Bifurcation analysis and phase diagram of a spin-string model with buckled states

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We analyze a one-dimensional spin-string model, in which string oscillators are linearly coupled to their two nearest neighbors and to Ising spins representing internal degrees of freedom. String-spin coupling induces a long-range ferromagnetic interaction among spins that competes with a spin-spin antiferromagnetic coupling. As a consequence, the complex phase diagram of the system exhibits different flat rippled and buckled states, with first or second order transition lines between states. The two-dimensional version of the model has a similar phase diagram, which has been recently used to explain the rippled to buckled transition observed in scanning tunnelling microscopy experiments with suspended graphene sheets. Here we describe in detail the phase diagram of the simpler one-dimensional model and phase stability using bifurcation theory. This gives additional insight into the physical mechanisms underlying the different phases and the behavior observed in experiments.

I. INTRODUCTION

Rippling and buckling of suspended graphene sheets is an active research topic [1–9]. Recent scanning tunnelling microscopy (STM) experiments show that local heating induces a transition from a soft rippled state to a hard buckled graphene membrane [9]. While heating certainly increases thermal fluctuations, in this case and quite counterintuitively, it produces a more ordered phase. We have interpreted the STM experiments as the result of driving the system through a first order phase transition between flat and buckled membrane states [10]. We have used a phenomenological spin-membrane model of the graphene sheet that exhibits such a first order phase transition [10], for there is no first principles derivation thereof. More specifically, spin-string [11] and spin-membrane models [6,10,12] display first and second order buckling transitions depending on the precise interactions among spins. In fact, spin-spin interactions and spin-membrane are reminiscent of the effective interactions among out of plane displacements in 2d systems, which appear after electrons and in plane phonons are integrated out in electron-phonon models [4,13]. Also, mechanical systems coupled to spins have been employed to describe structural phase transitions in other physical contexts [14–25].

In these models, the membrane is a system of mass points on a lattice that move vertically and are interconnected by linear springs. There is a pseudo-spin at each lattice node, which represents in a simple way some internal degrees of freedom, that pushes the point mass located there either upwards or downwards. If the pseudo-spins are coupled only to mass points but not among themselves, there is a second order buckling transition below a critical temperature [11]. This is also the case for a membrane described by Föppl-von Kármán equations on a hexagonal lattice with vertical displacements coupled to the local spin on the same lattice node [9]. This second order transition arises because the spin-membrane brings about a long-ranged ferromagnetic interaction among the pseudo-spins. Furthermore, additional short range antiferromagnetic couplings among the pseudo-spins produce different phases and first or second order transitions among them [10,12].

One drawback of the two-dimensional (2d) spin-membrane models with antiferromagnetic coupling is that most results are obtained from numerical simulations. In this work, we study analytically the corresponding one-dimensional (1d) spin-string model, in terms of the dimensionless temperature θ and the spin-spin antiferromagnetic coupling κ. As already said above, for κ = 0 there is a second order phase transition at θ = 1 from a flat string configuration (stable for θ > 1) to stable buckled string states that exist for θ < 1. This second order phase transition is a supercritical pitchfork bifurcation [26]. For κ ≠ 0, we find and analyze subcritical pitchfork bifurcations corresponding to first order phase transitions between flat and buckled phases. This situation is similar to the 2d case but, in 1d, we are able to obtain bifurcation lines, bifurcation diagrams and the different phases by analytical methods. The order parameter spin magnetization acts as the norm of the solution in bifurcation diagrams [26].

We show that the flat string configuration is the only stable phase except for a finite region within the first quadrant κ > 0, θ > 0 of the (κ,θ) plane. The flat string configuration is unstable inside a smaller region κ ∈ (0,κn), θ ∈ (0,1), which is bounded by a two-valued curve θb(κ) joining the origin to (κ,θ) = (0,1). This curve is a locus of pitchfork bifurcations from flat to...
buckled states. Bifurcations are subcritical at the low $\theta$ branch of the curve. At the high branch, they are supercritical for $0 < \kappa < \kappa_c$ and subcritical for $\kappa_c < \kappa < \kappa_\nu$. The tricritical point $[27, 28] (\kappa_c, \theta_c)$ has codimension two and we can use two-parameter perturbation theory to analyze the change from super to subcritical pitchfork bifurcation. The result is that the branch of unstable buckled states that stem from the flat configuration for $\theta < \theta_c$ coalesce with a branch of stable buckled states at a curve $\theta_M(\kappa)$ that is above the bifurcation curve $\theta_0(\kappa)$. This signals a first order phase transition and bistability between flat and buckled states. As the low and high temperature branches of $\theta_0(\kappa)$ coalesce at the turning point $(\kappa_n, \theta_n)$, the corresponding subcritical bifurcations merge and disappear. Analysis of this new codimension two point shows that there exist an isola of buckled states coalescing at a sufficiently large temperature at the curve $\theta_M(\kappa)$.

The first order phase transition occurring in this 1d spin-string model is akin to that found numerically in the 2d spin-membrane model. Our explanation of Schoelz et al’s experiments [9] is that the STM drives the system dynamically across the first order phase transition appearing in a certain range of antiferromagnetic coupling $\kappa$. The same situation occurs in the 1d spin-string model.

The paper is organized as follows. In Sec. [I] we define the model and introduce the free energy density controlling its equilibrium behavior, together with the corresponding Euler-Lagrange equation governing the equilibrium profiles. Also, we briefly discuss the flat solution and its stability. Section [II] puts forward the main results of our study, including a discussion of main elements of the phase diagram of the system, leaving the derivations for the later sections. We analyze in detail the bifurcation from the flat solution in Sec. [III] and the emergence of a (tri)critical point, at which the transition changes from second-order to first-order. In Sec. [IV] we study the low temperature limit of our system, focusing on the spin configurations underlying the parabolic profiles of the string. We present the main conclusions of our work in Sec. [V]. The appendices deal with some technical details and calculations that are omitted in the main text.

II. CONTINUUM LIMIT OF THE SPIN-STRING MODEL

We consider a spin-string system with Hamiltonian

$$\mathcal{H}(u, p, \sigma) = \sum_{j=0}^{N} \left[ \frac{p_j^2}{2m} + \frac{k}{2}(u_{j+1} - u_j)^2 - f(u_j \sigma_j + J \sigma_{j+1} \sigma_j) \right].$$

(1)

Here, $u_j$ and $p_j$, $j = 1, \ldots, N$, are the string vertical displacements and their conjugate momenta, respectively, and $\sigma_j = \pm 1$ are pseudo-spin variables [11][12]. The latter represent internal degrees of freedom arising from internal forces that push the atoms along the vertical direction. Therefore, we have: (i) a nearest-neighbor harmonic interaction between the elastic variables, $k(u_{j+1} - u_j)^2$, (ii) an on-site interaction between the elastic and the internal variables, $-f u_j \sigma_j$, and (iii) a nearest-neighbor spin-spin interaction, $J \sigma_{j+1} \sigma_j$. We have clamped boundary conditions at the string ends, $u_0 = p_0 = \sigma_0 = u_{N+1} = p_{N+1} = \sigma_{N+1} = 0$.

The string variables $u_j$ and $p_j$ satisfy Hamilton’s equations of motion, whereas the pseudo-spins $\sigma_j$ evolve following Glauber dynamics [29] at the thermal bath temperature $T$ [12]. Then the system reaches equilibrium in the long time limit. The probability density of finding the system in a certain configuration $(u, p, \sigma)$ is given by $e^{-\mathcal{H}/T}$, where $Z$ is the partition function and we have set $k_B = 1$. For $J = 0$ and temperature below $T_0 = \frac{\tilde{\kappa}^2 N^2}{4\pi^2}$, the system exhibits stable ripples [11]. Under these conditions, energy variables dimensionless by measuring them in units of $T_0$. The dimensionless coupling constant $\kappa$ and temperature $\theta$ are

$$\kappa = \frac{J}{T_0}, \quad \theta = \frac{T}{T_0}.$$

(2)

Suitable units are introduced for the remaining variables. Further details can be found in Ref. [12].

In this paper, we investigate the equilibrium states and the different phases of the model in the limit as $N \gg 1$ with $x = i/N \in [0, 1]$ [12]. We integrate out the pseudo-spins and the canonical momenta. Then the resulting equilibrium probability density $P[u]$ of finding the string with a certain profile $u(x)$ is $P[u; \theta, \kappa] \propto \exp \left( -F[u; \theta, \kappa]/\theta \right)$, in which

$$F[u; \theta, \kappa] = \int_0^1 dx \ f(u, u'; \theta, \kappa),$$

(3a)

$$f(u, u'; \theta, \kappa) = \frac{(u')^2}{2\pi^2} - \theta \ln \left( \frac{u}{\theta} \right) \left( \frac{\kappa}{\theta} \right),$$

(3b)

$$\zeta \left( \frac{u}{\theta} \frac{\kappa}{\theta} \right) = \exp \left( \frac{-\kappa}{\theta} \right) \cos \left( \frac{u}{\theta} \right) + \exp \left( \frac{\kappa}{\theta} \right) \sqrt{1 + \exp \left( -\frac{4\kappa}{\theta} \right) \sinh^2 \left( \frac{u}{\theta} \right)}.$$
Further information is given by the parameter \( \xi(u; \theta, \kappa) \), and it is therefore an order parameter. Net magnetization distinguishes between buckled and flat profiles; there are no internal nodes. The absolute value of the total magnetization sets the local value of the string curvature, which is the local value of the magnetization. Clearly, the magnetization is described by the pseudo-spins partition function per site, respectively.

