

# Thermodynamics of quantum crystalline membranes

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We investigate the thermodynamic properties and the lattice stability of two-dimensional crystalline membranes, such as graphene and related compounds, in the low temperature quantum regime  $T \rightarrow 0$ . A key role is played by the anharmonic coupling between in-plane and out-of-plane lattice modes that, in the quantum limit, has very different consequences from those in the classical regime. The role of retardation, namely of the frequency dependence, in the effective anharmonic interactions turns out to be crucial in the quantum regime. We identify a crossover temperature,  $T^*$ , between classical and quantum regimes, which is  $\sim 70 - 90$  K for graphene. Below  $T^*$ , the heat capacity and thermal expansion coefficient decrease as power laws with decreasing temperature, tending to zero for  $T \rightarrow 0$  as required by the third law of thermodynamics.

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## I. INTRODUCTION

The study of the mechanical and thermodynamic properties of membranes is a problem of broad interest in physics, being at the interface of statistical mechanics, condensed matter and field theory. Recent experimental developments in growing and isolating single layers of crystalline materials, such as graphene, MoS<sub>2</sub>, WS<sub>2</sub>, BN and similar materials<sup>1</sup>, have revived the interest in the properties of crystalline membranes. The very thermodynamic stability of these two-dimensional (2D) crystals has been a matter of debate (for a review see Refs. 2 and 3). At the harmonic level, the out-of-plane modes and the in-plane modes are completely decoupled, and the contribution of both modes to the mean-square atomic displacement diverges. In this situation, anharmonic coupling between them should be taken into account<sup>4</sup>. This coupling suppresses the out-of-plane instability but increases the in-plane instability. As a result, strictly speaking, no long-range-order exists at finite temperature in agreement with the Mermin-Wagner theorem. This fact implies that Bragg peaks are not infinitely sharp in the thermodynamic limit, as in 3D ideal crystals, but for stiff membranes such as graphene they are still narrow and centred at the regular reciprocal lattice sites. This situation defines precisely what we call 2D crystals<sup>2,3</sup>. The anharmonic coupling between in-plane and out-of-plane modes is reflected in the onset of out-of-plane ripples at any finite temperature<sup>5</sup>. The impact of corrugations on electronic transport, as well as on the mechanical properties of graphene, is a subject of intense investigation<sup>6-16</sup>. Ripples have been indeed measured in atomically thick materials such as graphene<sup>17</sup> or MoS<sub>2</sub><sup>18</sup>, although it is still experimentally unclear whether they are mostly thermal in nature or due to strain.

A crystalline membrane is a strongly anharmonic system, and these anharmonic effects must be taken into account beyond the usual quasi-harmonic approximation (which ignores phonon-phonon interaction). However,

the role of strong anharmonic effects in crystalline membranes has almost exclusively been theoretically investigated in the classical regime<sup>4,19-37</sup>. An exception to this are the recent works Refs. 38 and 39, where both quantum and anharmonic effects are taken into account. Nevertheless, Ref. 39 neglects some relevant anharmonic terms, while both Refs. 38 and 39 only partially take into account quantum fluctuations, neglecting effects of retardation in the interactions.

The limitation of the classical approaches to high temperatures makes them unsuitable to investigate the stability and thermodynamic properties of such compounds in the very low temperature regime, where quantum effects are dominant. Even the temperature above which quantum fluctuations can be neglected and the classical analysis becomes valid has not been known until now. However, taking graphene as an example, a simple estimation of its Debye temperature for the out-of-plane mode gives us a value of the order of 1000 K, which hints that quantum fluctuations should be relevant even at relatively high temperatures.

A quantum analysis can be easily performed at the harmonic level, but the lack of coupling between in-plane and out-of-plane modes leaves the system unstable. This is reflected, for instance, in the fact that, in the thermodynamic limit and at a quasi-harmonic level, a divergent negative areal thermal expansion  $\alpha_V = -\infty$  is obtained<sup>40</sup>, in violation of the third law of thermodynamics, which implies that the thermal expansion should vanish at  $T = 0$ . In Ref. 40, the effects of the interaction between out-of-plane and in-plane modes have been included simply by means of a reasonable infrared (IR) cutoff in the available momentum space of the harmonic model. This approach does not solve the problem because it leads to a temperature independent (up to logarithmic accuracy) thermal expansion<sup>40</sup>. This difficulty is due to the use of the classical anharmonic theory of a crystalline membrane, which cannot be extrapolated to the  $T \rightarrow 0$  limit.

Another important quantity is the specific heat. The harmonic theory predicts that at very low temperature, it should be dominated by the out-of-plane mode and, due to its quadratic dispersion relation at long wavelength, the heat capacity should behave as  $c_p \sim T^{40-43}$ . It is important to understand how this picture changes once we include the effects of anharmonic interactions, since we know that they drastically change the properties of the out-of-plane modes<sup>19,20,24,26,30,44</sup>.

A robust description of the lattice properties of 2D crystalline membranes, satisfying the third law of thermodynamics in the low temperature limit and properly including both quantum effects and the anharmonic coupling between in-plane and out-of-plane modes, is still lacking.

In this paper, we develop a theory for anharmonic crystalline membranes in the quantum regime. Toward this end, we derive an effective quantum field theory governing the dynamics of the out-of-plane modes. The in-plane modes can be integrated out rigorously leading to an effective retarded (i. e., frequency dependent) interaction between out-of-plane modes. Then, we study the effect of the anharmonicities by computing the self-energy to first order in perturbation theory, obtaining the corresponding corrections to the elastic constants. It is known that perturbation theory is insufficient to describe the physics of the classical version of this problem<sup>4</sup>, making it necessary to use some other techniques such as  $\epsilon = 4 - D$  expansion<sup>20</sup> (where  $D$  is the membrane dimension), the self-consistent screening approximation (SCSA)<sup>24</sup>, or the non-perturbative renormalization group method<sup>26</sup>. Therefore, we have further worked on the first step beyond perturbation theory, by using a one-loop self-consistent theory, without including any renormalization of the in-plane Lamé constants, which can be viewed as the generalization of the Nelson and Peliti approximation<sup>19</sup> to the quantum regime. The present work can therefore be seen as the first stage of the full description of quantum crystalline membranes. However, the perturbative calculation is already useful to study two problems: (i) assess the effect of retardation in the effective interaction between out-of-plane modes; (ii) investigate the momentum space associated with anharmonic effects by applying a Ginzburg criterion. Comparing the perturbative calculation performed in the quantum regime at  $T = 0$ , with the result from the classical theory, allows us to determine a cross over temperature  $T^*$ , below which quantum effects become dominant. Finally, we study the effect of anharmonicities on the thermal expansion and specific heat of quantum crystalline membranes, solving the contradiction with the third law of thermodynamics.

## II. MODEL

We start our analysis from the standard continuum theory for crystalline elastic membranes and thin

plates<sup>2,4,19,20,45,46</sup>. The lattice deformations of the membrane are expressed in terms of an in-plane 2D vector displacement field  $\vec{u}$  and an out-of-plane (flexural) displacement field  $h$ . We will use the imaginary time functional path integral formalism, which is particularly convenient to study thermodynamic quantities. The Euclidean action can be written as  $\mathcal{S}[\vec{u}, h] = \int_0^\beta d\tau \int d^2x \mathcal{L}[\vec{u}, h]$ , where  $0 < \tau < \beta$  is the imaginary time and  $\beta = 1/(k_B T)$  is the inverse temperature, with Lagrangian density

$$\mathcal{L}[\vec{u}, h] = \mathcal{L}_h^0[h] + \mathcal{L}_u^0[\vec{u}] + \mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h] + \mathcal{L}_{\text{int}}^{(4)}[h]. \quad (1)$$

Here,  $\mathcal{L}_h^0[h]$  and  $\mathcal{L}_u^0[\vec{u}]$  are the quadratic Lagrangian densities for the out-of-plane and in-plane displacement fields,

$$\mathcal{L}_h^0[h] = \frac{1}{2}\rho\dot{h}^2 + \frac{1}{2}\kappa(\partial^2 h)^2, \quad (2)$$

$$\mathcal{L}_u^0[\vec{u}] = \frac{1}{2}\rho\dot{\vec{u}}^2 + \frac{1}{2}c^{ijkl}\partial_i u_j \partial_k u_l, \quad (3)$$

and  $\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h]$  and  $\mathcal{L}_{\text{int}}^{(4)}[h]$  are anharmonic terms.  $\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h]$  contains cubic interactions between in-plane and out-of-plane modes, and  $\mathcal{L}_{\text{int}}^{(4)}[h]$  accounts for a quartic local interaction for the out-of-plane field. Explicitly we have

$$\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h] = \frac{1}{2}c^{ijkl}\partial_i u_j (\partial_k h \partial_l h), \quad (4)$$

$$\mathcal{L}_{\text{int}}^{(4)}[h] = \frac{1}{8}c^{ijkl}(\partial_i h \partial_j h)(\partial_k h \partial_l h). \quad (5)$$

In the above expressions,  $\rho$  is the mass density,  $\kappa$  is the bending rigidity,  $c^{ijkl} = \lambda\delta^{ij}\delta^{kl} + \mu(\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk})$  is the elastic moduli tensor,  $\mu$  and  $\lambda$  are Lamé coefficients<sup>47</sup>. The latin indices ( $i, j, \dots$ ) run over the spatial coordinates  $x, y$ , and we use the convention where repeated indices are to be summed over. In addition, we write  $\dot{O} \equiv \partial O / \partial \tau$  ( $O = h, \vec{u}$ ).

It is known that in the classical problem both anharmonic terms  $\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h]$  and  $\mathcal{L}_{\text{int}}^{(4)}[h]$  are equally relevant<sup>19,20,23</sup>. Inclusion of  $\mathcal{L}_{\text{int}}^{(4)}[h]$  is also needed in order to make the Euclidean action bounded from below, and therefore to have a well defined ground state. Therefore, we keep both terms in the quantum theory. It is worthwhile noting that the term  $\mathcal{L}_{\text{int}}^{(4)}[h]$  was not considered in Ref. 39.

The partition function is written as the functional integral  $Z = \int D[\vec{u}, h] \exp(-\mathcal{S}[\vec{u}, h])$ . The classical treatment formally corresponds to neglecting all kinetic terms in the Lagrangian density. To be able to reach the low temperature limit, it is necessary to take into account quantum fluctuations of the fields  $h$  and  $\vec{u}$ , by retaining the kinetic terms in the Euclidean action. It is convenient to express the fields in Fourier components

$$O(\vec{x}, \tau) = \frac{1}{\sqrt{\beta V}} \sum_{\mathbf{k}} O_{\mathbf{k}} e^{i\vec{k}\cdot\vec{x}} e^{-ik_n \tau}, \quad (6)$$

where  $k_n = 2\pi n/\beta$ , with  $n \in \mathbb{Z}$ , are bosonic Matsubara frequencies,  $V$  is the area of the undistorted membrane and we have used the shorthand notation  $\mathbf{k} = (ik_n, \vec{k})$  with  $\sum_{\mathbf{k}} = \sum_{ik_n, \vec{k}}$ . We will later see that the thermodynamic quantities we are interested in can be expressed via the two-point correlation functions (propagators)  $G_{\mathbf{k}} = \langle h_{\mathbf{k}} h_{-\mathbf{k}} \rangle$  and  $D_{\mathbf{q}}^{ij} = \langle u_{\mathbf{q}}^i u_{-\mathbf{q}}^j \rangle$ , where  $\langle O \rangle = Z^{-1} \int D[\vec{u}, h] O \exp(-S[\vec{u}, h])$ . At the level of the harmonic theory, the correlation functions are given by

$$G_{\mathbf{k}}^0 = \left( -\rho (ik_n)^2 + \rho \omega_{k,F}^2 \right)^{-1}, \quad (7)$$

$$D_{\mathbf{q}}^{0,L} = \left( -\rho (iq_n)^2 + \rho \omega_{q,L}^2 \right)^{-1}, \quad (8)$$

$$D_{\mathbf{q}}^{0,T} = \left( -\rho (iq_n)^2 + \rho \omega_{q,T}^2 \right)^{-1}, \quad (9)$$

