Scaling behavior and strain dependence of in-plane elastic properties of graphene

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We show by atomistic simulations that, in the thermodynamic limit, the in-plane elastic moduli of graphene at finite temperature vanish with system size \( L \) as a power law \( L^{-n_{\eta}} \) with \( n_{\eta} \approx 0.325 \), in agreement with the membrane theory. Our simulations clearly reveal the size and strain dependence of graphene’s elastic moduli, allowing comparison to experimental data. Although the recently measured difference of a factor 2 between the asymptotic value of the Young modulus for tensilely strained systems and the value from \textit{ab initio} calculations remains unsolved, our results do explain the experimentally observed increase of more than a factor 2 for a tensile strain of only a few permille. We also discuss the scaling of the Poisson ratio, for which our simulations disagree with the predictions of the self-consistent screening approximation.

Mechanical and structural properties of graphene form an intriguing and highly non-trivial aspect of its physics. The structure of a two-dimensional (2D) material embedded in a 3D space gives room to special features, related to large out-of-plane deformations, in particular thermal ripples \cite{1} and static ripples and wrinkles \cite{2}. A crucial difference with 3D (or strictly 2D) crystals is that, for graphene, out-of-plane atomic displacements \( h \) and in-plane displacements \( u \) have different wavevector dependence of the energy cost in the long wavelength limit \( q \rightarrow 0 \), namely \( \propto q^2 \) and \( \propto q \) respectively, the latter being the normal behavior for acoustic phonons. Hence, at finite temperature, the long wavelength out-of-plane fluctuations are much larger than the in-plane ones, so that some small wavevector \( q \) the first anharmonic coupling term of the form \( u h^2 \) will dominate over the “normal” harmonic terms \( u^2 \), with important consequences for the elastic behavior\cite{3} \cite{4} \cite{5} \cite{6}. In particular, the wavevector dependence of the anharmonic coupling strength leads to expect a power law behavior of the size dependence of the elastic properties.

Contrary to the temperature dependence \cite{7} \cite{8}, so far the size dependence of the in-plane elastic moduli of graphene has been hardly studied nor measured \cite{9} until recent experiments seem to indicate that such a size dependence does exist for graphene \cite{10} \cite{11}. From indentation experiments on graphene drums with sizes of the order of 1 \( \mu \text{m} \), the Young modulus \( Y \) was found to vary between 250 N/m and 700 N/m with increasing strain \cite{12}, the latter value being much higher than the currently accepted value for flat sheets of ~340 N/m obtained in previous measurements \cite{9} or \textit{ab initio} calculations \cite{13}.

Here we study the size dependence of the in-plane elastic moduli of graphene at room temperature \( T=300\, \text{K} \) by means of atomistic Monte Carlo (MC) simulations based on the realistic interatomic potential LCBOP II \cite{14}, as used in previous works \cite{15} \cite{16} \cite{17}. We obtain explicit expressions for the size and strain dependence of graphene’s in-plane elastic moduli, providing a benchmark and tools for the analysis of experiments for systems of any size.

Theoretically, the mentioned size dependence has been studied within the continuum elastic theory of thin plates and membranes, described by the Hamiltonian \cite{18}:

\[
H = \frac{1}{2} \int \! d\mathbf{r} \left( \kappa (\nabla^2 h)^2 + \lambda u_{\alpha\alpha}^2 + 2\mu u_{\alpha\beta}^2 \right) \tag{1}
\]

where \( \mathbf{r} \) is the 2D position vector, \( \kappa \) is the bending rigidity, \( \lambda \) and \( \mu \) are Lamé coefficients, with \( \mu \) the shear modulus, and

\[
u_{\alpha\beta} = \frac{1}{2} \left( \partial_{\alpha} u_{\beta} + \partial_{\beta} u_{\alpha} + \partial_{\gamma} h \partial_{\gamma} h \right) \tag{2}
\]

is the strain tensor.

