Nanoscale Directional Motion towards Regions of Stiffness

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(Received 2 April 2014; published 7 January 2015)

How to induce nanoscale directional motion via some intrinsic mechanisms pertaining to a nanosystem remains a challenge in nanotechnology. Here we show via molecular dynamics simulations that there exists a fundamental driving force for a nanoscale object to move from a region of lower stiffness toward one of higher stiffness on a substrate. Such nanoscale directional motion is induced by the difference in effective van der Waals potential energy due to the variation in stiffness of the substrate; i.e., all other conditions being equal, a nanoscale object on a stiffer substrate has lower van der Waals potential energy. This fundamental law of nanoscale directional motion could lead to promising routes for nanoscale actuation and energy conversion.

DOI: 10.1103/PhysRevLett.114.015504 PACS numbers: 62.25.-g, 68.35.Af, 68.35.Gy

Understanding the underlying physics and potential applications of directional motion is of particular importance for human life. One of the most common directional motions in nature is the motion of an object guided by gravity. Since it was realized that the downhill flow of water could generate power, waterwheels were developed and then served as the primary source of power supply for the world until the beginning of the Industrial Revolution in the 18th century, and they are widely regarded as the forerunner of modern hydroelectric turbines which have substantially changed our life. The emergence of nanotechnology has resulted in an increasing focus on nanoscale directional motion, owing to its importance to nanoscale actuation and energy conversion. Tremendous progress has been made in recent years to induce the nanoscale directional motion using applied voltage [1–3], electric current [4–7], thermal energy [8–12], or biological processes [13]. However, challenges still exist in producing nanoscale directional motion via an intrinsic mechanism similar to the downhill flow of water.

Here we show via molecular dynamics simulations that there in fact exists a fundamental nanoscale directional motion guided by stiffness gradient; i.e., a nanoscale object on a substrate would move spontaneously from a soft region to a hard region. In this phenomenon, termed *nanodurotaxis*, a stiffness gradient provides a gradient in the effective potential energy which the adsorbate responds to, resulting in an intrinsic mechanism for nanoscale directional motion that has general implications for nanoscale actuation and energy conversion.

In the simulations (details can be found in the Supplemental Material [14]), we employ a model system [Fig. 1(a)] that involves a short graphene sheet with an edge along the x axis oriented in the zigzag direction, the *slider*, initially placed at the center of a long strip of the graphene sheet with an armchair edge, the *substrate*. The incommensurate registry between the slider and substrate allows easy slide with reduced energy barriers [19–21]. To introduce a stiffness gradient, each substrate atom is linked to an underlying spring such that the substrate is anchored on a bed of springs with linearly graded stiffness k along the length (z direction) of the substrate [Fig. 1(b)]. The simulations show that the slider moves spontaneously in the direction of increasing stiffness along the substrate, i.e., from the soft side to the hard side of the substrate [Fig. 1(c)], much like a macroscopic object sliding down a curved ramp [Fig. 1(d)].

Figure 2(a) shows some snapshots of the moving slider along the linearly graded substrate (a movie is presented in the Supplemental Material [14]). The initial speed of the slider is zero and, once the motion starts, it accelerates toward the hard side of the substrate. When it reaches the end of the substrate, the slider rebounds (due to a retraction force when the slider tends to be extruded [22]) and decelerates toward the soft side. The bouncing behavior of the slider clearly shows that a persistent force is exerted on the slider toward the region of higher stiffness on the substrate.

The displacements and velocities of the slider are shown in Figs. 2(b) and 2(c) for substrates with different values of stiffness k_m at the midpoint along the length of the substrate and stiffness gradient $\gamma = \partial k/\partial z$. The simulations show that a larger γ or a smaller k_m leads to faster movement, indicating that a larger driving force can be generated by a larger stiffness gradient or a smaller local stiffness.

