

Irreversibility in Response to Forces Acting on Graphene Sheets

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The amount of rippling in graphene sheets is related to the interactions with the substrate or with the suspending structure. Here, we report on an irreversibility in the response to forces that act on suspended graphene sheets. This may explain why one always observes a ripple structure on suspended graphene. We show that a compression-relaxation mechanism produces static ripples on graphene sheets and determine a peculiar temperature T_c , such that for $T < T_c$ the free-energy of the rippled graphene is smaller than that of roughened graphene. We also show that T_c depends on the structural parameters and increases with increasing sample size.

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Introduction.—Two-dimensional graphene crystals [1] have attracted considerable attention both experimentally and theoretically, due to their unusual electronic properties [2]. Ripples or undulations were first observed in freely suspended graphene flakes in experiments [3]. The ripples affect the electronic properties [4], such as the conductivity and the quantum transport properties. Charge inhomogeneities due to the ripples have also been observed in graphene [5]. A new method to fabricate periodically rippled graphene on Ru(0001) under ultrahigh vacuum conditions was reported in [6]. The ripples in graphene were studied theoretically [7], and it was claimed that the ripples may be explained as a consequence of adsorbed molecules sitting on random sites.

There are two points of view on the physics of the ripples. Meyer *et al.* [3] proposed that the reproducible appearance of the ripples across samples indicates that it is an intrinsic effect. They emphasized that the homogeneity and isotropy of the ripples are not compatible with the assumption of an incompressible sheet. They estimated a local strain of up to 1% for a single-layer flake. Using the generic free energy for the long wavelength deformations [8], Castro Neto and Kim [9], on the other hand, argued that graphene may be considered as an atomic thin membrane, with its physics being also similar to a soft membrane. In this point of view the ripples are not intrinsic and can be the results of the environment, such as the substrate in the system.

Recently, direct observation and controlled creation of periodic ripples in suspended graphene sheet was reported [10] by using both spontaneously and thermally generated strains via varying the substrate and annealing conditions. The experimental measurements indicated that the ripples were induced by the preexisting longitudinal strains in graphene. It was observed at temperatures about 500 K that graphene sheets are flat, however, upon cooling down to room temperature, the ripples invariably appear.

In this Letter we report on an irreversibility in response to forces that act on the suspended graphene sheets that may explain why one always observes the rippled structure on graphene in experiments. We show that a compression-relaxation mechanism can produce static ripples on graphene sheets. We determine a peculiar temperature T_c such that for temperatures less than T_c the free energy of the rippled graphene is smaller than that of roughened graphene. We also show that for sample with size 400×200 atoms, $T_c \simeq 90$ K and, moreover, T_c is an increasing function of the sample size.

Theory and model.—We used molecular dynamics (MD) simulations with the empirical interatomic interaction potential due to Brenner [11], i.e., carbon-carbon interaction in hydrocarbons that contains three-body interaction. Many-body effects of electron system, on average, are considered in the Brenner potential through the bond-order term. We employed the Nosé-Hoover thermostat to control the temperature, when we used a canonical (NVT) ensemble in the MD simulations. We note that although the Brenner potential is not entirely a quantum mechanical potential, it predicts the correct mechanical properties of the structures with carbon atoms by using the classical MD simulations [12].

Here, we show that the compression and then relaxation in one or two directions [x (armchair) and y (zigzag)] of graphene sheet can produce static ripples, which means that there is an irreversibility in response to forces acting on segments of the graphene sheets. Indeed, we have found that if one compress the surface in one direction, say the x direction (armchair), after compressing about $0.13\%L$, where L is the size of the simulation sample, the ripples will appear. After the ripples emerge, we move back the boundaries to their *initial* positions. We then observe that after doing the compression-relaxation processes, the ripples *survive*, hence implying that the compression process is not reversible. It is worthwhile mentioning that we also

simulated tethered membranes [13] and repeated the compression-relaxation procedure. We obtained no any indication of irreversibility in response to the forces acting on the membranes.

In the case of graphene, if the compression amount becomes larger than the critical value (here, $0.13\%L$, which also depends on the temperature and the size of simulation sample), the graphene sheet bends and, therefore, no ripple appears. The typical height variance of the rippled graphene is about 5 \AA at $T = 50 \text{ K}$. Our simulation results show that the wavelength of the static ripples do not change with the size of the sample. Moreover, we observe that the surface roughness (the variance of the height fluctuations) does not change after the relaxation and, therefore, the ripples are static. Thus, we might state that any primary stress on graphene sheet, for example, in its preparation in the experiments, can *construct* ripples that will *survive* during the experimental measurements (see, for example, [14]).