The harmonic approximation neglects the non-linear \( h^2 \) term, decoupling the bending and stretching modes. Then the correlation functions for out-of-plane displacements, \( H_0(q) = \langle |h_{\mathbf{q}}|^2 \rangle_0 \), and for in-plane displacements, \( D_{\alpha\beta}(q) = \langle u_{\alpha q} u_{\beta q} \rangle_0 \), can be derived by Gaussian integration \cite{19} \cite{20}:

\[
H_0(q) = \frac{k_B T}{\kappa q^4} \tag{3}
\]

and:

\[
D_{\alpha\beta}(q) = \frac{P_{\alpha\beta}(q) k_B T}{(\lambda + 2\mu) q^2} + \frac{(\delta_{\alpha\beta} - P_{\alpha\beta}(q)) k_B T}{\mu q^2} \tag{4}
\]

with \( P_{\alpha\beta}(q) = q_{\alpha} q_{\beta} / q^2 \). The average height fluctuation behaves as \( \langle h^2 \rangle_0 = \sum_q \langle |h_{\mathbf{q}}|^2 \rangle_0 \sim L^2 \), implying instability of a membrane as a flat phase.

Due to the large out-of-plane fluctuations, however, the harmonic behavior is not valid for small \( q \) and one has to keep the \( h^2 \) term in eq. 2. Since \( H \) remains quadratic in \( u \), these degrees of freedom can still be integrated out. This leads to a Hamiltonian in Fourier space which is a function of \( h_{\mathbf{q}} \) only:

\[
\hat{H} = \frac{1}{2} \sum_{\mathbf{q}} |\kappa q|^2 |h_{\mathbf{q}}|^2 + \frac{Y}{8} \sum_{\mathbf{q}, \mathbf{k}, \mathbf{k}'} \mathcal{R}(\mathbf{q}, \mathbf{k}, \mathbf{k}') h_{\mathbf{q}} h_{\mathbf{k}^-} h_{\mathbf{k}'} h_{\mathbf{q}^-} \tag{5}
\]
where $Y$ is the 2D Young modulus and $R(q, k, k') = (q \times k)(q \times k')/q^4$. The anharmonic, quartic term reduces the height fluctuations, stabilizing the flat phase, effectively described by a renormalized bending rigidity $\kappa_R(q) \sim q^{-\eta}$ with positive $\eta$. Hence, the height correlation $H(q)$ for $q \to 0$ has the same form as $H_0(q)$ in eq. [3] but with $\kappa$ replaced by $\kappa_R(q)$ [11]. Likewise, $D_u^\alpha(q)$ can be described by renormalized $\lambda_R(q), \mu_R(q) \sim q^{\eta_0}$ in eq. [4] with $\eta_0 > 0$. From rotational invariance it follows that $\eta$ and $\eta_0$ should satisfy the scaling relation $\eta_0 = 2 - 2\eta$ [23].

Within the self-consistent screening approximation (SCSA) [13], the exponent was estimated as $\eta \approx 0.821$ [13]; next-order corrections reduce it slightly to $\eta \approx 0.789$ [14]. A renormalization group approach gives $\eta = 0.849$ [24] and MC simulations for self-avoiding membranes $\eta \approx 0.72$ [25]. With $q > 0$, $\langle h^2 \rangle \sim L^{2-\eta}$, is much smaller than $\langle h^2 \rangle_0 \sim L^2$ for large $L$, stabilizing the flat phase.

Although it is a priori not obvious whether the membrane theory applies to an atomic-layer-thick 2D crystal like graphene, atomistic MC simulations confirm the scaling behavior of $H(q)$ with $\eta \approx 0.85$ [4]. The scaling of in-plane elastic moduli, however, has not yet been studied nor confirmed for graphene. Contrary to $\kappa_R$ which increases with increasing system size, making the membrane more resistant against bending, $\lambda_R$ and $\mu_R$ decrease with system size. Hence, if graphene follows the membrane theory, the in-plane elastic moduli vanish for large system sizes, an unthinkable situation for 3D crystals!

