Grüneisen parameter of the $G$ mode of strained monolayer graphene

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We present a detailed analysis of the effects of uniaxial and biaxial strain on the frequencies of the $G$ mode of monolayer graphene, using first principles calculations. Our results allow us to explain discrepancies in the experimentally determined values of the Grüneisen parameter. The direction and strength of the applied strain, Poisson’s ratio of the substrate, and the intrinsic strain in different experimental setups turn out to be important. A reliable determination of the Grüneisen parameter is a prerequisite of strain engineering.

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I. INTRODUCTION

Since it was first obtained in 2004,1 graphene has attracted tremendous interest, reflected by many theoretical and experimental studies. This is due to its unique electronic properties arising from the hexagonal honeycomb lattice structure, which makes the electrons behave as massless relativistic fermions, satisfying the Dirac equation.2 On the other hand, strain is known to give rise to surprising effects on the electronic properties of carbon nanotubes,3–7 It has been demonstrated theoretically that local strain can be used as a means of tailoring the electronic structure and transport characteristics of graphene devices to generate confined states, quantum wires, and electron-beam collimation.8 Therefore it is essential to impose and/or probe the strain in graphene. Uniaxial strain can be induced by bending the substrate such that the graphene sheet is elongated without slippage.9–11 Biaxial strain can be induced by adhering the graphene to the bottom of a small aspect ratio depression12 or by utilizing piezoelectric actuators.13,14 To probe uniaxial or biaxial strain in graphene, Raman spectroscopy has proven to be a powerful and nondestructive tool, as two distinct Raman active modes [G mode and 2D mode] will shift and/or split when strain is applied.9–13

Both to impose and to probe the strain in graphene, the Grüneisen parameter is a crucial quantity because it represents the rate of phonon mode softening (hardening) under tensile (compressive) strain and determines the thermomechanical properties.10,13–15 However, there is a significant discrepancy among the reported Grüneisen parameters.10,13–16,17 For example, the experimental value of the $G$ mode is 2.4 as extrapolated from biaxial strain data by Metzger et al.,12 while Ding et al.,13 find a value of 1.80. The discrepancy of different experimental as well as calculated values of the Grüneisen parameter calls for clarification.

In this work we present a theoretical study of the effect of uniaxial strain along arbitrary direction as well as biaxial strain on the $G$ mode frequencies. We will show that Poisson’s ratio of graphene has a noticeable downward trend at large uniaxial strain and behaves anisotropically. The shifts of the splitted $G$ mode frequencies depend on the direction of the uniaxial strain, which is the intrinsic reason for the discrepancies reported for the Grüneisen parameter. The determination of Poisson’s ratio of the substrate also affects the Grüneisen parameter in uniaxial strain measurements. The discrepancies of biaxial strain measurements may result from different intrinsic strains in the graphene samples.

II. COMPUTATIONAL DETAILS

Our calculations are performed by means of the Quantum-Espresso code18 within the framework of ab initio pseudopotential density-functional theory.19 Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ)-type20 norm-conserving pseudopotentials are employed together with the generalized gradient approximation in the Perdew, Burke, and Ernzerhof parametrization.21 A 60-Ry plane-wave cutoff energy and a 16 $\times$ 16 $\times$ 1 Monkhorst-Pack mesh of $k$ points for the Brillouin-zone integration are used. The estimated self-consistency energy error is less than 10$^{-10}$ a.u. The structure is relaxed until the total energy change is less than 10$^{-5}$ a.u. and the components of the forces are smaller than 10$^{-4}$ a.u. We use the calculated equilibrium lattice constant $a = 2.46$ Å and an interlayer spacing of 15 Å to avoid artifacts of the weak van der Waals interaction.

