PRL 107, 236102 (2011) PHYSICAL REVIEW LETTERS week ending 2 DECEMBER 2011

Sticking of Hydrogen on Supported and Suspended Graphene at Low Temperature

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(Received 22 June 2011; published 30 November 2011)

The physisorption of atomic hydrogen on graphene is investigated quantum mechanically using a semiempirical model for the lattice dynamics. A thermally averaged wave packet propagation describes the motion of the H atoms with respect to the membrane. Two graphene configurations, either supported on a silicone oxide substrate or suspended over a hole in the substrate, are considered. In both cases, the phonon spectrum is modified in such a way that graphene is stabilized with respect to thermal fluctuations. The sticking probabilities of hydrogen on these stabilized membranes at 10 K are high at low collision energies, and larger than on graphite.

DOI: 10.1103/PhysRevLett.107.236102 PACS numbers: 68.49.Bc

Graphene, a two-dimensional layer of carbon atoms, has become the subject of intense investigations. Recent reviews describe its unusual electronic, mechanical, and thermal properties [1,2]. We focus here on the sticking of hydrogen atoms on graphene at low temperature (10 K). We show that the forces exerted on supported and suspended graphene by the substrate not only stabilize its two-dimensional structure but also modify H atom sticking, which is enhanced relative to that on graphite. Another motivation is the recent discovery of graphane, obtained by hydrogenation of graphene under hydrogen plasma exposure [3]. When a H atom chemisorbs onto an unhydrogenated membrane, the carbon atom closest to the H puckers out of the plane of the membrane [4,5]. As a result, the chemisorption of H onto graphene has a thermal activation of nearly 0.2 eV, and this hydrogenation mechanism is not effective at room temperature and lower. Under such conditions, however, physisorption can be efficient, as H atoms trap in the shallow potential well [6] resulting from the weak van der Waals interaction between H and graphene. These trapped states might serve as precursors to hydrogenation at edge or defect sites, or adjacent to chemisorbed H atoms, where the barriers to chemisorption are small. A third motivation is the recent development of graphene-based nanoelectromechanical devices (NEMS) used as mass sensors [7,8]. Operated at low temperatures, such devices are very sensitive detectors of stuck atoms and molecules on the graphene membrane through measurement of the shifts in its resonant vibrational frequency. This study is a prototype of the general NEMS-atom or molecule sticking process induced by van der Waals interactions. Understanding the conditions under which sticking occurs is important in the design and operations of such systems.

Sticking requires dissipation of the H atoms' energy into the lattice phonons, and an accurate phonon model is necessary to describe this correctly. Previous studies of hydrogen sticking on carbon surfaces [9–11] used models for (bulk) graphite phonons that cannot accurately describe the behavior of the low frequency phonons in single layer graphene. We consider here only the acoustic modes of flexural type (labeled ZA), corresponding to motion of the carbon atoms out of the membrane plane, as they are the only ones to be significantly excited by the incoming H atom. We use the semiempirical valence force field model of Aizawa *et al.* [12]. It relies on two spring constants describing changes in the potential due to deformation of the membrane. One characterizes the displacement of each carbon atom out of the plane formed by its three neighbors ($\gamma = 2.11$ eV), and one describes twisting ($\delta = 1.98$ eV), similar to the force making ethylene flat. This model has accurately reproduced the measured phonon dispersion curves of graphite monolayers on several substrates [12], and is in excellent agreement with first-principles calculations, particularly for the low frequency modes important in H atom sticking [13]. The dispersion relation for the ZA branch obtained by diagonalization of the dynamical matrix is shown in Fig. 1. Using a first order Taylor expansion, a compact relation between phonon frequency ω and wave vector norm Q can be derived close to the Γ point: $\omega \approx [\frac{a^4}{48m}(\frac{9\gamma}{a^2} + \frac{12\delta}{a^2})]^{1/2} Q^2$, where $a = 2.46$ Å is the lattice parameter and m the carbon mass. The dispersion is therefore quadratic, as opposed to the usual linear form ([14] and references therein). This unusual dispersion compromises the stability of graphene as a freestanding two-dimensional crystal [15]. This can be shown by considering the thermal average of the relative displacement from equilibrium perpendicular to the membrane plane $\langle (u_i - u_j)^2 \rangle$ of two atoms at sites $\mathbf{s_i}$ and $\mathbf{s_j}$ [16]. This quantity describes how order is preserved in the