### A. Euler-Lagrange equation for the equilibrium profiles

The equilibrium profiles \( u_{eq}(x) \) solve the Euler-Lagrange equation,

\[
\frac{1}{\pi^2} u''_{eq} = -\mu(u_{eq}; \theta, \kappa), \quad u_{eq}(0) = u_{eq}(1) = 0.
\]

where

\[
\mu(u; \theta; \kappa) = \frac{-\partial f(u, u'; \theta, \kappa)}{\partial u} = \frac{e^{-\kappa/\theta} \sinh(y)}{\sqrt{e^{-\kappa/\theta} \sinh^2(y) + 1}},
\]

is the local value of the magnetization. Clearly, the magnetization sets the local value of the string curvature.

Let us consider only the first buckled mode that has no internal nodes. The absolute value of the total magnetization distinguishes between buckled and flat profiles and it is therefore an order parameter

\[
M(\theta; \kappa) = \left| \int_0^1 dx \mu(u_{eq}; \theta, \kappa) \right|.
\]

Further information is given by the parameter

\[
\mathcal{D}\mathcal{L}(\theta; \kappa) = \frac{1}{2} \left( 1 - \theta \int_0^1 dx \left. \frac{\partial \ln \xi}{\partial \kappa} \right|_{u=u_{eq}} \right),
\]

which is zero for perfect anti-ferromagnetic order, 1/2 for a random configuration of the pseudo-spins, and 1 for perfect ferromagnetic order [12]. Recall that \( C = -\theta \partial_\kappa \ln \xi \) gives the correlation of nearest-neighbor pseudo-spins.

The free energy functional \( F[u] \) has a relative (or weak) minimum for the curve \( u = u_{eq}(x) \) provided the following two conditions are satisfied:

1. The curve \( u_{eq}(x) \) must satisfy the Euler-Lagrange equation \([4]\).
2. The linearised Euler-Lagrange equation about \( u_{eq}(x) \),

\[
\delta u'' = -\pi^2 \left. \left( \frac{\partial \mu}{\partial u} \right) \right|_{u=u_{eq}} \delta u, \quad \delta u(0) = \delta u(a) = 0,
\]

must have only the trivial solution \( \delta u(x) \equiv 0, \forall x \), for all \( a \leq 1 \).

Considered separately, each condition is necessary for \( F[u] \) to have a weak minimum (with the nuance \( a < 1 \) instead of \( a \leq 1 \) in the second one) [30].

### B. Flat string profile and its stability

The flat string profile \( u_L(x) \equiv 0, \forall x \), is always a solution of the Euler-Lagrange equation, which we call phase L [31]. It is (locally) stable if it corresponds to a minimum of the free energy functional. For phase L and any \( a \leq 1 \), the boundary value problem \([5]\) is

\[
\delta u'' = -\pi^2 \theta^{-1} \exp(-2\kappa/\theta) \delta u, \quad u(0) = u(a) = 0.
\]

Aside from the trivial solution \( \delta u(x) \equiv 0 \), we may have solutions

\[
\delta u(x) = A \sin \left[ \pi \theta^{-1/2} \exp(-\kappa/\theta) x \right],
\]

where \( A \) is an arbitrary constant and \( a \) is such that

\[
\theta^{-1/2} \exp(-\kappa/\theta) a = n, \quad n \in \mathbb{N}, \ a \leq 1.
\]

Thus, first, the flat solution produces a relative minimum of the free energy if \( \theta^{-1/2} \exp(-\kappa/\theta) < 1 \). In this region of the \((\kappa, \theta)\) plane, the only solution of \([4]\) is the trivial one. Second, if \( \theta^{-1/2} \exp(-\kappa/\theta) > 1 \), there is at least one nontrivial solution of \([4]\), provided we choose \( a = \theta^{1/2} \exp(\kappa/\theta) < 1 \) and the flat profile is no longer stable.

Buckled equilibrium profiles may bifurcate at the curve \( \theta^{1/2} \exp(\kappa/\theta) = 1 \), which is a bifurcation line in the \((\kappa, \theta)\) plane enclosing Region II in Fig. [1]. Points \((\kappa_b, \theta_b)\) on this line satisfy

\[
\theta_b \exp \left( \frac{2\kappa_b}{\theta_b} \right) = 1, \text{ or } \kappa_b = -\frac{1}{2} \theta_b \ln \theta_b.
\]

The bifurcation line has two branches \( \theta^{(2)}(\kappa) < \theta^{(1)}(\kappa) \) that coalesce at the turning point (“nose”) \( \mathcal{N} \equiv (\kappa_n = (2e)^{-1}, \theta_n = e^{-1}) \). For \( \kappa > \kappa_n \), the free energy has a local minimum at the flat solution, regardless of the temperature. For \( \kappa < \kappa_n \), the flat solution is unstable if \( \theta^{(2)}(\kappa) < \theta < \theta^{(1)}(\kappa) \), and locally stable otherwise, see Fig. [4]. Note that \( \theta^{(2)} < 2k < \theta^{(1)} \). The tangent to the bifurcation line at \((\kappa_b, \theta_b)\) verifies

\[
2 \delta \kappa_b + (1 + \ln \theta_b) \delta \theta_b = 0.
\]

Here, \( \delta \theta_b \) and \( \delta \kappa_b \) are the (small) deviations from \((\kappa_b, \theta_b)\) over the tangent.

### III. RESULTS: PHASE DIAGRAM

This section describes the main results of this paper, leaving derivations for later sections. There are three different phases in the system: the flat phase L and two buckled phases, which we denote \( B^+ \) and \( B^- \) (for low temperatures they are the string profiles shown in Fig. [5]). The points and lines governing the existence and stability of the different phases are shown in Fig. [7]. It shows the bifurcation line \( \kappa_b(\theta) \) and the turning point \( \mathcal{N} \) that
Definition |
--- | --- |
B+, B-, L | κ<κ |
Most stable | Unstable | Metastable |
--- | --- | --- |
I | κ > κ_b(κ) \( θ > θ_c \) \( \kappa > \kappa_M(\kappa) \) \( θ < θ_c \) | L | L | None | None |
II | κ < κ_b(κ) | B+ L | B+ | L | None |
IIIa | κ_b(κ) < κ < κ_l(κ) \( \kappa_M(\kappa) \) | B+ B-, L | B+ | B- | L |
IIIb | κ_l(κ) < κ < κ_M(κ) | B+ B-, L | L | B- | B+ |

TABLE I. Summary of the different regions, phases (flat \( L \), stable buckled \( B+ \) and unstable buckled \( B− \)) and their relative stability.

A summary of the above discussion is shown in Table I. Fig. 2(a) and (b) show the bifurcation diagram of magnetization as a function of \( \theta \) and \( \kappa \). Panels (c)-(f) depict the magnetization as a function of the temperature for several relevant values of \( \kappa \). The bifurcation is always supercritical for the lower branch of the bifurcation curve. As \( \kappa > 0 \) increases, the bifurcation at the upper branch changes from super to subcritical at the tricritical point \( \kappa_c \approx 0.159 \). The two subcritical bifurcation points merge at the nose point \( \kappa_n \approx 0.184 \). At higher \( \kappa \), the buckled phases form an isola separated from the flat configuration. The turning point \( \theta_M(\kappa) \) at which buckled phases \( B− \) and \( B+ \) coalesce marks the boundary between Regions IIIb and I. This is the first-order curve \( \kappa_M(\theta) \).

A complementary description to bifurcation diagrams is given in Figs. 3 and 4. Figure 3 depicts the phase diagram of the model showed in Figure 1 superimposed on the density plot of phase \( B+ \) magnetization (top panel) and free energy (bottom panel). In both panels, it is clearly observed the change of nature of the transition, from second to first-order, at the tricritical point \( K \). In the bottom panel, the change of relative stability between phases \( B+ \) and \( L \) at the coexistence line \( \kappa_L(\theta) \) is neatly seen, since \( \Delta F \) vanishes. Figure 4 is completely analogous to Fig. 3 but for the phase \( B− \). Note that phase \( B− \) only exists in region III and is always unstable, \( \Delta F > 0 \) everywhere.