III. RESULTS AND DISCUSSION

Graphene can be represented by two sublattices, $A$ and $B$, as illustrated in Fig. 1. The four- and the two-atom unit cells with lattice vectors $a_1$ and $a_2$ in the nondeformed reference configuration are shown in Figs. 1(a) and 1(b), respectively. Calculations performed for both cells yield the same results.22 For simplicity the two-atom unit cell is used in the following. We describe the uniaxial strain in terms of the angle $\theta$ between the strain direction and the lattice vector $a_1$, see Fig. 1(b). The general three-dimensional Hooke’s law connects the stress tensor $\sigma$ to the strain tensor $\varepsilon$ via the stiffness tensor $c$ as $c_{ijkl} \varepsilon_{kl}$. The tensile strain in the zigzag direction ($\theta = 0^\circ$) of the graphene sheet can be expressed via a two-dimensional tensor $\varepsilon = \{(\varepsilon_0, 0), (0, -\varepsilon_0\nu)\}$, where $\nu$ is Poisson’s ratio. Since we want to study arbitrary strain directions, given by the angle $\theta$, the strain tensor has to be rotated according to $\varepsilon = R^{-1} \varepsilon R$, where $R(\theta) = [(\cos \theta, -\sin \theta), (\sin \theta, \cos \theta)]$ is the rotational matrix. For strain in arbitrary directions the point group reduces from $D_{4h}$
to \(C_{2h}\), i.e., only the \(C_2\) rotation and inversion are retained. For strain along the \(\theta = 0^\circ\) (zigzag) and \(\theta = 30^\circ\) (armchair) directions additional mirror planes are retained, resulting in a \(D_{2h}\) symmetry. Phonon instability occurs at 19.4\% along the \(x\) direction and at 26.6\% along the \(y\) direction under uniaxial strain.\(^\text{22}\)

In Fig. 2, we show the phonon band structures of unstrained graphene and of strained graphene under \(\varepsilon = 5\%\) tensile strain along the zigzag direction. The strain induces the following principal modifications of the phonon band structure: (i) We observe for the optical bands a clear trend of softening, which is expected because all C-C in-plane distances increase uniformly. (ii) At the \(\Gamma\) point, the twofold degenerate \(E_{2g}\) mode splits into two different modes, which we will discuss later. (iii) The Kohn anomalies of the highest optical branches at \(\Gamma\) and at \(K\) do not vanish, which suggests that no band gap opens and that the Dirac point will also appear in the electronic band structure of strained graphene.\(^\text{16}\)

The Raman \(G\) mode of graphene results from the twofold degenerate \(E_{2g}\) mode corresponding to C-C bond stretching. Figs. 3(a) and 3(b) schematically display the atomic displacements associated with the two eigenmodes. Under uniaxial strain, the hexagonal symmetry of graphene is broken, which splits the twofold degenerate \(E_{2g}\) mode (\(G\) mode) into two modes. These two modes possess eigenvectors parallel and perpendicular to the strain direction, as displayed in Figs. 3(c) and 3(d). The parallel (perpendicular) mode is denoted \(G^- (G^+)\), analogous with the nanotube denotation.\(^\text{23}\)

The 2D mode is due to two phonons with opposite momentum in the highest optical branch near the \(K\) point of the Brillouin zone.\(^\text{24}\) In the case of uniaxially strained graphene, the shift of the 2D mode in the Raman spectrum should be due to the 2D phonon shift and an additional shift resulting from the fact that the relative movement of the Dirac cones alters the phonon wave vector.\(^\text{13}\) Under biaxial strain, the point group remains \(D_{6h}\), and the \(G\) mode does not split. The \(G\) mode therefore can be used to probe uniaxial versus biaxial strain in flat graphene.

It is reported that no \(G\) mode splitting can be observed in experiment if the uniaxial tensile strain is small (<1\%).\(^\text{11}\) This is due to the overlap of the \(G^+\) and \(G^-\) bands in this case. On the contrary, the \(G\) mode splitting can be observed clearly if a uniaxial strain of \(~1.3\%\) is applied to the graphene monolayer.\(^\text{2,10}\) Figure 4(a) shows the \(G^+(G^-)\) frequency shift with respect to the frequency of the equilibrium structure as a function of the uniaxial tensile strain (<1.5\%), together with data from Ref. 10. We find that the split \(G^+\) and \(G^-\) modes both soften with increasing strain. It has been claimed that the shift of the \(G^+(G^-)\) mode is independent of the strain direction for small uniaxial tensile strain (<1\%).\(^\text{3,11,16}\) From Fig. 4(a), we find that the softening of the \(G^-\) mode varies little for
different strain directions. In contrast, the $G^+$ mode shows an anisotropic behavior with strong variations in different strain directions. With increasing uniaxial strain (<5%), the shifts of both the $G^+$ and $G^-$ mode frequencies behave anisotropically; see Fig. 4(b). The shift of the $G^+$ mode frequency increases with the angle $\theta$, while that of the $G^-$ mode frequency decreases. Moreover, with increasing $\theta$ the slope $\Delta \omega_{G^-}/\varepsilon$ decreases; compare the inset of Fig. 4(b). It has been reported that the relative intensities of the split $G$ modes depend on the light polarization, which provides a useful tool to probe the crystallographic orientation of the graphene sheet with respect to the strain.9,10 Because the shift of the $G$ mode behaves anisotropically under increasing uniaxial strain, theoretically, this anisotropy likewise could be used to probe the orientation. However, we find that the $G^+$ and $G^-$ mode frequencies are almost identical for strain between $\theta = 20^\circ$ and $\theta = 30^\circ$, which suggests that it is difficult to distinguish the strain direction in this range.

