

# A perspective on the statistical mechanics of 2D materials



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## ABSTRACT

2D materials are fascinating for numerous reasons. Their geometrical and mechanical characteristics along with other associated physical properties have opened up fascinating new application avenues ranging from electronics, energy harvesting, biological systems among others. Due to the 2D nature of these materials, they are known for their unusual flexibility and the ability to sustain large curvature deformations. Further, they undergo noticeable thermal fluctuations at room temperature. In this perspective, we highlight both the characteristics and implications of thermal fluctuations in 2D materials and discuss current challenges in the context of statistical mechanics of fluid and solid membranes.

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## 2D materials as elastic sheets

2D materials may be mechanically described as elastic sheets that are resistant to areal change (in-plane deformations), but are quite flexible and can therefore bend easily. Solid 2D membranes<sup>1</sup> include materials such as graphene, Boron Nitride, MoS<sub>2</sub> among many others. Fluid membranes, such as lipid bilayer membranes, are relatively easier to describe mathematically as they are isotropic<sup>2</sup> and often only bending elastic energy has to be

accounted for and in-plane stretching, even if incorporated, may be regarded as uncoupled with bending deformation.<sup>3</sup> Specifically, the well-known Helfrich–Canham [1,2] theoretical framework parametrizes the bending energy cost of a tensionless patch of a fluid membrane by a quadratic function of the curvature:

$$F_b = \int \left[ \frac{1}{2} \kappa_b (H - H_0)^2 + \kappa_G (K - K_0) \right] dA. \quad (1)$$

Here  $\kappa_b$  and  $\bar{\kappa}$  are the bending moduli that, respectively, correspond to the energy change due to changes in the mean ( $H$ ) and Gaussian ( $K$ ) curvatures. The corresponding spontaneous curvatures are denoted by  $H_0$  and  $K_0$ .

The *directional* curvature of a surface can be described as gradient of the normal vector, along a given direction. There are always two orthogonal directions that the corresponding curvatures are extremals and are referred to as principal curvatures, denoted by

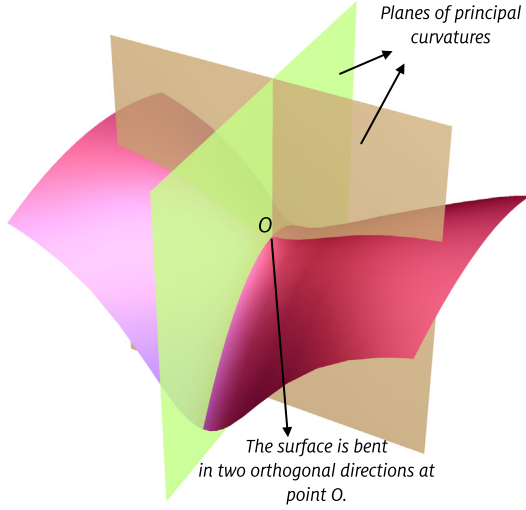
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<sup>1</sup> The word “membrane” has a different connotation in the area of solid mechanics than in physics. In solid mechanics, plates, shells and membranes are carefully distinguished. In the physics literature, essentially any 2D elastic sheet is referred to as a membrane and we have adopted this practice here.

<sup>2</sup> Fluid membranes are usually isotropic within the plane. Among solid membranes, graphene exhibits in-plane isotropy while most other solid 2D materials are anisotropic.

<sup>3</sup> We will revisit the complexity surrounding the modeling of solid membranes later in the perspective.



**Fig. 1.** This figure depicts the principal directions on a surface at a given point  $O$ . The directions of the normal planes where the curvature takes its extremum (maximum and minimum) values are called principal directions. The corresponding curvatures are principal curvatures, for which their summation gives the mean curvature and their product yields the Gaussian curvature at the given point  $O$ .

$c_1$  and  $c_2$  (Fig. 1). The mean and Gaussian curvatures are then defined as:  $H = c_1 + c_2$ ,  $K = c_1 c_2$  [3].

The spontaneous curvature models the situation where the minimizer of energy (in the absence of an external stimuli) corresponds to a preferred curvature. This is quite common for asymmetric membranes, where the molecular structure varies asymmetrically along the thickness.