FIG. 1. Phase diagram in the \((\kappa, \theta)\) plane. We have marked the tricritical point \( K \) and the turning point \( N \) over the bifurcation curve \( \kappa_b(\theta) \) (dashed line). Also plotted are the coexistence line \( \kappa_c(\theta) \) (solid line) and the first-order line \( \kappa_M(\theta) \) (dotted line). Note that \( \kappa_b(\theta) < \kappa_c(\theta) < \kappa_M(\theta) \). The definition of the different regions I, II and III in the phase diagram, as well as the existing phases in each region and their stability is summarised in Table I. In addition, the values of \( \kappa \) controlling the low temperature behavior, \( \kappa^{(0)}_c = 3\pi^2/128 \) and \( \kappa^{(0)}_M = \pi^2/32 \), are shown with points.

 separates its two branches \( \theta^{(1)}(\kappa) > \theta_n \) and \( \theta^{(2)}(\kappa) \leq \theta_n \).

The interior of the bifurcation curve is Region II. We shall now anticipate some results that will be discussed in detail in Section [IV]. A key element in the phase diagram is the existence of a tricritical point \( K \), \( K \equiv (\kappa_c = \sqrt{3}\ln 3/12, \theta_c = 1/\sqrt{3}) \), at which the three phases \( L, B+ \) and \( B− \) coalesce [27, 28]. For \( \theta > \theta_c \), the bifurcation at \( \theta^{(1)}(\kappa) \) is supercritical, a stable buckled profile \( B+ \) stems continuously from the flat solution in region II. For \( \theta < \theta_c \), the bifurcation becomes subcritical. Then an unstable buckled profile \( B− \) issues from the flat solution at \( \theta > \theta^{(1)}(\kappa) \) (upper bifurcation branch) and and at \( \theta < \theta^{(2)}(\kappa) \) (lower branch). The stable buckled phase \( B+ \) does not disappear at \( K \). Instead, \( B+ \) and the unstable state \( B− \) coalesce at a temperature \( \theta_M(\kappa) \) (dotted red line in Fig. 1) higher than \( \theta^{(1)}(\kappa) \) for \( \kappa > \kappa_c \). The transition at \( K \) changes to first order. The phase \( B+ \) exists inside the bifurcation curve (region II) and also outside it (region III). For \( \kappa > \kappa_M(\theta) \), we have only the flat phase \( L \). In region III, there are three phases: \( B− \) is unstable, whereas phases \( L \) and \( B+ \) are both locally stable as they correspond to local minima of the free energy. Their relative stability depends on \( \kappa \); in fact, there appears a coexistence line \( \kappa_c(\theta) \) (solid blue in Fig. 1) at which both phases are equiprobable. In region IIIa, \( \kappa_b(\kappa) < \kappa < \kappa_c \), phase \( B+ \) provides the absolute minimum and phase \( L \) is metastable, while in region IIIb, \( \kappa_l < \kappa < \kappa_M \), the situation is reversed.
IV. BIFURCATIONS FROM THE FLAT STRING CONFIGURATION

In this section, we calculate the buckled phases that issue from the flat string near the bifurcation line described in Section III. Considerations on the stability of the phases are included in Appendix D.

A. Pitchfork bifurcations from the flat string configuration

Firstly, we expand the free energy about the flat string configuration in powers of $u(x) = \epsilon U(x)$, $\epsilon \ll 1$ and $U = O(1)$, in which $\epsilon$ measures the amplitude of the string vertical displacement. We define the excess free energy density $\Delta f$ from the flat configuration (that has

$$\Delta f(u, u'; \kappa, \theta) \equiv f(u, u'; \kappa, \theta) - f_L(\kappa, \theta), \quad (14)$$

$$f_L(\kappa, \theta) \equiv f(0, 0; \kappa, \theta) = -\theta \ln \left(2 \cosh \frac{\kappa}{\theta}\right). \quad (15)$$

This leads to

$$\Delta f(u, u'; \kappa, \theta) = \frac{\epsilon^2}{2\pi^2} (U')^2 + \frac{\epsilon^2}{2} f_2(\kappa, \theta) U^2 + \frac{\epsilon^4}{4!} f_4(\kappa, \theta) U^4 + \frac{\epsilon^6}{6!} f_6(\kappa, \theta) U^6 + O(\epsilon^8), \quad (16)$$

FIG. 2. Bifurcation diagrams numerically computed from eq. (4). Figures 2(a) and 2(b) show the total magnetization of the buckled solutions versus $\kappa$ and $\theta$. The upper yellow (lower blue) surface stand for the stable (unstable) solution, two different profiles of such solutions at low temperatures can be found in figure 3. Panels (c)-(f) are bifurcation diagrams for increasing values of $\kappa$ depicting subcritical and supercritical bifurcations. For $\kappa > \kappa_n \sim 0.184$, the subcritical bifurcations at the two branches of the bifurcation curve coalesce and an isola stems from the $M = 0$ plane. Symmetric results with negative magnetization are omitted for clarity.

FIG. 3. Density plot of the magnetization $M$ (top panel) and the free energy difference $\Delta F$ (bottom panel) over the numerical solution of the Euler-Lagrange equation for the phase B+. Also depicted are (i) the bifurcation line (solid) $\kappa_b(\theta)$, (ii) the coexistence line (dotted) $\kappa_c(\theta)$ that separates Regions IIIa and IIIb, at which $\Delta F = 0$, and (iii) the limit line $\kappa_M(\theta)$ (dotted). In the free energy panel, we have also plotted the analytical expressions close to the critical point for the first-order transition lines $\kappa_c(\theta)$ and $\kappa_M(\theta)$, derived in Appendix D, but extended up to low temperatures, namely for $\theta \geq 0.08$. 

energy density $f_L$) as
ing Eq. (5), we obtain 

Here \( \mu \) is the local magnetization. Using Eq. (5), we obtain

\[
\begin{align*}
f_2(\kappa, \theta) &= -e^{-2\kappa/\theta}, \tag{18a} \\
f_4(\kappa, \theta) &= e^{-6\kappa/\theta} \left(3 - e^{4\kappa/\theta}\right), \tag{18b} \\
f_6(\kappa, \theta) &= -e^{-10\kappa/\theta} \frac{1}{\theta^5} \left(45 - 30e^{4\kappa/\theta} + e^{8\kappa/\theta}\right). \tag{18c}
\end{align*}
\]

The values of \( f_n \) at the bifurcation line are

\[
\begin{align*}
f_{2,b} &= -1, \tag{19a} \\
f_{4,b} &= \frac{3\theta_b^2 - 1}{\theta_b^2}, \tag{19b} \\
f_{6,b} &= -45\theta_b^4 + 30\theta_b^2 - 1. \tag{19c}
\end{align*}
\]

Secondly, we expand \( \kappa \) and \( \theta \) in powers of \( \epsilon \):

\[
\begin{align*}
\delta \kappa(\epsilon) &\equiv \kappa(\epsilon) - \kappa_b = \epsilon^2 \kappa_2 + \epsilon^4 \kappa_4 + O(\epsilon^6), \tag{20a} \\
\delta \theta(\epsilon) &\equiv \theta(\epsilon) - \theta_b = \epsilon^2 \theta_2 + \epsilon^4 \theta_4 + O(\epsilon^6). \tag{20b}
\end{align*}
\]

The relation between \( \delta \kappa \) and \( \delta \theta \) fixes the direction in which we enter the different regions of the phase diagram. We anticipate that terms containing odd powers of \( \epsilon \) vanish because \( \Delta f \) is invariant under the transformation \( U \rightarrow -U \).

We now expand \( \Delta f \) up to \( O(\epsilon^4) \) near the bifurcation line by inserting (20) into (18) and using (19a) with

\[
\delta f_{2,b} = f_2(\kappa, \theta) - f_{2,b} = \frac{2}{\theta_b} \delta \kappa + \frac{1 + \ln \theta_b}{\theta_b} \delta \theta. \tag{21}
\]

The result is

\[
\Delta f = \frac{\epsilon^2}{2} \left( \frac{U''}{\pi^2} - U^2 \right) + \epsilon^4 \left( \frac{\varphi_2}{2} \frac{U^2}{\pi^2} + \frac{f_{4,b}}{24} U^4 \right) + O(\epsilon^6), \tag{22}
\]

where

\[
\varphi_n = \frac{2\kappa_n + \theta_n (1 + \ln \theta_b)}{\theta_b}. \tag{23}
\]

The corresponding Euler-Lagrange equation, to be solved with clamped boundary conditions, is

\[
\frac{U''}{\pi^2} + U = \epsilon^2 \left( \varphi_2 U + \frac{f_{4,b}}{6} U^3 \right) + O(\epsilon^4). \tag{24}
\]

We now insert in this equation the ansatz

\[
U(x; \epsilon) = U_0(x) + \epsilon^2 U_2(x) + O(\epsilon^4). \tag{24}
\]

All coefficients of powers of \( \epsilon \) are zero separately, which supplies the hierarchy of equations

\[
\begin{align*}
\frac{U''}{\pi^2} + U_0 &= 0, \tag{25a} \\
\frac{U''}{\pi^2} + U_2 &= \varphi_2 U_0 + \frac{f_{4,b}}{6} U_0^3, \tag{25b}
\end{align*}
\]

and so on. The boundary conditions are \( U_0(0) = U_0(1) = 0 \). The solution of the first equation is \( U_0(x) = A \sin \pi x \). Eq. (25b) has a solution with \( U_2(0) = U_2(1) = 0 \) if its right hand side (rhs) is orthogonal to \( \sin \pi x \). This yields the bifurcation equation

\[
\varphi_2 A + \frac{f_{4,b}}{6} A^3 = 0. \tag{26}
\]

Its non-vanishing solutions obey

\[
0 < A^2 = \frac{8\varphi_2}{f_{4,b}} - \frac{8\kappa_2 + \theta_2 (1 + \ln \theta_b)}{3\theta_b^4 - 1}, \tag{27}
\]
provided \( f_{4,b} \neq 0 (\theta_b \neq \theta_c) \). In (27) we have substituted \( \varphi_2 \) and \( f_{4,b} \) by their explicit expressions.