Theoretically, the shift of the split $E_{2g}$ mode frequency under uniaxial strain is

$$\Delta \omega_{E_{2g}}/\varepsilon = -\omega_0^0 \gamma_{E_{2g}} (1 - \nu) \pm \omega_0^0 \beta_{E_{2g}} (1 + \nu)/2,$$  

(1)

where $\omega_0^0$ is the $G$ mode frequency without strain, $\varepsilon$ is the uniaxial strain, $\gamma_{E_{2g}}$ is the Gr"uneisen parameter for the $E_{2g}$ mode, $\beta_{E_{2g}}$ is the shear deformation potential for the $E_{2g}$ mode, and $\nu$ is Poisson’s ratio.10 From Eq. (1), we obtain

$$\gamma_{E_{2g}} = -(\Delta \omega_{G^+}/\varepsilon + \Delta \omega_{G^-}/\varepsilon)/[2\omega_0^0 (1 - \nu)],$$  

(2)

and

$$\beta_{E_{2g}} = (\Delta \omega_{G^+}/\varepsilon - \Delta \omega_{G^-}/\varepsilon)/[\omega_0^0 (1 + \nu)].$$  

(3)

To obtain the Gr"uneisen parameter $\gamma_{E_{2g}}$ and the shear deformation potential $\beta_{E_{2g}}$ for uniaxially strained graphene, hence, Poisson’s ratio $\nu$ of free-standing graphene is needed. For small strain we obtain for the isotropic Poisson’s ratio $\nu$ of the substrate a value of $\nu_0 = 0.167$, which is consistent with previous $ab$ initio results, as listed in Table I. Under small uniaxial tensile strain (<1.5%) our calculation yields $\Delta \omega_{G^-}/\varepsilon = -34$ cm$^{-1}$/% and $\Delta \omega_{G^+}/\varepsilon = -17$ cm$^{-1}$/%, in excellent agreement with the calculated values from Refs. 10 and 16; see Table I. Using the calculated value $\omega_0^0 = 1575$ cm$^{-1}$, we obtain the Gr"uneisen parameter $\gamma_{E_{2g}} = 1.86$ and the shear deformation potential $\beta_{E_{2g}} = 0.96$ according to Eqs. (2) and (3).

Our calculated values of $\Delta \omega_{G^-}/\varepsilon$ and $\Delta \omega_{G^+}/\varepsilon$ are consistent with the values reported in Refs. 10 and 16. However, other experiments point to smaller slopes of $\Delta \omega_{G^-}/\varepsilon = -12.5$ cm$^{-1}$/% and $\Delta \omega_{G^+}/\varepsilon = -5.6$ cm$^{-1}$/% (Ref. 9) or $\Delta \omega_{G^-}/\varepsilon = -31.7$ cm$^{-1}$/% and $\Delta \omega_{G^+}/\varepsilon = -10.8$ cm$^{-1}$/% (Ref. 10), for example. The question now is why the calculated values of $\Delta \omega_{G^+}/\varepsilon$ show such large discrepancies as compared to experimental findings. Of course, the graphene sheet is attached to some substrate in the experiment, whereas the calculations assume free-standing graphene. When ideally contacted to a substrate, graphene should consistently deform with the substrate in uniaxial strain experiments. However, because Poisson’s ratio of the substrate is always higher than that of graphene, the graphene sheet is not really uniaxially strained in the experiments. The discrepancy between the

\[
\begin{array}{cccccc}
\nu & \Delta \omega_{G^-}/\varepsilon & \Delta \omega_{G^+}/\varepsilon & \Delta \omega_{G^+}/\varepsilon & \gamma_{E_{2g}} & \beta_{E_{2g}} \\
\hline
\text{This work} & 0.167 & -33 & -15 & -59 & 1.86 & 0.96 \\
\text{Ref. 9} & 0.16 & -12.5 & -5.6 & 0.69 & 0.38 \\
\text{Ref. 10} & 0.33 & -31.7 & -10.8 & 1.99 & 0.99 \\
\text{Ref. 10} & 0.13 & -36.4 & -18.6 & 1.99 & 0.99 \\
\text{Ref. 16} & 0.163 & -34 & -14.5 & & & \\
\text{Ref. 12} & & -77 & 2.4 & & & \\
\text{Ref. 13} & & -57.3 & 1.80 & & & \\
\end{array}
\]

Substrate.