There are numerous ways to parametrize a surface and the particular choice depends on the objective of the mathematical description. Perhaps, the one used most often in the literature is the so-called Monge representation [3], which is convenient for surfaces with a flat equilibrium (ground) state. In this representation, the surface is characterized by a height function  $h(\mathbf{x})$ , with  $\mathbf{x}$  being the position of each point on the surface. The mean and Gaussian curvatures can then be expressed in terms of  $h(\mathbf{x})$  [3]:

$$H = \nabla \cdot \left( \frac{\nabla h(\mathbf{x})}{\sqrt{1 + |\nabla h(\mathbf{x})|^2}} \right)$$

$$K = \frac{\det(\nabla \nabla h(\mathbf{x}))}{(1 + |\nabla h(\mathbf{x})|^2)^2}. \quad (2)$$

The above expressions are the general nonlinear forms of the mean and Gaussian curvatures. If the deformations are “small” enough, upon linearization, Eq. (2) reduces to:

$$H = \nabla^2 h(\mathbf{x}), \quad K = \frac{\partial^2 h}{\partial x^2} \frac{\partial^2 h}{\partial y^2} - \left( \frac{\partial^2 h}{\partial x \partial y} \right)^2. \quad (3)$$

Eq. (1) may be used to evaluate the energy change due to flexural deformations of both fluid and (isotropic) solid membranes. Unlike fluid membranes, for solid membranes, in addition to Eq. (1), the in-plane stretching energy should be also accounted for in the total elastic energy. A more detailed description of the elasticity of solid membranes is given later, where we present how the bending energy in Eq. (1) is coupled with the in-plane strain energy.

### Why does an elastic sheet fluctuate at finite temperature?

Eq. (1) has been extensively used to describe the mechanics of fluid and biological membranes. Typical bending modulus ( $k_b$ ) of most lipid-bilayers is between 5 and  $25k_B T$ —small enough

compared to the thermal energy scale that membranes undulate or fluctuate noticeably at physiological temperatures [4–8]. Bending rigidity of 2D crystalline graphene has also been measured by atomistic and quantum simulations [9–11]. Reported values for graphene bending rigidity at zero Kelvin, range from (1.2–1.6 eV) [9–11]—just a few times larger than the bending rigidity of biological membranes (at room temperature).<sup>4</sup> Thus, the energy cost for bending deformations of these materials is typically very low.

Consider a toy model of an elastic sheet—shown in Fig. 2. At zero Kelvin, the sheet will adopt the configuration corresponding to minimum bending energy. If spontaneous curvature is absent then an infinite elastic sheet will simply minimize its energy by adopting a perfectly flat configuration. At a non-zero temperature, however, there is a *finite* probability that even a non-zero bending-energy-state can occur—some illustrative samples are given in Fig. 2. The probability of occurrence of any of these deformation modes is dictated by the Boltzmann factor [8]:

$$p_i \propto \exp(-E_i/k_B T) \quad (4)$$

where  $p_i$  is the probability of occurrence of state  $i$ ,  $E_i$  is its associated elastic energy cost and  $k_B T$  is the thermal energy scale. The notion expressed in Eq. (4) can be elaborated further. The probability distribution can be normalized to 1 with a normalizing factor  $1/Z$ , where  $Z$  is known as the partition function and is obtained by summing over all possible states<sup>5</sup>:

$$Z = \sum_i \exp(-E_i/k_B T). \quad (5)$$

Further, the ensemble average of any physical quantity  $X$  can be obtained using the probability distribution:

$$\langle X \rangle = \sum_i X_i p_i = \frac{1}{Z} \sum_i X_i \exp(-E_i/k_B T). \quad (6)$$

For deformation modes that correspond to extensive curvature changes, the energetic cost can be fairly high and the probability of its occurrence (accordingly) very low but nevertheless, all states are, in principle, *possible*. At any given time, if a 2D membrane is observed at a finite temperature, there is a finite probability that one of the infinite set of modes will be observed (as opposed to just the flat state at zero Kelvin). Accordingly, 2D sheets always appear to be fluctuating in a random manner around the ground (equilibrium-minimized) state. Even though the average of the height field  $\langle h \rangle$  is zero, the fluctuations,  $\langle h^2 \rangle$  around the flat state are nonzero and depend on the membrane size, temperature as well as the mechanical properties of the sheet. The relatively low bending modulus of many 2D materials ensures that fluctuations are noticeable at room temperature.

