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Determining the Gaussian Modulus and Edge Properties of 2D Materials: From Graphene to Lipid Bilayers

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The quest for (and some surprises in) the determination of the Gaussian modulus and edge tension of 2D materials—from graphene to lipid bilayers

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The dominant deformation behavior of two-dimensional materials (bending) is primarily governed by just two parameters: bending rigidity and the Gaussian modulus. These properties also set the energy scale for various important physical and biological processes such as pore formation, cell fission and generally, any event accompanied by a topological change. Unlike the bending rigidity, the Gaussian modulus is however notoriously difficult to evaluate via either experiments or atomistic simulations. In this work, recognizing that the Gaussian modulus and edge tension play a non-trivial role in the fluctuations of a 2D material edge, we derive closed-form expressions for edge fluctuations. Combined with atomistic simulations, we use the developed approach to extract Gaussian modulus and edge tension at finite temperature for both graphene and various types of lipid bilayers. Our results possibly provide the first reliable estimate of this elusive property at finite temperature and appear to suggest that earlier estimates must be revised. In particular, we show that if previously estimated properties are employed, graphene free edge will exhibit unstable behavior at room temperature. Remarkably, in the case of graphene, we show that the Gaussian modulus and edge tension even change *sign at finite temperature*.

Two-dimensional (2D) materials[1]with thickness at the atomistic scale are highly flexible and bend quite easily. This mechanical characteristic, in addition to other physical and chemical attributes, has opened up an entirely new field of research in the sciences with tantalizing applications that range from next-generation electronics, drug delivery, energy harvesters, to structural composites[2–5]. Graphene is a prototypical crystalline 2D material and the lipid bilayer membrane, the key ingredient of a biological cell, is arguably its counterpart in the soft matter world. Phenomenologically, the elastic energy cost to bend an isotropic 2D material can be well described by [6]:

$$F_b = \int \frac{1}{2} \kappa_b H^2 + \kappa_G K \quad (1)$$

Here κ_b and κ_G are the bending and Gaussian moduli that, respectively, correspond to the change in energy due to changes in the mean (H) and Gaussian (K) curvatures.

Equation (1) has been extensively used to described the mechanics of both biological and isotropic crystalline membranes[7]. Bending modulus is *relatively* simple to estimate—be it from atomistic simulations or from experimental methods[8, 9]. For example, measurement of thermal fluctuations of 2D materials provides a facile route to estimate the bending modulus [10, 11]. The typical bending modulus (κ_b) of most 2D materials is small enough compared to the thermal

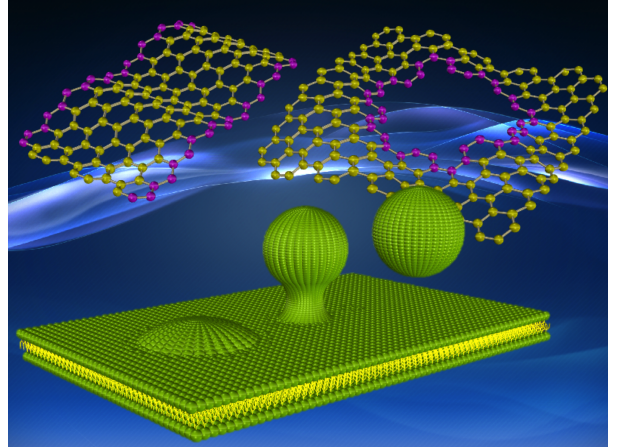


FIG. 1: Gaussian modulus and edge properties play a central role in physical processes that involve topological changes or deformation of an open edge e.g. pore formation, structural deformation of a finite nanoribbon, cell fission and fusion.

energy scale that they undulate noticeably even at room temperature[11, 12]. For an infinitely large membrane, the following result for the fluctuations of the out-of-plane displacement field (h) may be derived based on the linearized version of Equation (1): $\langle h^2 \rangle \propto kT/\kappa_b$ [13]. With this expression, either atomistic computation of the fluctuation spectra, or experimental measurements, can be used to estimate