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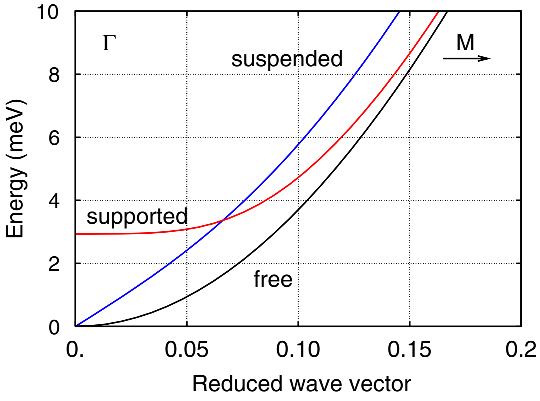

FIG. 1 (color online). Phonon dispersions for freestanding (black line), suspended (blue line), and substrate supported (red line) graphene, near the Γ point and along the Γ-*M* direction in reciprocal space. The reduced wave vector is the amplitude of the wave vector, normalized to be 0.5 at the *M* point.

material over distance, and is proportional to $\int d\omega \rho(\omega) \times \frac{\{1-\cos[\mathbf{Q}(\mathbf{s}_i-\mathbf{s}_j)]\}}{\omega^2}$, where $\rho(\omega)$ is the phonon density of states, shown in Fig. 2. Close to the Γ point, $\rho(\omega)$ is nonzero, as $\rho(\omega) = \frac{2\pi Q dQ}{d\omega} \propto \omega^0$. The integrand is singular for $\omega = 0$ and the relative deviation $\langle (u_i - u_j)^2 \rangle$ diverges for all length scales. Thermal fluctuations thus destroy order at any length scale [15].

It is thus necessary to identify conditions under which flat graphene is stabilized with respect to these thermal fluctuations. One possibility is to support graphene on a substrate, say, a silicon oxide layer. The weak van der Waals interaction between graphene and a SiO_2 substrate has been measured to be ≈ 0.1 J/m^2 [17] for an average separation of ≈ 0.42 nm [18]. In the harmonic approximation, this corresponds to a force constant $k^{\rm sub} = 0.4$ N/m linking each carbon atom to the substrate [17]. The modified dispersion relation now involves three force constants and is shown in Fig. 1. Close to the Γ point, we have $\omega^2 \approx \frac{k^{\rm sub}}{m} + \frac{a^4}{48m}(\frac{9\gamma}{a^2} + \frac{12\delta}{a^2})Q^4$. The presence of the substrate modifies the phonon dispersion relation mainly near the Γ point in such a way that there is now a nonzero minimum frequency for $Q = 0$. Even with the resulting van Hove singularity in the density of states for this minimum frequency (Fig. 2), the expression for the relative deviation is now integrable. This restores stability to the two-dimensional crystal. It has been confirmed experimentally that ultraflat graphene can be obtained under such conditions [19].

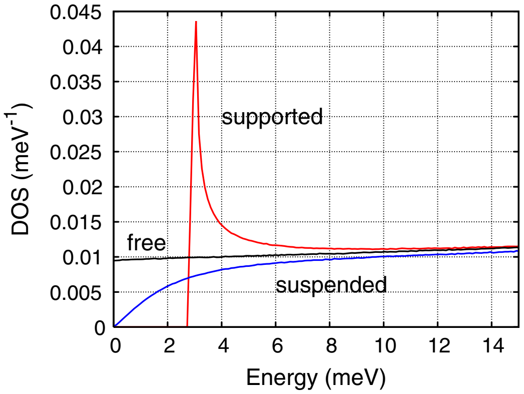

FIG. 2 (color online). Phonon density of states (DOS) for the 3 configurations considered in Fig. 1. The density of states are normalized such that the integral over energy is 1.

