thus appears valid. In particular, metallic carbon nanotubes show nearly the full shear splitting expected from *ab initio* calculations for E_{2g} modes with eigenvectors pointing along the axis and perpendicular to it.

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[1] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, M.S. Dresselhaus, and G. Dresselhaus, Science **275**, 187 (1997).
[2] F. Tuinstra and J.L. Koenig, J. Chem. Phys. **53**, 1126 (1970).
[3] C. Thomsen, Phys. Rev. B **61**, 4542 (2000).
[4] D. Sánchez-Portal, E. Artacho, J. Soler, A. Rubio, and P. Ordejón, Phys. Rev. B **59**, 12 678 (1999).
[5] S. Reich, C. Thomsen, and P. Ordejón, Phys. Rev. B **64**, 195416 (2001).
[6] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rinzler, R.E. Smalley, and P.C. Eklund, Phys. Rev. B **59**, 10 928 (1999).
[7] C. Thomsen, S. Reich, A.R. Goñi, H. Jantoljak, P.M. Rafailov, I. Loa, K. Syassen, C. Journet, and P. Bernier, Phys. Status Solidi B **215**, 435 (1999).
[8] S. Reich, H. Jantoljak, and C. Thomsen, Phys. Rev. B **61**, R13 389 (2000).
[9] S. Reich and C. Thomsen, in *Proceedings of the XV International Winterschool on the Electronic Properties of Novel Materials*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (AIP, Woodbury, New York, 2001), p. 129.
[10] F. Cerdeira, C.J. Buchenauer, F.H. Pollack, and M. Cardona, Phys. Rev. B **5**, 580 (1972).
[11] M. Hanfland, H. Beister, and K. Syassen, Phys. Rev. B **39**, 12 598 (1989).
[12] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[13] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[14] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
[15] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J.M. Soler, Phys. Status Solidi B **215**, 809 (1999).
[16] Y.X. Zhao and I.L. Spain, Phys. Rev. B **40**, 993 (1989).
[17] J.C. Boettger, Phys. Rev. B **55**, 11 202 (1997).
[18] E. Anastassakis, in *Dynamical Properties of Solids*, edited by G. Horton and A. Maradudin (North-Holland, Amsterdam, 1980), Vol. 4, p. 157.