To verify that the driving force stems from the stiffness difference, we further investigate a system in which half of

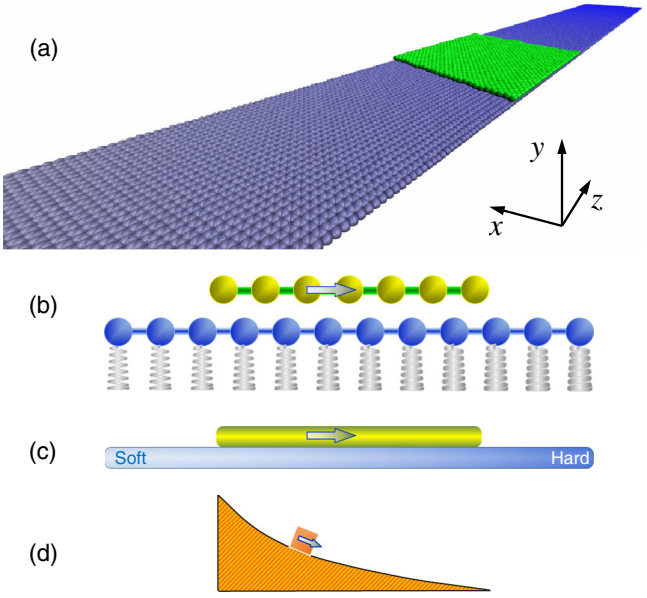

FIG. 1 (color online). A model slider-substrate system. (a) Configuration of a short graphene slider on a long graphene substrate for molecular dynamics simulations. (b) Atoms of the substrate are anchored on an array of springs with linearly graded stiffness along the length direction of the substrate. (c) Stiffness guided nanoscale directional motion, i.e., nanodurotaxis, of an object from the soft side to the hard side of the substrate. (d) A macroscopic object slides down on a curved ramp guided by gravity.

the substrate atoms are linked to springs with identical but relatively low stiffness while the other half are linked to springs with identical but relatively large stiffness, as illustrated in the inset of Fig. 3(a). In this case, there is a sharp stiffness jump in the middle of the substrate, instead of a continuous stiffness gradient along the length of the substrate, corresponding to a piecewise homogeneous substrate divided into a uniformly soft region and a uniformly hard region by a sharp interface. We find that the slider moves to the harder side of the substrate. It is not surprising to see that the displacement of the slider on the substrate linked to springs with 0.801 nN/nm on the soft side and 4.005 nN/nm on the hard side (labeled as 0.801/4.005) is approximately equal to the sum of the displacements for the sliders on the 0.801/2.403 and 2.403/4.005 substrates, because the stiffness difference in the former system is just the superposition of the stiffness differences in the latter two systems. It should be noted that, although the stiffness difference is the same in the 0.801/2.403 substrate and the 2.403/4.005 substrate, the acceleration of the slider on the 0.801/2.403 substrate is substantially larger due to smaller overall stiffness. We show also that, at a higher temperature but the same stiffness difference, the slider moves faster, suggesting that increasing system temperature may increase the driving force.

The driving mechanism of the motion guided by the stiffness difference can be further elucidated by considering