Let \( \kappa \) be the bifurcation parameter, so that \( \theta_2 = 0 \). For \( \theta_b > \theta_c \), Eq. (27) produces \( \kappa_2 < 0 \). Then \( \kappa < \kappa_b \), and the buckled phases exist only inside Region II of Figure 1 where the flat string is unstable, i.e., the bifurcation is supercritical. For \( \theta_b < \theta_c \) (which also occurs at the whole lower branch of the bifurcation line), we obtain \( \kappa_2 > 0 \), so that \( \kappa > \kappa_b \). The buckled phase bifurcates outside Region II where the flat string is stable, i.e., the bifurcation is subcritical. Clearly the bifurcating branches scale as \( |\kappa - \kappa_b|^{1/2} \), the usual scaling for a pitchfork bifurcation.

### B. Bifurcation at the tricritical point

At the tricritical point \( K \), the coefficient of \( A^2 \) in the bifurcation equation (26) vanishes. We can unfold this bifurcation by expanding the free energy up to \( O(\epsilon^6) \) terms and rescaling the bifurcation parameters. If we set \( \theta_b = \theta_c + \epsilon \chi \), with \( \chi = O(1) \), then (27) becomes \( O(\epsilon^2) \). Then, the leading terms of the coefficients of \( U^4 \) and \( U^6 \) in \( \Delta f \) are both \( O(\epsilon^3) \). Assuming that \( \delta \kappa \) and \( \theta \) are also \( O(\epsilon^2) \), we obtain

\[
\theta = \theta_b + \epsilon \chi, \quad \kappa = \kappa_b + \epsilon \kappa_4 + O(\epsilon^6),
\]

(28a)

(28b)

Keeping terms up to \( O(\epsilon^5) \), we obtain

\[
\Delta f = \frac{\epsilon^2}{2} \frac{[(U')^2 - U^2]^2}{\pi^2} + O(\epsilon^6),
\]

(29)

where we have omitted \( O(\epsilon^5) \) terms and introduced the notation

\[
\varphi_{4,c} \equiv \varphi_4|_{\theta_b=\theta_c} = \frac{\sqrt{3}}{2} [4 \kappa_4 + \theta_4(2 - \ln 3)].
\]

(30)

The corresponding Euler-Lagrange equation is

\[
\frac{U''}{\pi^2} + U = \epsilon^4 \left[ \varphi_{4,c} U + \sqrt{3} \chi U^3 + \frac{3}{10} U^5 \right] + O(\epsilon^6),
\]

to be solved with clamped boundary conditions. We now insert in this equation the ansatz

\[
U(x; \epsilon) = U_0(x) + \epsilon^4 U_4(x) + O(\epsilon^6),
\]

(31)

thereby obtaining a hierarchy of equations. The equation for \( U_0 \) is the same as before, whereas \( U_4 \) solves

\[
\frac{U_4''}{\pi^2} + U_4 = \varphi_{4,c} U_0 + \sqrt{3} \chi U_0^3 + \frac{3}{10} U_0^5. \]

(32)

The condition that the rhs of this equation be orthogonal to \( \sin \pi x \) produces the equation for \( A \). For \( A \neq 0 \), it is

\[
A^4 + 4 \sqrt{3} \chi A^2 + \frac{8}{\sqrt{3}} [4 \kappa_4 + \theta_4(2 - \ln 3)] = 0.
\]

(33)

Here we have substituted the explicit expression for \( \varphi_{4,c} \).

Let us analyze the solutions of Eq. (33) for \( \theta_4 = 0 \). Then \( A \) is a function of \( \chi \) and \( \kappa_4 \). In Fig. 1 the system is just above (below) of the critical point for \( \chi > 0 \) (\( \chi < 0 \)) and just outside (inside) the bifurcation curve for \( \kappa_4 > 0 \) (\( \kappa_4 < 0 \)). For \( \chi > 0 \), Eq. (33) has one positive solution \( A^2 > 0 \) if \( \kappa_4 < 0 \) (\( A^2 = 0 \) for \( \kappa_4 = 0 \)). No real solutions exist if \( \kappa_4 > 0 \). For \( \chi < 0 \), Eq. (33) has one positive solution \( A^2 > 0 \) if \( \kappa_4 < 0 \) (corresponding to the stable phase \( B^+ \)). Depending on the sign of the discriminant of the biquadratic equation, Eq. (33) has two or zero positive solutions \( A^2 > 0 \) for \( \kappa_4 > 0 \) (corresponding to stable and unstable phases \( B^+ \) and \( B^- \)). The discriminant of Eq. (33) vanishes at the curve

\[
\kappa_M(\theta) = \kappa_b(\theta) + \frac{3 \sqrt{3}}{8} (\theta - \theta_c)^2.
\]

(34)

Specifically, there are two solutions for \( \kappa < \kappa_M(\theta) \), denoted by \( A_+^2, A_-^2 < A^2 \), and no solutions for \( \kappa > \kappa_M(\theta) \). For \( \kappa < \kappa_M \), the solution \( A_+ \) corresponds to phase \( B^- \) and it issues from the flat configuration as an unstable subcritical bifurcation at \( \theta = \theta_b \). The solution \( A_- \) corresponds to phase \( B^- \) and it matches at \( \theta \) the only unique phase existing for \( \theta > \theta_c \). At the line \( \kappa_M(\theta) \), phases \( B^- \) and \( B^+ \) coalesce and disappear, which is consistent with the physical picture of a first-order phase transition. For more details, see Appendix D.

Note that Eq. (33) becomes

\[
A^2 \sim -\frac{2}{3 \chi} [4 \kappa_4 + \theta_4(2 - \ln 3)],
\]

(35)

as \( \chi \gg 1 \). This relation follows from (27) if we substitute \( \theta_b = \theta_c + \epsilon \chi, \theta_2 = \epsilon^2 \chi, \theta_4 = \epsilon^4 \chi \) and \( \kappa_2 = \epsilon^2 \kappa_4 \) therein. Therefore, as expected, the bifurcating solution of (33) matches the solution of the bifurcation equation (27) as we move away from the tricritical point.

### C. Bifurcation at the turning point

At the turning point \( N \), the coefficient of \( A \) in the bifurcation equation (26) becomes \( 2 \kappa_2 \), independent of \( \theta_2 \). We can unfold this bifurcation by rescaling the bifurcation parameter

\[
\kappa = \frac{1}{2 \epsilon} + \epsilon \frac{\kappa_4}{\kappa_2} + O(\epsilon^6),
\]

(36)

and expanding the coefficient of \( U^2 \) in the free energy up to \( O(\epsilon^3 \theta_2^2) \) terms. Inserting the result in Eq. (27), we obtain

\[
\Delta f = \frac{\epsilon^2}{2} \frac{[(U')^2 - U^2]}{\pi^2} + \epsilon^4 \left[ \kappa_4 + \frac{\epsilon \theta_2^2}{4} \right] U^2 + \frac{3 - \epsilon^2 \theta_2^2}{24} U^4 + O(\epsilon^6) \]

(37)
The corresponding Euler-Lagrange equations are

\[ \frac{U''}{\pi^2} + U = \epsilon^2 \left[ 2e \left( \kappa_4 + \frac{e^2}{4} \right) U - \frac{\epsilon^2 - 3}{6} U^3 \right] + O(\epsilon^4), \]

to be solved with clamped boundary conditions. Inserting (24) into this formula and equating like powers of \( \epsilon \), we obtain a hierarchy of equations.

Again, the solution of the first equation of the hierarchy with clamped boundary conditions is \( U_0(x) = A \sin \pi x \). The second equation is

\[ \frac{U''}{\pi^2} + U_2 = 2e \left( \kappa_4 + \frac{e^2}{4} \right) U_0 - \frac{\epsilon^2 - 3}{6} U_0^3. \]

This equation has a solution that satisfies clamped boundary conditions provided its rhs is orthogonal to \( \sin \pi x \), which yields

\[ 2e \left( \kappa_4 + \frac{e^2}{4} \right) A - \frac{\epsilon^2 - 3}{8} A^3 = 0. \]

The nontrivial solution of this equation satisfies

\[ 0 < A^2 = \frac{4e(4\kappa_4 + e^2)}{\epsilon^2 - 3}. \] (38)

Note that \( \kappa_4 = -e^2/4 \) is nothing but the lowest approximation to the bifurcation curve in the vicinity of the nose, written in the scaled variables.