For a 2D system, the 2D bulk modulus $B$, the uniaxial modulus $C_{11}$ and $Y$ are related to $\lambda$ and $\mu$ as:

$$B = \lambda + \mu \ , \ C_{11} = B + \mu \quad \text{and} \quad Y = \frac{4B\mu}{B+\mu} \quad (6)$$

implying that $B$, $C_{11}$ and $Y$ scale as $\lambda$ and $\mu$. Another relevant quantity is the 2D Poisson ratio $\nu$:

$$\nu = \frac{B - \mu}{B + \mu} \quad (7)$$

The SCSA predicts a universal, negative Poisson ratio $\nu = -1/3$ for $L \to \infty$ [13], as later confirmed by MC simulation of self-avoiding membranes [26]. For graphene, however, so far only positive values were reported ($\nu = 0.15 - 0.46$) [15, 27, 28].

In Fig.1 we show the in-plane correlation function $D_u^\alpha(q)$ ($\alpha = x, y$) calculated by NPT MC simulations at pressure $P = 0$ and $T = 300$ K with isotropic volume fluctuations for roughly square samples of $N = 37888$ atoms using periodic boundary conditions. Besides displacement moves we apply also collective wave moves for small $q$ as in Ref. [4]. For the calculation of $D_u^\alpha(q) = \langle |u^\alpha|^2 \rangle = (1/N)\langle \sum_{i=1}^{N} u_{i\alpha} \exp(iq_{\alpha,0}) \rangle^2$ with $\{r_{i,0}\}$ the ground state positions, the in-plane displacement field was scaled as $u_{i\alpha} = s r_{i\alpha} - r_{i\alpha,0}$ where $s = \sqrt{A_0/A}$ scales the area $A$ at $T=300$ K to the ground state area $A_0$ of a flat sample. The behavior of $D_u^\alpha(q)$ for small $q$ is consistent with a power law with exponent $\eta_0 \approx 0.3$, indicating that graphene follows the membrane theory also for in-plane correlations.

In Fig.2 we show the pressure as a function of size in NPT simulations (symbols) with (a) isotropic and (b) uniaxial size fluctuations for approximately square systems with $N = 24, 112, 336, 1008, 4032, 12096$ and 37888 atoms. The lines are best fits to eq. [11]. The inset gives the equilibrium sizes $s_{eq} = s(P = 0)$ (symbols) as a function of $L_0$ and the fit (solid line) according to the expression in Table I.

The size and strain dependence of the elastic properties can be computed simultaneously by NPT MC simulations for different sizes with isotropic area fluctuations at several pressures $P$. The resulting average area $A$ gives the
equation of state (EOS), \( A(P) \) and thus also \( P(A) \) from which \( B \) can be calculated as:

\[
B = -\frac{\partial P}{\partial A} = \frac{s}{2} \frac{\partial P}{\partial s}
\]

where \( s = L/L_0 \) is the relative linear size with \( L_0 = \sqrt{N/\rho_0} \) the ground state system size, \( \rho_0 \simeq 0.3819 \, \text{Å}^{-2} \) being the 2D ground state atomic density of graphene. To obtain both \( B \) and \( C_{11} \), we also performed NPT simulations for uniaxial pressure \( P_z \), applying fluctuations of \( L_z \) in the \( x \)-direction, while keeping \( L_y \) fixed. Then \( C_{11} \) follows from:

\[
C_{11} = -L_z \frac{\partial^2 P}{\partial L_x \partial P} \bigg|_P = -s_x \frac{\partial^2 P}{\partial s_x} \bigg|_P \simeq -s_x \frac{\partial P}{\partial s} \bigg|_{s_x=s_{eq}}
\]

where \( s_x = L_x/L_{0,0} \), with \( L_{0,0} \) the ground state dimensions, and where \( s_{eq} = s(P=0) \) is the equilibrium size obtained from the isotropic NPT simulations at \( P = 0 \). The subscript “\( P \)” in eq. 9 indicates that \( L_y \) should be taken equal to \( s_y = s(P) \) resulting from isotropic NPT simulations at pressure \( P \) and that \( P \) should be varied around \( P = 0 \). However, since we verified that the dependence of \( \partial P/\partial s_x \) on \( s_y \) is very weak we adopted the last approximation in eq. 9 which is exact for \( P = 0 \).