where we have split  $D_{\mathbf{q}}^{ij,0}$  in its longitudinal ( $L$ ) and transverse ( $T$ ) components with respect to the vector  $\vec{q}$ . The bare dispersion relations for the flexural ( $F$ ) and in-plane longitudinal/transverse modes are, respectively,  $\omega_{k,F} = \sqrt{\kappa/\rho} k^2$  and  $\omega_{q,L/T} = c_{L/T} q$ , with  $c_L = \sqrt{(\lambda + 2\mu)/\rho}$  and  $c_T = \sqrt{\mu/\rho}$ . When anharmonic effects are taken into account, the two point correlation functions are given by the Dyson equations,

$$G_{\mathbf{k}}^{-1} = (G_{\mathbf{k}}^0)^{-1} + \Sigma_{\mathbf{k}}, \quad (10)$$

$$(D_{\mathbf{q}}^L)^{-1} = (D_{\mathbf{q}}^{0,L})^{-1} + \mathcal{P}_{\mathbf{q}}^L, \quad (11)$$

$$(D_{\mathbf{q}}^T)^{-1} = (D_{\mathbf{q}}^{0,T})^{-1} + \mathcal{P}_{\mathbf{q}}^T, \quad (12)$$

where  $\Sigma_{\mathbf{k}}$  is the self-energy for the out-of-plane mode and  $\mathcal{P}_{\mathbf{q}}^{L/T}$  is the self-energy for the in-plane longitudinal/transverse mode. Since the Euclidean action (1) is quadratic in the field  $\vec{u}$ , the latter can be integrated out exactly, so that we are left with an effective theory only involving the flexural field  $h$ . Doing this (details given in Appendix A), the effective theory is described by the action

$$\begin{aligned} \mathcal{S}_{\text{eff}}[h] = & \frac{1}{2} \sum_{\mathbf{k}} \left( -\rho (ik_n)^2 + \kappa k^4 \right) h_{\mathbf{k}} h_{-\mathbf{k}} \\ & + \frac{1}{8\beta V} \sum_{\mathbf{k}, \mathbf{p}, \mathbf{q} \neq 0} R_{\mathbf{q}}^{ijkl} (k+q)_i k_j (p-q)_k p_l \\ & \times h_{\mathbf{k}+\mathbf{q}} h_{-\mathbf{k}} h_{\mathbf{p}-\mathbf{q}} h_{-\mathbf{p}} \end{aligned} \quad (13)$$

where  $R_{\mathbf{q}}^{ijkl}$  is the effective interaction tensor between out-of-plane modes that takes into account both interaction channels: the quartic local interaction (5) and the in-plane mode mediated interaction due to the cubic interaction (4). Just like in the classical theory, the  $\mathbf{q} = 0$  component was excluded from the interaction term (see Appendix A and Ref. 4). The tensor  $R_{\mathbf{q}}^{ijkl}$  obeys the same symmetries of the elastic moduli tensor, namely  $R_{\mathbf{q}}^{ijkl} = R_{\mathbf{q}}^{jikl} = R_{\mathbf{q}}^{klij}$ . For a physical 2D membrane,

$R_{\mathbf{q}}^{ijkl}$  has four independent components, which are most conveniently written in the basis defined by the momentum vector  $\vec{q}$ ,  $\{\hat{e}_{\parallel}, \hat{e}_{\perp}\}$ , with  $\hat{e}_{\parallel} = (q_x, q_y)/|\vec{q}|$  and  $\hat{e}_{\perp} = (-q_y, q_x)/|\vec{q}|$ . These are given by<sup>48</sup>

$$R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{cl}} = \frac{4\mu(\lambda + \mu)}{(\lambda + 2\mu)} \quad (14)$$

$$R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{qt}} = -\rho (iq_n)^2 \frac{\lambda^2}{\lambda + 2\mu} D_{\mathbf{q}}^{0,L} \quad (15)$$

$$R_{\mathbf{q}}^{\parallel\parallel\parallel\parallel} = -\rho (iq_n)^2 (\lambda + 2\mu) D_{\mathbf{q}}^{0,L}, \quad (16)$$

$$R_{\mathbf{q}}^{\perp\perp\parallel\parallel} = -\rho (iq_n)^2 \lambda D_{\mathbf{q}}^{0,L}, \quad (17)$$

$$R_{\mathbf{q}}^{\perp\parallel\perp\parallel} = -\rho (iq_n)^2 \mu D_{\mathbf{q}}^{0,T}, \quad (18)$$

where we have written the  $R_{\mathbf{q}}^{\perp\perp\perp\perp}$  component as  $R_{\mathbf{q}}^{\perp\perp\perp\perp} = R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{cl}} + R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{qt}}$ . The term  $R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{cl}}$  is frequency independent, and coincides with the 2D Young modulus. This term is already present in the classical statistical mechanics problem<sup>4,19</sup>, and this is why we denote it by the superscript cl, from *classical*. The remaining interaction terms,  $R_{\mathbf{q}}^{\perp\perp\perp\perp, \text{qt}}$ ,  $R_{\mathbf{q}}^{\parallel\parallel\parallel\parallel}$ ,  $R_{\mathbf{q}}^{\perp\perp\parallel\parallel}$  and  $R_{\mathbf{q}}^{\perp\parallel\perp\parallel}$ , are new terms that do not occur in the classical theory, for which reason we will refer to them as *quantum*. The *quantum* terms (15)-(18) all have the same structure, depending on the Matsubara frequency and become zero for  $iq_n = 0$ . Therefore the term  $R_{\mathbf{q}}^{ijkl} (k+q)_i k_j (p-q)_k p_l$  that appears in (13) can be written as

$$R_{\mathbf{q}}^{ijkl} (k+q)_i k_j (p-q)_k p_l = \sum_M g_{\vec{k}, \vec{q}, \vec{p}}^M R_{\mathbf{q}}^M, \quad (19)$$

with  $M$  running over  $\{\perp\perp\perp\perp, \parallel\parallel\parallel\parallel, \perp\perp\parallel\parallel, \perp\parallel\perp\parallel\}$ ,  $g_{\vec{k}, \vec{q}, \vec{p}}^M$  given by

$$g_{\vec{k}, \vec{p}, \vec{q}}^{\perp\perp\perp\perp} = k^2 p^2 \sin^2 \theta_{k,q} \sin^2 \theta_{p,q}, \quad (20)$$

$$\begin{aligned} g_{\vec{k}, \vec{p}, \vec{q}}^{\parallel\parallel\parallel\parallel} = & k p \cos \theta_{k,q} \cos \theta_{p,q} \times \\ & \times (k \cos \theta_{k,q} + q) (p \cos \theta_{p,q} - q), \end{aligned} \quad (21)$$

$$\begin{aligned} g_{\vec{k}, \vec{p}, \vec{q}}^{\perp\perp\parallel\parallel} = & k^2 p \sin^2 \theta_{k,q} \cos \theta_{p,q} (p \cos \theta_{p,q} - q) \\ & + p^2 k \sin^2 \theta_{p,q} \cos \theta_{k,q} (k \cos \theta_{p,q} + q), \end{aligned} \quad (22)$$

$$\begin{aligned} g_{\vec{k}, \vec{p}, \vec{q}}^{\perp\parallel\perp\parallel} = & k p \sin \theta_{k,q} \sin \theta_{p,q} \times \\ & \times (2k \cos \theta_{k,q} + q) (2p \cos \theta_{p,q} - q), \end{aligned} \quad (23)$$

where  $\theta_{k,q}$  and  $\theta_{p,q}$  are, respectively, the angle between  $\vec{k}$  and  $\vec{q}$ , and the angle between  $\vec{p}$  and  $\vec{q}$ . It is important to emphasize that both the quartic local interaction (5) and the in-plane mode mediated interaction (4) contribute to all the interaction terms (14)-(18). In Appendix A we show the individual contributions from the quartic local interaction and from the in-plane mediated channel.

### III. CLASSICAL VERSUS QUANTUM REGIMES

In the high temperature limit,  $T \rightarrow \infty$ , the main contribution to the self-energy of the out-of-plane mode

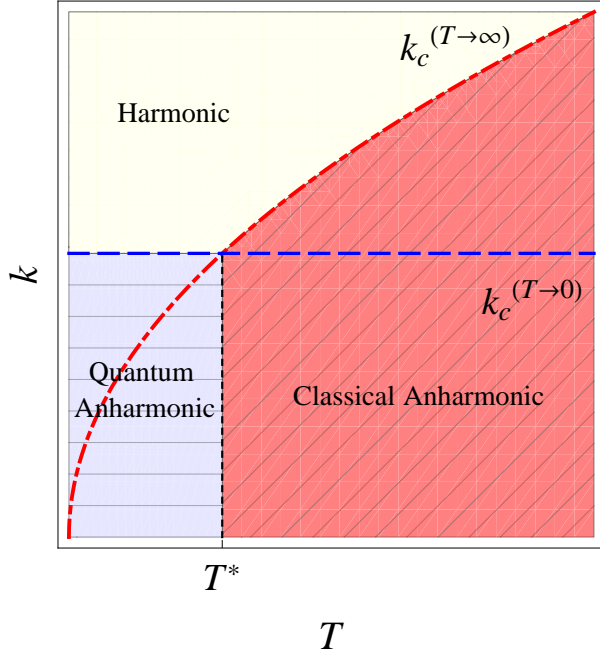


FIG. 1. Phase diagram in  $(T, k)$  space for the harmonic/anharmonic and quantum/classical regimes. The harmonic-to-anharmonic crossover momenta  $k_c^{(T \rightarrow \infty)}$  (28) and  $k_c^{(T \rightarrow 0)}$  (29) are displayed by the dot-dashed red and dashed blue lines, respectively. The vertical line shows the classical-to-quantum crossover temperature  $T^*$ . In the region labelled *Harmonic*, anharmonic effects are weak and the membrane is nearly harmonic. In the region labelled *Quantum Anharmonic*, anharmonic effects dominate and the main contribution comes from the  $T \rightarrow 0$  quantum terms, Eq. (25). In the region labelled *Classical Anharmonic*, anharmonic effects dominate and the main contribution comes from the  $T \rightarrow \infty$  classical term, Eq. (24).

comes from the only interaction term that occurs in the classical theory,  $R_q^{\perp\perp\perp\perp, \text{cl}}$  (see Appendix B 1 for an analysis of the remaining terms). To first order in perturbation theory, after an analytic continuation to real frequencies  $ik_n \rightarrow \omega + i0^+$ , we obtain the well known result<sup>4</sup>

$$\lim_{T \rightarrow \infty} \text{Re}\Sigma_k(\omega) \simeq \frac{4\mu(\lambda + \mu)}{(\lambda + 2\mu)\kappa} \frac{3k_B T}{16\pi} k^2, \quad (24)$$

which is frequency independent. In the low temperature limit,  $T \rightarrow 0$ , to first order in perturbation theory, the main contribution to the on-shell self-energy ( $\omega = \omega_{k,F}$ ) in the physically relevant long wavelength limit does not result from the  $R_q^{\perp\perp\perp\perp}$  component, but from the quantum terms  $R_q^{\parallel\parallel\parallel\parallel}$  and  $R_q^{\perp\perp\parallel\parallel}$ , due to the factors  $g_{\vec{k}, -\vec{k}, \vec{q}}^{\parallel\parallel\parallel\parallel}$  and  $g_{\vec{k}, -\vec{k}, \vec{q}}^{\perp\perp\parallel\parallel}$  that behave as  $\sim k^2$  for  $k \rightarrow 0$ . In this limit,

we obtain (see Appendix B 1)

$$\lim_{T \rightarrow 0} \text{Re}\Sigma_k(\omega_{k,F}) \simeq \frac{\hbar\kappa^{1/2}k^2}{8\pi\rho^{1/2}} \times \left[ q_L^4 f\left(\frac{\Lambda}{q_L}\right) + q_T^4 f\left(\frac{\Lambda}{q_T}\right) \right], \quad (25)$$

where we have imposed an ultraviolet (UV) momentum cutoff  $\Lambda$  (which should be of the order of the Debye momentum,  $q_D$ ), and we have defined the function