### What do the fluctuations tell us about the mechanical properties?

In the case of a large, nearly flat membrane, occupying a domain of  $\{\mathbf{x} \in \mathbb{S} | \mathbb{S} = [0, L]^2\}$ , with periodic boundary condition in all directions, the out-of-plane displacement field  $h(\mathbf{x})$ , can be expanded in Fourier series as<sup>6</sup>:

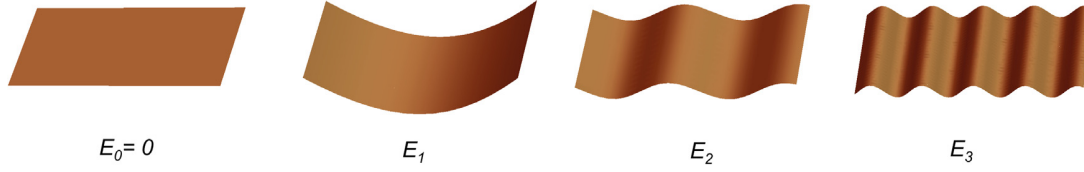
$$h(\mathbf{x}) = \sum_{\mathbf{q} \in \mathbb{K}} \bar{h}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}). \quad (7)$$

<sup>4</sup> Graphene's larger apparent bending stiffness originates from the nonlinear coupling of in-plane stretching deformation and out-of-plane bending.

<sup>5</sup> Since we have used a *field theory* as a starting point, the number of possible deformation states or deformation modes are infinite

<sup>6</sup>  $\mathbf{q} := |\mathbf{q}| \in [q_{\min}, q_{\max}]$ , i.e.

$\mathbb{K} = \{\mathbf{q} : \mathbf{q} = \frac{2\pi}{L} (v_x, v_y), v_x, v_y \in \mathbb{Z}, |\mathbf{q}| \in [q_{\min}, q_{\max}]\}$ .



**Fig. 2.** An elastic sheet at finite temperature undergoes out-of-plane undulations. All deformation modes are possible with a probability that is proportional to the Boltzmann factor ( $\propto \exp(-E_i/k_B T)$ ). Deformations with higher energy cost are less probable and the equilibrium state that minimizes the energy, is the most probable state.

The Fourier transform of the height function then is:

$$\bar{h}(\mathbf{q}) = \frac{1}{L^2} \int_{\mathcal{S}} h(\mathbf{x}) \mathbf{e}^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x}. \quad (8)$$

Assuming linearized elasticity, described in Eq. (3), the energy formulation in Eq. (1) can be expanded in Fourier space as follows<sup>7</sup>:

$$E_b = L^2 \sum_{\mathbf{q} \in \mathbb{K}} \frac{1}{2} \kappa_b |\mathbf{q}|^4 |\bar{h}(\mathbf{q})|^2. \quad (9)$$

We remark that the contribution from the Gaussian curvature vanishes for a system with no boundaries [3]. The mean square of the amplitude in each mode  $\langle |h_{\mathbf{q}}|^2 \rangle$  can be then evaluated from Eq. (6).<sup>8</sup> More frequently, the phase averages are computed by taking recourse to the so-called equipartition theorem [8,12], that states that the thermal energy is equally shared among all the modes of deformations.<sup>9</sup> Accordingly, the average of the energy in each mode is:

$$\left\langle \frac{L^2}{2} \kappa_b |\mathbf{q}|^4 |\bar{h}(\mathbf{q})|^2 \right\rangle := \frac{1}{2} k_B T. \quad (11)$$

Consequently, the mean-square average of the fluctuations of each mode may be obtained as:

$$\langle |\bar{h}(\mathbf{q})|^2 \rangle = \frac{k_B T}{L^2 \kappa_b |\mathbf{q}|^4}. \quad (12)$$

Eq. (12), implies that for smaller  $\mathbf{q}$ , the amplitude is larger and dominant. Further, for a periodic geometry, the fluctuations at all