The results are shown in Fig. 2. The inset shows that the previously found negative thermal expansion [15] is also size dependent, but tending to a constant for large \( L_0 \). On the basis of Fig. 2b, with the slope \( \partial P/\partial s \) as a function of \( s \), we propose the phenomenological relation for \( B(s) \)

\[
P(s) = -\frac{2}{D} \left( \frac{B_{eq}}{s_{eq}} - C \right) \ln(1 + D(s - s_{eq})) - 2C(s - s_{eq})
\]

Similarly, we write

\[
C_{11}(s_x) = \frac{s_x}{2} \left( \frac{C_{11,eq}}{s_{eq}} + \tilde{C} \tilde{D}(s_x - s_{eq}) \right)
\]

which substituted in eq. 9 gives an equation for \( P_z(s_x) \) similar to eq. 11 but with \( s, B_{eq}, C \) and \( D \) replaced by \( s_{eq}, C_{11,eq}/2, \tilde{C}/2 \) and \( \tilde{D} \). This form allows the excellent fits shown in Fig. 2 providing \( B_{eq} \) and \( C_{11,eq} \) as a function of \( L_0 \). In the left panels of Fig. 3 (left panels) we show that both \( B \) and \( C_{11} \) vanish for large \( L_0 \), decreasing as a power law \( \sim L^{-0.6} \), with \( \eta_0 \simeq 0.325 \) (insets). The right panels give the corresponding results for \( Y \) and \( \nu \) at \( P = 0 \), calculated using eqs. 6 and 7. Note that, according to LCBOPII, the in-plane elastic moduli of graphene at \( T = 0 \) K are \( B = 12.69 \, \text{eV/Å}^2 \) and \( \mu = 9.26 \, \text{eV/Å}^2 \), yielding \( Y = 21.41 \, \text{eV/Å}^2 = 343 \, \text{N/m} \) and \( \nu = 0.156 \), in agreement with ab initio data [20] and with the small size limit in Fig. 3 where \( Y \simeq 314 \, \text{N/m} \). By simulations at 1 K for \( N = 24 \) we verified that the remaining difference is due to temperature.

Interestingly, the power law decrease of \( B, C_{11} \) and \( Y_{eq} \) as a function of \( L_0 \) sets in from \( L_0 \simeq 20 \, \text{Å} \), a value twice smaller than the Ginzburg critical value \( L^* = 2\pi \sqrt{16\pi\kappa^2/(3Y_{eq}T)} \simeq 40 \, \text{Å} \) (using \( \kappa \simeq 1.1eV \) [2]) expected from membrane theory [11]. The Poisson ratio \( \nu \) for small sizes is close to its bare value and increases up to 0.275 for larger \( L_0 \), against the SCSA prediction \( \nu = -1/3 \). Since the scaling of \( B \) and \( \mu \) is consistent with the SCSA, it is very unlikely that \( \nu \) will reach the value -1/3 for \( L_0 \to \infty \), as the outcome of eq. 7 only depends on the prefactors.

