Thermal stiffening of clamped elastic ribbons

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We use molecular dynamics to study the vibrations of a thermally fluctuating two-dimensional elastic membrane clamped at both ends. We directly extract the eigenmodes from resonant peaks in the frequency domain of the time-dependent height and measure the dependence of the corresponding eigenfrequencies on the microscopic bending rigidity of the membrane, taking care also of the subtle role of thermal contraction in generating a tension when the projected area is fixed. At finite temperatures we show that the effective (macroscopic) bending rigidity tends to a constant as the bare bending rigidity vanishes, consistent with theoretical arguments that the large-scale bending rigidity of the membrane arises from a strong thermal renormalization of the microscopic bending rigidity. Experimental realizations include covalently-bonded two-dimensional atomically thin membranes such as graphene and molybdenum disulfide or soft matter systems such as the spectrin skeleton of red blood cells or diblock copolymers.

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I. INTRODUCTION

Since the discovery of graphene about ten years ago,1 atomically thin, two-dimensional (2D) crystals such as molybdenum disulfide,2 boron nitride,3 and black phosphorus4 have attracted considerable attention. While not atomically thin, the spectrin skeleton of red blood cells5 and diblock copolymer systems6 provide alternative arenas in which to investigate the physics of membranes and shells, in this case with thicknesses of order 1-10 nm. Self-consistent statistical field theory treatments of coarse-grained models of polymerized membranes, flexible elastic sheets and shells predict that thermally-driven shape undulations (sometimes called flexural phonons) generate a non-linear stretching term in the effective free energy in addition to the usual bending energy contribution.8–10 The isotropic shape corrugations generated by height fluctuations of these flexible elastic sheets render the dressed bending rigidity strongly scale-dependent, growing as a power law lβ, where l is a measure of the spatial extent of the shape fluctuations.11 12 The first treatment11 employed a one-loop expansion of the bending energy, within a self-consistent approximation, and gives η = 1. A more elaborate self-consistent theory allowing for the renormalization of the in-plane elastic constants yields η = 0.821.13 Other approaches lead to refined values of η analytically14 15 and allow comparisons with simulation results16 17.

A revealing proxy for the field theory calculation is a direct determination from computer simulations of the effective bending rigidity of a thermalized ribbon, clamped on two sides as in the experiments18, has, however, been lacking to this point. Here we use molecular dynamics (MD) to simulate the thermally induced shape fluctuations of atomically thin ribbons like graphene. Fourier analysis of the time-dependent height fluctuations, which is now far stiffer to bend19 and can indeed support its own weight. Field theory calculations indicate that thermally induced ripples have precisely the same dramatic effect on the bending modulus. Thermally fluctuating flexible elastic sheets are thus more rigid macroscopically than microscopically. As opposed to quenched static ripples resulting from, say, frozen-in grain boundaries arising during sample preparation, the thermally-induced ripples we study are dynamic, which allows us to study their height profile in frequency space. Recent room temperature experiments on micron-length graphene ribbons have carefully measured the macroscopic bending rigidity of the ribbons, finding values up to four orders of magnitude higher than the bare value, through the relative contribution from frozen static ripples and thermal fluctuations remains to be thoroughly explored.20

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methods outlined above.

Our method may be used for arbitrary boundary conditions but for simplicity here we clamp both ends of the ribbon across the whole width to avoid macroscopic crumpling at small bare bending rigidity and other complications that distract from the main task of uncovering the fluctuation-dressed effective bending rigidity. Our boundary conditions effectively impose a constraint of constant projected area on the ribbon. They can easily be achieved experimentally via the techniques of Ref. [22] by fixing the positions of gold pads that anchor the ends of otherwise freely suspended graphene ribbons in water at room temperature.