$$f(x) = \frac{1}{2}x(x-2) + \log(1+x), \quad (26)$$

and introduced the two momentum scales<sup>49</sup>

$$q_L = \sqrt{(\lambda + 2\mu)/\kappa} \\ q_T = \sqrt{\mu/\kappa}. \quad (27)$$

Notice [Eqs. (25) and (26)] that besides logarithmic UV divergences, we have also obtained power law divergences. Careful inspection allows us to see that the main  $\Lambda^2$  divergence comes from the quartic local interaction,  $\mathcal{L}_{\text{int}}^{(4)}[h]$ , while the  $\Lambda$  and  $\log(\Lambda)$  divergences come from the interaction of in-plane with out-of-plane modes,  $\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h]$ . To first order in perturbation theory, the dispersion relation,  $\Omega_k$ , of the physical excitations is given by  $\rho\Omega_k^2 = \kappa k^4 + \text{Re}\Sigma_k(\omega_{k,F})$ . Note that, for  $k \rightarrow 0$ ,  $\Omega_k \sim k$  instead of  $\omega_{k,F} \sim k^2$ . It can be checked that, in the long wavelength limit, the result from Eq. (25) is the same as that obtained by setting  $\omega = 0$  in  $\Sigma_k(\omega)$ . This tells us that, for physical excitations, the frequency dependence of the self-energy can be neglected in the low temperature and long wavelength limit. We can estimate, in both the high temperature and low temperature limits, the momentum scale,  $k_c$ , below which anharmonic effects become dominant, as determined by the Ginzburg criterion<sup>4</sup>  $\Sigma_{k_c}(\omega_{k_c,F}) = \kappa k_c^4$ . By doing such analysis, we obtain<sup>50</sup>

$$k_c^{(T \rightarrow \infty)} \simeq \sqrt{\frac{3k_B T}{16\pi} \frac{4\mu(\lambda + \mu)}{\kappa^2(\lambda + 2\mu)}}, \quad (28) \\ k_c^{(T \rightarrow 0)} \simeq \sqrt{\frac{\hbar}{8\pi\rho^{1/2}\kappa^{1/2}} \left[ q_L^4 f\left(\frac{\Lambda}{q_L}\right) + q_T^4 f\left(\frac{\Lambda}{q_T}\right) \right]^{1/2}}. \quad (29)$$

For typical graphene values we obtain  $k_c^{(T \rightarrow \infty)} \simeq 0.17 \text{\AA}^{-1}$  at  $T = 300\text{K}$  (in agreement with what was found in Ref. 27), and setting  $\Lambda = q_D$ , we obtain  $k_c^{(T \rightarrow 0)} \simeq 0.1 \text{\AA}^{-1}$  at  $T = 0$ . It is useful to write approximate expressions for  $k_c$  in the limit  $T \rightarrow 0$  when  $\Lambda/q_{T/L} \gg 1$  and  $\Lambda/q_{T/L} \ll 1$ . Expanding the function  $f(x)$ , we obtain the following approximate expressions:

$$k_c^{(T \rightarrow 0)} \simeq \begin{cases} \left( \frac{\hbar}{16\pi\sqrt{\rho\kappa}} \frac{\lambda+3\mu}{\kappa} \right)^{1/2} \Lambda, & \Lambda \gg q_{T/L}, \\ \left( \frac{\hbar}{24\pi\sqrt{\rho\kappa}} \right)^{1/2} (q_L + q_T)^{1/2} \Lambda^{3/2}. & \Lambda \ll q_{T/L}. \end{cases} \quad (30)$$

To determine the actual importance of the anharmonic effects in suspended samples of crystalline membranes, one has to compare the anharmonic scale  $k_c$ , with the minimum momentum allowed by the finite size of the sample  $\sim 1/L$  and with the momentum scale due to residual strains  $\sim q_L \bar{u}$ , where  $\bar{u}$  is the strain<sup>13</sup>. We can also estimate the temperature,  $T^*$ , at which the crossover from the classical to the quantum regime occurs, by equating  $\lim_{T \rightarrow \infty} \text{Re} \Sigma_k(\omega_k, F) = \lim_{T \rightarrow 0} \text{Re} \Sigma_k(\omega_k, F)$ . Since, in both regimes, the leading contribution to the self-energy goes like  $k^2$ , this is equivalent to comparing  $k_c^{(T \rightarrow \infty)}$  with  $k_c^{(T \rightarrow 0)}$ . We obtain

$$T^* \simeq \frac{2\hbar}{3k_B \rho^{1/2} \kappa^{1/2}} \frac{(\lambda + 2\mu) \kappa^2}{4\mu(\lambda + \mu)} \times \left[ q_L^4 f\left(\frac{\Lambda}{q_L}\right) + q_T^4 f\left(\frac{\Lambda}{q_T}\right) \right], \quad (31)$$

a quantity that depends on the UV cutoff  $\Lambda$ . Expanding once again the function  $f(x)$  we obtain

$$T^* \simeq \begin{cases} \frac{\hbar \kappa^{1/2}}{3k_B \rho^{1/2}} \frac{(\lambda + 2\mu)(\lambda + 3\mu)}{4\mu(\lambda + \mu)} \Lambda^2, & \Lambda \gg q_T/L, \\ \frac{2\hbar \kappa}{9k_B \rho^{1/2}} \frac{\lambda + 2\mu}{4\mu(\lambda + \mu)} (\sqrt{\lambda + 2\mu} + \sqrt{\mu}) \Lambda^3, & \Lambda \ll q_T/L. \end{cases} \quad (32)$$

For typical graphene values, setting  $\Lambda = q_D$ , we obtain a value of  $T^* \sim 70 - 90$  K (depending on the values we take for the elastic constants, which depend themselves on the temperature<sup>5,44</sup>). Below this temperature, the contribution to the self-energy from the quantum interaction terms  $R_q^{\parallel\parallel\parallel\parallel}$  and  $R_q^{\perp\perp\perp\perp}$  should become dominant. Fig. 1 shows the different regions in the  $(T, k)$  space where anharmonic and quantum effects give the main contribution.

It is interesting to notice that both in the classical and in the quantum regime, the self-energy has the same  $k^2$  dependence, with negligible frequency dependence. However, it must be kept in mind that the main contributions to the self-energy have very different origins. In fact, it can be checked (see Appendix B1) that the contribution of the interaction term  $R_q^{\perp\perp\perp\perp, \text{cl}}$  for  $T \rightarrow 0$  goes as  $\Sigma_k^{\text{cl}} \propto k^4 \log(\Lambda/k)$ . In this  $T \rightarrow 0$  limit, it is clear that the contribution to the self-energy from  $R_q^{\parallel\parallel\parallel\parallel}$  and  $R_q^{\perp\perp\perp\perp}$  (25), dominates over the contribution from  $R_q^{\perp\perp\perp\perp, \text{cl}}$  at small momenta. If we would extend the result (25) to large  $k$ , going beyond its long wavelength validity region, it is clear that it would also dominate over the contribution from  $R_q^{\perp\perp\perp\perp, \text{cl}}$ , for large enough  $k$ . One could think that there might exist an intermediate momentum region where  $\Sigma_k^{\text{cl}}$  actually dominates over the term (25). It can be checked however that for usual graphene values Eq. (25) always dominates and that increasing the bending rigidity,  $\kappa$ , (i.e. to account for stiffer crystalline membranes as single-layer MoS<sub>2</sub>) makes this dominance even stronger.

The next step to go beyond first order perturbation theory for  $T \rightarrow 0$ , is to perform a simple self-consistent calculation in the spirit of what was done by Nelson and

Peliti in Ref. 19. First, we notice that in first order perturbation theory, the in-plane mode propagator has only logarithmic corrections due to anharmonic effects. This is a much weaker effect than for the out-of-plane phonons and therefore we will ignore it. Furthermore, we also neglect the frequency dependence of the out-of-plane self-energy and write the full out-of-plane correlation function as  $G_{\mathbf{k}} \simeq \left( -\rho (ik_n)^2 + \rho \omega_{k,F}^2 + \kappa k_c^\eta k^{4-\eta} \right)^{-1}$ , where we have written the self-energy as  $\Sigma_k = \kappa k_c^\eta k^{4-\eta}$ , with  $k_c$  the harmonic-to-anharmonic crossover momentum, and  $\eta$  a characteristic exponent, both to be determined in a self-consistent way. The main contribution to the self-energy in the long wavelength limit still comes from  $R_q^{\parallel\parallel\parallel\parallel}$  and  $R_q^{\perp\perp\perp\perp}$ , and since the factors  $g_{\vec{k}, -\vec{k}, \vec{q}}^{\parallel\parallel\parallel\parallel}$  and  $g_{\vec{k}, -\vec{k}, \vec{q}}^{\perp\perp\perp\perp}$  behave as  $\sim k^2$  for  $k \rightarrow 0$ , we obtain a value of  $\eta = 2$ , in agreement with first order perturbation theory. This is an important result which justifies the use of first order perturbation theory contrary to the classical regime, where the *perturbative*  $\eta = 2$  exponent is changed to  $\eta = 1$  when the same kind of self-consistent calculation is performed<sup>19</sup>. The present result of  $\eta = 2$  indicates that quantum anharmonic effects act as an effective positive external strain, which contributes to the stabilization of the 2D phase of the membrane (see also Ref. 32).

Furthermore, the corresponding  $k_c$  in this self-consistent approximation is determined by the condition

$$k_c^2 = \frac{(\lambda + 2\mu) \hbar k^2}{8\pi \rho^{1/2} \kappa^{3/2}} \int \frac{dq q^3}{\sqrt{q^4 + k_c^2 q^2 + q_L q}} + \frac{\mu \hbar k^2}{8\pi \rho^{1/2} \kappa^{3/2}} \int \frac{dq q^3}{\sqrt{q^4 + k_c^2 q^2 + q_T q}}. \quad (33)$$

Notice that the integral over  $q$  is convergent in the  $q \rightarrow 0$  limit and does not depend on  $k$ . In the classical theory, instead, the integral is singular in  $k$  as  $k^{\eta-2}$  and  $0 < \eta \leq 2$ <sup>19</sup>. In fact, in the integral (33), the term  $q_L q$  dominates the denominator of the integrand for small  $q$ , while  $q^2$  dominates for large  $q$ . Therefore, the term  $k_c^2 q^2$  will only contribute for intermediate values of  $q$  and the integral should be weakly dependent on  $k_c$ . Performing the integral over momentum we obtain

$$k_c^2 = \frac{\hbar}{8\pi \rho^{1/2} \kappa^{1/2}} \left[ q_L^4 F\left(\frac{\Lambda}{q_L}, \frac{k_c}{q_L}\right) + q_T^4 F\left(\frac{\Lambda}{q_T}, \frac{k_c}{q_T}\right) \right], \quad (34)$$

where we have defined the function

$$F(x, y) = \frac{1}{2} x \left( \sqrt{x^2 + y^2} - 2 \right) + \frac{1}{2} (2 - y^2) \sinh^{-1} \left( \frac{x}{y} \right) + \sqrt{1 - y^2} \tanh^{-1} \left( \frac{x}{\sqrt{1 - y^2}} \right) - \sqrt{1 - y^2} \tanh^{-1} \left( \frac{x}{\sqrt{(1 - y^2)(x^2 + y^2)}} \right). \quad (35)$$

The function  $F(x, y)$  reduces to  $f(x)$  in the limit of  $y \rightarrow 0$ . Solving the self-consistent condition (34) for  $k_c$  we obtain a value that, for typical graphene parameters, is nearly unchanged with respect to the perturbative result  $k_c \approx 0.1 \text{ \AA}^{-1}$ . The relative difference between the perturbative and self-consistent value is of the order of  $10^{-4}$ .

We are now in a position to calculate thermodynamics quantities as the thermal expansion,  $\alpha_V$ , and the specific heat,  $c_p$ , in the low temperature quantum regime, which will be the focus of the next section.