\bb Free-standing graphene.
calculated and experimental slopes $\Delta \omega_{G}/\varepsilon$ therefore can be attributed to different Poisson’s ratios of the graphene sheet and the substrate.

To illustrate this point clearly, the slopes $\Delta \omega_{G}/\varepsilon$ and $\Delta \omega_{G}/\varepsilon$ are plotted in Fig. 5 as a function of Poisson’s ratio $\nu$ of the substrate. The results are obtained from Eq. (1), using the experimental value of $\omega_{0}^{0} = 1585$ cm$^{-1}$, which yields the calculated Gr"uneisen parameter $\gamma_{E_{g}} = 1.86$, and the shear deformation potential $\beta_{E_{g}} = 0.96$. With increasing Poisson’s ratio $\nu$ of the substrate the slopes decrease. In Ref. 10, the substrate is polyethylene terephthalate (PET) with a Poisson’s ratio of about 0.33, which yields $\Delta \omega_{g}/\varepsilon = -29.8$ and $\Delta \omega_{g}/\varepsilon = -9.6$ in agreement with experiment. In Ref. 9 the substrate is polydimethylsiloxane (PDMS) with a Poisson’s ratio of about 0.5, which yields $\Delta \omega_{g}/\varepsilon = -26.2$ and $\Delta \omega_{g}/\varepsilon = -3.5$. These values cannot be compared to the experimental results of $-12.5$ and $-5.6$, respectively, because the sample of Ref. 9 includes patterned narrow Ti stripes which modify the behavior.

From Eqs. (2) and (3), we obtain $\gamma_{E_{g}} = 1.86$ and $\beta_{E_{g}} = 0.96$ for graphene under small uniaxial strain, as listed in Table I. Our calculated values are in agreement with the calculated values $\gamma_{E_{g}} = 1.87$ and $\beta_{E_{g}} = 0.92$ and the experimental values $\gamma_{E_{g}} = 1.99$ and $\beta_{E_{g}} = 0.99$ reported by Mohiuddin and co-workers. However, there are other experimental values which exhibit significant discrepancies, for example $\gamma_{E_{g}} = 0.69$ and $\beta_{E_{g}} = 0.38$ as reported in Ref. 9. They are due to different values of Poisson’s ratio used to calculate $\gamma_{E_{g}}$ and $\beta_{E_{g}}$. In Ref. 9 Poisson’s ratio of free-standing graphene, $\nu = 0.16$, is used, while in Ref. 10 Poisson’s ratio of the substrate is used. Assuming that graphene is not really uniaxially strained in the experiments, see our above discussion, applying the value of the substrate should be more realistic.

To calculate the Gr"uneisen parameter for the $E_{2g}$ mode of graphene under large uniaxial strain, Poisson’s ratio $\nu$ under large uniaxial strain is needed. Liu et al. have reported that $\nu$ shows a noticeable downward trend at large strain and is smaller in the zigzag ($\theta = 0^\circ$) than in the armchair ($\theta = 30^\circ$) direction. However, data for Poisson’s ratio in arbitrary direction under large strain are missing up to now. Poisson’s ratio $\nu(\varepsilon)$ for strain up to 20% is shown in Fig. 6(a) for different directions. We find that $\nu(\varepsilon)$ exhibits a noticeable decrease at large strain (>5%) and that the slope increases linearly with $\theta$, indicating that Poisson’s ratio behaves anisotropically. The derivative $\partial \nu/\partial \varepsilon$ as a function of $\theta$ is shown in the inset of Fig. 6(a). The linear dependence is well fitted by $\partial \nu/\partial \varepsilon = 0.0073-\theta$ for $0^\circ \leq \theta \leq 30^\circ$.