We can also calculate \( Y \) as a function of tensile strain, using eqs. 10 and 12 with the best fit parameters. We should use the \( B(s) \) and \( C_{11}(s_x) \) at equal pressure by solving \( P_z(s_x) = P \) for \( s_x \) at given \( s \). Due to the approximation in eq. 9 \( s_x \neq s \) unless \( s = s_{eq} \). An approximation of \( s_x(s) \) is given in Table I. The \( Y(s) \) obtained from the data of Fig. 2 are shown in Fig. 4 for different sizes. Symbols mark the results at \( s = s_{eq} \). Notice the strong increase of \( Y(s) \) for large sizes. For \( N = 37888 \) (\( L_0 \simeq 315 \, \text{Å} \)), \( Y \) increases from \( \sim 100 \, \text{N/m} \) at \( s_{eq} \simeq 0.9985 \) to \( 220 \, \text{N/m} \) at \( s = 0.9995 \), i.e. more than a factor 2 for a stress \( \epsilon = s - s_{eq} = 0.001 \) (0.1 %)! This strong dependence is in full qualitative agreement with the recent experimental claims [18, 19]. A quantitative comparison will be discussed below.

Since \( B_{eq} \) and \( C_{11,eq} \), as well as \( s_{eq}, C, D, \tilde{C} \) and \( \tilde{D} \) turn out to depend smoothly on \( L_0 \), we can approximate...
These expressions apply to any size and give appropriate asymptotics with $\lambda R$ in $\text{eV/Å}$. The inset of Fig. 4 shows the resulting $Y(s)$ for a size $L_0 = 1 \mu m \sim N = 3.8 \times 10^7$, calculated using eqs. 10 and 12 and the expressions in Table I. The upper axis of the inset gives the strain $\varepsilon = s - s_{eq}$.

\begin{align*}
s_{eq} &= 0.99838 + \frac{4.295 \times 10^{-3}}{1+18142 L_0^{-6}}, \quad D = \frac{392.3+1.2510 \times 10^{-15} L_0^2}{1+1750 \times 10^{-13} L_0^2}, \\
B_{eq} &= 12.2-5.5 \times 10^{-3} \frac{1+28.6(L_0/14.4)^2}{L_0^{-6}}, \quad C = 12.1, \\
C_{11,eq} &= 20.35-7.5 \times 10^{-3} \frac{1+47 \times 10^{-4}+48.8(L_0/31.6)^2}{L_0^{-6}}, \quad s_x(s) = 1.15(s-s_{eq}) + s_{eq}.
\end{align*}

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<thead>
<tr>
<th>$L_0$</th>
<th>$Y(s)$</th>
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<tbody>
<tr>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8</td>
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TABLE I. Size dependent parameters for $B(s)$ and $C_{11}(s_x)$ according to eqs. 10 and 12 for $L_0$ in Å, $B_{eq}$, $C_{11,eq}$, $C$ and $D$ are calculated with $s_{eq}$ given in Table 1.

The inset of Fig. 4 shows the resulting $Y(s)$ for a size $L_0 = 1 \mu m \sim N = 3.8 \times 10^7$, calculated using eqs. 10 and 12 and the expressions in Table I. The upper axis of the inset gives the strain $\varepsilon = s - s_{eq}$.

unexplained and requires further investigations. We note that our values of the bare elastic moduli agree with the experimental phonon spectrum [50, 51] of graphite, where anharmonic effects are suppressed by interlayer interactions.

In conclusion, we have shown by atomistic simulations that the in-plane elastic moduli of graphene vanish with size as $L_0^{-nu}$ with $\eta_0 \approx 0.325$, confirming that graphene follows membrane theory within the SCQA in this respect. The critical exponent $\eta_0$, together with the independent estimate of $\eta \approx 0.85$ [4], supports the scaling relation $\eta_0 = 2 - \eta$. In contrast, our results do not support the SCQA prediction $\nu = -1/3$ for $L \to \infty$. We remark that $\nu = -1/3$ in eqs. 6 and 7 leads to $B_R = -\lambda R$ and $\lambda_R = 2B_R - C_{11}$, implying that $\lambda_R$ should be negative for stability while in Fig. 3 $2B_R - C_{11,R}$ remains positive for any $L_0$. We also find that suppression of anharmonicity requires a tensile strain 10-50 times larger than predicted by SCQA.

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