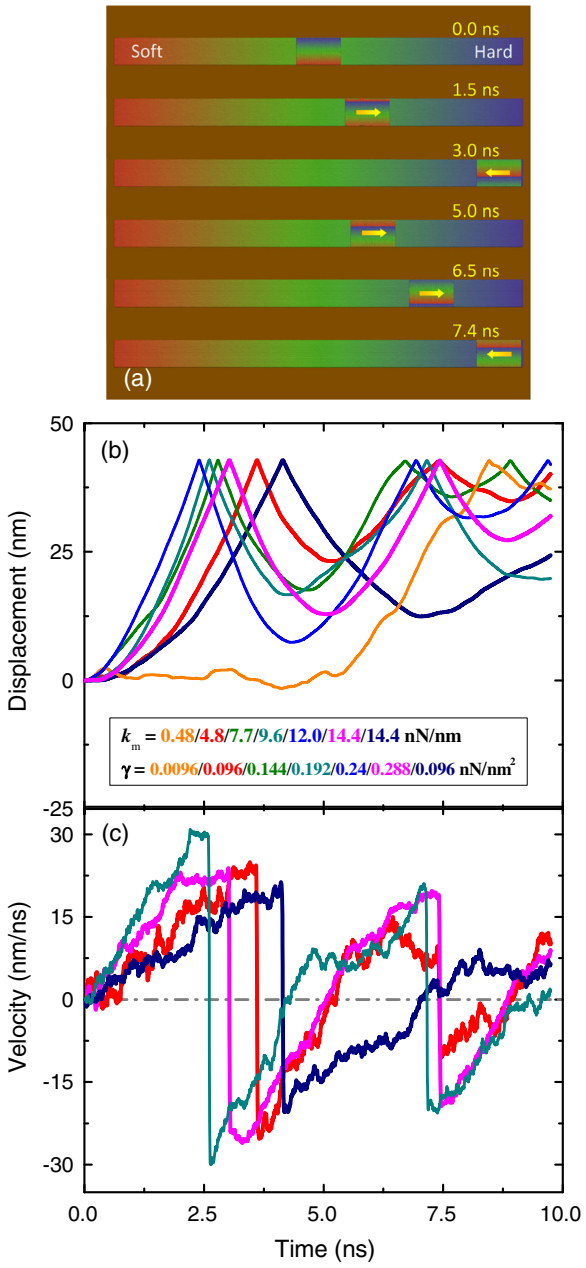

FIG. 2 (color online). Nanodurotaxis of a 10 nm long slider on a 97 nm long substrate with a linear stiffness gradient. (a) Snapshots of a typical system in which the stiffness gradient γ is 0.288 nN/nm^2 and the stiffness at the midpoint of the substrate k_m is 14.4 nN/nm. The displacements and velocities of the slider on different substrates are shown in (b) and (c), respectively.

the motion of the slider on an alternate-patterned, piecewise homogeneous substrate in the length direction. In this case, the substrate is divided into alternate stiff and soft regions along the length direction (via a periodic boundary condition in simulations), as shown in the inset of Fig. 3(b). It can be seen that the slider shuttles on the substrate with a frequency of ~ 0.3 GHz, similar to a high frequency oscillator composed of multiwalled carbon nanotubes

[22]. Whenever the slider spans across a stiffness jump (with one end on the soft region and the other on the hard region), its velocity changes almost linearly, implying that the slider experiences an approximately constant acceleration (~ 40 nm/ns^2, corresponding to a driving force of ~ 0.6 pN/nm per width). However, when the slider lies entirely within the hard region of the substrate, its velocity is almost unchanged. This conclusively shows that the driving force is induced by the stiffness difference, directed from the softer side toward the harder side of the substrate.

Stiffness guided directional motion, termed *durotaxis*, was first found in living cells which tend to move to stiffer parts of a substrate [23]. The mechanism of durotaxis of living cells is still unknown, although it is generally believed to involve active sensing and locomotion [23,24]. Simple liquid droplets undergo reverse durotaxis [25], due to the fact that the contact angle of the droplets increases with the substrate stiffness. In the present system of two graphene layers in contact, there is neither active sensing nor wetting. So what is the driving force for the observed nanoscale durotaxis?

To elucidate the underlying physics of nanodurotaxis, we plot in Fig. 4(a) the interlayer van der Waals (vdW) potential energy between the slider and substrate. It is found that different values of the effective vdW potential can be induced by different substrate stiffness: the larger the stiffness, the lower the interlayer vdW potential. This can be confirmed by a recent analytical model [26] that showed that the vdW potential between two adjacent graphene layers is a decreasing function of the stiffness. A lower potential energy means a more stable state, which is why a slider moves toward the position of largest stiffness on the substrate. To correlate the change in vdW potential with the dynamics of substrate atoms, we show in Fig. 4(a) also the standard deviations of the vibration magnitudes of substrate atoms outside and within