As we demonstrate explicitly with our simulations (see Fig. 1), the effect of the clamped boundary conditions is to generate a uniaxial tension that depends on the ratio of $k_B T$ to the bare bending rigidity $\kappa$. This tension acts like an ordering field on membrane normals. The effect of an isotropic version of this remarkable entropically generated tension was studied years ago by Guitter et al. [23], who uncovered a “crumpling transition” associated with constraints that impose a fixed projected area on the flat phase of thermally wrinkled materials. See Refs. [24] and [25] for recent studies of the (nonlinear) response of thermalized atomically-thin free-standing materials to both isotropic and uniaxial tensions. Bonilla and Ruiz-Garcia [26] have used the saddle point method of Ref. [27] to calculate the fluctuation-dressed effective bending rigidity. Our method may be used for arbitrary boundary conditions as our primary goal. With graphene as a concrete example, we set the equilibrium spring length $a$ to be $\sqrt{3}a_0$, where $a_0 = 1.42 \text{ Å}$ is the carbon-carbon bond length in graphene – thus $a \approx 2.46 \text{ Å}$. The triangular lattice we employ is the dual of graphene’s honeycomb lattice. To give the correct graphene density we take the mass of every vertex to be $m = 2m_C \approx 4 \times 10^{-26} \text{ kg}$, where $m_C$ is the mass of a carbon atom. In Ref. [43], it was shown that this simplified dual model gives results consistent with graphene simulations [44] that incorporate explicitly the energetics of carbon-carbon bonds. We choose $a$ and $m$ as our units of length and mass and set $a = 1$ and $m = 1$ in all simulations. Figure 1(a) displays the initial, zero-temperature flat configuration of the membrane in the $x-y$ plane, with $n_1 = 32$ vertices in the long direction and $n_2 = 11$ vertices staggered along the short direction ($L_0 \approx 30a \approx 74 \text{ Å}$ and $W_0 = 5\sqrt{3}a \approx 21 \text{ Å}$). There are 347 vertices in total. We clamp the edge vertices along the two zigzag boundaries indicated by the orange lines in Fig. 1 and tag a marked vertex (shown in red). We perform MD simulations using the HOOMD-blue [45–47] and the LAMMPS software packages [48], both giving consistent results. We choose $E_0 = 1 \text{ eV}$ as the unit of energy and $k_B T = 0.025 \text{ eV}$ (corresponding to room temperature) in all simulations. The elastic free energy is calculated as the sum of the stretching and bending energies given in Eqs. (1) and (2), with unrenormalized elastic parameters $\kappa = 1.2 \text{ eV} = 48 k_B T$ [49] [50] and $Y = 20 \text{ eV/Å}^2 = 800 k_B T/\text{Å}^2$ [51] [52] as parameter estimations for graphene. The discrete parameters $\varepsilon$ and $\kappa$ follow from the relations above. After giving the free vertices a small random out-of-plane displacement, we update their positions in the constant temperature (NVT) ensemble. The simulation unit of time thus corresponds to a real time $t_0 = m a^2/E_0 \approx 0.12 \text{ ps}$. Finally we set the integration time step to be 0.005. Every simulation timestep $\tau$ thus corresponds to a real time $\tau = 0.005 t_0 \approx 0.6 \text{ ns}$ (movie 1).
III. RESULTS AND DISCUSSION