## IV. THERMODYNAMIC QUANTITIES

### A. Thermal expansion

The areal thermal expansion coefficient is defined as

$$\alpha_V = \frac{1}{V} \left( \frac{\partial \Delta V}{\partial T} \right)_p, \quad (36)$$

where  $\Delta V$  is the change in the area of the membrane (to be understood as the area of the membrane projected onto the reference  $x-y$  plane),  $V$  is the area of the undistorted membrane, and the index  $p$  indicates that the process occurs at constant pressure/stress. Recalling that the relative change of area is given by  $\Delta V/V = \langle \partial_i u_i \rangle$ , the thermal expansion can be most efficiently computed by adding to the Euclidean Lagrangian (1) an extra term of the form  $\mathcal{L}_\sigma[\vec{u}] = -\sigma \partial_i u_i$ , that describes an externally applied homogeneous and isotropic stress  $\sigma$  to the membrane. The relative expansion at zero external stress can therefore be obtained from

$$\frac{\Delta V}{V} = \frac{1}{\beta V} \frac{\partial}{\partial \sigma} \log Z[\sigma] \Big|_{\sigma=0}, \quad (37)$$

where  $Z[\sigma] = \int D[\vec{u}, h] \exp(-\mathcal{S}[\vec{u}, h] - \mathcal{S}_\sigma[\vec{u}])$ , with  $\mathcal{S}_\sigma[\vec{u}] = -\sigma \int_0^\beta d\tau \int d^2x \partial_i u_i$ . Notice that  $\sigma$  couples to the  $\mathbf{q} = 0$  component of  $\partial_i u_i$ . Therefore, we can perform a shift of  $\partial_i u_j$  in the functional path integral  $\partial_i u_j \rightarrow \partial_i u_j + c_{ijkl}^{-1} \delta^{kl} \sigma$ , where  $c_{ijkl}^{-1}$  is the inverse of the elastic moduli tensor), and cancel the linear term in  $\partial_i u_i$  of  $\mathcal{S}_\sigma[\vec{u}]$  at the expense of generating two new terms in the Euclidean Lagrangian density: (i) one of the form  $-\sigma^2 c_{ijjj}^{-1}/2$ , which does not lead to any thermal expansion, (ii) and another term of the form  $\sigma \partial_i h \partial_i h/2$ , which is the term responsible for the thermal expansion. Therefore we can write the thermal expansion at zero external stress as<sup>40</sup>

$$\alpha_V = -\frac{1}{2} \frac{\partial}{\partial T} \left( \frac{1}{\beta V} \sum_{\mathbf{k}} k^2 G_{\mathbf{k}} \right). \quad (38)$$

Replacing in Eq. (38) the full out-of-plane correlation function (10) by the bare, harmonic, one (7) is equivalent to performing a quasi-harmonic treatment of the thermal

expansion of a membrane<sup>40</sup>. In the quasi-harmonic approximation one obtains

$$\alpha_V^{\text{qh}} = -\frac{\hbar^2}{8\rho k_B T^2} \int_{q_{\min}}^\Lambda \frac{d^2 k}{(2\pi)^2} \frac{k^2}{\sinh^2(\hbar\omega_{k,F}/(2k_B T))}, \quad (39)$$

where the UV momentum cutoff is of the order of the inverse lattice spacing,  $\Lambda \sim 1/a$ , and the IR cutoff is of the order of the inverse of the membrane size,  $q_{\min} \sim 1/L$ . For not too high temperatures, we can safely take the limit  $\Lambda \rightarrow \infty$  in Eq. (39), but the integral is divergent for  $q_{\min} \rightarrow 0$ . Keeping  $q_{\min}$  finite, we can perform the integration analytically. In the quasi-harmonic approximation, the thermal expansion is given by  $\alpha_V^{\text{qh}} = -k_B \mathcal{I}(t)/(8\pi\kappa)$ , where

$$\mathcal{I}(t) = \int_{\frac{1}{2t}}^\infty \frac{dx}{\sinh(x)^2} = \frac{1}{2t} \coth\left(\frac{1}{2t}\right) - \log \left[ 2 \sinh\left(\frac{1}{2t}\right) \right], \quad (40)$$

and  $t = (k_B T \rho^{1/2}) / (\hbar \kappa^{1/2} q_{\min}^2)$ . The fact that ignoring anharmonic effects makes the membrane unstable, is reflected in that the limits  $T \rightarrow 0$  and  $L \rightarrow \infty$  do not commute. As a matter of fact for  $t \gg 1$  we have  $\mathcal{I}(t) \sim 1 + \log(t)$  while for  $t \ll 1$  we have  $\mathcal{I}(t) \sim e^{-1/t}/t$ . Therefore, in the quasi-harmonic approximation the thermal expansion depends crucially on the size of the membrane even for  $L \rightarrow \infty$ . This fact is important when interpreting numerical results for the thermal expansion of membrane like materials based on the quasi-harmonic theory. In these numerical calculations the thermal expansion is calculated by (finite difference) differentiation of the temperature dependence of the lattice parameter calculated for finite size supercells<sup>43,51,52</sup>. We will now see how going beyond the quasi-harmonic approximation will make the limits  $T \rightarrow 0$  and  $L \rightarrow \infty$  commute so that the thermodynamic limit can be taken without ambiguity and at the same time satisfying the third law of thermodynamics. Taking into account the results from Eqs. (24) and (25), we neglect the frequency dependence of the self-energy, writing the full out-of-plane correlation function as  $G_{\mathbf{k}}^{-1} = -\rho (ik_n)^2 + \rho \Omega_{\mathbf{k}}^2$ , with  $\Omega_{\mathbf{k}} = \sqrt{(\kappa k^4 + \Sigma_{\mathbf{k}})/\rho}$ . Since, according to Eq. (25), the self-energy  $\Sigma_{\mathbf{k}}$  goes to a constant at  $T = 0$ , we will ignore the temperature dependence of the self-energy for  $T \simeq 0$ , approximating  $\partial \Omega_{\mathbf{k}}/\partial T \simeq 0$ . With this approximations, the thermal expansion is given by Eq. (39) with the replacement  $\omega_{k,F} \rightarrow \Omega_{\mathbf{k}}$ . Now the integral is finite both in the IR and in the UV and we can take  $q_{\min} \rightarrow 0$  and  $\Lambda \rightarrow \infty$ . Since in the  $T \rightarrow 0$  limit the main contribution will come from small momentum modes, we approximate  $\rho \Omega_{\mathbf{k}}^2 = \kappa k^4 + \Sigma_{\mathbf{k}} \simeq \kappa k_c^\eta k^{4-\eta}$ , where  $\eta$  is a characteristic exponent whose value depends on the approximation used to solve the theory. After a straightforward calculation we obtain

$$\alpha_V = -\frac{k_B}{2\pi(4-\eta)\kappa} \left( \frac{2\rho^{1/2} k_B T}{\hbar \kappa^{1/2} k_c^2} \right)^{2\eta/(4-\eta)} I_\eta, \quad (41)$$

where we have defined  $I_\eta = \int_0^\infty dx x^{(4+n)/(4-n)} / \sinh^2(x)$ , which for  $\eta = 2$  evaluates to  $I_2 = 3\zeta(3)/2$ . Since we have obtained  $\eta = 2$  within first order perturbation theory as well as in the partially self-consistent approximation, we obtain that  $\alpha_V \propto -T^2$  at low temperature. Most importantly, this result correctly predicts a vanishing thermal expansion coefficient for  $T \rightarrow 0$ , satisfying the third law of thermodynamics even in the limit of an infinite membrane,  $L \rightarrow \infty$ .

## B. Specific heat

Another important thermodynamic physical property, probing the low-energy elementary excitations in the system, is the specific heat. We are working in an ensemble with constant external stress  $\sigma_{ij}$ . The specific heat at constant pressure/stress can be computed from

$$c_p = \left( \frac{\partial H}{\partial T} \right)_p, \quad (42)$$

where  $H = U - u_{ij}\sigma_{ij}$  is the enthalpy of the system per unit area, with  $U$  the total energy of the system per unit area. Since we are working at zero external stress, the enthalpy coincides with the total internal energy. The total energy of the system can be expressed in terms of two-point correlation functions, using a modified Migdal-Galitskii-Koltun energy sum rule<sup>53,54</sup>. The total energy of the membrane per unit area can be written as  $U = U^{(\text{out})} + U^{(\text{in})}$  with (see Appendix C for the proof)

$$U^{(\text{out})} = \frac{1}{4} \frac{1}{\beta V} \sum_{\mathbf{k}} \left( 3\rho (ik_n)^2 + \kappa k^4 \right) G_{\mathbf{k}}, \quad (43)$$

$$U^{(\text{in})} = \frac{1}{\beta V} \sum_{\mathbf{q}} \rho (iq_n)^2 D_{\mathbf{q}}^{ii}. \quad (44)$$

Although in the anharmonic theory in-plane and out-of-plane modes are coupled, we can attribute  $U^{(\text{out})}$  mostly to out-of-plane modes and  $U^{(\text{in})}$  mostly to in-plane modes. In the same way, the specific heat can also be split in these two contributions,  $c_p = c_p^{(\text{out})} + c_p^{(\text{in})}$ , where  $c_p^{(\text{out})} = \partial U^{(\text{out})} / \partial T$  and  $c_p^{(\text{in})} = \partial U^{(\text{in})} / \partial T$ . As previously, we ignore the frequency dependence of the self-energy, and obtain the energy per unit area

$$U^{(\text{out})} = \frac{\hbar}{4} \int \frac{d^2k}{(2\pi)^2} \frac{\coth(\beta\hbar\Omega_k/2)}{2\rho\Omega_k} (3\rho\Omega_k^2 + \kappa k^4). \quad (45)$$

In the  $T \rightarrow 0$  limit, making the same approximations as for the thermal expansion, we can write the specific heat at constant pressure per unit area as

$$c_p^{(\text{out})} = \frac{3}{8\pi} k_B k_c^2 \left( \frac{2\rho^{1/2} k_B T}{\hbar \kappa^{1/2} k_c^2} \right)^{4/(4-\eta)} L_\eta, \quad (46)$$

where  $L_\eta = \int_0^\infty dx x^{(8-\eta)/(4-\eta)} / \sinh^2(x)$ . For  $\eta = 2$ , which is the value corresponding to the approximations

used in this paper, we have  $L_2 = 3\zeta(3)/2$  and  $c_p^{(\text{out})} \propto T^2$ . This result is to be contrasted with the one obtained at the harmonic level, which would predict  $c_p^{(\text{out})} \propto T$ . It is a consequence of the change of dispersion of flexural modes from  $\sim k^2$  to  $\sim k$  as discussed after Eq.(27). Regarding the contribution mostly due to in-plane modes, we can check that interactions lead only to a logarithmic correction of the in-plane modes correlation function (see Appendix B), which we will neglect. Therefore, the contribution mostly due to the in-plane modes reduces to the non-interacting one, which for  $T \rightarrow 0$  reduces to the expected  $T^2$  dependence

$$c_p^{(\text{in})} = k_B \left( \frac{2k_B T}{\hbar} \right)^2 \left( \frac{\rho}{\lambda + 2\mu} + \frac{\rho}{\mu} \right) L_2. \quad (47)$$

Therefore, taking into account at the same level anharmonic and quantum effects, one predicts an intermediate behavior  $T < T^{4/(4-\eta)} \leq T^2$  resulting from the coupling between in-plane and out-of-plane modes. To first order in perturbation theory, both  $c_p^{(\text{out})}$  and  $c_p^{(\text{in})}$  are proportional to  $T^2$ . Notice, that the harmonic theory calculated for graphene<sup>42,43</sup>, predicts  $c_p \propto T$  up to temperatures as high as 100 K which is about our  $T^*$ . That is why we believe that the linear  $T$  dependence should not be observable in graphene for which we predict instead a  $T^2$  dependence.

## V. CONCLUSIONS

In summary, in this paper we have calculated several thermodynamic properties of crystalline membranes in the low temperature quantum regime. Toward that end we have employed both a first order perturbation theory as well as a one-loop self-consistent approximation in which we have ignored any possible renormalization of the in-plane Lamé elastic constants. We have derived the effective action for the out-of-plane modes by integrating out exactly the in-plane modes. This procedure leads to frequency dependent anharmonic interactions (retardation effects) which we have shown to be the dominant effect in the zero temperature limit. This is to be contrasted with the high temperature classical regime, where retardation can be ignored. We have further evaluated the leading of the anharmonic out-of-plane mode self-energy in the  $T \rightarrow 0$  limit and estimated the available phase space, described by a crossover momentum  $k_c$ , which defines a wavelength above which anharmonic effects dominate the theory in the quantum regime. For graphene we estimate  $k_c \sim 0.1 \text{ \AA}^{-1}$ , about 0.6 of the value estimated for the crossover from the harmonic to the anharmonic regime in the classical case at room temperature<sup>27</sup>. Based on this result, we estimate a crossover temperature  $T^*$  between the classical and quantum regimes. For typical graphene parameters, this crossover temperature is  $T^* \sim 70 - 90 \text{ K}$ .