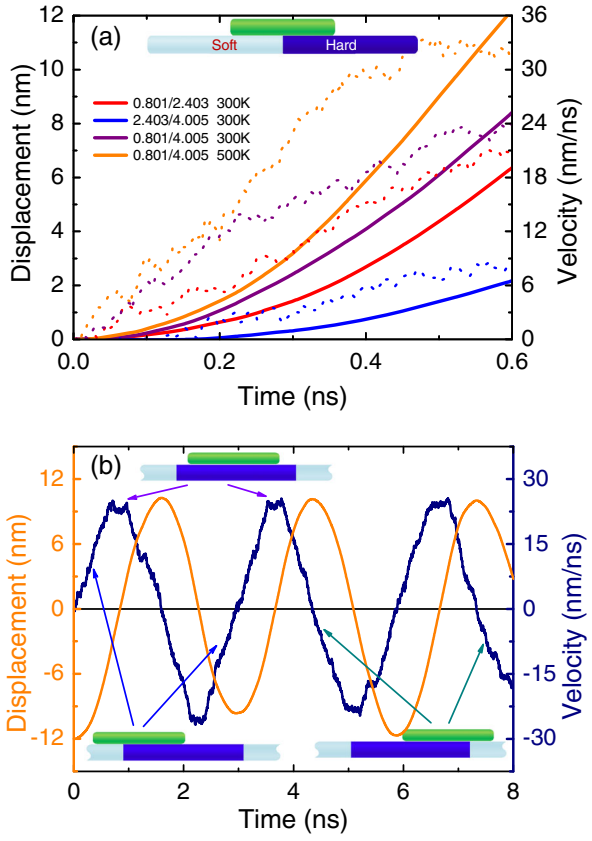

FIG. 3 (color online). Nanodurotaxis of a 19 nm long slider on a 48 nm long substrate with stiffness jumps across piecewise homogeneous regions. The displacements (solid lines) and velocities (dot lines) of the slider on substrates with different stiffness jumps are shown in (a). The shuttle behavior of the slider on a substrate with alternate soft or hard (0.801/2.403) regions are shown in (b), where the displacement is measured from the center of the hard region.

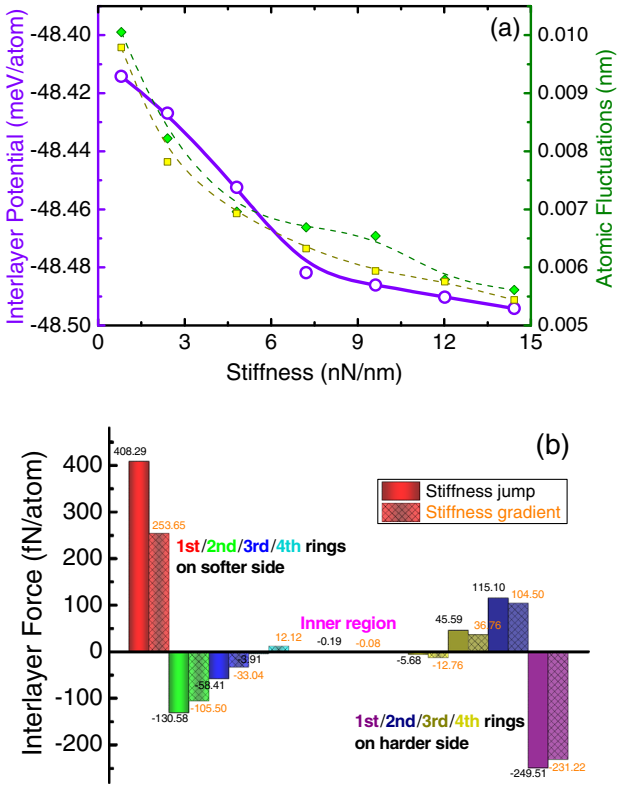

FIG. 4 (color online). Interlayer interactions between the slider and the substrate. (a) The interlayer vdW potential and the standard deviations of the vibration magnitudes of substrate atoms outside (diamond) and within (square) the contact area against the spring stiffness. (b) The interlayer vdW forces (a positive value indicates that the force points towards the hard side) exerted on different regions of the sliders for the system of a 19 nm long slider on a 48 nm long substrate with a stiffness jump (0.801/4.005) across piecewise homogeneous regions and for the system of a 10 nm long slider on a 97 nm long substrate with a stiffness gradient 0.096 nN/nm^2 and a midpoint spring stiffness of 4.8 nN/nm. In both cases, the average velocity of the slider is about 8.8 nm/ns.

the contact area. It is seen that atoms residing on softer springs exhibit larger magnitudes of vibration and consequently result in larger effective potential.