Concerning freestanding membranes, it has been suggested that thermal fluctuations can be limited by anharmonic coupling between bending and stretching. Freestanding graphene would exist but would exhibit ripples [15,20]. It was then shown that the ripples could be controlled by tuning the strain applied to the membrane, which resulted from the differing thermal expansion coefficients of the graphene and the surrounding substrate [21]. This suggests that the substrate plays a significant role even in the case of "freestanding" graphene, and for this reason, we prefer to call it "suspended" graphene in the following, reserving the term "free" for the (unrealistic) situation where there is no substrate. Experimentally, flat suspended graphene can be obtained by mechanical deposition onto a SiO_2 layer patterned with holes [22,23]. Interestingly, graphene adheres to the vertical walls of the holes over several nanometers because of the van der Waals interactions between the membrane and the substrate. This interaction can induce a strain on the order of 1% and a biaxial stress σ in the suspended membrane which can reach several N/m (but which adds to a pretension which can be compressive). We model this situation by adding a constant force σa, exerted by each C atom on each of its 3 neighbors, to the expression for the dynamical matrix. We choose $\sigma = 4$ N/m for the biaxial tension applied to the membrane from its rim to be representative of experimental conditions. The resulting dispersion relation for the ZA branch is shown in Fig. 1. Close to the Γ point we have $\omega^2 \approx \frac{\sqrt{3}\sigma a^2}{4m} Q^2 + \frac{a^4}{192m}(\frac{36\gamma}{a^2} + \frac{48\delta}{a^2} - \sqrt{3}\sigma)Q^4$. The application of tensile stress restores an approximately linear relation between the ZA phonon frequency and the wave vector norm near the Γ point, proportional to σ. The corresponding phonon density of states is shown in Fig. 2. It is proportional to frequency close to the Γ point. This provides convergence of the integral involved in the relative deviation $\langle (u_i - u_j)^2 \rangle$ and improves the stability of flat graphene. Note that this result is obtained within a purely harmonic phonon model, without the introduction of bending-stretching anharmonic couplings. Note also that supported graphene is subjected to stress and strain induced by lattice mismatch with the underlying substrate, so that the stress stabilization effect described here in the suspended case should also be efficient in the supported one [24].

We now describe a quantum model for the sticking of hydrogen on supported and suspended graphene, based on the close coupling wave packet method [25,26]. Our Hamiltonian is $H = H_s + H_b + V_c$. H_s describes the incoming hydrogen atom and its interaction with a static but corrugated membrane. Similar to the study of Ref. [10], our potential energy surface is fit to the high-level *ab initio* calculations of Ref. [27], and has a physisorption well of 40 meV. H_b is the Hamiltonian of the harmonic bath, supported or suspended graphene, as described above. The system-bath coupling is a complicated function of the coordinates of the lattice atoms, given by their displacements from equilibrium, $\mathbf{u_i}$, and the location of the incoming particle, $\mathbf{r} = (\mathbf{R}, z)$, where $\mathbf{R} = (x, y)$ is the atom's position projected onto the membrane plane, and z is the atom's distance above this plane. It is reasonable to expand this to first order in the carbon displacements, to get [11]

$$V_c(\mathbf{r}, \{\mathbf{u_i}\}) = D(z)\sum_{\mathbf{Q}} \frac{e^{-(1/2)(\mathbf{Q}^2/Q_c^2)} e_z(\mathbf{Q})}{\omega_{\mathbf{Q}}^{1/2}} e^{i\mathbf{QR}}(a_{\mathbf{Q}} + a^{\dagger}_{-\mathbf{Q}}). \tag{1}$$

$D(z)$ is a decreasing function of z parametrizing the strength of the coupling, Q_c is related to the lateral extension of the interaction between hydrogen and carbon atoms, $a_{\mathbf{Q}}$ and $a^{\dagger}_{-\mathbf{Q}}$ are phonon annihilation and creation operators, on which carbon atom displacements $\mathbf{u_i}$ are expanded. $e_z(\mathbf{Q})$ is the sum of the z components of the polarization vectors of both atoms in the elementary unit cell. This function is nearly constant and equal to $\sqrt{2}$ throughout the first Brillouin zone, except close to its edge.

A wave function describing an atom incident on a substrate is expanded in a product basis of nearly 2000 phonon states (necessary for convergence near the Γ point) and 200 particle states describing the interaction of the H atom with the corrugated rigid membrane. These states are eigenfunctions of H_b and H_s, respectively. The coefficients in the expansion are solutions to a set of time dependent first order differential equations. Sticking probabilities are extracted after time propagation of an initially Gaussian 0.9 meV wide wave packet. These probabilities correspond to H atoms irreversibly trapped in the physisorption well. These trapped states are characterized by two approximate quantum numbers: v describes H vibration perpendicular to the membrane, and the other gives the diffraction state for H motion parallel to the membrane (and restricted to 2 values here, "g" for ground or "e" for excited [11]). Our main approximation is the truncation of the phonon basis: only states involving a difference of zero or one phonon with respect to the initial occupation numbers are considered. This is, however, appropriate here given the low mass, collision energy, and membrane temperature [11].