By using the calculated correlation functions in the quantum anharmonic regime, we establish the tempera-

ture dependence of thermodynamic properties. In the  $T \rightarrow 0$  limit, we find a power-law behavior for both the thermal expansion coefficient  $\alpha_V$  and the specific heat  $c_p$ . In general they are characterized by an anomalous exponent related to the characteristic exponent  $\eta$  of the elementary excitations, namely  $\alpha_V \propto T^{2\eta/(4-\eta)}$  and  $c_p \propto T^{4/(4-\eta)}$ . To first order perturbation theory, as well as in the one-loop self-consistent approximation we find  $\eta = 2$ , which means that both  $\alpha_V$  and  $c_p$  are proportional to  $T^2$ .

This work is a first step towards the full understanding of the physics of a quantum crystalline membrane. We know that for a classical crystalline membrane, it is necessary to go beyond perturbation theory and use a more elaborate technique, such as a full self-consistent calculation. Also for the quantum case, more advanced methods such as quantum Monte Carlo or functional renormalization group are needed to solve the problem quantitatively. Nevertheless, the perturbative calculation that we have presented is already sufficient to show that a simultaneous treatment of quantum and anharmonic effects is necessary to have a vanishing thermal expansion and specific heat at zero temperature, in accordance with the third law of thermodynamics. This approach also allows us to estimate the crossover temperature between the classical and the quantum regime.

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### Appendix A: Derivation of effective action for the out-of-plane modes

In this appendix, we briefly summarize the steps performed to derive the effective action (13). Notice that the cubic action  $S_{\text{int}}^{(3)}[\vec{u}, h]$ , corresponding to Eq. (4), can be written in terms of Fourier components as

$$S_{\text{int}}^{(3)}[\vec{u}, h] = \frac{i}{2\sqrt{\beta V}} \sum_{\mathbf{k}, \mathbf{q}} u_{\mathbf{q}}^i c^{ijkl} q_j (k - q)_k k_l h_{\mathbf{k} - \mathbf{q}} h_{-\mathbf{k}}, \quad (\text{A1})$$

where we have introduced the elastic moduli tensor for an isotropic membrane  $c^{ijkl} = \lambda \delta^{ij} \delta^{kl} + \mu (\delta^{ik} \delta^{jl} + \delta^{il} \delta^{jk})$ . Integrating out the field  $\vec{u}$ , amounts to performing a Gaussian integration of the form  $\int dx e^{-\frac{1}{2a}x^2 - bx} = e^{\frac{1}{2}b^2a} \left( \int dx e^{-\frac{1}{2a}x^2} \right)$ . As a result, the partition function can be written as

$$Z = \int D[\vec{u}, h] \exp(-S[\vec{u}, h]) \\ = Z_0[\vec{u}] \int D[h] \exp(-S_{\text{eff}}[h]), \quad (\text{A2})$$

where  $Z_0[\vec{u}] = \int D[\vec{u}] \exp\left(-\int_0^\beta d\tau \int d^2x \mathcal{L}_u^0[\vec{u}]\right)$  is the non-interacting partition function for the in-plane modes. Integrating out the in-plane modes will therefore generate a new quartic interaction term for the out-of-plane modes that is mediated by the in-plane modes. Therefore, we obtain an effective Euclidean action of the form of Eq. (13), with the interaction tensor given by

$$R_{\mathbf{q}}^{ijkl} = c^{ijkl} - c^{ijj'j'} \langle u_{ij'j', \mathbf{q}} u_{k'l', -\mathbf{q}} \rangle_0 c^{k'l'kl}, \quad (\text{A3})$$

where  $\langle \rangle_0$  represents averaging with respect to the harmonic theory and  $u_{ij} = (\partial_i u_j + \partial_j u_i)/2$  is the in-plane strain tensor. The first term of  $R_{\mathbf{q}}^{ijkl}$  is due to the quartic interaction  $\mathcal{L}_{\text{int}}^{(4)}[h]$ , as given by Eq. (5), while the second term is the in-plane mode mediated interaction due to the cubic term  $\mathcal{L}_{\text{int}}^{(3)}[\vec{u}, h]$ , Eq. (4). From Eq. (A3), it is easy to see that  $R_{\mathbf{q}}^{ijkl}$  obeys the same symmetries as the elastic moduli tensor  $c^{ijkl}$ , i.e.,  $R_{\mathbf{q}}^{ijkl} = R_{\mathbf{q}}^{jikl} = R_{\mathbf{q}}^{klij}$ . Just like in the classical problem, it is necessary to analyse the cases  $\mathbf{q} \neq 0$  and  $\mathbf{q} = 0$  separately<sup>4</sup>. The in-plane strain tensor  $u_{ij}$  must be split into its  $\mathbf{q} = 0$  homogeneous component,  $u_{ij}^0$ , and  $\mathbf{q} \neq 0$  components, which can be expressed in terms of phonon modes. For  $\mathbf{q} \neq 0$ , we have

$$\langle u_{ij, \mathbf{q}} u_{kl, -\mathbf{q}} \rangle_0 = \frac{1}{2} q^2 D_{\mathbf{q}}^{L,0} (P_{ik}^L P_{jl}^L + P_{jk}^L P_{il}^L) \\ + \frac{1}{2} q^2 D_{\mathbf{q}}^{T,0} (P_{ik}^L P_{jl}^T + P_{jk}^L P_{il}^T) \quad (\text{A4})$$

where  $P_{ij}^L = q_i q_j / q^2$  and  $P_{ij}^T = \delta_{ij} - q_i q_j / q^2$  are, respectively, the longitudinal and transverse projectors along the vector  $\vec{q}$ . Therefore, for  $\mathbf{q} \neq 0$ , the in-plane mode mediated interaction can be written as

$$c^{ijj'j'} \langle u_{ij'j', \mathbf{q}} u_{k'l', -\mathbf{q}} \rangle_0 c^{k'l'kl} = \\ = \lambda^2 q^2 D_{\mathbf{q}}^{L,0} P_{ij}^T P_{kl}^T + (\lambda + 2\mu)^2 q^2 D_{\mathbf{q}}^{L,0} P_{ij}^L P_{kl}^L \\ + \lambda (\lambda + 2\mu) q^2 D_{\mathbf{q}}^{L,0} (P_{ij}^L P_{kl}^T + P_{ij}^T P_{kl}^L) \\ + \mu^2 q^2 D_{\mathbf{q}}^{T,0} (P_{ik}^T P_{jl}^L + P_{il}^T P_{jk}^L + P_{jk}^T P_{il}^L + P_{ik}^L P_{jl}^T). \quad (\text{A5})$$

The elastic moduli tensor can also be decomposed in terms of longitudinal and transverse projectors

$$c^{ijkl} = \lambda P_{ij}^T P_{kl}^T + \mu (P_{ik}^T P_{jl}^T + P_{il}^T P_{jk}^T) \\ + (\lambda + 2\mu) P_{ij}^L P_{kl}^L + \lambda (P_{ij}^T P_{kl}^L + P_{ij}^L P_{kl}^T) \\ + \mu (P_{ik}^T P_{jl}^L + P_{ik}^L P_{jl}^T + P_{il}^T P_{jk}^L + P_{il}^L P_{jk}^T). \quad (\text{A6})$$



In 2D, we have  $P_{ij}^T P_{kl}^T = P_{ik}^T P_{jl}^T = P_{il}^T P_{jk}^T$ . Therefore, in 2D  $R_{\mathbf{q}}^{ijkl}$  has only 4 independent components. As a result, the effective interaction for  $\mathbf{q} \neq 0$  can be expressed in the basis  $\{\hat{e}_{\parallel}, \hat{e}_{\perp}\}$  as

$$\begin{aligned} R_{\mathbf{q}}^{ijkl} &= R_{\mathbf{q}}^{\perp\perp\perp\perp} \hat{e}_{\perp}^i \hat{e}_{\perp}^j \hat{e}_{\perp}^k \hat{e}_{\perp}^l + R_{\mathbf{q}}^{\parallel\parallel\parallel\parallel} \hat{e}_{\parallel}^i \hat{e}_{\parallel}^j \hat{e}_{\parallel}^k \hat{e}_{\parallel}^l \\ &+ R_{\mathbf{q}}^{\perp\perp\parallel\parallel} \left( \hat{e}_{\perp}^i \hat{e}_{\perp}^j \hat{e}_{\parallel}^k \hat{e}_{\parallel}^l + (ij \leftrightarrow jl) \right) \\ &+ R_{\mathbf{q}}^{\perp\parallel\perp\parallel} \left( \hat{e}_{\perp}^i \hat{e}_{\parallel}^j \hat{e}_{\perp}^k \hat{e}_{\parallel}^l + (i \leftrightarrow j) + (k \leftrightarrow l) + (ij \leftrightarrow jl) \right), \end{aligned} \quad (\text{A7})$$

with  $R_{\mathbf{q}}^{\perp\perp\perp\perp}$ ,  $R_{\mathbf{q}}^{\parallel\parallel\parallel\parallel}$ ,  $R_{\mathbf{q}}^{\perp\perp\parallel\parallel}$  and  $R_{\mathbf{q}}^{\perp\parallel\perp\parallel}$  given by Eqs. (14)-(18). Notice that for the generalized problem of a  $D > 2$  dimensional membrane,  $R_{\mathbf{q}}^{ijkl}$  will have an extra independent component which involves only the shear modulus  $\mu$ . For the  $\mathbf{q} = 0$  component, the quadratic Lagrangian density (3) reads  $\mathcal{L}_u^0 [u_{ij}^0] = \frac{1}{2} c_{ijkl} u_{ij}^0 u_{kl}^0$ . Therefore,  $\langle u_{ij}^0 u_{kl}^0 \rangle_0$  is simply the tensor  $c_{ijkl}^{-1}$ , which for an isotropic membrane reads  $c_{ijkl}^{-1} = -\frac{\lambda}{4\mu(\lambda+\mu)} \delta_{ij} \delta_{kl} + \frac{1}{4\mu} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$ . For  $\mathbf{q} = 0$ , we have  $R_{\mathbf{q}=0}^{ijkl} = c^{ijkl} - c^{ij'j'} c_{i'j'k'l'}^{-1} c^{k'l'kl} = 0$ . This justifies the exclusion of the  $\mathbf{q} = 0$  component from the interaction term in Eq. (13), just as in the classical problem.