<sup>7</sup> Note that we have used the orthogonality property of the Fourier transformation that decouples the modes in a quadratic energy formulation:

$$\begin{aligned} \int (\nabla^2 h)^2 d\mathbf{x} &= \sum_{\mathbf{q}, \mathbf{q}'} |\mathbf{q}|^2 |\mathbf{q}'|^2 \bar{h}(\mathbf{q}) \bar{h}(\mathbf{q}') \int \mathbf{e}^{i(\mathbf{q}+\mathbf{q}') \cdot \mathbf{x}} d\mathbf{x} \\ &= L^2 \sum_{\mathbf{q}} |\mathbf{q}|^4 \bar{h}(\mathbf{q}) \bar{h}(-\mathbf{q}) \delta(\mathbf{q}, -\mathbf{q}'). \end{aligned}$$

Also, note that  $\bar{h}(-\mathbf{q}) = \bar{h}^*(\mathbf{q})$  are conjugates and hence we can set  $\bar{h}(\mathbf{q}) \bar{h}(-\mathbf{q}) = |\bar{h}(\mathbf{q})|^2$ .

<sup>8</sup> The partition function is calculated as:

$$\begin{aligned} Z &= \int_{-\infty}^{\infty} \mathbf{e}^{-\frac{L^2}{2k_B T} \sum_{\mathbf{q} \in \mathbb{K}} \kappa_b |\mathbf{q}|^4 |\bar{h}(\mathbf{q})|^2} \prod_{\mathbf{q} \in \mathbb{K}} d\bar{h}_{\mathbf{q}} \\ &= \prod_{\mathbf{q} \in \mathbb{K}} \sqrt{\frac{2\pi k_B T}{L^2 \kappa_b |\mathbf{q}|^4}} \end{aligned} \quad (10)$$

where  $\mathbb{K} := \{\mathbf{q} = 2\pi(v_x, v_y)/L : v_x, v_y \in \mathbb{Z}, |\mathbf{q}| \geq 2\pi/L\}$ . Then the average of the square of the amplitude in each mode is obtained as:

$$\begin{aligned} \langle |\bar{h}_{\mathbf{q}}|^2 \rangle &= \frac{1}{Z} \int_{-\infty}^{\infty} |\bar{h}_{\mathbf{q}}|^2 \mathbf{e}^{-\frac{L^2}{2k_B T} \sum_{\mathbf{q} \in \mathbb{K}} \kappa_b |\mathbf{q}|^4 |\bar{h}(\mathbf{q})|^2} \prod_{\mathbf{q} \in \mathbb{K}} d\bar{h}_{\mathbf{q}} \\ &= \frac{k_B T}{L^2 \kappa_b |\mathbf{q}|^4} \end{aligned}$$

<sup>9</sup> This is however, valid only when the energy is a quadratic function of uncoupled degrees of freedom.

points are identical, i.e.  $\langle h(\mathbf{x}_1)^2 \rangle = \langle h(\mathbf{x}_2)^2 \rangle$  and is represented by a spatial average as<sup>10</sup>:

$$\begin{aligned} \langle h^2 \rangle &= \frac{1}{L^2} \int \langle h(\mathbf{x})^2 \rangle d\mathbf{x} \\ &\propto \frac{k_B T}{\kappa_b} L^2. \end{aligned} \quad (14)$$

Eq. (14) is a critical result with many applications. For example, the thermal fluctuation spectra may be measured by experimental methods or computed using atomistic simulations and the above formula can then be used to estimate the bending rigidity of membranes [14–17]. This result has been also extended to other contexts providing a facile route to extract useful information about membranes e.g. the incorporation of electromechanical coupling [18], tilt of lipids [19,20], presence of heterogeneities [21–23], proximity to substrates or other vesicles [24,25] among others.

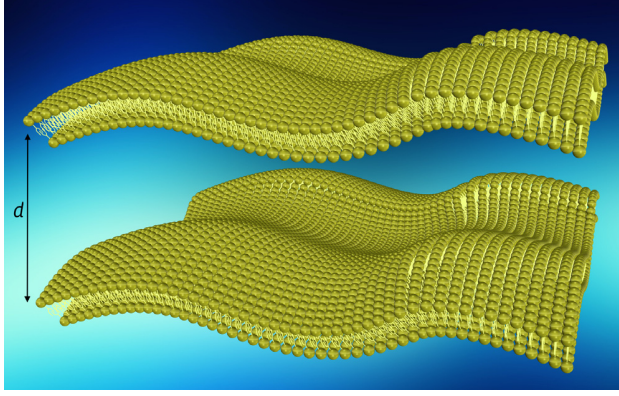
### What are the implications of thermal fluctuations in material science and biology?