Equation (38) implies that buckled solutions stem continuously from the parabola \( \kappa_4 = -e^2/4 \) and exist outside it. These buckled states (corresponding to phase \( B^- \)) bifurcate subcritically at \( \theta_2^{(3,2)} = \pm 2\sqrt{-\kappa_4/\epsilon} \). The corresponding temperatures are on the upper and lower branches of the bifurcation curve, respectively. At the turning point \( \kappa_4 = 0 \) and the two bifurcation points merge. For \( \kappa_4 > 0 \) (\( \kappa > \kappa_4 \)), there is a single unstable buckled state given by (38), for points close enough to the bifurcation curve.

Note that the stable phase \( B^+ \) cannot be predicted by the bifurcation analysis near the nose, since the corresponding string profile is not close to the flat solution therein. We know that, for fixed \( \kappa > \kappa_4 \), both buckled phases \( B \pm \) coalesce at the boundary between Regions IIIb and I in Figure 3. These buckled string configurations persist as the temperature \( T \) → 0 + for all spin-spin couplings \( \kappa < \kappa_M^{(0)} = \pi^2/32 \), as indicated in Section IV A.

V. LOW TEMPERATURE BEHAVIOR

A. Low temperature profiles: Exact solution of the Euler-Lagrange equation

At very low temperatures, such that \( \exp(-2\kappa/\theta) < 1 \) in Fig. 1, there are buckled solutions in addition to the stable flat profile. We calculate exactly their profiles below.

In fact, for \( \theta \ll |u| \), the local magnetization \( \mu \) of Eq. (4) reduces to

\[ \mu(u; \kappa, \theta = 0^+) = \text{sgn}(u) \eta(|u| - 2\kappa), \] (39)

where \( \eta(x) \) is the Heaviside step function. Substituting Eq. (39) into (4), we find \( u'' = 0 \) if \( |u| < u_0 = 2\kappa \), and \( u'' = \pm \pi^2 \) if \( |u| > 2\kappa \). Then \( u(x) \) is a linear function if \( |u| < 2\kappa \), and a parabola if \( |u| > 2\kappa \). Due to the clamped boundary conditions, buckled solutions with a single extremum (no internal nodes) are linear close to the boundaries, \( x \in (0, x_0) \) or \( x \in (1 - x_0, 1) \), and have a parabolic profile in the bulk \( x \in (x_0, 1 - x_0) \). The condition \( |u(x_0)| = 2\kappa \) produces the condition \( \pi^2 x_0 (1 - 2x_0) = 4\kappa \) whose solutions \( x_{0,1} \) and \( x_{0,2} \) are

\[ x_{0,j} = \frac{1}{4} \left( 1 + (-1)^j \sqrt{1 - \frac{\kappa}{\kappa_M^{(0)}}} \right), \quad j = 1, 2, \] (40)

for \( \kappa < \kappa_M^{(0)} = \pi^2/32 \). We have \( x_{0,1} < 1/4 < x_{0,2} < x_{0,1} + x_{0,2} = 1/2 \). If \( \kappa > \kappa_M^{(0)} \), these rippled low-temperature profiles are not possible and the only solution is \( u = 0 \).

Fig. 5 shows two of these profiles for an appropriate value of \( \kappa \). The same functions multiplied by -1 are also stationary solutions. In these string profiles, the pseudo-spins exhibit antiferromagnetic order close to the boundaries and ferromagnetic order in the bulk, see below.

The profiles with \( x_{0,1} < 1/4 \) produce a relative minimum of the free energy and are stable whereas those with \( x_{0,2} > 1/4 \) are unstable [32], as proven in Appendix A.

Thus, for \( \kappa < \kappa_M^{(0)} \), the buckled profiles with \( x_{0,1} < 1/4 \)
and the flat string are stable and the unstable profiles with \( x_{0,2} > 1/4 \) separate them. The stable and unstable buckled profiles coalesce and disappear at \( \kappa = \kappa_M^{(0)} \) \( (x_{0,1} = x_{0,2} = 1/4) \). This allows us to identify the buckled profiles with \( x_{0,1} \) and \( x_{0,2} \) as the low temperature limits of phases \( B^+ \) and \( B^- \), respectively.

By direct integration, we can show that the absolute minimum of the free energy corresponds to the buckled configurations with \( x_{0,1} \) if \( 0 < \kappa < \kappa_M^{(0)} = 3\pi^2/128 \) \( (0 < x_{0,1} < x_t = 1/8) \). For \( \kappa_t^{(0)} < \kappa < \kappa_M^{(0)} \) \( (x_t < x_{0,1} < 1/4) \), the free energy of the flat string is smaller than that of the buckled configurations with \( x_0 = x_{0,1} \). Thus the flat string profile is metastable for \( 0 < \kappa < \kappa_t^{(0)} \) and stable for \( \kappa_t^{(0)} < \kappa < \kappa_M^{(0)} \). The situation is reversed for the buckled configurations with \( x_0 = x_{0,1} \). At \( \kappa = \kappa_t^{(0)} \) there is a first order phase transition, where the buckled phase with \( x_{0,1} \) and the flat string coexist. Consistently, the first-order derivatives of the free energy change discontinuously at \( \kappa = \kappa_t^{(0)} \). In fact, as \( \kappa \) increases past \( \kappa_t^{(0)} \), \( M \) and \( \mathcal{D} \mathcal{L} \) jump from \( M = 3/4 \) and \( \mathcal{D} \mathcal{L} = 3/4 \) (buckled phase with \( x_{0,1} \)) to \( M = 0 \) and \( \mathcal{D} \mathcal{L} = 1/2 \) (flat phase).

### B. Spin configurations of the low temperature buckled string states

What are the spin configurations at buckled string states? It turns out that the spins form antiferromagnetic domains near the boundaries and ferromagnetic domains in the central region of the string. To see this, we derive their marginal probability \( \mathcal{P}(\sigma) \) by integrating the canonical distribution \( \exp(-\mathcal{H}/T) \) over the string degrees of freedom. The result is

\[
\mathcal{P}(\sigma) \propto e^{-\mathcal{H}_{\text{eff}}(\sigma)/\theta}, \quad \mathcal{H}_{\text{eff}}(\sigma) = \kappa \sigma^T J \sigma - \frac{\pi^2}{2N^2} \sigma^T \Lambda \sigma. \quad (41)
\]

Here, the effective spin Hamiltonian \( \mathcal{H}_{\text{eff}}(\sigma) \) contains the nearest neighbor antiferromagnetic interaction given by

\[
J_{ij} = \frac{1}{2} (\delta_{i,j+1} + \delta_{i,j-1}) \quad (42)
\]

and a long-ranged ferromagnetic interaction given by

\[
\Lambda_{ij} = \frac{1}{N+1} \delta(N-i+1) > 0, \quad \forall i \geq j, \quad \Lambda_{ij} = \Lambda_{ji}, \quad (43)
\]

which is derived in Appendix C. Phase transitions in a one-dimensional model stem from this effective long range interaction, similarly to the situation found in other spin-oscillator models \[11,14,15\].

We focus on the low temperature limit as \( \theta \to 0^+ \); therein, the equilibrium probability concentrates in the spin configuration that corresponds to the absolute minimum of \( \mathcal{H}_{\text{eff}} \). The long-range ferromagnetic interaction \( (43) \) is stronger for the pseudo-spins located near the center of the system than for those close to the boundaries.

Therefore, as the intensity of the antiferromagnetic interaction \( \kappa \) increases, the absolute minimum of \( \mathcal{H}_{\text{eff}} \) moves from the completely ferromagnetic configuration to one that is antiferromagnetic at the boundaries and ferromagnetic in the bulk. See Appendix C for details.

In light of the previous discussion, we restrict ourselves to states that are antiferromagnetic at the boundaries and ferromagnetic in the center. Note that this restriction includes completely antiferromagnetic and ferromagnetic states. We label the states by the number \( n_a = 1, 3, 5, \ldots, N/2 \) of spins at the antiferromagnetic boundary regions; see Fig. 6. Moreover, we denote by \( \mathcal{H}_{\text{eff}}(n_a) \) the effective potential for such a configuration. In Appendix C, we find

\[
\mathcal{H}_{\text{eff}}(n_a) = (n_a - 1) \left\{ \frac{\pi^2}{6N^2} [N(3 + n_a)3 - 21 - 13n_a] - 4n_a^2 - 4\kappa \right\}. \quad (44)
\]

The origin of energy is such that \( \mathcal{H}_{\text{eff}}(n_a = 1) = 0 \).

