Buckled graphene for efficient energy harvest, storage and conversion

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Abstract

Buckling is one of the most common phenomena in atom-thick layered structures like graphene. While the buckling phenomenon usually causes disaster for most nanodevices, we illustrate one positive application of buckled graphene for energy harvest, storage and conversion. More specifically, we perform molecular dynamical simulations to show that buckled graphene can be used to collect wasted mechanical energy and store the energy in the form of internal knotting potential. Through strain engineering, the knotting potential can be converted into useful kinetic energy that is highly concentrated at the free edges of buckled graphene. The present study demonstrates potential applications of buckled graphene for converting dispersed wasted mechanical energy into concentrated useful kinetic (thermal) energy.

Keywords: buckled graphene, energy harvest, energy storage, energy conversion

(Some figures may appear in colour only in the online journal)

Graphene is a quasi-two-dimensional (2D) honeycomb lattice structure of high in-plane stiffness [1] but very small bending modulus [2–5]. As a result of the quasi-2D nature, buckling becomes the most common phenomenon in graphene. For buckling instability, Euler buckling theory [6] states that the critical compression strain, above which graphene will be buckled, is inversely proportional to the in-plane stiffness \( C_{11} \) and is proportional to the bending modulus \( D \); i.e. \( \epsilon_c \propto D/C_{11} \). According to the Euler buckling theory, the critical strain for graphene is very small; i.e. the buckling phenomenon can easily take place in graphene. Consequently, the buckling process can be induced by very weak external disturbance like the thermal expansion effect [7].

The buckling of graphene has attracted intensive research interest in the past few years [8–19]. In most of these existing works, buckling brings negative effects on the mechanical, thermal, or electronic properties of graphene. However, in the present work, we will show that buckled graphene can collect wasted mechanical energy and convert it into useful concentrated kinetic energy.

It has been found that the conversion of energy on the nanoscale level plays an important role in supporting the engineering of nanodevices. Chang performed molecular dynamics simulations to examine the domino-like energy transformation between van der Waals potential and kinetic (thermal) energy in single-walled carbon nanotubes [20]. Many works have proposed to use graphene-based materials as flexible supercapacitors for energy storage and conversion [21–25].

In this paper, we demonstrate a mechanical route for the application of graphene for energy collection, storage, and conversion. More specifically, buckled graphene can be used to collect wasted mechanical energy, which is stored in the form of knotting potential. The energy stored in the buckled graphene can be converted into kinetic energy concentrated at the free edges of graphene. We also investigate possible methods to increase the efficiency of energy conversion from the dispersed mechanical energy into concentrated kinetic energy.

The left structure in figure 1(a) shows the thermalized configuration for graphene of dimension \( 30 \times 200 \) Å. Both ends in the \( x \)-direction are fixed, while free boundary conditions are applied in the \( y \)- and \( z \)-directions. The whole system is divided into top, middle (mid), and bottom (bot) regions. Free edges are at the top and bottom regions. The interactions between carbon atoms in graphene are described by the second generation Brenner potential [26]. The standard Newton equations of motion are integrated in time using the velocity

\[
\frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla V_i - \frac{1}{m} \mathbf{F}_i + \frac{1}{m} \mathbf{F}_{ext}
\]

where \( \mathbf{r}_i \) is the position of the atom, \( V_i \) is the potential energy, \( m \) is the mass of the atom, and \( \mathbf{F}_{ext} \) is the external force. The external force is applied at each atom, and the equations of motion are solved using the Velocity-Verlet algorithm [27].
Verlet algorithm with a time step of 1 fs. The Nosé–Hoover [27, 28] thermostat is used for maintaining constant temperature at 1 K and constant pressure of 0 Pa. Molecular dynamics simulations are performed using the publicly available simulation code LAMMPS [29]. The OVITO package is used for visualization [30].