Thermal fluctuations appear to have several fascinating implications in material science and biology. In the context of 2D crystalline materials, of which graphene is a good example, its morphology is strongly dictated by thermal fluctuations at room temperature. Graphene can be experimentally made in different geometries such as rectangular sheet and ribbons. However, it is found that at finite temperature, graphene sheet cannot exist in perfectly flat state and there is always intrinsic rippling on the surface of a graphene sheet [26]. This has been explained theoretically by nonlinear elasticity theory of crystalline membranes, where the in- and out-of-plane deformations are coupled and at finite temperature result in permanent ripples in graphene sheet. Further, graphene nano-ribbons exhibit self-folding and warping at finite temperature. In this case, the edge effects along with thermal fluctuations, render the ribbon geometry to be unstable. Consequently, with small twisting stimuli, the ribbon can be transformed into a nano-tube—a more stable configuration without any edge [27]. Accordingly, the morphology of graphene is highly affected by temperature, and the temperature dependence of the graphene morphology can be used as a method in experiments for graphene-based structures [28].

<sup>10</sup> Also, since the two-point correlation function is translationally and rotationally invariant, it only depends on the distance between the two points,  $r = |\mathbf{r}| = |\mathbf{x} - \mathbf{x}'|$ , rather than their positions  $(\mathbf{x}, \mathbf{x}')$ :

$$\begin{aligned} \langle h(\mathbf{x}) h(\mathbf{x}') \rangle &= \sum_{\mathbf{q}, \mathbf{q}' \in \mathbb{K}} \langle \bar{h}_{\mathbf{q}} \bar{h}_{\mathbf{q}'} \mathbf{e}^{i(\mathbf{q} \cdot \mathbf{x} + \mathbf{q}' \cdot \mathbf{x}')} \rangle \\ &= \frac{k_B T}{L^2 \kappa_b} \sum_{\mathbf{q} \in \mathbb{K}} \frac{\mathbf{e}^{i\mathbf{q} \cdot \mathbf{r}}}{|\mathbf{q}|^4} \end{aligned} \quad (13)$$

which is clearly independent of the position of the two points. We remark that in case of finite membranes, where pertinent boundary conditions must be accounted for, these simple results are no longer valid.



**Fig. 3.** While a single membrane fluctuates freely, its undulations are impeded when it is close to another surface or, for example, another fluctuating membrane. This “hindrance” results in the decrease of the total system entropy and thus increases the overall free energy of the system. The increase in free energy depends on the inter-membrane distance and can be interpreted as a repulsive force that acts to push the membranes apart. Source: Adapted from Ref. [13].

Many physiological processes are involved with thermal fluctuations such as exo and endo-cytosis, membrane fusion, pore formation, cell adhesion, binding–unbinding transitions, self assembly and vesicle size distributions among many others. These aforementioned biophysical phenomena are governed by a complex interplay between the various attractive and repulsive forces that mediate between biological membranes. A key role is played by a repulsive force termed “steric hindrance”, or simply entropic pressure, the origins of which lie in the thermally excited fluctuations of membranes (see Fig. 3). As mentioned earlier, biological membranes are quite flexible and fluctuate noticeably at room temperature. While a single membrane fluctuates freely, its undulations are impeded when it is close to another surface or another fluctuating membrane. This hindrance decreases the entropy and the ensuing overall increase of the free-energy of the membrane system, which depends on the intermembrane distance, leads to a repulsive force that tends to push the membranes apart. Stated differently, a finite external pressure is required to maintain the mean distance between the interacting membranes. Accordingly, the study of thermal fluctuations and entropic effects has been one of the cornerstones of biophysical research on membranes [13,29–34].

A more recent topic of growing interest is the entropic interaction of ultra-thin 2D nano-materials such as graphene with cellular membranes and its study has implications for several biomedical applications such as biosensors [35], tissue scaffolds [36,37], carriers for drug delivery [38,39] and gene therapy [40]. The graphene sheet undergoes thermal motion in the vicinity of the cellular membrane. Rather than adhering to cellular membrane, graphene sheet is observed to penetrate the bilayer, through one of its sharp corner [41]. We speculate that this type of interaction (which does not change the total elastic energy) is primarily controlled by entropic effects arising from thermal undulations of both the membrane and the graphene sheet. Generally speaking, adhesion and cellular uptake of nano-materials, depending on their shapes and sizes, can be strongly affected by thermal fluctuations [42].