## Appendix B: Perturbative evaluation of the self-energies

### 1. Out-of-plane mode self-energy

To first order in the interaction, the self-energy of the out-of-plane mode is given by

$$\Sigma_{\mathbf{k}} = \frac{1}{\beta V} \sum_{\mathbf{q}} R_{\mathbf{q}}^{ijkl} (k+q)_i k_j (k+q)_k k_l G_{\mathbf{k}+\mathbf{q}}^0, \quad (\text{B1})$$

which can be decomposed into the sum of one *classical* term plus 4 *quantum* terms

$$\Sigma_{\mathbf{k}} = \Sigma_{\mathbf{k}}^{\text{cl}} + \Sigma_{\mathbf{k}}^{\perp\perp\perp\perp, \text{qt}} + \Sigma_{\mathbf{k}}^{\parallel\parallel\parallel\parallel, \text{qt}} + \Sigma_{\mathbf{k}}^{\perp\perp\parallel\parallel, \text{qt}} + \Sigma_{\mathbf{k}}^{\perp\parallel\perp\parallel, \text{qt}}, \quad (\text{B2})$$

where the *classical* contribution is given by

$$\Sigma_{\mathbf{k}}^{\text{cl}} = \frac{4\mu(\lambda+\mu)}{\lambda+2\mu} \frac{1}{\beta V} \sum_{\mathbf{q}} g_{\vec{k}, -\vec{k}, \vec{q}}^{\perp\perp\perp\perp} G_{\mathbf{k}+\mathbf{q}}^0 \quad (\text{B3})$$

and the *quantum* terms have the general form

$$\Sigma_{\mathbf{k}}^{M, \text{qt}} = C^M \frac{1}{\beta V} \sum_{\mathbf{q}} g_{\vec{k}, -\vec{k}, \vec{q}}^M \frac{-\rho (iq_n)^2}{-\rho (iq_n)^2 + \rho \omega_{q, M}^2} G_{\mathbf{k}+\mathbf{q}}^0, \quad (\text{B4})$$

with the label  $M$  running over  $\{\perp\perp\perp\perp, \parallel\parallel\parallel\parallel, \perp\perp\parallel\parallel, \perp\parallel\perp\parallel\}$ .  $g_{\vec{k}, \vec{p}, \vec{q}}^M$  are given by Eqs. (20)-(23);  $C^M$  are given by  $C^{\perp\perp\perp\perp} = \lambda^2/(\lambda+2\mu)$ ,  $C^{\parallel\parallel\parallel\parallel} = \lambda+2\mu$ ,  $C^{\perp\perp\parallel\parallel} = \lambda$ ,  $C^{\perp\parallel\perp\parallel} = \mu$ ; and  $\omega_{q, M} = \omega_{q, L}$  for  $M = \perp\perp\perp\perp, \parallel\parallel\parallel\parallel, \perp\perp\parallel\parallel$  while  $\omega_{q, \perp\parallel\perp\parallel} = \omega_{q, T}$ .

a. *Contribution from classical term:  $\Sigma_{\mathbf{k}}^{\text{cl}}$*

Performing the sum over Matsubara frequencies for the *classical* contribution one obtains

$$\Sigma_{\mathbf{k}}^{\text{cl}} = \frac{4\mu(\lambda+\mu)}{\lambda+2\mu} \hbar \int \frac{d^2 q}{(2\pi)^2} k^4 \sin^4 \theta \frac{\coth(\beta \hbar \omega_{k+q, F}/2)}{2\rho \omega_{k+q, F}}. \quad (\text{B5})$$

In the high-temperature limit,  $T \rightarrow \infty$ , we have  $\coth(\beta \hbar \omega/2) \simeq 2k_B T/(\hbar \omega)$ , and we recover the well known result<sup>4</sup>

$$\lim_{T \rightarrow \infty} \Sigma_{\mathbf{k}}^{\text{cl}} \simeq \frac{4\mu(\lambda+\mu)}{(\lambda+2\mu)\kappa} \frac{3k_B T}{16\pi} k^2. \quad (\text{B6})$$

In the zero temperature limit,  $T \rightarrow 0$ , we have  $\coth(\beta \hbar \omega/2) \simeq 1$ . Therefore, the *classical* contribution becomes

$$\lim_{T \rightarrow 0} \Sigma_{\mathbf{k}}^{\text{cl}} \simeq \frac{4\mu(\lambda+\mu)}{\lambda+2\mu} \frac{\hbar}{2\sqrt{\rho\kappa}} \frac{3}{16\pi} k^4 \log\left(\frac{\Lambda}{k}\right), \quad (\text{B7})$$

where  $\Lambda$  is a UV momentum cutoff, which we identify as the Debye momentum. This *classical* contribution has to be compared with the *quantum* ones.

b. *Contribution from quantum terms:  $\Sigma_{\mathbf{k}}^{\perp\perp\perp\perp, \text{qt}}$ ,  $\Sigma_{\mathbf{k}}^{\parallel\parallel\parallel\parallel, \text{qt}}$ ,  $\Sigma_{\mathbf{k}}^{\perp\perp\parallel\parallel, \text{qt}}$  and  $\Sigma_{\mathbf{k}}^{\perp\parallel\perp\parallel, \text{qt}}$*

Performing the sum over Matsubara frequencies for the *quantum* contributions one obtains [with a small change of notation  $\Sigma_{\mathbf{k}} = \Sigma_{\mathbf{k}}(ik_n)$ ]

$$\begin{aligned} \Sigma_{\mathbf{k}}^{M, \text{qt}}(ik_n) &= \frac{\text{P}}{V} \sum_{\vec{q}} g_{\vec{k}, -\vec{k}, \vec{q}}^M \int \frac{dy}{\pi} b(y) \text{Im} R_{\mathbf{q}}^{M, \text{qt}}(y + i0^+, q) G_{\mathbf{k}+\mathbf{q}}^0(ik_n + y) \\ &+ \frac{\text{P}}{V} \sum_{\vec{q}} g_{\vec{k}, -\vec{k}, \vec{q}}^M \int \frac{dy}{\pi} b(y) R_{\mathbf{q}}^{M, \text{qt}}(y - ik_n, q) \text{Im} G_{\mathbf{k}+\mathbf{q}}^0(y + i0^+), \end{aligned} \quad (\text{B8})$$

where P denotes Cauchy principal value. Performing the analytic continuation  $ik_n \rightarrow \omega + i0^+$  and taking the real

part we obtain

$$\text{Re} \Sigma_{\mathbf{k}}^{M, \text{qt}}(\omega) = \frac{C^M}{\rho} \frac{\text{P}}{V} \sum_{\vec{q}} g_{\vec{k}, -\vec{k}, \vec{q}}^M \mathcal{K}^{M, \text{qt}}(\omega, k, q), \quad (\text{B9})$$

where we have defined

$$\begin{aligned} \mathcal{K}^{M,\text{qt}}(\omega, k, q) = & -\frac{\hbar b(\omega_{q,M})}{2\omega_{q,(A)}} \frac{\omega_{q,M}^2}{-(\omega + \omega_{q,M})^2 + \omega_{k+q,F}^2} \\ & + \frac{\hbar b(-\omega_{q,M})}{2\omega_{q,(A)}} \frac{\omega_{q,M}^2}{-(\omega - \omega_{q,M})^2 + \omega_{k+q,F}^2} \\ & + \frac{\hbar b(\omega_{k+q,F})}{2\omega_{k+q,F}} \frac{-(\omega_{k+q,F} - \omega)^2}{-(\omega_{k+q,F} - \omega)^2 + \omega_{q,M}^2} \\ & - \frac{\hbar b(-\omega_{k+q,F})}{2\omega_{k+q,F}} \frac{-(-\omega_{k+q,F} - \omega)^2}{-(-\omega_{k+q,F} - \omega)^2 + \omega_{q,M}^2}, \end{aligned} \quad (\text{B10})$$

with  $b(\omega) = (\exp(\beta\hbar\omega) - 1)^{-1}$  the Bose-Einstein distribution function. In the high temperature limit, we have  $b(\omega) \simeq k_B T / (\hbar\omega)$  and we obtain

$$\mathcal{K}_{T \rightarrow \infty}^{M,\text{qt}}(\omega, k, q) = \frac{k_B T}{\omega_{k+q,F}^2} \frac{\omega^2 (\omega^2 - \omega_{q,M}^2 - \omega_{k+q,F}^2)}{[(\omega_{k+q,F} + \omega_{q,M})^2 - \omega^2] [(\omega_{k+q,F} - \omega_{q,M})^2 - \omega^2]}. \quad (\text{B11})$$

In this form we can see explicitly that for  $\omega = 0$  we have  $\mathcal{K}_{T \rightarrow \infty}^{M,\text{qt}}(0, k, q) = 0$ , and the *quantum* terms do not give any contribution to the self-energy in the  $T \rightarrow \infty$  limit. Notice, however, that even if we take  $T \rightarrow \infty$  but keep  $\omega \neq 0$ , we obtain a non zero value of  $\text{Re}\Sigma_k^{M,\text{qt}}(\omega)$ . The analysis of this situation is subtle. One can check that for finite  $\omega$ , the integrations over momentum involved in computing  $\Sigma_{\mathbf{k}}^{\parallel\parallel\parallel\parallel,\text{qt}}$  and  $\Sigma_{\mathbf{k}}^{\parallel\perp\perp\perp,\text{qt}}$  are logarithmically divergent due to the point  $\vec{q} = -\vec{k}$ . This is a pathology of the first order perturbation theory that should disappear if a more complete self-consistent calculation is performed. If we replace the dispersion relation of the out-of-plane modes  $\omega_{k,F} \rightarrow \Omega_k \propto k^{(4-\eta)/2}$ , for any

$\eta > 0$ , the integrals become finite. Assuming that such regularization is performed, and to lowest order in the frequency, the quantum contributions are suppressed by a factor of  $\omega^2 / (c_{L/T} k)^2 \log(c_{L/T} k / \omega)$  when compared with the contribution from  $\Sigma_k^{\parallel}$  in the  $T \rightarrow \infty$  limit. We remind the reader that the dispersion of the physical excitation is obtained, to first order in perturbation theory, by  $\Omega_k^2 = \omega_{k,F}^2 + \text{Re}\Sigma_k(\omega_{k,F}) / \rho$ . Therefore, for the relevant long wavelength limit,  $k \rightarrow 0$ , the quantum contributions can be ignored in the  $T \rightarrow \infty$  limit, as expected. However, this situation changes dramatically in the quantum,  $T \rightarrow 0$ , limit. In this limit, we have  $b(\omega) \simeq -\Theta(-\omega)$ , where  $\Theta(x)$  is the step function, and therefore we obtain

$$\mathcal{K}_{T \rightarrow 0}^{M,\text{qt}}(\omega, k, q) = \frac{\hbar}{2\omega_{k+q,F}} \frac{\omega_{k+q,F} (\omega_{k+q,F} + \omega_{q,M}) - \omega^2}{(\omega_{k+q,F} + \omega_{q,M})^2 - \omega^2}. \quad (\text{B12})$$

We can see that we obtain finite contributions even if we set  $\omega = 0$ , in which case we have

$$\mathcal{K}_{T \rightarrow 0}^{M,\text{qt}}(0, k, q) = \frac{\hbar}{2} \frac{1}{\omega_{k+q,F} + \omega_{q,M}}. \quad (\text{B13})$$

With this in mind we will focus on the static,  $\omega = 0$ , behavior of the self-energy, which will be the dominant one in the long wavelength limit,  $k \rightarrow 0$ . Therefore, we set  $\omega = 0$  and expand to lowest order in  $k$ . The different

*quantum* contributions to the self-energy yield

$$\Sigma_{k,T \rightarrow 0}^{\perp\perp\perp\perp,\text{qt}}(0) \simeq \frac{\hbar}{2\sqrt{\rho\kappa}} \frac{\lambda^2}{\lambda + 2\mu} \frac{3k^4}{16\pi} \log\left(1 + \frac{\Lambda}{q_L}\right), \quad (\text{B14})$$

$$\Sigma_{k,T \rightarrow 0}^{\parallel\parallel\parallel\parallel}(0) \simeq \frac{\hbar}{2\sqrt{\rho\kappa}} \frac{(\lambda + 2\mu)^2}{\kappa} \frac{k^2}{4\pi} f\left(\frac{\Lambda}{q_L}\right), \quad (\text{B15})$$

$$\Sigma_{k,T \rightarrow 0}^{\perp\perp\parallel\parallel}(0) \simeq \frac{\hbar}{2\sqrt{\rho\kappa}} \frac{\lambda k^4}{8\pi} \left( \frac{2\Lambda}{q_L + \Lambda} - \log\left(1 + \frac{\Lambda}{q_L}\right) \right), \quad (\text{B16})$$

$$\Sigma_{k,T \rightarrow 0}^{\perp\parallel\perp\parallel}(0) \simeq \frac{\hbar}{2\sqrt{\rho\kappa}} \frac{\mu^2}{\kappa} \frac{k^2}{4\pi} f\left(\frac{\Lambda}{q_T}\right). \quad (\text{B17})$$

where we have once again imposed an UV momentum cutoff  $\Lambda$ , with  $f(x)$  and  $q_{L/T}$  as given by Eqs. (26) and (27), respectively. Therefore, for  $T \rightarrow 0$ , the main contribution in the long wavelength limit comes from  $\Sigma_k^{\parallel\parallel\parallel\parallel}(0)$  and  $\Sigma_k^{\perp\perp\perp\perp}(0)$ .

For the on-shell case  $\omega = \omega_{k,F}$  and in the long wavelength limit  $k \rightarrow 0$ , the results (B14)-(B17) are not changed. This tells us that, at least at the perturbative level, the frequency dependence of the self-energy can be neglected for physical excitations in the long wavelength limit.