Figure 1 displays the whole energy collection, storage, and conversion process in five simulation steps. First, the system is thermalized to the targeted pressure and temperature within the NPT (i.e. the particle number $N$, the pressure $P$ and the temperature $T$ of the system are constant) ensemble for 200 ps. Second, graphene is buckled by compression along the $x$-direction for 200 ps at a strain rate of $10^{-4}$ ps$^{-1}$, which results in a final compressive strain of 2% in the system. The structure is allowed to be fully relaxed in lateral directions during mechanical loading. The buckled structure is shown by the right configuration in figure 1(a).

In the third step, the buckled graphene is indented by a spherical indenter tip. The indenter is moving toward the buckled graphene at a constant speed of 0.01 Åps$^{-1}$. Figure 1(b) shows that, during the indentation process, two knots (indicated by stars) are created in the middle region and these knots will move to the top and bottom regions in the buckled graphene. This step is to mimic the collection of wasted mechanical energy. More specifically, the buckled graphene is hit by the indenter (with wasted mechanical energy) at the central position, which leads to the formation of two knots, i.e. the wasted mechanical energy can be collected and stored as the potential for these two knots (indicated by stars). We note that the third structure shown in figure 1(b) is very stable, which indicates that buckled graphene can store energy in the form of potential energies for knots near the edge.

In the fourth step, the buckled graphene with two knots are thermalized within the NPT ensemble for another 200 ps. In the fifth step, the system is compressed again in the $x$-direction, and the knots will be loosened eventually. As a result, the knotting potential energy is released as kinetic energy, most of which concentrates at the free edges of graphene. The fifth step is to mimic the usage of the knotting potential through mechanical engineering.

We now illustrate the whole process by examining the potential energy and kinetic energy during these five simulation steps. Figure 2 shows the potential per atom for graphene during the whole simulation process, which indicates that the wasted mechanical energy is transformed into the knotting potential in the middle region at $t = 600$ ps.
knots move to the top and bottom regions at $t \approx 856$ ps as shown in figure 3(a), at which the potential of the top and bottom regions increases suddenly while the potential of the middle region decreases. The potential energies of these two knots are recorded in figure 3(b), giving a speed of 430 ms$^{-1}$ for the motion of the knot. Both knots are loosened at $t \approx 1300$ ps, when the potential energies of the top and bottom regions decrease suddenly as shown in figure 2(a).

The evolution of the total kinetic energy is shown in figure 4. We focus on the time around 1300 ps, when the kinetic energies of the top and bottom regions show a sudden increase, which indicates the occurrence of the loosening phenomenon. The change of the kinetic energy in the middle region is much smaller than the kinetic energy variations in the top or bottom region. It means that the knotting potential is converted into kinetic energy for atoms in the edge (top and bottom) region. From this simulation step, we learn that the wasted mechanical energy is eventually converted into concentrated kinetic (thermal) energy, which is useful for engineering nanodevices.

We further examine possible effects from using different simulation parameters. In the above second simulation step, graphene is buckled by compressive strain $\varepsilon$ along the $x$-direction. We find that the magnitude of the strain has a considerable effect on the efficiency of the energy conversion. Figure 5 shows that the potential variation during knot formation is $\Delta V_1$, while the potential variation during loosening is $\Delta V_2$. The efficiency ($\eta = \Delta V_1/\Delta V_2$) of energy collection is displayed in the inset.
as high as 47% for $\epsilon = 0.021$. This efficiency is obviously larger than the energy conversion efficiency of solar cells, which is typically lower than 30% [31].

Figure 6 shows that the position of the indenter during the indentation process is not important. The buckled graphene is indented at different positions, but the same knotting structure is formed in the end. Figure 7 shows that the evolution of the potential per atom is almost the same for the buckled graphene that is indented at different positions. The position insensitivity is a nice property for energy collection in the sense that the buckled graphene can collect wasted mechanical energy that is dispersed in the space. Figure 8 shows that the width of graphene has no effect on the whole energy collection and conversion processes either. However, the energy harvest/storage/conversion processes are dependent on the creation of knots, that can be stable at the edges of the graphene ribbons. The knots are created in the middle of the graphene ribbon, and the knots will travel to and stay at the free edges. Thus a proper width to length ratio is required for the knots to be stable at the edges of the graphene ribbon.