Let us first determine the average wavelength of the ripples after relaxing the system. To do so we calculate the two-dimensional Fourier components of the height-height correlations, $G(|\mathbf{q}|) = \langle |h(\mathbf{q})|^2 \rangle$. Figure 1 shows $G(|\mathbf{q}|)$ as a function of $|\mathbf{q}|/q_0$, in logarithmic scales, for both the roughened (no ripples) and relaxed states in which we have stable ripples. Here $q_0 = 2\pi/L$, with L being the length of graphene in the x direction. In the inset of Fig. 1 the same plot in linear scale for $|\mathbf{q}|$ is shown to clarify a peak around $|\mathbf{q}| \approx 10q_0$ that corresponds to about 85 \AA at 50 K . This is the average wavelength of the ripples and is near to the value observed experimentally [3] and calculated numerically [15,16]. In addition, one can derive the wavelength of the ripples by calculating the first minimum of the second moments of the height increments fluctua-

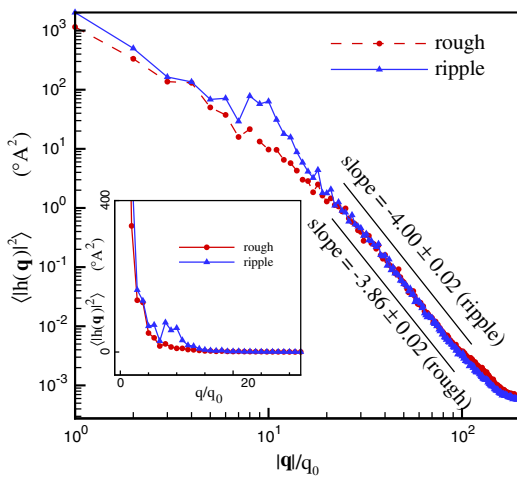


FIG. 1 (color online). Log-log plot of $\langle |h(\mathbf{q})|^2 \rangle$ as a function of $|\mathbf{q}|/q_0$ (log scaled) both in the rough and ripple cases. In the inset, $\langle |h(\mathbf{q})|^2 \rangle$ is shown as a function of $|\mathbf{q}|/q_0$ to clarify a peak around $|\mathbf{q}| \approx 10q_0$. A graphene sheet incorporates 80 000 atoms at 50 K .

tions $\langle |h(x_1) - h(x_2)|^2 \rangle$ with respect to relative distance, $|x_1 - x_2|$.

The scale-dependence of $\langle |h(\mathbf{q})|^2 \rangle$ is proportional to $1/|\mathbf{q}|^\alpha$, where $\alpha \approx 4$ at temperature 50 K . Consequently, our results predict that the bending rigidity term prevails with respect to the surface tension in graphene at short distances [17]. Note that the contribution of surface tension is a term like $T/\sigma|\mathbf{q}|^2$, whereas the contribution of the bending rigidity is $T/\kappa|\mathbf{q}|^4$, where σ and κ are the interfacial tension and bending modulus, respectively [17]. The exponent α might generally be smaller than 4, due to thermal fluctuations, surface tension and anharmonic corrections [8]. We estimate κ , the bending rigidity or bending modulus, using the relation, $\kappa^{-1} \approx |\mathbf{q}|^4 \langle |h(\mathbf{q})|^2 \rangle / Nk_B T$. Plotting κ vs $|\mathbf{q}|/q_0$ shows that the bending rigidity is almost constant for $20 < |\mathbf{q}|/q_0 < 100$, with $\kappa \approx 1 \text{ eV}^{-1}$.

Thus, for a given temperature, the compression-relaxation mechanism produces the ripples, and graphene has at least two “states” simultaneously, the “rough” or normal sheet (no ripple) and the “rippled” structure. The question now is, which state is more stable? To answer this question one should calculate the free energies of the two states and determine which state has a smaller free energy. In what follows we calculate the free-energy difference of the rippled and roughened states of graphene sheets.