Depending on the value of \( \kappa \), \( \mathcal{H}_{\text{eff}}(n_a) \) has one or two minima, as seen in Fig. 7. For \( \kappa = 0 \), the completely ferromagnetic configuration gives the minimum of \( \mathcal{H}_{\text{eff}} \), as expected on physical grounds. On the other hand, as \( \kappa \) increases, there appear several relevant values of \( \kappa \), namely

\[
\kappa_0 = \frac{\pi^2}{4N(N+1)}, \quad \kappa_1 = \frac{\pi^2}{384} \frac{9N^2 + 6N - 47}{N^2}, \quad \kappa_2 = \frac{\pi^2}{96} \frac{3N^2 + 6N - 5}{N^2}. \quad (45a, 45b, 45c)
\]

The physical meaning of which are discussed below. First, for \( \kappa = \kappa_0 \), the configurations with \( n_a = 1 \) and \( n_a = 0 \)
share the same value of $\mathcal{H}_{\text{eff}}$. This marks the onset of the antiferromagnetic ordering at the boundaries, although for a large system this ordering is only relevant when $n_a/N$ becomes of the order of unity. In fact, for large $N$, $\kappa_0$ is proportional to $N^{-1}$, whereas both $\kappa_1$ and $\kappa_2$ become independent of $N$. Second, at $\kappa_1$, the relative minimum of $\mathcal{H}_{\text{eff}}$ has the same value as the completely antiferromagnetic configuration. Finally, at $\kappa_2$, this relative minimum disappears and the only stable configuration is that of the absolute minimum for $n_a = N/2$, that is, the completely antiferromagnetic configuration.

The situation described above is illustrated in Fig. 7, in which we plot $\mathcal{H}_{\text{eff}}$ as a function of $n_a$, for different values of $\kappa$. Of course, in the large $N$ limit, the values of $\kappa$ at which there are changes in the stability of the solution are in perfect agreement with those obtained from the analysis of the solution of the Euler-Lagrange equation for the string profile: $\kappa_1$ and $\kappa_2$ tend to $\kappa_0^{(0)}$ and $\kappa_M^{(0)}$, respectively. The completely antiferromagnetic configuration leads to an almost flat, wrinkled, string whereas the completely ferromagnetic distribution corresponds to a buckled configuration, with a definite sign of the curvature. Accordingly, the low temperature phase, comprising antiferromagnetic boundaries and a ferromagnetic bulk yields a buckled string with linear ($u^r = 0$) boundaries, as depicted in Figs. 5 and 6.

VI. CONCLUSIONS

Despite its simplicity, the 1d string model contains the key ingredients that lead to the emergence of wrinkled and buckled phases in graphene. The transversal displacements $u_i$ are coupled to internal degrees of freedom, modeled by spin variables $\sigma_i$. The latter have two competing interactions: (i) an on-site interaction with their corresponding displacements, and (ii) an antiferromagnetic interaction (of strength $\kappa$) between nearest neighbor spins.

A coarse-grained approach, where internal degrees of freedom are integrated out to give rise to an effective free energy for the string deformation, entails that the string curvature is controlled by the local magnetization and the flat string phase $L$ becomes unstable inside a bifurcation line $\kappa_b(\theta)$ whose inverse function is two-valued. For a given $\kappa$, lowering the temperature $\theta$ produces buckled string profiles with non-zero global magnetization. For low enough temperatures, the short-ranged antiferromagnetic interaction: (i) modifies the buckled profiles, introducing an antiferromagnetic region close to the boundaries, and (ii) makes the flat string metastable.

Fig. 1 and Table I provide a summary of the different phases, their domains of existence and their stability. In region I, the antiferromagnetic interaction prevails and only the flat phase $L$ exists. In region II, the long-range ferromagnetic interaction dominates and there appears a stable buckled phase $B^+$. For each $\theta$ in Region III, there is a competition between the ferromagnetic interaction that induces global buckling and the antiferromagnetic interaction that favors the flat phase. Therein, both the flat phase $L$ and the buckled phase $B^+$ are locally stable minima of the free energy. In addition, there appears an unstable buckled phase $B^-$ that separates these minima.

A key element in the observed behavior is the existence of a tricritical point $K$, at which all phases coalesce. As shown by Figs. 1 and 3 three lines emanating from $K$ control the different phases: the bifurcation line $\kappa_b(\theta)$, the coexistence line $\kappa_c(\theta)$ and the first-order line $\kappa_M(\theta)$, $\kappa_b(\theta) < \kappa_c(\theta) < \kappa_M(\theta)$. We have obtained an exact expression for $\kappa_b(\theta)$ and approximate analytical expressions for $\kappa_c(\theta)$ and $\kappa_M(\theta)$ near the critical point. As shown in Fig. 3, their continuation far from $K$ describes better the coexistence line $\kappa_c(\theta)$ than the first-order-line $\kappa_M(\theta)$. This is logical because they follow from a Landau-like expansion of the free energy around the flat solution.
The above phase diagram is qualitatively similar to that found numerically in a 2d version of the model, built on a hexagonal lattice to model buckling and rippling in graphene [10]. It is the qualitative shape of this phase diagram that explains the emergence of the rippled to buckled transition when the system is heated, recently observed in STM experiments [9]. The key point is the existence of values of the antiferromagnetic parameter $\kappa$ (Region IIIa in Fig. 1), for which the flat phase is locally stable at low temperature but becomes unstable and is replaced by a buckled phase when the temperature is increased. For sufficiently low initial temperature, we may prepare the string in a rippled flat profile that is a metastable equilibrium state. As the temperature slowly increases past the bifurcation line, the string suddenly jumps to and remains in a buckled state.

In light of the above discussion, it is tempting to conjecture that the actual phase diagram of graphene is similar to the one found here. The crux of the argument is the existence of some internal degrees of freedom analogous to pseudo-spins. For them: (i) their direct short-rage interaction (of strength $\kappa$) favors rippling, but (ii) their couplings to the elastic modes produce a long-range interaction that favors buckling. It is this competition that leads to a phase diagram like ours, in which there appear first order phase transitions below some temperature. Then there appears a STM-like rippled-to-buckled transition as described in the previous paragraph.

In suspended graphene sheets, buckling instabilities may be due to residual stresses produced by the electron-phonon interaction [8]. This conclusion is based on a linear stability analysis of the flat configuration solution of saddle-point equations for phases in thermal equilibrium (first deduced in [13]). Whether buckling states bifurcate sub or supercritically from the flat membrane requires a study of not yet deduced small amplitude equations.

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Appendix A: Stability of the low temperature string profiles

At low temperatures $\theta \to 0^+$, the Euler-Lagrange equation becomes equivalent to

$$\frac{1}{\pi^2} u'' + \text{sgn}(u)\eta(|u| - 2\kappa) = 0, \ u(0) = u(1) = 0. \quad (A1)$$

The solutions without internal nodes are [12]

$$u^{(0)}(x) = \pm \begin{cases} \pi^2(1-2\kappa)x & x < x_0, \\ 2\kappa + \frac{\pi^2(x-x_0)(1-x_0-x)}{2}, & x_0 < x < 1-x_0, \\ \pi^2(1-2\kappa)(1-x) & x > 1-x_0. \end{cases} \quad (A2)$$

The relation $u(x_0) = 2\kappa$ produces the following equation for $x_0$:

$$\frac{\pi^2}{2} x_0(1-2x_0) = 2\kappa, \quad (A3)$$

Provided $\kappa < \kappa_M = \pi^2/32$, there are two solutions $x_{0,j}$, $j = 1, 2$, given by Eq. (40), which are symmetrical with respect to $1/4$, $x_{0,1} < 1/4 < x_{0,2}$. For $\kappa > \kappa_M$, there are no buckled solutions and $x_{0,1} = x_{0,2} = 1/4$ if $\kappa = \kappa_M$.

Let $u^{(0)}(x)$ be one of these buckled stationary profiles characterised by the sign in (A2) and the value of $x_0$. To study its linear stability, we consider a small disturbance to it, $u(x) = u^{(0)}(x) + \Delta u(x)$. According to the stability conditions described in Sec. [11], we have to solve the linear boundary value problem (BVP)

$$\frac{1}{\pi^2} \Delta u'' + \delta(u^{(0)}(x) - 2\kappa)\Delta u = 0. \quad (A4a)$$

$$\Delta u(0) = \Delta u(a) = 0, \quad a \leq 1. \quad (A4b)$$

Equation (A4a) is the linearisation of Eq. (A1) around (A2) (with positive sign). The profile $u^{(0)}(x)$ is stable if, for any $a \leq 1$, $\Delta u(x) \equiv 0$ is the unique solution of this BVP. On the contrary, if the BVP has a non-trivial solution for some $a < 1$, then $u^{(0)}(x)$ is unstable.

Integrating (A4a) from $x_j$ to $x_{j+1}$ ($x_j$ is either $x_0$ or $1 - x_0$), we find the jump conditions:

$$\Delta u'(x_{j+1}) - \Delta u'(x_j) = -\frac{2}{1-2x_0} \Delta u(x_j). \quad (A5)$$

As the solution of (A4a)-(A4b) is unique up to a multiplicative constant factor, we can fix the slope at $x = 0$ to be $\Delta u'(0) = 1$ [30]. Then $\Delta u(0^+) > 0$. If we find $\Delta u(1) < 0$, then $\Delta u(a) = 0$ at some intermediate point $a \leq 1$ and the profile $u^{(0)}(x)$ is unstable.