the bending modulus [11, 13]. In sharp contrast, however, the estimation of the Gaussian modulus is quite difficult. For example, the aforementioned thermal fluctuation spectra result is independent of the Gaussian modulus. This is a consequence of a more general principle—the so-called Gauss-Bonnet theorem[14] which states that the integration of the Gaussian curvature over the surface *without edge* is invariant under any deformation that is not involved with topological transformations. To quote Hu et. al.[15], this is “*both a blessing and a curse*”. That is, we can safely ignore the contribution due to the Gaussian curvature in several practical situations unless there is a change in topology. However, due to this very reason, Gaussian modulus is notoriously difficult to measure. To understand this, it is worthwhile to mention some of the physical processes where it *does* matter: pore formation, structural deformation of a finite ribbon, cellular uptake of macromolecules, cell fusion and fission are some examples (Figure 1). However, there are no clear experimental or simulation procedures that can readily use these aforementioned events to estimate this elusive material property. While most of the experimentally measured values of Gaussian modulus for lipid membranes are reported for monolayers[16–22], there are no experimental or computational estimates of Gaussian modulus for crystalline membranes at *nonzero* temperatures.

Despite the attendant complexities of the endeavor, numerous attempts have been made to evaluate the Gaussian modulus of biological membranes[15, 18, 21–23]. We highlight here the work by Deserno and co-workers [15, 23] who provide a thoughtful review of the subject and propose a strategy to estimate this property for lipid bilayers[24]. Using coarse-grained molecular dynamics (MD), Hu et. al.[23] monitored the tendency of a flat finite size-membrane patch to close and form a vesicle in order to reduce the total edge energy. A theoretical result is then used to link this probability to the Gaussian modulus. Despite the pioneering nature of work by Deserno and co-workers[15, 23], several issues pertaining to this approach suggest that another independent estimate is warranted. The theoretical model by Deserno and co-workers[15, 23] is a ground-state model (i.e. zero Kelvin) while simulations are performed at finite temperature and accordingly disregard entropic corrections and there is thus an inconsistency between their atomistic simulations and the matching theoretical model. The authors carefully choose very small size membrane patches to minimize the effect of thermal fluctuations. Nevertheless, the sensitivity of their results to a finite temperature correction is not immediately

obvious. Furthermore, since rather small patches must be used, there is also a likelihood that their estimates are plagued by size-effects. Even with a small patch, while surface fluctuations may be minimized, the edge fluctuations may still be large (as we will show in this work). Finally, the size of the patch in simulations is restricted by a range of edge tension and Gaussian modulus and thus, in case any of these properties turn out to be beyond these ranges, the correct estimations cannot be obtained by the initially imposed patch size.

In the context of graphene, a couple of key works have recently appeared in the literature. Wei et. al.[25], using quantum calculations, estimated the Gaussian modulus at zero Kelvin ($\sim -1.52\text{eV}$) by comparing the potential energy of graphene for different topological structures. Davini et. al.[26] used a rather interesting approach where they derived a continuum model linked with the 2nd-generation reactive empirical bond-order (REBO) interatomic potential[27] to extract the Gaussian modulus at zero Kelvin and find its value to be around -1.62eV . These approaches exclude entropic contributions. As we will show, entropic effects make a decisive contribution to the physically relevant finite temperature Gaussian modulus and edge properties. In short, the quest for the true Gaussian modulus still remains an active research topic.

We propose an entirely different approach from the ones in the literature and show that monitoring the thermal fluctuations of the *edge* of a 2D material provides all the requisite information necessary to determine the elusive Gaussian modulus and the edge tension. Inspired by an earlier work of Gompper and Kroll[28], we derive the necessary theoretical relations and carry out MD simulations to yield arguably the first reliable finite temperature estimates of these properties. While our approach predicts values well within the experimental range, they are markedly different from past works. In particular, we show that the currently estimated values for the Gaussian modulus can lead to physical inconsistencies at room temperature—e.g. in the case of graphene, unstable edge behavior will ensue. An additional key outcome of the work is that our relations for the edge fluctuations provide a rather reliable metric to bracket the physically plausible range of these properties.

**Thermal fluctuations of a free edge—
theoretical model.** Consider an open finite 2D elastic membrane, with a smooth and orientable surface Ω , enclosed by a space curve $\partial\Omega$ that represents the edge of the surface. Let ψ and ϕ be the areal and lineal energy density, respectively, of the surface and the edge. Up to quadratic order, ψ is simply the

integrand of Equation (1). Then the total elastic energy can be split into two parts as:

$$F = F_b + \int_{\partial\Omega} \phi. \quad (2)$$

The edge energy density can be expressed as [29, 30]: $\phi = \phi_0 + \frac{1}{2}\kappa_s(\kappa_n^2 + \kappa_g^2) + \dots$, where ϕ_0 is the so-called edge(line) tension. Further, κ_n, κ_g are the normal and geodesic curvatures, respectively and κ_s can be defined as the bending *modulus* of the edge. Minimization of the total elastic energy then leads to the ground-state Euler-Lagrange equations (not shown, see Supplementary Information (SI)-Section 2, Equations (9, 10), which includes Ref. [29]) and a rather complicated set of boundary conditions on the *free* edge [29]:

$$(\mathbf{L}\nabla_S\psi_K - \frac{1}{2}\nabla_S\psi_H - 2H\nabla_S\psi_K) \cdot \nu + \phi_{\kappa_n}\kappa_n^2 + \phi_{\kappa_g}\kappa_n\kappa_g - \phi_{\kappa_n} - \phi_{\kappa_n}'' = 0 \quad (3a)$$

$$\frac{1}{2}\psi_H + \psi_K\kappa_n + \phi_{\kappa_n}\kappa_g - \phi_{\kappa_g}\kappa_n = 0, \quad (3b)$$

and $\{h = 0, \nabla_S h \cdot \nu = 0\}$ for constrained edges. In Equation (3), all the subscripts denote derivatives and the superscript "", denotes second derivative with respect to the arc length of the free edge. Also, \mathbf{L} is the curvature tensor, ∇_S denotes surface gradient operator and ν is the unit vector, normal to the edge curve and tangent to the surface (see SI-Section 2, Equations (2, 3), which includes Ref. [29]).

As usual, the partition function Z is defined as $\int e^{-F[h]/kT} \mathcal{D}[h]$ where $\mathcal{D}[h]$ denotes path integration over all *possible* functions, $h(\mathbf{x})$, that *satisfy* the free boundary conditions in Equation (3) or the constrained edge conditions. While the statistical mechanics analysis of thermal fluctuations is relatively simple for an infinitely large elastic sheet, the path integral is difficult to evaluate in the present case due to the rather complicated boundary conditions at the edge. It is therefore worthwhile to briefly touch upon the infinite sheet case (i.e. periodic boundary conditions) to connect with the typical practice in the literature. In that scenario, the boundary conditions at the edge vanish and the displacement correlation in terms of the Fourier vector \mathbf{q} can be calculated analytically to be: $\langle h(\mathbf{x})h(\mathbf{x}') \rangle = \sum_{\mathbf{q}} \frac{kT e^{i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')}}{L^2 \kappa_b |\mathbf{q}|^4}$. This expression has traditionally been used to extract the bending stiffness of elastic membranes from either experiments or molecular dynamics simulations[10, 11, 31]. In the present work, we will derive the displacement correlation function for a *free edge* at finite temperature and show that both the Gaussian modulus and edge tension can be obtained from the de-

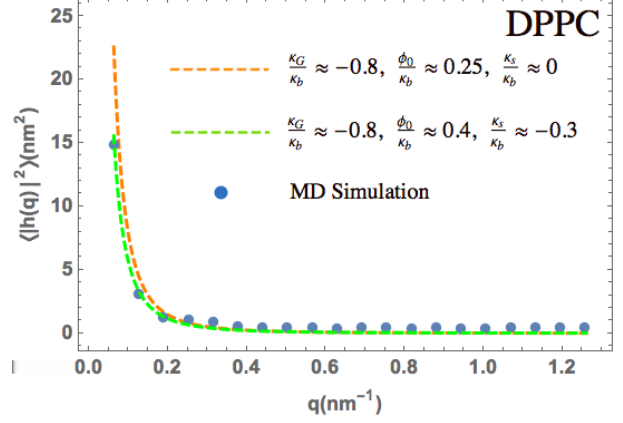


FIG. 2: We extract the Gaussian modulus and edge properties from MD simulations for lipid membrane DPPC by fitting our analytical results. Our fit is found to be more sensitive to edge tension compared to the edge moduli and hence the green dashed line yields a better fit.

rived result[32]. In what follows, we choose a simplified geometry to carry out our analysis. In principle we can choose any geometry and the main consideration for a particular configuration is the ease of carrying out the atomistic simulations. Accordingly, we consider a rectangular membrane with a free edge of size L and a clamped (opposite) edge. The objective is to study the fluctuation behavior of the membrane at (and near) the free edge. In order to make analytical progress, we model this case with a semi-infinite sheet with one free edge. The semi-infinite sheet is embedded in the domain $\Omega^1 := [\mathbf{x} = (x, y); -\infty < x < 0, -\infty < y < \infty]$, with a free edge at $\partial\Omega^1 := [\mathbf{x} = (0, y); -\infty < y < \infty]$. Therefore, we have periodic boundary conditions only in y direction. The derivation is long and tedious however the final result is exceptionally simple which we quote here and leave it to the reader to pursue the details in SI-Section 4, Equations (38-61). At the edge $\mathbf{x} = \mathbf{x}' = (0, y)$, the displacement self-correlation is simply:

$$\langle |h(\mathbf{q})|^2 \rangle = \frac{2kT\kappa_b}{Lq^2 (2\kappa_b(\phi_0 - 2q\kappa_G + q^2\kappa_s) - q\kappa_G^2)}, \quad (4)$$

which unlike the infinite membrane case, contains the contributions from not only the bending modulus κ_b , but also the Gaussian modulus κ_G as well as the edge properties (ϕ_0, κ_s) [33].

MD simulations of a fluctuating free edge. In

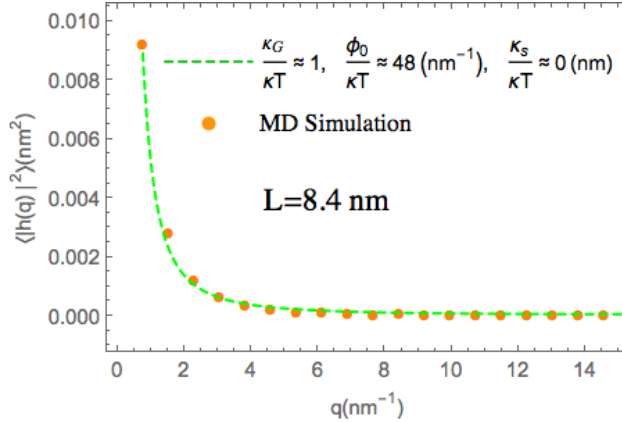


FIG. 3: Fluctuations of the free edge of graphene monolayer with size of $L = 8.4 \text{ nm}$.

order to use the derived fluctuation relations in the preceding paragraphs, we perform MD simulations on graphene monolayer and three types of lipid bilayers. The details of the simulation approach, force-field used, the manner in which the edge conditions were imposed and other details are in SI-Section 5, which includes Refs. [34–39]. For lipid bilayers, calculations were performed with the freely available software GROMACS, using the coarse-grained MARTINI force field[40, 41]. We chose three types of lipid: DPPC, DOPC and DOPE. We expect different properties for the three bilayers and since any particular one is fine for “proof-of-concept”, we focus on the details of only DPPC. For the others, the results can be found in the SI-Section 5. We perform MD simulations of monolayer graphene using LAMMPS [42]. The second-generation reactive empirical bond-order (REBO) potential [27] is used for the multibody C–C interactions. In graphene, unlike lipid bilayers, the in and out-of-plane deformations are coupled in a nonlinear fashion. MD simulations of *infinitely large* graphene monolayers show that at finite temperature, depending on the size of the sheet and the temperature, they exhibit marked stiffening[11] [43]. To minimize the effects arising from nonlinearities, we perform MD simulations under NPT ensemble—zero pressure—to relax the in-plane stress field. Further details related to graphene MD simulations are in the SI-Section 6, which includes Refs.[27, 42, 44].

Results and discussions. We fit our theoretical expression in Equation (4) to the data from MD simulations. The details on transforming the MD data into Fourier space can be found in SI-Section 7. Results are shown in Figure 2 for lipid bilayers.

The fluctuation spectra can be described by a power law as: $\langle |h(q)|^2 \rangle \propto 1/q^\eta$. For long wave-length fluctuations, the dominant term is the edge tension, as it couples with q^2 , while at short wave-length fluctuations, the edge modulus κ_s , coupled with q^4 becomes the dominant term. Unfortunately, there are no reports on the edge modulus of lipid membranes in the literature. For DPPC lipid membrane, we obtained the bending modulus $\kappa_b = 36kT$ and the edge tension is estimated as: $\phi_0 = 14.4kT/\text{nm}$ which is about an order of magnitude larger than what has been obtained by Hu et.al.[15]. In the intermediate region, the Gaussian modulus, determines the decaying trend of the fluctuations, i.e. the value of η and how fast the fluctuations decay. Interestingly, the Gaussian modulus does not have significant impact on the *overall* fluctuations, but strongly affects only its *rate of decay* with respect to the wave number and is estimated to be $\kappa_G = -28.8kT$ for DPPC lipid membrane. Our fitted parameters are indeed in the range of reported data for lipid membranes[16–22], but slightly different from those reported by Hu et.al.[15]. We have investigated the properties for other types of lipids as well (SI-Section 5). While our estimates on Gaussian modulus and edge tension for DPPC are in reasonable agreement with existing values in the literature, *reported values of these properties for DOPC and DOPE in the literature, cannot explain our MD observations.*