## 2. In-plane mode self-energy

Notice, that although  $\vec{u}$  no longer appears in  $\mathcal{S}_{\text{eff}}[h]$ , that does not mean that it is not affected by the inter-

actions. When computing any correlation function, one must remember that in the process of integrating out the in-plane modes, they were shifted by

$$u_{\mathbf{q}}^i \rightarrow v_{\mathbf{q}}^i + \frac{i}{2\sqrt{\beta V}} \sum_{\mathbf{k}, \mathbf{q}} (D_{\mathbf{q}}^0)^{ij} c^{jklm} q_k (k+q)_l k_m h_{\mathbf{k}+\mathbf{q}} h_{-\mathbf{k}}, \quad (\text{B18})$$

where the field  $v_{\mathbf{q}}^i$  is a free field, with Lagrangian given by the in-plane harmonic one,  $\mathcal{L}_u^0[\vec{u}]$ , as given by Eq. (3). Therefore, the full in-plane correlation function is given by

$$D_{\mathbf{q}}^{ij} = (D_{\mathbf{q}}^0)^{ij} + \frac{1}{4\beta V} (D_{\mathbf{q}}^0)^{ik} c^{klmn} q_l \sum_{\mathbf{k}, \mathbf{p}, \mathbf{q}} (k+q)_m k_n (p-q)_{m'} p_{n'} \langle h_{\mathbf{k}+\mathbf{q}} h_{-\mathbf{k}} h_{\mathbf{p}-\mathbf{q}} h_{-\mathbf{p}} \rangle c^{k'l'm'n'} q_{l'} (D_{\mathbf{q}}^0)^{k'j}. \quad (\text{B19})$$

To first order in perturbation theory, we decouple the four-point correlation function and obtain

$$D_{\mathbf{q}}^{ij} = (D_{\mathbf{q}}^0)^{ij} + (D_{\mathbf{q}}^0)^{ik} q_l c^{klmn} \Pi_{\mathbf{q}}^{mnm'n'} c^{m'n'k'l'} q_{k'} (D_{-\mathbf{q}}^0)^{l'j}, \quad (\text{B20})$$

where

$$\Pi_{\mathbf{q}}^{ijkl} = \frac{1}{2\beta V} \sum_{\mathbf{k}} (k+q)_i k_j (k+q)_k k_l G_{\mathbf{k}} G_{\mathbf{k}+\mathbf{q}}. \quad (\text{B21})$$

Just like in the harmonic theory, isotropy allows us to split  $D_{\mathbf{q}}^{ij}$  in a longitudinal and a transverse component,  $D_{\mathbf{q}}^{ij} = D_{\mathbf{q}}^L P_{ij}^L + D_{\mathbf{q}}^T P_{ij}^T$ , where  $P_{ij}^L = q_i q_j / q^2$  and  $P_{ij}^T = \delta_{ij} - q_i q_j / q^2$  are the longitudinal and transverse projectors, respectively. To lowest order in perturbation theory, the self-energies for the in-plane modes are given by

$$\mathcal{P}_{\mathbf{q}}^L = -q^2 \lambda^2 \Pi_{\mathbf{q}}^{\perp\perp\perp\perp} - q^2 (\lambda + 2\mu)^2 \Pi_{\mathbf{q}}^{\parallel\parallel\parallel\parallel} - q^2 \lambda (\lambda + 2\mu) \Pi_{\mathbf{q}}^{\perp\perp\parallel\parallel}, \quad (\text{B22})$$

$$\mathcal{P}_{\mathbf{q}}^T = -q^2 \mu^2 \Pi_{\mathbf{q}}^{\perp\parallel\perp\parallel}, \quad (\text{B23})$$

where

$$\Pi_{\mathbf{q}}^M = \frac{1}{2\beta V} \sum_{\mathbf{k}} g_{\mathbf{k}, -\mathbf{k}, \mathbf{q}}^M G_{\mathbf{k}}^0 G_{\mathbf{k}+\mathbf{q}}^0. \quad (\text{B24})$$

Performing the sum over Matsubara frequencies, making the analytic continuation,  $iq_n \rightarrow \omega + i0^+$ , and taking the real part, we obtain

$$\text{Re}\Pi_{\mathbf{q}}^M(\omega) = \frac{\text{P}}{V} \sum_{\vec{k}} g_{\vec{k}, -\vec{k}, \vec{q}}^M \mathcal{F}(\omega, q, k), \quad (\text{B25})$$

with

$$\begin{aligned} \mathcal{F}(\omega, q, k) &= \frac{\hbar}{2\rho^2 \omega_{k,F} - (\omega_{k,F} + \omega)^2 + \omega_{k+q,F}^2} \frac{b(\omega_{k,F})}{b(\omega_{k,F})} \\ &- \frac{\hbar}{2\rho^2 \omega_{k,F} - (-\omega_{k,F} + \omega)^2 + \omega_{k+q,F}^2} \frac{b(-\omega_{k,F})}{b(-\omega_{k,F})} \\ &+ \frac{\hbar}{2\rho^2 \omega_{k+q,F} - (\omega_{k+q,F} - \omega)^2 + \omega_{k,F}^2} \frac{b(\omega_{k+q,F})}{b(\omega_{k+q,F})} \\ &- \frac{\hbar}{2\rho^2 \omega_{k+q,F} - (-\omega_{k+q,F} - \omega)^2 + \omega_{k,F}^2} \frac{b(-\omega_{k+q,F})}{b(-\omega_{k+q,F})}. \end{aligned} \quad (\text{B26})$$

We focus on the  $T \rightarrow 0$  limit, where  $\mathcal{F}(\omega, q, k)$  simplifies to

$$\mathcal{F}_{T \rightarrow 0}(\omega, q, k) = \frac{\hbar}{2\rho^2} \frac{\omega_{k,F} + \omega_{k+q,F}}{\omega_{k,F} \omega_{k+q,F} \left[ (\omega_{k,F} + \omega_{k+q,F})^2 - \omega^2 \right]}, \quad (\text{B27})$$

Focusing on the case with  $\omega \rightarrow 0$  and  $q \rightarrow 0$ , the integration over momentum is effectively cutoff at small momenta by the largest of these quantities. Therefore, apart from a numerical factor coming from the angular integration, we obtain

$$\lim_{T \rightarrow 0} \text{Re}\Pi_{\mathbf{q}}^M(\omega) \propto \frac{\hbar}{2\rho^{1/2} \kappa^{3/2}} \log \left( \frac{\Lambda^2}{\max(\sqrt{\kappa/\rho\omega}, q^2)} \right). \quad (\text{B28})$$

Therefore, we will just have a weak logarithmic correction to the correlation function of the in-plane modes. Notice that the minus sign in Eqs. (B23) and (B22) leads

to a reduction of the in-plane elastic constants. To first order in perturbation theory, the in-plane mode dispersion relations would be modified to  $\omega_{q,L/T}^2 \rightarrow \omega_{q,L/T}^2 + \mathcal{P}^{T/L}(\omega_{q,L/T})/\rho$ . Taking the limit  $q \rightarrow 0$ , we would obtain a negative dispersion relation, indicating that the theory is unstable. We attribute this, not to a physical instability of the membrane, but to a breakdown of the perturbation theory, showing that one should go beyond the first order.

### Appendix C: Migdal-Galitskii-Koltun energy sum

In this appendix, we will prove Eqs. (43) and (44). The Migdal-Galitskii-Koltun energy sum<sup>53,54</sup> allows one to express the total energy of a system with quartic interactions just in terms of two-point correlation functions. In the following, we will prove a similar result but for the case of a crystalline membrane, which contains both quartic and cubic interactions. In the canonical quantization formalism, the Hamiltonian for a crystalline membrane is given by

$$H = \int d^2x \left[ \frac{1}{2\rho} (\pi_h^2 + \vec{\pi}_u^2) + \frac{1}{2} \left( \kappa (\partial^2 h)^2 + c^{ijkl} \partial_i u_j \partial_k u_l \right) \right] + \int d^2x \left[ \frac{1}{2} c^{ijkl} \partial_i u_j (\partial_k h \partial_l h) + \frac{1}{8} c^{ijkl} (\partial_i h \partial_j h) (\partial_k h \partial_l h) \right], \quad (\text{C1})$$

where  $\pi_h$  and  $\vec{\pi}_u$  are, respectively, the canonical conjugate momenta of  $h$  and  $\vec{u}$ , which obey the equal time commutation relations  $[h(x), \pi_h(x')] = i\hbar\delta^{(2)}(x-x')$  and  $[u^i(x), \pi_u^j(x')] = i\hbar\delta^{ij}\delta^{(2)}(x-x')$ . The proof is based on the Heisenberg equation of motion for the operators, and the crucial point for the proof is that the Hamiltonian (C1) has a quartic interaction for the  $h$  field and a cubic interaction involving  $h$  and  $\vec{u}$ , such that  $\vec{u}$  appears only once in the cubic interaction. In other words,  $\vec{u}$  is an interaction mediating field. To keep the notation simple and since the essential of the proof is not altered, instead of working with Hamiltonian (C1), we use the Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{1}{2}k_1x_1^2 + \frac{p_2^2}{2m_2} + \frac{1}{2}k_2x_2^2 + \frac{g}{2}x_1^2x_2 + \frac{w}{8}x_1^4, \quad (\text{C2})$$

with  $p_a$  the canonical conjugate momentum of  $x_a$ , obeying the equal time commutation relations  $[x_a, p_b] = i\hbar\delta_{ab}$  ( $a = 1, 2$ ). Notice that the Hamiltonian (C2) has the same structure as (C1) if we replace  $x_1 \leftrightarrow h$  and  $x_2 \leftrightarrow \vec{u}$ . We wish to evaluate the expectation value of the energy  $\langle H \rangle = T_1 + V_1 + T_2 + V_2 + W_3 + W_4$ , where we have the kinetic energy of the fields,  $T_a = \langle p_a^2 \rangle / (2m_a)$ , the potential energy  $V_a = k_a \langle x_a^2 \rangle / 2$ , the interaction energy due to the cubic interaction  $W_3 = g \langle x_2 x_1^2 \rangle / 2$  and the interaction energy due to the quartic interaction  $W_4 = w \langle x_1^4 \rangle / 8$ . In the imaginary time formalism, operators evolve according to the Heisenberg equation  $\partial O(\tau) / \partial \tau = [H, O(\tau)]$ . The Heisenberg equations for

the operators read

$$i\partial_\tau x_1 = \frac{p_1}{m_1}, \quad (\text{C3})$$

$$-i\partial_\tau p_1 = k_1 x_1 + g x_1 x_2 + \frac{w}{2} x_1^3, \quad (\text{C4})$$

$$i\partial_\tau x_2 = \frac{p_2}{m_2}, \quad (\text{C5})$$

$$-i\partial_\tau p_2 = k_2 x_2 + \frac{g}{2} x_1^2, \quad (\text{C6})$$

from which the second order equation for  $x_1$  and  $x_2$  can be obtained

$$m_1 \partial_\tau^2 x_1 = k_1 x_1 + g x_1 x_2 + \frac{w}{2} x_1^3, \quad (\text{C7})$$

$$m_2 \partial_\tau^2 x_2 = k_2 x_2 + \frac{g}{2} x_1^2. \quad (\text{C8})$$

Now let us define the time ordered Green's functions (recall that a time ordered Green's function in the canonical quantization formalism, corresponds to a correlation function in the path integral formalism)

$$G_{ab}(\tau) = \langle T_\tau x_a(\tau) x_b(0) \rangle, \quad (\text{C9})$$

where  $T_\tau$  is the time ordering operator in imaginary time. Using the exact eigenbasis of the interacting Hamiltonian,  $H|n\rangle = E_n|n\rangle$ , a correlation function of the form  $C_{AB}(\tau) = \langle T_\tau A(\tau) B(0) \rangle$ , after a Fourier transform in  $\tau$ , has the following Lehmann representation

$$C_{AB}(i\omega_n) = \int_0^\beta e^{i\omega_n \tau} \langle T_\tau A(\tau) B(0) \rangle = \frac{1}{Z} \sum_{n,m} \frac{e^{-\beta E_m} - e^{-\beta E_n}}{i\omega_n + E_n - E_m} A_{nm} B_{mn},$$

where  $A_{nm} = \langle n|A|m\rangle$ ,  $Z = \sum_n e^{-\beta E_n}$  and  $\omega_n = 2\pi\beta n$  ( $n \in \mathbb{Z}$ ) are bosonic Matsubara frequencies. Now let us

study the quantity

$$\sigma_{AB}^{(2)} = \frac{1}{\beta} \sum_{i\omega_n} (i\omega_n)^2 C_{AB}(i\omega_n), \quad (\text{C10})$$