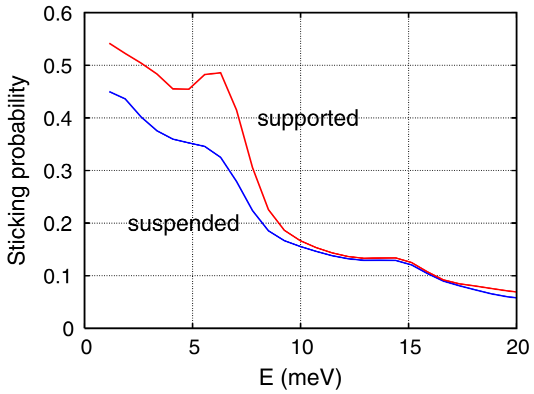

FIG. 3 (color online). Sticking as a function of the kinetic energy of the incoming H atom perpendicular to the membrane. Both suspended and supported (see Fig. 1) configurations are considered.

Figure 3 shows total sticking probabilities as a function of the incident hydrogen atom energy, summed over all possible stuck states $(v, g/e)$. This probability is high, reflecting an efficient energy dissipation mechanism, and decreases with energy. As the collision energy increases, higher frequency phonons are needed to absorb the energy, and it can be seen from Eq. (1) that coupling is then smaller. Low frequency phonons near the Γ point therefore play an essential role in the process. The modifications made to our phonon model to limit thermal fluctuations are also necessary for convergence of the sticking probabilities. These sticking probabilities are much larger than those of Ref. [11], especially at low energy. This is mainly due to the use of a different model for the polarization vector in Ref. [11], namely, $e_z(\mathbf{Q}) = [\sin(\frac{\pi Q}{2Q_{\max}})]^{1/2}$, which goes to 0 near the Γ point. This corresponds to a Rayleigh mode for a thick graphite slab that loses its surface character at low Q [28], and which obviously does not exist in the present two-dimensional problem. This provides a vanishing coupling at the Γ point and thus less efficient energy dissipation by low frequency phonon excitation. By contrast, the present $e_z(\mathbf{Q})$ remains almost constant ($\sqrt{2}$) near the Γ point, leading to more efficient low frequency phonon excitation and higher low energy sticking. Note that sticking is slightly lower in the suspended case because the phonon density of states is slightly reduced in the low energy portion of the spectrum (see Figs. 1 and 2).

The sticking probability does not decrease monotonically throughout the entire energy range. For collision energies near 7 and 15 meV, the H atom can be temporarily trapped on the membrane in the excited diffraction states $(v = 1, e)$ and $(v = 2, e)$, respectively. This trapping gives more time for the system to dissipate energy into the phonons and to relax from the $(v = 1, e)$ and $(v = 2, e)$ states down to the $(v = 0, e)$, enhancing sticking in the $(v = 0, e)$ state near 7 and 15 meV. This diffraction mediated selective adsorption [29] has been studied for H on graphite [10,11], and is illustrated clearly in the state selected sticking probabilities of Fig. 4 for the supported graphene case. In the absence of resonances, individual populations are typically decreasing functions of energy,

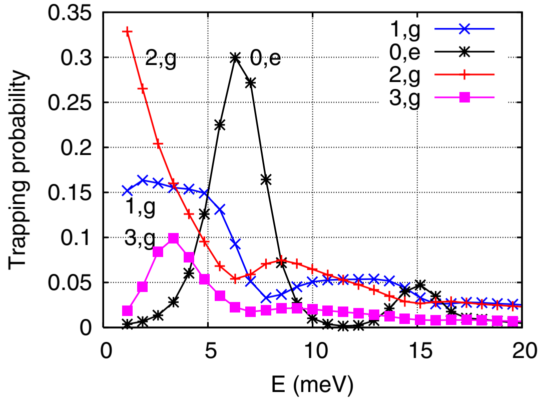

FIG. 4 (color online). Sticking populations for individual H-graphene adsorbed states, as a function of the incident H atom kinetic energy perpendicular to the membrane. Graphene is supported on a SiO_2 substrate. Each state has two labels. The first is the vibrational excitation of H perpendicular to the membrane, and g/e corresponds to the ground or excited diffraction state.

though the $(3, g)$ population is small at low energy due to the absence of low frequency phonons in the supported case (Fig. 2).

In conclusion, we present harmonic phonon models for suspended and supported graphene. We describe how interactions with the substrate can limit thermal fluctuations and stabilize flat graphene without assuming anharmonic couplings between bending and stretching. These suspended and supported graphene models were used to study the sticking of hydrogen atoms on a 10 K membrane. We showed that sticking is efficient at low energies (≤ 10 meV) due to the unusual nature of the lattice vibrations. This suggests that sticking should be enhanced at low collision energies for many other atomic and molecular species on graphene-based NEMS operated at low temperature. These findings await experimental verification.

The authors thank D. Lemoine for useful discussions. B. J. gratefully acknowledges support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy under Grant No. DE-FG02-87ER13744.

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