To compute the free energy, we employed a well-known method (cf., Haile [18]) in which one defines a continuous variable λ for distinguishing two different states [19]. Suppose that by varying an external parameter, such as slow compression and relaxation of the graphene, the system can go from an initial state i (rough) to a final state f (rippled). When the parameters are changed infinitely slowly along the some path from i to f in the parameter space, then the total work W performed on the system is equal to the Helmholtz free-energy difference between the initial and final configurations. In contrast, when the parameters are switched along the path at a finite rate, Jarzynski found that [19]:

$$\Delta A = -\frac{1}{\beta} \overline{\ln \exp(-\beta W)}, \quad (1)$$

where the overbar denotes an average over an ensemble of measurements of W . We ran the MD simulation to very long times in order to slowly pass the intermediate quasi-stable states. In practice, for every step of compression relaxation, we checked whether the system was in equilibrium. We ensured the existence of the true equilibrium condition by checking the stability of the internal-energy fluctuations. Eventually, the problem of calculating ΔA is the same as calculating the averaged W .

In Fig. 2 the free-energy differences $A_{\text{ripple}} - A_{\text{rough}}$ is given as a function of T . We used the numerical results for a graphene sheet incorporating $N = 80\,000$ atoms (400×200) at various temperatures. It appears that the ripples are stable at low temperatures, namely, below $T_c \approx 90 \text{ K}$, such

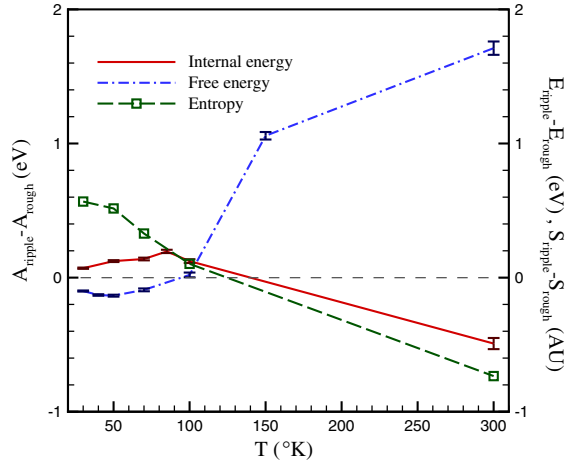


FIG. 2 (color online). The dependence of the free-energy and internal-energy (entropy) differences as a function of temperature.

that above T_c the rough state is more stable. This feature is in good agreement with recent experimental observation [10]. Here, we would like to point out that the potential energy of the carbon-carbon interaction in the compression process is different from that in the relaxation process since the relative positions of the atoms in these two configurations are different. Note that the morphology of the surface depends strongly to the potential energy.

We also tested the dependence of T_c on the size of the samples by simulating the systems with 600×200 and 800×200 atoms, and found their characteristic temperatures to be $T_c \approx 115$ and $T_c \approx 140$, respectively. Moreover, we found that the wavelength of the ripples depends on T as $\lambda \approx 35 \ln(T) - 55$, but it does not depend on the system size. Accordingly, we calculated the entropy difference of the two states and showed that for temperatures less than T_c , the rippled state has a higher entropy and is stable. We plotted the internal-energy difference of the two states is shown in Fig. 2. The value of T_c can be also determined from the local stored stress on a graphene sheet; we will report the results elsewhere [20].

We may expect that similar to second-order phase transitions the probability distribution function (PDF) of the total internal energy possesses different shapes for rough and ripple states, and exhibit non-Gaussian behavior. In Fig. 3 the PDF of the total internal energy E for the ripple and rough states are presented for $T = 30, 50, 70, 85, 100,$ and 300 K. To calculate the PDF, we used 200 ensembles of roughened and rippled graphenes, incorporating 400×200 atoms. We observed that the PDF has a Gaussian form for both states indicating that there is no longer second-order phase transition in the system. We also checked the Gaussian nature of the PDF by using the χ^2 test [21]. The dashed curves represent the Gaussian PDF.

As we argued earlier, there are at least two states for graphene sheets for a given temperature. A question raised

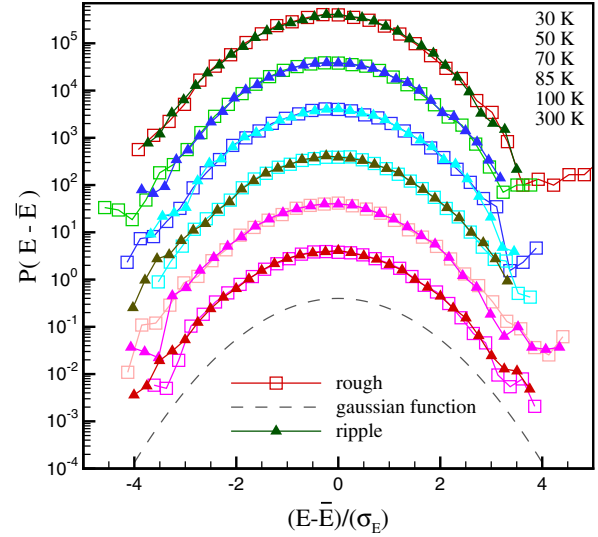


FIG. 3 (color online). Probability distribution function of the total energy E for the rippled and rough states for $T = 30, 50, 70, 85, 100,$ and 300 K (from top to bottom). The dashed curves are the Gaussian probability distribution function. For clarity, the PDFs were shifted upward.