Equation (A4a) tells us that $\Delta u(x)$ is composed of straight lines, with slope jumps at the points $x_0$ and $1 - x_0$ determined by Eq. (A5). Therefore, $\Delta u = \left\{ \begin{array}{ll} x, & 0 < x < x_0, \\ x_0 + c_1(x-x_0), & x_0 < x < 1-x_0, \\ x_0 + c_1(1-2x_0) + c_2(x-1+x_0), & 1-x_0 < x < 1. \end{array} \right.$ (A6)

The jump conditions (A5) readily yield

$$c_1 = \frac{1-4x_0}{1-2x_0}, \quad c_2 = -1. \quad (A6)$$
Then, \[
\Delta u(1) = 1 - 4x_0. \tag{A7}
\]
Thus the stationary profile having \(x_0 > 1/4\), corresponding to \(x_{0,2}\) in Eq. (40), produces \(\Delta u(1) < 0\) and it is unstable as explained above. For the other stationary profile, corresponding to \(x_{0,1} < 1/4\), \(\Delta u(x)\) is positive for \(0 < x < 1\) and the only solution of the BVP is \(\Delta u = 0\). Therefore this stationary profile is linearly stable.

Appendix B: Effective Hamiltonian for the pseudo-spins

We start by deriving the pseudo-spins’ marginal probability \(\mathcal{P}(\sigma)\) by integrating the canonical distribution \(\mathcal{P}(u, p, \sigma)\) over the string degrees of freedom. To do so, we rewrite Eq. (4) in matrix form,

\[
\mathcal{H} = \frac{1}{2m} p^T p + \frac{k}{2} u^T K u - f u^T \sigma + J \sigma^T J \sigma, \tag{B1}
\]

in which \((u, p, \sigma)\) are now column matrices of dimension \(N\), \((u^T, p^T, \sigma^T)\) are their respective transpose matrices, and \(J\) and \(K\) are symmetric matrices of dimension \(N\), namely

\[
J = \begin{bmatrix}
0 & \frac{1}{2} & \frac{1}{2} & \cdots & \frac{1}{2} \\
\frac{1}{2} & 0 & \frac{1}{2} & \cdots & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & 0 & \cdots & \frac{1}{2} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \cdots & 0
\end{bmatrix}, \quad K = \begin{bmatrix}
2 & -1 & & & \\
-1 & 2 & -1 & & \\
& -1 & 2 & -1 & \\
& & -1 & 2 & \\
& & & -1 & 2
\end{bmatrix}. \tag{B2}
\]

Also, we make the following change of variables, \(u = v + \frac{k}{f} \Lambda \sigma\), where \(\Lambda\) is the inverse of the matrix \(K\),

\[
\Lambda_{ij} = \frac{1}{N + 1} j(N - i + 1) > 0, \forall i \geq j, \quad \Lambda_{ij} = \Lambda_{ji}, \tag{B3}
\]

see below for details on the derivation of the elements of \(\Lambda\).

Interestingly, the variables \((v, p)\) and \(\sigma\) become decoupled in the Hamiltonian, making it easy to integrate the canonical distribution over \((v, p)\). The result is

\[
\mathcal{P}(\sigma) \propto e^{-\mathcal{H}_{\text{eff}}(\sigma)/\beta}, \quad \mathcal{H}_{\text{eff}}(\sigma) = \kappa \sigma^T J \sigma \frac{\pi^2}{2N^2} \sigma^T \Lambda \sigma, \tag{B4}
\]

which is Eq. (41) of the main text.

Now, we derive the explicit expression of the elements of the matrix \(\Lambda = K^{-1}\). From equation Eq. (B2), we can directly calculate the determinant of the matrix \(K_n\) (\(K\)-matrix with dimension \(n\)) as

\[
\det(K_1) = 2, \quad \det(K_2) = 3, \tag{B5a}
\]
\[
\det(K_n) = 2 \det(K_{n-1}) - \det(K_{n-2}). \tag{B5b}
\]

Hence,

\[
\det(K_n) = n + 1. \tag{B6}
\]

We take advantage of \(K\) being a symmetric matrix \(K = K^T\), and impose \(i \geq j\) when calculating \(\Lambda_{ij}\), which is also symmetric. Then, for dimension \(N\)

\[
\Lambda_{ij} = \frac{1}{N + 1} (-1)^{i+j} \det(K_{j-i})(-1)^{i-j} \det(K_{N-i}) = \frac{1}{N + 1} j(N - i + 1), \tag{B7}
\]

where we have made use of

\[
\det \begin{bmatrix}
A & 0 \\
B & C
\end{bmatrix} = \det(A) \det(C), \tag{B8}
\]

in which \(A\), \(B\) and \(C\) are non-zero matrices and \(0\) the zero matrix.

Appendix C: Effective Hamiltonian landscape

We want to characterise the \(\mathcal{H}_{\text{eff}}\) landscape as \(\kappa\) is modified, where the phase space is formed by all possible configurations of \(\sigma\). For small enough \(\kappa\), the completely ferromagnetic configuration with all the pseudo-spins pointing up (or down) minimises Eq. (B4). On the other hand, as \(\kappa\) increases the configuration minimising Eq. (B4) changes. Let us start from a completely ordered ferromagnetic configuration \(\sigma_{\text{ferro}}\), in which \(\sigma_i = +1, \forall i\), and change the sign of \(\sigma_i\), thereby obtaining the configuration \(R_i \sigma_{\text{ferro}}\). The additional contribution to the free energy is

\[
\Delta \mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{eff}}(R_i \sigma_{\text{ferro}}) - \mathcal{H}_{\text{eff}}(\sigma_{\text{ferro}}) = \frac{\pi^2}{2N^2} \sum_{i \neq l} \Lambda_{i,i} - \kappa, \tag{C1}
\]

where

\[
\sum_{i \neq l} \Lambda_{i,i} = \frac{(N - 1)(N + 1 - l)}{2(N + 1)}. \tag{C2}
\]

This positive expression has a maximum at the centre, \(l = (N + 1)/2\), and therefore \(\Delta \mathcal{H}_{\text{eff}}\) is minimum when the flipping pseudo-spins are those at the borders of the chain. This suggests that, as \(\kappa\) increases, the most probable (minimum free energy) state will become antiferromagnetic at both boundaries while remaining ferromagnetic in the bulk.

Now we can analyze the behavior of this global minimum with increasing \(\kappa\). In light of the discussion above, we restrict ourselves to configurations in which \(n_a\) consecutive antiferromagnetic links have been created at each boundary, see Fig. 6. We denote by \(\mathcal{H}_{\text{eff}}(n_a)\) the value of the effective Hamiltonian for such a configuration.
Since \( n_a \) increases by two, we are interested in evaluating \( \mathcal{H}_{\text{eff}}(n_a) - \mathcal{H}_{\text{eff}}(n_a - 2) \). Using Eq. (B4), taking into account the symmetries of \( K \) and \( J \), and that we only have to take care of the terms that change their sign from \( \mathcal{H}_{\text{eff}}(n_a) \) to \( \mathcal{H}_{\text{eff}}(n_a - 2) \), we get the expression

\[
\mathcal{H}_{\text{eff}}(n_a) - \mathcal{H}_{\text{eff}}(n_a - 2) = \frac{4\pi^2}{N^2} \left[ \sum_{j=1}^{n_a-1} (-1)^j (N - n_a + 1) + \sum_{i=n_a+1}^{N-n_a} \frac{n_a(N - i + 1)}{N + 1} + \sum_{i=N-n_a+2}^{N} (-1)^{i+1} \frac{(N - i + 1)n_a}{N + 1} \right] - 8\kappa.
\]

After some simplifications,

\[
\mathcal{H}_{\text{eff}}(n_a) - \mathcal{H}_{\text{eff}}(n_a - 2) = \frac{2\pi^2}{N^2} \left[ -1 + (1 + N - 2n_a) n_a \right] - 8\kappa.
\]

Iteration of this recurrence relation gives Eq. (44).

### Appendix D: Stability of the phases

Here we determine the stability of the different phases whose approximate profiles near bifurcation points,

\[ u_S(x; C) = C \sin(\pi x), \]

solve the Euler-Lagrange equations for the total free energy (see Sec. IV). Phase L (flat string profile) has \( C = 0 \), whereas \( C \neq 0 \) for the buckled phases \( B_\pm \). We shall calculate the total free energy for \( u_S \) as a function of \( C \) and determine whether it is a relative maximum or a minimum. The obtained stability results are consistent with the principle of exchange of stabilities in bifurcation theory [26].