We log a sample configuration every 100 simulation timesteps. Figure 1(b) shows the kinetic, stretching and bending energy profiles for the first $8 \times 10^5$ timesteps in a run of $10^7$ timesteps in all. The ribbon equilibrates after roughly $3 \times 10^5$ timesteps. Figure 1(c) displays the time-dependent height ($z$-coordinate) of a tagged vertex (the red vertex in Fig. 1(a)) for $10^5$ timesteps after equilibration. The vertex fluctuates about the $x-y$ plane ($z=0$). To get a better understanding of the height fluctuations, we Fourier transform the height profile of Fig. 1(c) and plot the amplitude of the first six peaks in frequency space in Fig. 1(d). The root mean square height of the membrane (Fig. 2(a)) has contributions from all the excited modes. To extract the contribution from a given mode we select the appropriate peak in the frequency domain by applying a window function as illustrated by the light green shading centered on peak 2 (p2) in Fig. 1(d). We then inverse Fourier transform to extract the time profile of the height for this mode. The same window
filter is used for all vertices. Figure 2(b) displays the first six modes. As stiff, atomically thin materials like graphene bend more readily than they stretch, the in-plane displacements of a vertex are small compared to the out-of-plane displacement, and we can neglect variations of the $x$ and $y$ coordinates of vertices when plotting Fig. 2. The frequency of a peak is determined as the center of the best fit to a Gaussian. On the other hand, we clamp the two opposite ends at, e.g., the length of the longer $L_0$ direction (using the lineforce command in LAMMPS) and choose the edges connecting these vertices to have a high spring constant. These vertices will then move together horizontally. We have taken into consideration the corresponding subtraction of the total number of degrees of freedom in the simulation. When $\kappa$ is large the sliding end fluctuates and the amplitude of fluctuation is small (movie 2). As $\kappa$ decreases, the amplitude of fluctuations gets larger until $\kappa \lesssim 1 k_B T$, where the ribbon crumples (movie 3 and 4). We then add a horizontal force on the sliding end. We increase the force gradually until the ribbon is pulled back to have projected length $L_p$ equal to its zero-temperature length $L_0$. The crumpled ribbon becomes flat when the force is large enough (movie 5). Figure 3 plots the measured force $F$ on each vertex at the sliding end as a function of $\kappa$. When $\kappa$ is large the force is small. As $\kappa$ decreases, the force increases until the small $\kappa$ range, where the force tends to a constant. The response of thermalized ribbons to this type of pulling (as well as bending) has been analyzed in Ref. [24] and the non-Hookean statistical mechanics of thermalized ribbons clamped at one end only, with the associated scale-dependent stiffening of the bending rigidity, studied in Ref. [33].

We then use COMSOL to solve the vibration of a plate
subjected to an in-plane tension along the long direction. We use the 2D Plate modulus in COMSOL to simulate the ribbon subject to an in-plane stress given by $11F/W_0$, corresponding to a force on each of the 11 vertices on the right side of the ribbon (inset to Fig. 4). We sweep over the bending rigidity $\kappa_C$ ($C$ is short for COMSOL, to distinguish it from the bending rigidity in MD simulations) of the ribbon, until the frequency of a certain mode matches that of the MD simulation. We call this $\kappa_C$ the effective bending rigidity $\kappa_{\text{eff}}$. As an example, Fig. 5 plots $\kappa_{\text{eff}}$ of the (1,1) mode as a function of $\kappa$. In the small $\kappa$ range $\kappa_{\text{eff}}$ tends to be constant and is of order several $k_B T$ (see inset of Fig 5). On the other hand, the self-consistent theory of elastic membranes implies that non-linear stretching results in a renormalized bending rigidity $\kappa_R$ determined by the integral equation [11].

$$\kappa_R(\vec{q}) = \kappa + k_B T \left( \frac{d^2k}{(2\pi)^2} \kappa_R(\vec{q}+\vec{k})|\vec{q}+\vec{k}|^4 + \sigma_{ij}(\vec{q}+\vec{k})_i(\vec{q}+\vec{k})_j \right)$$

where $\vec{q}$ is the wave vector, $\hat{q}$ is the corresponding unit vector, $P^{ij}_{\vec{q}}(\vec{k}) = \delta_{ij} - k_i k_j/k^2$ is the transverse projection operator and $\sigma_{ij}$ is an external edge tension [2] [62]. In our case $\sigma_{xx} = 11F/W_0$ and other components of $\sigma_{ij}$ vanish. When $\kappa$ is large, the correction term is small compared to the bare $\kappa$ and thus $\kappa_R(\vec{q}) \approx \kappa$. In the small $\kappa$ limit, as the external force tends to a constant (Fig. 4), we expect from Eq. (3) that $\kappa_R(\vec{q})$ will also tend to a constant. We now estimate this limiting value. Taking, as the lowest order approximation, $\kappa_R(\vec{q}+\vec{k}) \approx \kappa_R(\vec{q})$ on the right hand side of Eq. (3) and approximating the (1,1) mode shape by $\vec{q} = \left( \pi/L_0, \pi/W_0 \right)$, with the upper and lower limits for $\vec{k}$ being $k_{\text{max}} = \pi/a$ and $k_{\text{min}} = \pi/L_0$, we solve Eq. (3) numerically and obtain $\kappa_R(\vec{q}) \approx 21k_B T$. With $k_{\text{max}} = \pi/a$ and $k_{\text{min}} = \pi/W_0$, $\kappa_R(\vec{q}) \approx 13k_B T$. Thus $\kappa_R(\vec{q})$ is consistent with our determination of the effective bending rigidity. There are, however, several possible sources of discrepancy. There may be higher order corrections to $\kappa_R(\vec{q})$. In addition, the frequency given by COMSOL is only accurate for small amplitudes, whereas we necessarily have finite amplitudes. There may also be corrections due to the scale dependence of the Young’s modulus and the Poisson ratio which we neglect. Finally, there can be finite-size effects associated with the boundary conditions.