### What are the differences between solid and fluid membranes?

Elasticity of solid membranes, is somewhat more complicated compared to their fluid counterparts. Unlike fluid membranes, in addition to bending and stretching rigidities, solid membranes

may also exhibit non-trivial in-plane shear resistance. While the bending energy is parametrized by Eq. (1), the elastic energy cost for their in-plane deformations must be also accounted for and is non-nonlinearly coupled to the out-of-plane displacement field. The von Karman nonlinear plate theory [43] is usually employed to describe the elasticity of 2D solid materials. The displacement field in its general form can be expressed as:

$$\mathbf{u} = (u_x, u_y, h) \quad (15)$$

where  $u_x$  and  $u_y$  are displacement fields along  $x$  and  $y$  directions, respectively and  $h$  is the out-of-plane displacement field. Then the in-plane strain field is defined as:

$$\varepsilon_{\gamma\delta} = \frac{1}{2} \left( \frac{\partial u_\gamma}{\partial x_\delta} + \frac{\partial u_\delta}{\partial x_\gamma} + \frac{\partial h}{\partial x_\gamma} \frac{\partial h}{\partial x_\delta} \right). \quad (16)$$

The resulting stress tensor, assuming isotropy, can be written as:

$$\sigma_{\gamma\delta} = \frac{E}{1-\nu^2} \left( \varepsilon_{\gamma\delta} + \frac{\nu}{1-\nu} \varepsilon_{kk} \delta_{\gamma\delta} \right) \quad (17)$$

where  $E$  and  $\nu$  are the elastic Young modulus and Poisson ratio of the solid sheet, respectively. The total energy is then:

$$\begin{aligned} F_{\text{tot}} &:= F_b + F_s \\ &= \int \left[ \frac{1}{2} \kappa_b H^2 \right] dA + \int \left[ \frac{1}{2} \sigma_{\gamma\delta} \varepsilon_{\gamma\delta} \right] dA \end{aligned} \quad (18)$$

which implies that even in the absence of explicit in-plane deformation – i.e.  $u_x = u_y = 0$  – the out-of-plane deformations results in a *quartic* stretching energy. The total energy in the absence of in-plane displacement fields ( $u_x = u_y = 0$ ) is:

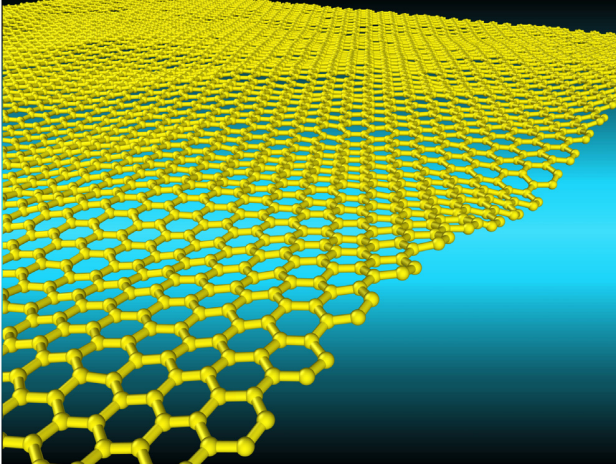
$$\begin{aligned} F_{\text{tot}} &:= F_b + F_s \\ &= \int \left[ \frac{1}{2} \kappa_b (\nabla^2 h)^2 + \frac{E}{8(1-\nu^2)} |\nabla h|^4 \right] dA. \end{aligned} \quad (19)$$

Due to the nonlinear contribution of the stretching energy, the thermal fluctuations spectra of solid membranes like graphene monolayers cannot be obtained analytically and Eq. (12) is invalid. The fluctuations in solid membranes are suppressed when compared to their fluid counterparts [44]. Molecular dynamics simulations of graphene monolayers (shown in Fig. 4), with periodic boundary conditions in all directions, show that the apparent bending stiffness of graphene at finite temperature is much larger than its bare value—at zero kelvin [45]. This can be physically explained by the fact that graphene's in-plane Young's modulus is relatively high and involved in the energy cost of the out-of-plane deformations—as evident from Eq. (19). Consequently, at finite temperature, the fluctuations are suppressed due to these nonlinearities. Typically, the out-of-plane fluctuations for solid membranes are described as a power law; i.e.  $\langle h^2 \rangle \propto L^\eta$ , with  $L$  being the in-plane size of the sheet. Within the harmonic approximation, the exponent  $\eta$  is equal to 2—as evident from Eq. (12). Due to anharmonicity,  $\eta$  is smaller than 2 for solid membranes. Several works have numerically studied this scaling and its entropic consequences [44–48]. Typical values of  $\eta$  for graphene are found to range from (0.7–1.2) [44–48].