For a device based on nanodurotaxis, it is important to understand how the contact layers interact with each other. Shown in Fig. 4(b) is the distribution of the interlayer vdW forces on the slider in the length direction. Two cases are considered: the slider initially placed on the interface of a substrate with a stiffness jump, and the slider initially placed at the center of a substrate with a stiffness gradient. It is seen that, in both cases, the slider experienced remarkable edge forces (defined by the force exerted on the last-four-ring atoms near each end of the slider), similar to the case of a thermal gradient driven nanodevice [26,27]. The physical origin of edge force is clarified in the Supplemental Material [14]. In particular, the edge force on the soft side is significantly higher than that on the hard side. For the case of stiffness jump in Fig. 4(b), the unbalanced edge force is 0.996 pN/nm, higher than the global net driving force, 0.868 pN/nm, because the slider experienced also a frictional force as it is moving toward the hard side. The force on the inner atoms, −0.19 fN/atom, should be largely the frictional force. For the case of the stiffness gradient, the unbalanced edge force is 0.201 pN/nm, higher than the global net driving force, 0.174 pN/nm, too. The force on the inner atoms is −0.08 fN/atom, providing again a resistance force to the slider motion, although it is smaller than that with stiffness jump (due to the existence of the stiffness gradient that provides additional driving force to oppose the friction).

The driving force induced by substrate stiffness gradient can actually be quite large. For instance, a 0.801/2.403 difference can generate a force of ~ 4 pN for a 6 nm wide slider (~ 320 kPa per unit area). By comparison, a 1 K/nm thermal gradient in a carbon nanotube cargo [10] generates a force of ~ 5 pN for a nanotube with diameter of 2 and length of 8 nm (~ 100 kPa per unit area), the driving force generated in a protein biomotor [13,28] is typically up to ~ 10 pN (~ 400 kPa per unit area), and the traction force per unit area exerted by a living cell [23,24,29,30] on a substrate is ~ 2 μN (2 kPa per unit area).

Nanodurotaxis can have great potential in nanodevice applications. Stiffness differences exist widely in materials and structures, e.g., in a functionally graded material or across the interface of two materials with different elastic moduli. It could also be generated through aligned nanotube [31], nanopillar [32], or nanoporous [33] arrays with a change in their density or size. Using these various forms of stiffness difference, it should be possible to design nanomotors and nanocargos for nanoscale actuation or energy conversion. The concept can also be used to design nanomechanical diodes to control the direction of nanoscale motion. Unlike thermal [10] or electrical [4,6] gradients, the stiffness gradient need not be maintained by external powers. In addition, stiffness tuning by electrical, magnetic, or mechanical (see Supplemental Material for an example [14]) approaches may lead to controllable delivery of nanoscale objects (e.g., DNA molecules [34,35]) and provide a possibility of *stiffness engineering* for functional materials and nanodevices.

In summary, by investigating the sliding of a graphene flake on a graphene strip via molecular dynamics simulations, we report a fundamental law of nanoscale directional motion: nanodurotaxis—a nanoscale object on a substrate would move spontaneously from a soft region to a hard region. The underlying physics is that increased stiffness in the substrate renders effectively a lower potential energy on the adsorbate, and the driving mechanism is closely related to the edge force. Nanodurotaxis is an intrinsically produced nanoscale directional motion, and it need not be maintained by an external potential, nor does it involve any biological activity, and may open a new way for nanodevices of actuation and energy conversion.

The authors acknowledge financial support from the NSF (Grants No. 11425209, No. 11172160) of China, Fok Ying Tung Education Foundation (Grant No. 121005), Shanghai Pujiang Program (Grant No. 13PJD016), and Shanghai Leading Academic Discipline Project (Project No. S30106). H. G. acknowledges support from the Center of Mechanics and Materials at Tsinghua University.

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