The order of the modes also puts constraints on $\kappa_{\text{eff}}$.
However, at $\kappa_C = \kappa_{\text{eff}}$ not only the frequency matches but also the order of modes matches. More exactly, for small $\kappa$ range ($\kappa \leq 1k_B T$), if we only want the order of the modes in COMSOL to match that in MD simulation, then $\kappa_{\text{eff}}$ is confined to be about $2 \sim 12k_B T$ (see e.g., $\kappa_C = 5k_B T$ in Table. I). If there is no renormalization, the eigenmodes for small $\kappa_C$ values at this relatively large stress ($F = 0.768 \text{ev}/a$ corresponding to the force at $\kappa = 0.1k_B T$ in the MD simulation), exhibit wrinkles only along the unstrained direction (e.g., the (1,4), (1,5) modes at $\kappa_C = 0.1k_B T$ in Table. I). These modes are similar to the profile of an elastic membrane stretched along one direction (see, e.g., Ref. [63]). Thus the order of the modes also supports the presence of a strong thermal renormalization.

### IV. CONCLUSIONS

In summary, we have used molecular dynamics and a simple coarse-grained model to simulate atomically thin 2D membranes and study their thermally-induced fluctuations. We have identified the eigenmodes of the system and find that thermal effects significantly change the eigenfrequencies predicted by classical plate theory, qualitatively consistent with the scale-dependent renormalized bending rigidity predicted by the statistical field theory of elastic membranes.

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### Appendix A: Movies

Movie 1 shows the vibration of a two-end clamped ribbon with $\kappa = 48k_B T$ over a period of time after reaching equilibrium. The configuration is logged every 500\tau. Movies 2 to 4 show the evolution of a ribbon with one-clamped end and the opposite end sliding, and with $\kappa = 48, 1, 0.001k_B T$, respectively, starting from the initial perturbed configuration. As $\kappa$ decreases, the sliding end first fluctuates with a small amplitude, then with a larger amplitude, and finally crumples. The frequency of logging is 500\tau, 600\tau, 500\tau, respectively. Movies 5 has the same setup as that in movie 4, but with a horizontal force $F = 0.8 \text{ev}/a$ on each vertex at the sliding end. The ribbon remains flat over the simulation time. In all movies, the geometric parameters and the temperature are the same as those in the main text. The clamped ends are colored yellow and the sliding ends blue. Movies can be found in Ref. [64].

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### Table I. Lowest six modes ordered by frequency when sweeping over $\kappa_C$ in COMSOL, with the stress $11F/W_0$ and $F = 0.768 \text{ev}/a$ fixed.

| $\kappa_C (k_B T)$ | 1        | 2        | 3        | 4        | 5        | 6        |
|-------------------|----------|----------|----------|----------|----------|----------|
| 0.1               | (1,2)    | (1,3)    | (1,4)    | (1,5)    | (2,2)    | (2,3)    |
| 1                 | (1,0)    | (1,1)    | (1,2)    | (1,3)    | (2,0)    | (2,1)    |
| 5                 | (1,0)    | (1,1)    | (1,2)    | (2,0)    | (2,1)    | (2,2)    |
| 14.4              | (1,0)    | (1,1)    | (2,0)    | (2,1)    | (2,2)    | (2,2)    |
| 20.8              | (1,0)    | (1,1)    | (2,0)    | (2,1)    | (2,1)    | (3,0)    |