is whether or not there is any possibility of a transition from one state to another? One possible way for such a transition with a fixed graphene sheet size is to increase the temperature. For this purpose we simulated the graphene sheet with 80×40 atoms and, after carrying out the compression-relaxation process, the ripple structure appeared at $T = 55$ K (see the upper figure of Fig. 4). We then increased the temperature very slowly. As shown in Fig. 4, the ripples begin to disappear at high temperatures. At $T = 55$ K, we have almost two wavelength of the ripples; however, at higher temperatures there is one wavelength at $T = 320$ K, and finally one half of the wavelength at $T = 520$ K remains. The final step may be called rough state. Accordingly, the energy barrier of two states may be estimated by $465k_B = 0.04$ eV (or = 0.0125 meV per particle) for a sample with 3200 atoms, where k_B is the Boltzmann's constant. Such a transition has been observed experimentally in [10]. They argued that the disappearing of ripples in high temperature is due to the fact that graphene has negative thermal expansion coefficient.

As mentioned above, for temperatures less than T_c , the free energy of the rippled state is smaller than that of the free energy of the roughened graphene sheet. However, there is a possibility of having a transition from the rippled state to the roughened state, due to a tunneling-type transition. To detect this transition, we checked that the height fluctuations variance of the rippled graphene sheet is stable with time. A sample size of 80×40 atoms was used at $T = 55$ K. The simulations showed that there is no transition from the rippled to roughened state at a constant temperature T less than T_c , at least up to available time scales in the MD simulations. The probability for such

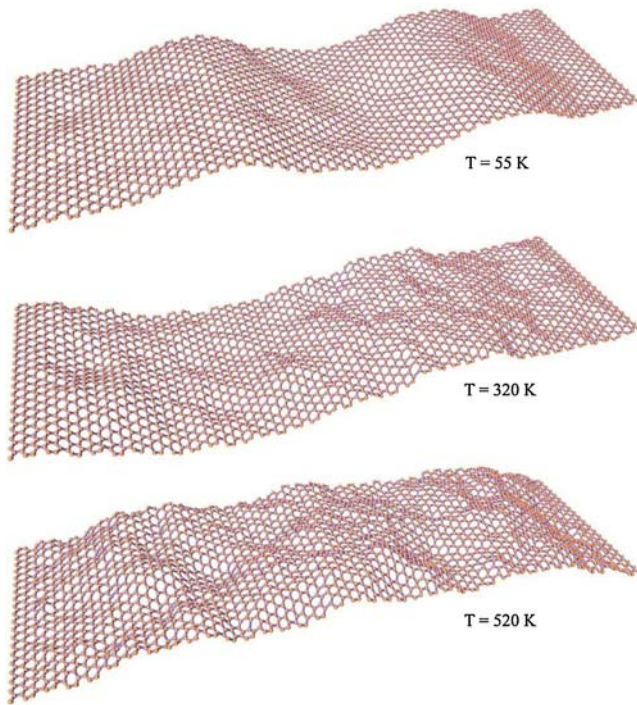


FIG. 4 (color online). Transition from rippled state (upper snapshot) to the rough state, due to the increasing of the temperature from 55 to 520 K.

transition is about $\exp(-465/T)$ for a sample with size 3200 atoms. We remind that the variance of height fluctuations in graphene are about 5 Å and 1 nm, for rough and rippled states, respectively.

In summary, we have used a compression-relaxation mechanism to produce rippled structures on graphene sheets. The constructed ripples *survive* even though the system is relaxed to its initial position. In the closed-path loop, we calculated the total work and, hence, the free-energy difference of the rippled and roughened states. Our numerical results show that for sample with 400×200 atoms and below $T_c \approx 90$ K, the rippled surface is stable and the entropy of the ripples should be larger than that of the rough state. However, above T_c the rough state is more stable. The rippled and rough structures are also related to the morphology of such systems and we, therefore, expect that the our simulations yield the correct and new results for the free energy of the rippled and roughened graphene. We have done similar simulations for a bilayer graphene and observed that, for a given temperature, the wavelength of the static ripples are larger than that for a monolayer graphene. We will report the results for bilayer graphene elsewhere.