(a factor of  $e^{i\omega_n\eta}$ , with  $\eta \rightarrow 0^+$ , should be added to this expression for convergence reasons<sup>55</sup>). Using contour integration to evaluate the Matsubara sum over frequencies we obtain

$$\sigma_{AB}^{(2)} = \frac{1}{Z} \sum_{n,m} (E_m - E_n)^2 e^{-E_m} A_{nm} B_{mn}. \quad (\text{C11})$$

Comparing this result with the Lehmann representation for  $\langle B[H, [H, A]] \rangle$  and  $\langle [H, B][H, A] \rangle$  we obtain the important result

$$\sigma_{AB}^{(2)} = \langle B\partial_\tau^2 A \rangle = -\langle \partial_\tau B \partial_\tau A \rangle. \quad (\text{C12})$$

Using (C12) with  $A = B = x_1$  and  $A = B = x_2$  together with the equations of motion (C7) and (C8) we obtain

$$m_1 \sigma_{11}^{(2)} = k_1 \langle x_1^2 \rangle + g \langle x_1^2 x_2 \rangle + \frac{w}{2} \langle x_1^4 \rangle \quad (\text{C13})$$

$$m_2 \sigma_{22}^{(2)} = k_2 \langle x_2^2 \rangle + \frac{g}{2} \langle x_1^2 x_2 \rangle \quad (\text{C14})$$

so that the interaction energies can be expressed as

$$W_3 = m_2 \sigma_{22}^{(2)} - 2V_2 \quad (\text{C15})$$

$$W_4 = \frac{1}{4} \left( m_1 \sigma_{11}^{(2)} - 2m_2 \sigma_{22}^{(2)} \right) - \frac{1}{2} V_1 + V_2. \quad (\text{C16})$$

The kinetic energy terms can also be expressed in terms of  $\sigma_{11}^{(2)}$  and  $\sigma_{22}^{(2)}$  using (C12) together with (C3) and (C5)

$$T_a = \frac{1}{2} m_a \sigma_{aa}^{(2)}, \quad (\text{C17})$$

and the potential energies are given by

$$V_a = \frac{1}{2} k_a \frac{1}{\beta} \sum_{i\omega_n} G_{aa}(i\omega_n). \quad (\text{C18})$$

Putting all the pieces together, the total energy is given by

$$\begin{aligned} \langle H \rangle &= \frac{1}{4\beta} \sum_{i\omega_n} \left( 3m_1 (i\omega_n)^2 + k_1 \right) G_{11}(i\omega_n) \\ &+ \frac{1}{\beta} \sum_{i\omega_n} m_2 (i\omega_n)^2 G_{22}(i\omega_n). \end{aligned} \quad (\text{C19})$$

Applying Eq. (C19) for the crystalline membrane Hamiltonian (C1), we obtain Eqs. (43) and (44) of the main text.

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<sup>1</sup> K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *Proc. Natl. Acad. Sci. (USA)* **102**, 10451 (2005).

<sup>2</sup> M. Katsnelson, *Graphene: Carbon in Two Dimensions* (Cambridge University Press, Cambridge, 2012).

<sup>3</sup> M. I. Katsnelson and A. Fasolino, *Acc. Chem. Res.* **46**, 97 (2013).

<sup>4</sup> D. Nelson, T. Piran, and S. Weinberg, eds., *Statistical Mechanics of Membranes and Surfaces* (World Scientific, Singapore, 2004).

<sup>5</sup> A. Fasolino, J. Los, and M. I. Katsnelson, *Nature materials* **6**, 858 (2007).

<sup>6</sup> M. Katsnelson and A. Geim, *Philos. Trans. R. Soc. A* **366**, 195 (2008).

<sup>7</sup> E.-A. Kim and A. H. C. Neto, *EPL (Europhysics Letters)* **84**, 57007 (2008).

<sup>8</sup> E. Mariani and F. von Oppen, *Phys. Rev. Lett.* **100**, 076801 (2008).

<sup>9</sup> D. Gazit, *Phys. Rev. B* **80**, 161406 (2009).

<sup>10</sup> D. K. Efetov and P. Kim, *Phys. Rev. Lett.* **105**, 256805 (2010).

<sup>11</sup> P. San-Jose, J. González, and F. Guinea, *Phys. Rev. Lett.* **106**, 045502 (2011).

<sup>12</sup> E. Mariani and F. von Oppen, *Phys. Rev. B* **82**, 195403 (2010).

<sup>13</sup> E. V. Castro, H. Ochoa, M. I. Katsnelson, R. V. Gorbachev, D. C. Elias, K. S. Novoselov, A. K. Geim, and F. Guinea, *Phys. Rev. Lett.* **105**, 266601 (2010).

<sup>14</sup> I. V. Gornyi, V. Y. Kachorovskii, and A. D. Mirlin, *Phys. Rev. B* **86**, 165413 (2012).

<sup>15</sup> M. Gibertini, A. Tomadin, F. Guinea, M. I. Katsnelson, and M. Polini, *Phys. Rev. B* **85**, 201405 (2012).

<sup>16</sup> B. Amorim and F. Guinea, *Phys. Rev. B* **88**, 115418 (2013).

<sup>17</sup> J. Meyer, A. Geim, M. Katsnelson, K. Novoselov, T. Booth, and S. Roth, *Nature* **446**, 60 (2007).

<sup>18</sup> J. Brivio, D. T. L. Alexander, and A. Kis, *Nano Lett.* **11**, 5148 (2011).

<sup>19</sup> D. Nelson and L. Peliti, *J. Phys. (Paris)* **48**, 1085 (1987).

<sup>20</sup> J. A. Aronovitz and T. C. Lubensky, *Phys. Rev. Lett.* **60**, 2634 (1988).

<sup>21</sup> M. Paczuski, M. Kardar, and D. R. Nelson, *Phys. Rev. Lett.* **60**, 2638 (1988).

<sup>22</sup> M. Paczuski and M. Kardar, *Phys. Rev. A* **39**, 6086 (1989).

<sup>23</sup> J. Aronovitz, L. Golubovic, and T. Lubensky, *J. Phys. France* **50**, 609 (1989).

<sup>24</sup> P. Le Doussal and L. Radzihovsky, *Phys. Rev. Lett.* **69**, 1209 (1992).

<sup>25</sup> Mark J. Bowick, Simon M. Catterall, Marco Falcioni, Gudmar Thorleifsson, and Konstantinos N. Anagnostopoulos, *J. Phys. I France* **6**, 1321 (1996).

<sup>26</sup> J.-P. Kownacki and D. Mouhanna, *Phys. Rev. E* **79**, 040101 (2009).

- <sup>27</sup> J. H. Los, M. I. Katsnelson, O. V. Yazyev, K. V. Zakharchenko, and A. Fasolino, *Phys. Rev. B* **80**, 121405 (2009).
- <sup>28</sup> F. L. Braghin and N. Hasselmann, *Phys. Rev. B* **82**, 035407 (2010).
- <sup>29</sup> D. Gazit, *Phys. Rev. E* **80**, 041117 (2009).
- <sup>30</sup> K. V. Zakharchenko, R. Roldán, A. Fasolino, and M. I. Katsnelson, *Phys. Rev. B* **82**, 125435 (2010).
- <sup>31</sup> S. Costamagna and A. Dobry, *Phys. Rev. B* **83**, 233401 (2011).
- <sup>32</sup> R. Roldán, A. Fasolino, K. V. Zakharchenko, and M. I. Katsnelson, *Phys. Rev. B* **83**, 174104 (2011).
- <sup>33</sup> N. Hasselmann and F. L. Braghin, *Phys. Rev. E* **83**, 031137 (2011).
- <sup>34</sup> V. V. Lebedev and E. I. Kats, *Phys. Rev. B* **85**, 045416 (2012).
- <sup>35</sup> A. Košmrlj and D. R. Nelson, *Phys. Rev. E* **88**, 012136 (2013).
- <sup>36</sup> K. Essafi, J.-P. Kownacki, and D. Mouhanna, *Phys. Rev. E* **89**, 042101 (2014).
- <sup>37</sup> A. Košmrlj and D. R. Nelson, *Phys. Rev. E* **89**, 022126 (2014).
- <sup>38</sup> F. Guinea, P. Le Doussal, and K. J. Wiese, *Phys. Rev. B* **89**, 125428 (2014).
- <sup>39</sup> E. I. Kats and V. V. Lebedev, *Phys. Rev. B* **89**, 125433 (2014).
- <sup>40</sup> P. L. de Andres, F. Guinea, and M. I. Katsnelson, *Phys. Rev. B* **86**, 144103 (2012).
- <sup>41</sup> J. Zimmermann, P. Pavone, and G. Cuniberti, *Phys. Rev. B* **78**, 045410 (2008).
- <sup>42</sup> V. N. Popov, *Phys. Rev. B* **66**, 153408 (2002).
- <sup>43</sup> N. Mounet and N. Marzari, *Phys. Rev. B* **71**, 205214 (2005).
- <sup>44</sup> K. V. Zakharchenko, M. I. Katsnelson, and A. Fasolino, *Phys. Rev. Lett.* **102**, 046808 (2009).
- <sup>45</sup> L. Landau and E. Lifshitz, *Course of Theoretical Physics vol. 7: "Theory of Elasticity"* (Pergamon Press, Oxford, 1959).
- <sup>46</sup> P. M. Chaikin and T. C. Lubetsky, *Principles of condensed matter physics* (Cambridge University Press, Cambridge, 2003).
- <sup>47</sup> We use graphene as an example of a crystalline membrane. Typical parameters for single-layer graphene at  $T = 0$  are taken (see Refs. 5 and 44):  $\mu = 9.44 \text{ eV } \text{Å}^{-2}$ ,  $\lambda = 3.25 \text{ eV } \text{Å}^{-2}$  and  $\kappa = 0.82 \text{ eV}$ . At  $T = 300\text{K}$  we used the values:  $\mu = 9.95 \text{ eV } \text{Å}^{-2}$ ,  $\lambda = 2.57 \text{ eV } \text{Å}^{-2}$  and  $\kappa = 1.1 \text{ eV}$ . Graphene has density  $\rho/\hbar^2 = 1104 \text{ eV}^{-1} \text{Å}^{-4}$  and its lattice constant is given by  $a = 2.46 \text{ Å}$ , from which we obtain a Debye momentum  $q_D = \sqrt{8\pi/(3^{1/2}a^2)} = 1.55 \text{ Å}^{-1}$ .
- <sup>48</sup> These terms are also given, in a somewhat different form, in Ref. 38.
- <sup>49</sup> For graphene values at  $T = 0$  we have  $q_L \simeq 5.2 \text{ Å}^{-1}$  and  $q_T \simeq 3.4 \text{ Å}^{-1}$ . Therefore, the momentum scales  $q_{L/T}$  are actually larger than graphene's Debye momentum.
- <sup>50</sup> There is a factor of  $1/\sqrt{2}$  missing in the expression for  $k_c^{(T \rightarrow \infty)}$  presented in Refs. 5, 30, and 32.
- <sup>51</sup> L. Karssemeijer, *Thermal expansion of carbon structures*, Master's thesis, Institute for Molecules and Materials - Radboud Univeristy Nijmegen (2010), can be found at [http://www.ru.nl/tcm/education\\_0/bachelor-master/](http://www.ru.nl/tcm/education_0/bachelor-master/).
- <sup>52</sup> L. Karssemeijer and A. Fasolino, *Surface Science* **605**, 1611 (2011), graphene Surfaces and Interfaces.
- <sup>53</sup> V. Galitski and A. Migdal, *Zh. Eksp. Teor. Fiz.* **34**, 139 (1958), [Engl. Transl.: *Sov. Phys. JETP* 7, 96 (1958)].
- <sup>54</sup> D. S. Koltun, *Phys. Rev. C* **9**, 484 (1974).
- <sup>55</sup> B. Henrik and K. Flensberg, *Many-Body Quantum Theory in Condensed Matter Physics* (Oxford University Press, New York, 2004).