With Poisson’s ratio in different strain directions, we obtain the Gr"uneisen parameter $\gamma_{E_{2g}}$ for the $E_{2g}$ mode for strain up to 20%, as shown in Fig. 6(b). First, we find that $\gamma_{E_{2g}}$ decreases in each direction with increasing uniaxial strain. It decreases more quickly for larger strain. Second, the behavior of $\gamma_{E_{2g}}$ is anisotropic from $\theta = 0^\circ$ to $20^\circ$, while the data for $\theta = 30^\circ$ exactly resemble those for $\theta = 20^\circ$. We stress that the Gr"uneisen parameter decreases with increasing uniaxial strain in the entire experimental range and behaves anisotropically, which is one reason for the observation of different values of the Gr"uneisen parameter in the experiments.

We next deal with biaxial strain. In this case, the point group remains $D_{6h}$ and the $G$ mode does not split. The Gr"uneisen parameter is given by

$$\gamma_{E_{2g}} = -\Delta \omega_{G}/(2\omega_{0}^{0}\varepsilon).$$

Since Poisson’s ratio does not enter Eq. (4), no difference is expected between free-standing graphene and graphene on a substrate which deforms isotropically under biaxial strain. Because graphene is not really uniaxially strained in uniaxial strain experiments, biaxial strain is more suitable for deducing $\gamma_{E_{2g}}$ from experiments.

Figure 7(a) shows the $G$ mode frequency shift $\Delta \omega_{G}$ with respect to the frequency of the equilibrium structure as a function of biaxial strain between $-0.2\%$ and $0.2\%$, together with results from Ref. 13. It is found that the slope $\Delta \omega_{G}/\varepsilon = -59$ cm$^{-1}/\%$ is consistent with the experimental value of $-57.3$ cm$^{-1}/\%$, obtained for graphene on a piezoelectric substrate. However, it deviates quite seriously from the experimental value of $-77$ cm$^{-1}/\%$ reported for graphene on a SiO$_2$/Si wafer. While the biaxial strain is small ($|\varepsilon| < 0.2\%$) in the experiments, we have also applied much larger strain from $-16\%$ to $20\%$ and present the effects on the $E_{2g}$ mode frequency in Fig. 7(b). Under large compressive (expansive)
bixial strain ($|\varepsilon| > 5\%$), the slope $\Delta \omega_G/\varepsilon$ is significantly smaller (larger) than for small strain.

The Grüneisen parameter $\gamma_{E_{2g}}$ derived according to Eq. (4) is shown in Fig. 7(b) as a function of the strain $\varepsilon$. We observe that $\gamma_{E_{2g}}$ decreases with increasing strain. The calculated Grüneisen parameter for small biaxial strain, $\gamma_{E_{2g}} = 1.86$, is identical to that for small uniaxial strain. In the experimental biaxial strain range ($-0.2\%$ to $0.2\%$) the calculated $\gamma_{E_{2g}}$ varies from 1.83 to 1.89. This is close to the experimental value, $\gamma_{E_{2g}} = 1.80$, reported by Ding et al.\textsuperscript{13} However, another experimental value of $\gamma_{E_{2g}} = 2.4$ is extrapolated from the data of Metzger et al.\textsuperscript{12} This discrepancy may be due to strain initially imposed to the graphene sheet by the substrate\textsuperscript{25,26} which would cause a change of $\omega_G^0$.

IV. CONCLUSION

In conclusion, we have presented a thorough analysis of the effects of uniaxial strain (along arbitrary directions) as well as biaxial strain on the frequency of the $G$ mode. Poisson’s ratio under uniaxial strain decreases with the strain, and shows an anisotropic behavior. Under large uniaxial strain ($>5\%$) the shifts of the split $G$ mode frequencies depend significantly on the direction of the strain. The following reasons have been identified for the inconsistency among the reported experimental values of the Grüneisen parameter for the $E_{2g}$ mode: (i) Direction of the applied strain: The Grüneisen parameter behaves anisotropically under uniaxial strain. (ii) Strength of the applied strain: The Grüneisen parameter decreases with increasing uniaxial and biaxial strain. (iii) Substrate: Uniaxial strain measurements cannot yield the Grüneisen parameter directly. Instead, it is required to account for Poisson’s ratio of the substrate. (iv) Intrinsic strain: It is likely that there is already intrinsic strain in the graphene sheet due to the contact with the substrate. This strain will depend on the details of the experimental setup. A correct measurement of the Grüneisen parameter is a prerequisite of strain engineering and therefore pave the way to graphene electronics.