### What is the effect of thermal fluctuations on the apparent bending modulus of 2D materials?

Consider a tensionless flat patch of membrane with vanishing spontaneous curvature. The energy required to deform the membrane into a non-zero curvature is given by Eq. (1). This is however, the ground state energy not the *free energy*. At finite temperature, due to thermal fluctuations, the free energy is not the same as the elastic energy in Eq. (1). The work required to





**Fig. 4.** Snapshot of graphene sheet in a molecular dynamics simulation. Graphene as a solid membrane, has shear resistance, that results in coupling between in and out-of-plane deformations. This leads to a nonlinear contribution from the in-plane stretching energy that suppresses the height field fluctuations, compared to the simple harmonic result in Eq. (12).

create any non-zero deformation in the presence of the thermal fluctuations is equivalent to the change in the *total free energy*. In this manner, at finite temperature, the thermal fluctuations change the total work required to develop a particular deformation mode—in contrast to the prediction by Eq. (1). Even though the average value of the curvature at finite temperature is zero, i.e.  $\langle \nabla^2 h \rangle = 0$ , the ensemble average of the square of curvature is nonzero i.e.  $\langle (\nabla^2 h)^2 \rangle \neq 0$ . In this sense, the fluctuations act like a pre-existing curvature, that reduces the work required to deform the membrane. This appears as if the apparent bending modulus is smaller than its bare value (in ground state) [49]. Several works have studied this softening effect [50–52]. The so-called *apparent* bending stiffness is expressed as [50]:

$$\kappa_{\text{eff}} = \kappa_b + \frac{\alpha}{8\pi} k_B T \log N \quad (20)$$

wherein  $\alpha$  is a universal constant and  $N$  is the number of degrees of freedom in the system. Within a linearized framework (i.e. small deviations from the flat-state), Helfrich [50] predicted  $\alpha = -1$ . Peliti and Leibler [51] also reexamined this problem and obtained  $\alpha = -3$ . Later on, Kleinert [52] rigorously discussed the origins of these discrepancies confirmed that  $\alpha = -3$ .

An alternative approach to study the softening effects of the thermal fluctuations is to investigate the persistence length of the membrane at finite temperature. Thermal fluctuations cause the orientation of the surface to change with respect to position. The local orientation of a surface can be characterized by its normal;  $\mathbf{n}(\mathbf{x})$ . If the membrane is flat, the product of the normal vectors at two positions;  $\mathbf{n}(\mathbf{x}_1) \cdot \mathbf{n}(\mathbf{x}_2)$  is independent of the positions of and distance between the two points. In the presence of the thermal fluctuations, however, the normal vectors (and consequently their scalar products) vary with position. The correlations of the normal vectors serve as a measure for surface fluctuations. In general, the normal–normal correlations can be expressed as [53]:

$$\langle \mathbf{n}(\mathbf{x}_1) \cdot \mathbf{n}(\mathbf{x}_2) \rangle \propto \exp(-|\mathbf{x}_1 - \mathbf{x}_2|/\xi_p) \quad (21)$$

where  $\xi_p$  is known as persistence length, beyond which the above correlation function vanishes. Using the height field correlation function, the normal–normal correlations is obtained as [53]:

$$\langle \mathbf{n}(\mathbf{x}_1) \cdot \mathbf{n}(\mathbf{x}_2) \rangle \sim 1 + \alpha \frac{k_B T}{\kappa_b} \log(|\mathbf{x}_1 - \mathbf{x}_2|/d) \quad (22)$$

where  $d$  corresponds to the short wave length undulations; ( $q_{\text{max}} = 2\pi/d$ ) and  $\alpha$  is a universal coefficient. Vanishing correlations occur at the same length scale as the renormalized bending rigidity in Eq. (20) become zero.