The results for the fluctuations of a graphene edge are shown in Figure 3. Existing values for graphene mechanical properties in the literature are reported at zero Kelvin. Due to nonlinearities, graphene monolayers exhibit stiffening at finite temperature. Similarly, the Gaussian modulus and edge properties also get renormalized at finite temperature. In fact, a free edge, influenced by edge forces, sustains ground-state non-zero deformations, that arise from the competition between in-plane stretching energy and the compressive edge force. The effect of the in-plane stretching energy can be implicitly captured by the edge modulus κ_s as well as ϕ_0 , representing the *apparent* edge tension. The variation of edge *modulus* appears to have negligible effect on the fitting of the MD results. Our results show that at finite temperature, the apparent edge tension—unlike its *bare* value at zero Kelvin $\sim -10 \text{ eV/nm}$ [45]—is *positive* with a value of $\sim 1.2 \text{ (eV/nm)}$ and thus provides stability to the edge. This is in sharp contrast to the negative edge tension that is believed to exist for graphene edges. For Gaussian modulus also, we obtained $\kappa_G \sim 1kT \sim 25\text{meV}$, which is positive and much larger than its predicted *bare* value at zero Kelvin ~ -1.52 to -1.62 eV [25, 26]. Our results bring

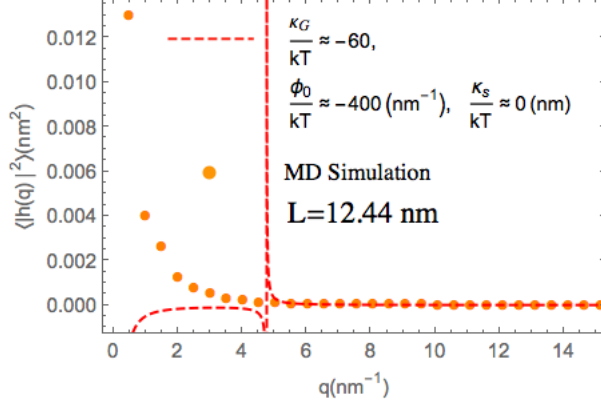


FIG. 4: This figure show the predictions of edge fluctuations of graphene if the currently accepted values of Gaussian modulus[25] and edge properties[45] in the literature are used. As evident, our atomistic simulations cannot be captured by those properties.

to fore that the negative value is not possible at finite temperature. In fact, we could not get a good fit with the reported negative values of Gaussian modulus in the literature. Indeed, the best fit is obtained with rather small, *positive* value for Gaussian modulus. The discrepancies between the zero and finite temperature Gaussian modulus and edge tension clearly reveal that entropic effects are significant. Even if we were to use the currently accepted properties, they would be incapable of explaining our simulations of the edge fluctuations (Figure 4) and in fact demonstrate unphysical instability at finite temperature. The red dashed line in Figure 4 is obtained by substituting the zero-Kelvin values into Equation (4). Note that the zero-Kelvin negative values of edge tension and Gaussian modulus, result is a singular point q^*

where the denominator of Equation (4) becomes zero. For all values of $q < q^*$ the correlation function become negative, which is an indicator of the instability of thermal fluctuations for long wave-lengths.

While not practical for lipid bilayers, at least in the context of graphene, it is of interest to investigate whether the Gaussian modulus does show a transition towards negative values as the temperature is lowered. As alluded to earlier, two notable (and congruent) estimates exist for the zero Kelvin value [25, 26]. Accordingly, we have also explored the temperature dependency of the Gaussian modulus and edge properties. The detailed results appear in the SI-Section 8. Our simulations suggest that as the temperature decreases below room temperature, these properties approach their zero Kelvin values and in particular, the Gaussian modulus *does* transition to a negative value. We remark that (as discussed in the SI-Section 8) our approach has limitations in that it cannot be used (in its present form) at ultra-low or very high temperatures. Future work extending our framework to incorporate stretch-bending coupling may partially mitigate this limitation.

In summary, our work provides a new and facile route—for the first time—to extract the edge properties and Gaussian modulus for both fluid and solid 2D membranes from fluctuations spectra. The obtained insights lay bare some of physical inconsistencies and paradoxes in the currently accepted mechanical properties for lipid bilayers and graphene.

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