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Abedpour, Asgari, and Tabar Reply: In his Comment [1] on our Letter [2] Neek-Amal raises questions about our discovery that the response to forces acting on suspended graphene sheets is irreversible. Here, we show that Neek-Amal's arguments and objections are invalid, and indeed are a mixture of contradictory arguments.

First of all, we would like to stress that the rippled state is determined by a Bragg peak in the spectral function, examples of which have been shown in Fig. 3 of Ref. [3] and Fig. 1 of Ref. [2]. Neek-Amal assumes that the graphene sheet subjected to the boundary stress [4] is in a rippled state. This is an *ad hoc* definition and incompatible with the well-defined standard definition in the condensed matter physics and statistical mechanics of membranes. We present the results for two counterexamples to this definition: (i) compression and relaxation mechanism (CRM) on a tethered membrane [5], and (ii) a graphene sheet with periodic boundary conditions (PBCs) in both directions.

(1) We simulated a tethered membrane by the same molecular dynamics (MD) method that we used for the graphene sheet, but found no evidence of the rippled state. It clearly means that Neek-Amal's definition is no longer valid. He claims that the irreversibility seen in our simulations is related to the presence of stress on the boundaries. To assess the validity of this conjecture, we also carried out extensive new MD simulations for the CRM on a graphene sheet with no boundary stress tensor [6]. We started off by simulating a graphene (200×400) with PBCs in both directions, and after carrying out the CRM, found a stable rippled state. The simulations were done by scaling the length along the armchair direction and rescaling the length to its initial box length [6]. In Fig. 1(a) the rippled state after the CRM with PBCs is shown. Note that, due to PBCs, the boundary along the y direction is no longer smooth. By plotting the structure function $G(|\mathbf{q}|)$ we found that the wavelength of the ripples in the simulated system is about the same as that reported in [2]. Neek-Amal could have plotted the structure function $G(|\mathbf{q}|)$ to prove his statement that the initial and final states are rippled, but he did not do so.

(2) It is known that the variance of the work is size dependent and depends on the trajectory of moving from the initial state i to the final state f (here the CRM state). We carried out three new series of MD simulations by starting from the size that Neek-Amal used and increased it up to 30 times larger to reach the size used in [2]. As shown in Fig. 1(b), the variance $\sigma_w = \sqrt{\langle (W - \langle W \rangle)^2 \rangle}$ per particle is a decreasing function of the sample size N . Therefore, Neek-Amal's finding of the fluctuations of the work is due to the very small size. (3) To verify results that appeared in Fig. 2 of our Letter, we examined ΔA during the CRM by using Eq. (1) of Ref. [2] and using the $\langle W \rangle$ for $N = 20\,000$ and $80\,000$. The new results support our conclusion that the ripples are stable at low temperatures. (4) Though Neek-Amal found that $\Delta A \neq 0$ during the CRM, he surprisingly

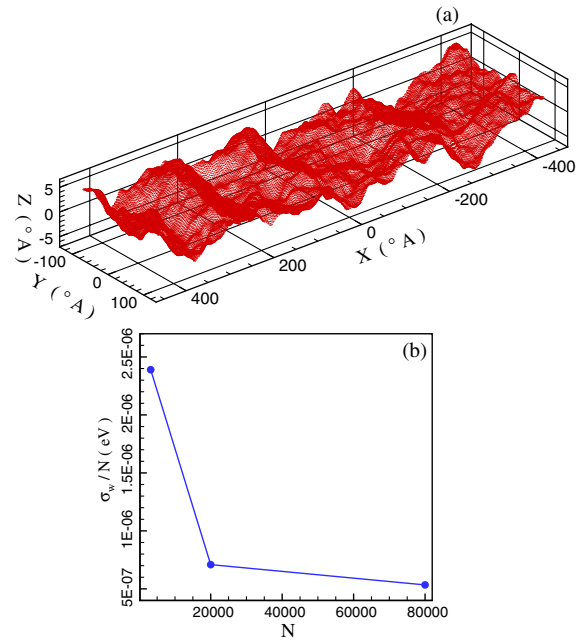


FIG. 1 (color online). (a) Rippled state of graphene sheet after the CRM with the PBCs. (b) Size dependence of the variance per particle of the work fluctuations.

concluded that “the process is reversible,” which is an unphysical statement in his Comment.

Here we reconfirm our conclusions in our Letter [2] and prove that Neek-Amal's findings are the artifact of his *ad hoc* definition of the ripple state and simulating of a very small size graphene.

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