Typical values for the persistence length of 2D membranes are beyond macroscopic scales ( $\sim \text{km}$  [53]). Though, this correction has a negligible impact on the bending rigidity, the entropic consequences of it, in biological phenomena are potentially important.

## Future directions

There exists a rich and extensive literature on thermal fluctuations of 2D materials. For a comprehensive review of this topic, the reader is referred to monographs by Safran [8] and Nelson et al. [54]. In the majority of the literature on this topic the Helfrich's classical quadratic energy function is used within the linearized elasticity approximation. Specifically, geometric and constitutive nonlinearities are not usually accounted for. Nevertheless, there are several cases where these simplifications cannot be made:

- The membrane is not always flat. In fact cellular membranes in reality are of ellipsoidal shape and sometimes even more complex. Biological vesicles also can exist in a wide range of sizes. Graphene sheets, can also appear in spherical and cylindrical shapes. These are the cases where the fluctuations occur within curved configurations and are coupled with the non-zero pre-existing curvature. Geometric nonlinearities of this kind, cannot be easily handled within conventional statistical mechanics, however, may result in important entropic effects. For example, it has been shown that the Gaussian size distribution of biological vesicles cannot be explained without incorporating the effects of geometric nonlinearities [55]. In the context of solid membranes, as another example, Paulose et al. [56] considered the nonlinearities introduced by curved background metric of spherical shells and suggested a new scaling behavior of their thermal fluctuations and buckling transitions in the presence of an external pressure.
- The quadratic Helfrich hamiltonian in Eq. (1) is the lowest order of the contribution of elastic energy to the total free energy. Generally, the expression for the bending energy can include higher orders of curvatures such as:  $\kappa^4, K\kappa^2, K^2$ . Though, in most cases the quadratic approximation is reasonable, at very high curvatures – such as for small biological vesicles or graphene nanotube – the higher order terms should be accounted for. These kind of constitutive nonlinearities, not only bring several equilibrium (ground state) solutions for the problem, but also, at finite temperature, can have significant entropic effects.
- There are cases, where the elastic energy is neither geometrically nor constitutively nonlinear, however, the total free energy formulation is a nonlinear function of the deformation. Constrained fluctuations are example of such cases where the path integration of the partition function should be carried out over all possible deformations that satisfy the corresponding constraints. For example, when the fluctuations of a graphene sheet occur in the vicinity of a substrate, they cannot exceed the distance between the membrane and the substrate. Also, when two fluctuating membranes approach each other, they cannot have overlap in their fluctuations. In these cases, the constraints result in suppression of the fluctuations and produce the so-called entropic pressure as a function of the inter-membrane distance. Typically, the partition function in such cases needs to be evaluated numerically. Alternatively, to make analytical progress, the effect of the entropic pressure can be mathematically captured by a nonlinear function in the total free energy.

Accordingly, due to nonlinearities the conventional equipartition theorem is not applicable and the development of approximate methods is an important research avenue.

- In the majority of the existing works in the literature, the membrane is assumed to be large enough that the effects of boundary conditions are negligible. In addition, far often than not, the boundary energy is ignored as well. In fact, periodic boundary conditions are usually assumed. In real cases, however, the fluctuations can be affected by different geometry and boundary conditions. Further, the periodic boundary conditions, automatically remove the contributions from Gaussian modulus and edge properties, since these parameters enter the equations only through boundary conditions. The statistical mechanics of a system, influenced by a set of boundary conditions, is hard to handle within conventional approaches. This is due to the fact that the partition function integration should be carried out over all possible deformation functions that do satisfy the boundary conditions. Accordingly, statistical mechanics of membranes near an open edge, pore or defect are still open questions in the literature and require further attention from both theoretical and atomistic point of views.
- Finally, we note that, the importance of thermal fluctuations is somewhat *universal* in all 2D materials. Solid membrane such as graphene – despite its nonlinear behavior – is the simplest example to study because of elastic isotropy. However, in the context of statistical mechanics, there exist unresolved challenges, even for this simplest case. For other 2D materials, such as MoS<sub>2</sub> and others, the nonlinear elastic energy formulation should also be modified to incorporate anisotropy. Nonetheless, the main challenges in the statistical mechanics of 2D materials, as emphasized in this perspective, are nonlinearities and the effects of boundary conditions.

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