The graphene ribbons illustrated in the figures are of armchair orientation along the x-direction. We show in figure 9 that the orientation of the graphene ribbon is not important for the performance of the energy device. We found similar energy collection, storage, and conversion processes in the graphene of zigzag orientation in the x-direction.

Considering the large Young’s modulus (about 1.0 TPa) for graphene, the internal stress (pressure) is usually several orders larger than the ambient pressure of 101.3 kPa. More specifically, for a typical strain $\epsilon = 0.01$ used in the present work, the internal stress is $\sigma = E\epsilon = 1.0$ TPa $\times$ 0.01 = 10 GPa, which is five orders larger than the ambient pressure. Hence, the ambient pressure is negligible. This speculation is verified in figure 10, which shows that the potential curve for pressure $P = 1$ atm is almost the same as the potential curve for $P = 0$.

We note that the working temperature for energy collection and conversion based on buckled graphene is related to the intrinsic energy scale in this energy device. More specifically, we have introduced the parameter $\eta = \Delta V_1/\Delta V_2$ as the efficiency for the energy device, with $\Delta V_1$ as the potential variation during knot formation and $\Delta V_2$ as the potential variation during unknotting. That is $\Delta V_1$ is the energy that can be collected by the buckled graphene, while $\Delta V_2$ is the external work to be done to explore the energy stored in the device. In other words, $\Delta V_2$ serves as a potential barrier for the knot. Hence, the working temperature should be lower than $T_C = \Delta V_2/k_B$. Otherwise, the knot can be loosened by thermal vibration, i.e. the knot becomes thermally unstable, if the thermal vibration energy is larger than the potential barrier $\Delta V_2$. From figure 10, we have $\Delta V_2 \approx 10$ meV, so the critical temperature is about $T_C \approx 116$ K. We have checked that the knot indeed becomes thermally unstable at room temperature, so the working temperature for the energy device should be lower than 116 K. From figure 5, the potential variation $\Delta V_2$ will increase with increasing strain $\epsilon$, so the critical temperature $T_C$ can be increased by increasing strain $\epsilon$. However, as shown in the above, the efficiency of the energy device will be decreased with the increase of $\Delta V_2$, so there is a trade-off between higher critical temperature and higher efficiency in the real-world.
application of the buckled graphene for energy harvest, storage, and conversion.

Finally, the energy harvest and storage will be valuable for some physical processes, especially on the nanoscale level. As an example, we propose one possible application of buckled graphene for energy harvest/storage/conversion in nanomechanical resonators, which can work at temperatures from room temperature down to 10 K [32, 33]. Resonant oscillation energy will decay into wasted mechanical energy after a long time, which can be harvested by the buckled graphene discussed in the present work. The harvested energy will be stored in the buckled graphene as knotting potential. We have found in our work that the stored energy can be converted into thermal vibration that is highly localized at the free edges, which will be useful for the actuation of some localized resonant oscillations of nanomechanical resonators [34].

Overall, we have demonstrated in the above that buckled graphene can be used to collect wasted mechanical energy. Dispersed mechanical energy can be collected through hitting the buckled graphene at various positions, which leads to the same final knotting configuration. The buckled graphene is long in the y-direction, and this large surface area is helpful for energy harvest. Furthermore, the collected energy can be converted into kinetic energy concentrated at the two free edges, which may be useful for mechanical engineering of nanodevices.

In conclusion, we have investigated the application of buckled graphene to collect dispersed mechanical energy. Mechanical energy is stored within buckled graphene in the form of knotting potential, which can be utilized as kinetic energy localized at the free edges of graphene. One advanced feature for the energy conversion process using buckled graphene is that such a system is able to collect mechanical energy that is highly dispersed in space, and convert the energy into highly localized kinetic (thermal) energy.

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