The difference of free energies between the sinusoidal and the flat profiles is given by

\[
\Delta F(C; \kappa, \theta) \equiv \int_0^1 dx \left[ f(u_S, u'_S; \kappa, \theta) - f_L(\kappa, \theta) \right].
\]

Note that \( \Delta F \) is no longer a functional but a function of the (unknown) amplitude \( C \). To simplify our notation, we omit the dependence on \( (\kappa, \theta) \) hereafter. Within the same level of approximation as we have been working throughout, we have

\[
\Delta F(C) \sim \int_0^1 dx \left( \frac{1}{2} \delta f_{2,b} u_S^2 + \frac{1}{4!} f_{4,b} u_S^4 + \frac{1}{6!} f_{6,b} u_S^6 \right) = \frac{1}{4} \delta f_{2,b} C^2 + \frac{1}{64} f_{4,b} C^4 + \frac{1}{2304} f_{6,b} C^6,
\]

where \( \delta f_{2,b} = f_2 - f_{2,b}, f_{n,b} \) is the value of \( f_n \) over the bifurcation curve, as introduced in Sec. IV, and we have neglected \( O(C^8) \) terms. The equilibrium values of \( C \), which we denote by \( C_{\text{eq}} \), are found by seeking the extrema of \( \Delta F(C) \), see below.

Far from the critical point, consistently with the procedure for solving perturbatively the Euler-Lagrange equation in Sec. IV, the term proportional to \( C^6 \) in Eq. (D3) can be neglected. Then, the non-vanishing values of \( C_{\text{eq}} \) obey

\[
C_{\text{eq}}^2 \sim -\frac{8 \delta f_{2,b}}{f_{4,b}}.
\]

Note that \( \delta f_{2,b} \) is of the order of \( \epsilon^2 \), cf Eqs. (21) and (20). Thus, \( C_{\text{eq}} \) is \( O(\epsilon) \) and with the substitution \( C_{\text{eq}} = \epsilon A \), the above equation is completely equivalent to Eq. (27).

Insertion of \( C_{\text{eq}} \) into Eq. (D3) gives the free energy difference between the buckled and the flat phase,

\[
\Delta F_{\text{eq}} \sim -\frac{\delta f_{2,b}^2}{f_{4,b}}.
\]

which shows that the sign of \( \Delta F_{\text{eq}} \) is controlled by the sign of \( f_{4,b} \).

The stability of the phases can be further elucidated by looking at the sign of the second derivative of \( \Delta F \) with respect to \( C \), which is given by

\[
\frac{\partial^2 \Delta F}{\partial C^2} \sim \frac{\delta f_{2,b}^2}{2} + \frac{3}{16} f_{4,b} C^2.
\]

Therefore,

\[
\left. \frac{\partial^2 \Delta F}{\partial C^2} \right|_{\text{eq}} = -\delta f_{2,b},
\]

and the stability is controlled by the sign of \( \delta f_{2,b} \). We recall that \( f_{4,b} \) vanishes at the critical point \( \kappa \), and that \( f_{4,b} > 0 \) (\( f_{4,b} < 0 \)) above (below) it. Then, above the critical point, the phase \( B^+ \) bifurcates inside the bifurcation line \( (\delta f_{2,b} < 0) \) where the flat phase L becomes unstable, and is thus stable: \( \partial^2_C F(C)|_{B^+} > 0 \) and, consistently, \( \Delta F_{\text{eq}}|_{B^+} < 0 \). To the right of the critical point, the phase \( B^- \) emerges outside the bifurcation line \( (\delta f_{2,b} > 0) \), where the flat phase is stable, and is unstable: \( \partial^2_C F(C)|_{B^-} < 0 \) and \( \Delta F_{\text{eq}}|_{B^-} > 0 \). The phase \( B^- \) is indeed unstable but it does not correspond to a (local) maximum of the free energy functional, but to some kind...
of “saddle point” extremum that is neither a minimum nor a maximum.\textsuperscript{[35]}

In the vicinity of the tricritical point $K$, we have to keep the $C^6$ terms, and substitute the coefficients of $\Delta F(C)$ with their leading behaviors. With the same notation as before,

$$\Delta F(C) \sim \frac{1}{4} \delta f_{2,c} C^2 + \frac{1}{64} f_{1,c}^{(1)} C^4 + \frac{1}{2304} f_{6,c} C^6. \quad \text{(D8)}$$

where

$$\delta f_{2,c} = \epsilon^4 \varphi_{4,c}, \quad f_{1,c}^{(1)} = \epsilon^2 6 \sqrt{3} \chi, \quad f_{6,c} = 36, \quad \text{(D9)}$$

and we have used Eqs.\textsuperscript{[20]} (with $\kappa_2 = \theta_0 = 0$),\textsuperscript{[25]} and\textsuperscript{[30]} Again, $C_{eq}$ is found by looking for the extrema of $\Delta F$, and $C_{eq} = O(\epsilon)$. By introducing $C_{eq} = \epsilon A$, we have that $A$ is the solution of the biquadratic equation\textsuperscript{[33]}.

Let us denote by $A_2^b$ the two solutions of Eq.\textsuperscript{[33]}, with $A_2^b > A_2$. As discussed in Sec.\textsuperscript{[14]} (i) above the critical point, $\chi > 0$, it is only $A_2^b$ that makes sense ($A_2^b < 0$) and (ii) below the critical point, $\chi < 0$, both $A_2^b$ and $A_2$ are positive in a certain domain.

Again, the local stability of the phases is given by the second derivative of $\Delta F$ at equilibrium. After a little algebra, one gets the result

$$\frac{\partial^2 \Delta F}{\partial C^2} \bigg|_{B^\pm} = \pm \frac{\sqrt{3}}{4} \epsilon^6 \tilde{A}_2^b \sqrt{9 \chi^2 - 4 \varphi_{4,c}}. \quad \text{(D10)}$$

Then the phase $B^+$ is locally stable and the phase $B^-$ is unstable within their respective domains of existence. Below the critical point, we recall that the phase $B^+$ exists for $\kappa < \kappa_M(\theta)$, where $\kappa_M(\theta)$ is the first-order line given by Eq.\textsuperscript{[24]}, whereas the phase $B^-$ only exists between the bifurcation line and the first-order line, $\kappa_b(\theta) < \kappa < \kappa_M(\theta)$. Over $\kappa_M(\theta)$, both phases $B^\pm$ merge, disappear and $\partial^2 \Delta F/\partial C^2|_{B^\pm} = 0$, because the argument of the square root becomes equal to zero. Above the critical point, only the plus sign is possible and Eq.\textsuperscript{(D10)} smoothly matches with Eq.\textsuperscript{(D7)}.

Let us focus on region III of the phase diagram in Fig.\textsuperscript{[1]} that is, between the bifurcation and the first-order line, $\kappa_b(\theta) < \kappa < \kappa_M(\theta)$. Further analysis is necessary to find out which of the two locally stable phases, the flat $L$ phase and the buckled $B^+$ phase, gives the absolute minimum of the free energy. The free energy difference $\Delta F$ is obtained by inserting $C_{eq} = \epsilon A$ in Eq.\textsuperscript{(D8)}, which yields

$$\Delta F_{B^\pm} = \frac{\epsilon^6}{48} \tilde{A}_2^b \left[ 8 \varphi_{4,c} \pm 3 \sqrt{9 \chi^2 - 4 \varphi_{4,c}} - 9 \chi^2 \right]. \quad \text{(D11)}$$

Recall that $\chi < 0$ below the critical point, and thus $\sqrt{9 \chi^2} = -3 \chi$. Consistently with its unstable character, $\Delta F_{B^-} \geq 0$, it varies from $\Delta F_{B^-} = 0$ over the bifurcation line $\kappa_b(\theta)$, at which $A_2^b$ vanishes, to the positive value $\Delta F_{B^+}^{\max} = 9 \epsilon^6 \tilde{A}_2^b \chi^2/48 > 0$ at the first-order line $\kappa_M(\theta)$. On the other hand, $\Delta F_{B^+} < 0$ at the bifurcation line, whereas $\Delta F_{B^+} = \Delta F_{B^+}^{\max}$ at the first order line because the phases $B^\pm$ merge. Thus, there must be a coexistence line at which $\Delta F_{B^+}$ vanishes and phases $B^+$ and $L$ are equally probable. Equation\textsuperscript{(D11)} determines the condition $\varphi_{4,c} = 27 \chi^2/16$ or

$$\kappa_2(\theta) = \kappa_b(\theta) + \frac{27 \sqrt{3}}{96} (\theta - \theta_c)^2, \quad \theta < \theta_c, \quad |\theta - \theta_c| \ll 1. \quad \text{(D12)}$$

For $\kappa_b(\theta) < \kappa < \kappa_2(\theta)$, the most stable phase is $B^+$, whereas the flat phase $L$ is metastable; the situation is just reversed in the region $\kappa_2(\theta) < \kappa < \kappa_M(\theta)$.

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[35] Note that the phase B+ cannot be produced by an expansion around the flat solution below the critical point, because its amplitude does not vanish at the bifurcation line. This is the reason why the solution obtained to the right of the critical point corresponds to the phase B-.