Hydrogen dynamics on defective monolayer graphene

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The hydrogen dynamics on a graphene sheet is studied in the presence of carbon vacancies. We analyze the motion of atomic H by means of molecular dynamics (MD) simulations, using a tight-binding Hamiltonian fitted to density-functional calculations. Hydrogen passivates the dangling bonds of C atoms close to a vacancy, forming C–H bonds with H located at one or the other side of the layer plane. The hydrogen dynamics has been studied from statistical analysis of MD trajectories, along with the autocorrelation function of the atomic coordinates. For a single H atom, we find an effective barrier of 0.40 eV for crossing the graphene layer, with a jump rate $\nu = 2 \times 10^6$ s$^{-1}$ at 300 K. The atomic jumps behave as stochastic events, and their number for a given temperature and time interval follows a Poisson probability distribution. For two H atoms close to a vacancy, strong correlations in the atomic dynamics are found, with a lower jump frequency $\nu = 7 \times 10^5$ s$^{-1}$ at room temperature. These results provide insight into the diffusion mechanisms of hydrogen on graphene, paving the way for a complete understanding of its motion through defective crystalline membranes.

Keywords: Graphene, atomic vacancies, hydrogen diffusion, molecular dynamics, permeability

I. INTRODUCTION

The study of hydrogen as an impurity in solids and on surfaces dates back to many years. Although it is one of the simplest impurities, a deep understanding of the physical and chemical properties of H-related defects is not obvious because of its low mass, and needs the application of advanced theoretical and experimental techniques. For two-dimensional (2D) systems, such as graphene, hydrogen chemisorption can nowadays be efficiently obtained in the laboratory by several routes. The resulting material may be suitable for catalytic reactions and turns out to be a good candidate for hydrogen storage.

Experimental and theoretical work indicates that a defect-free graphene sheet is impermeable to gases, even to small atoms such as He or H. For atomic H, in particular, the energy barrier for crossing a perfect graphene layer is about 4 eV, which makes permeation highly unlikely. Sun et al. have recently suggested that the effective barrier for this dynamic process could be lower, thus favoring jumping of atomic hydrogen from one side of the sheet to the other. Proton permeation across graphene and related materials under various conditions turns out to be more efficient than in the case of atomic hydrogen. This has been demonstrated in recent years by several research groups.

Permeation of atoms and molecules through crystalline membranes such as graphene is enhanced by the presence of nanomeshes, nanopores, and atomic-scale defects. This has attracted interest for its applications in gas separation and sieving of H isotopes. In connection with this, hydrogen is known to passivate vacancy defects and edges in graphene nanoribbons.

The properties of atomic and molecular hydrogen on graphene have been investigated by various research groups from a theoretical point of view, using ab-initio electronic structure methods, as well as semi-empirical potentials. In particular, introducing hydrogen molecules on the graphene surface, the permeation process is thought to consist of several steps, namely molecular dissociation, atomic diffusion on the surface, crossing of the layer, recombination, and desorption. The actual disposition of hydrogen atoms on graphene has been also studied by employing experimental techniques, such as scanning tunneling microscopy, electron diffraction, and photoemission spectroscopy.

In this paper, we study the motion of atomic hydrogen in defective graphene. In particular, we consider one and two H atoms close to a carbon vacancy and study their dynamics, with especial emphasis on the jump rate of hydrogen for crossing the graphene layer from one side to the other. We present results of tight-binding (TB) molecular dynamics (MD) simulations in a temperature range from 300 to 1200 K, obtained from a TB Hamiltonian employed earlier to study H diffusion in graphite, graphene, and diamond. In the case of two H atoms, we find a strong correlation in the jumps for both of them. As a check of the reliability of the TB Hamiltonian to describe C–C and C–H interactions in hydrogenated graphene, we have also carried out ab-initio density-functional theory (DFT) calculations to determine some relevant features of the energy surface, such as energy barriers. TB MD simulations similar to those presented here have been carried out earlier to study several finite-temperature properties of hydrogen-related defects in various types of materials, as well as on surfaces.

The paper is organized as follows. In Sec II we present the computational methods employed here, i.e., tight-binding molecular dynamics, DFT method, and harmonic linear-response procedure. In Secs III and IV, we give results for H impurities at $T = 0$ and finite tempera-
turers, respectively. The dynamics of the hydrogenic complexes with one and two H atoms is presented in Secs V and VI. The paper closes with a summary in Sec. VII.

II. COMPUTATIONAL METHODS

In this Section we present the methods employed in our calculations. In Sec. II.A we focus on molecular dynamics simulations and the tight-binding method used along the paper to describe the interatomic interactions. In Sec. II.B we briefly outline some aspects of the DFT calculations which we carried out to compare with the TB results at $T = 0$. In Sec. II.C we give a short account of the harmonic linear-response method used to obtain vibrational frequencies at finite temperatures.

A. Tight-binding molecular dynamics

We study equilibrium and dynamical properties of hydrogen in defective graphene by means of MD simulations. An important point in the MD procedure is a precise definition of interatomic interactions, which should be taken as realistic as possible. Using ab-initio density functional or Hartree-Fock based self-consistent potentials would largely reduce the length of the simulation trajectories required for a reasonable statistics of the considered variables. Thus, we derive the interatomic forces from an efficient tight-binding Hamiltonian, developed on the basis of density functional calculations.

The capacity of this kind of TB methods to describe various properties of molecular systems and condensed matter has been discussed by Goringe et al. and Colombo. The TB Hamiltonian employed here has been found earlier to reliably describe C–H interactions in carbon-based materials. As an example, for a methane molecule, it yields for $A_1$ and $T_2$ vibrational modes in a harmonic approximation (HA) frequencies of 3100 and 3242 cm$^{-1}$, respectively. The agreement with experimental frequencies of 2917 and 3019 cm$^{-1}$ can be considered to be good, taking into account the usual redshift of these modes due to anharmonicity. This TB Hamiltonian has been used in earlier work to describe C–H interactions in diamond, graphite, and graphene.

In this paper, TB MD simulations have been performed in the isothermal-isobaric ($NPT$) ensemble for a graphene rectangular supercell, containing 95 C and $n$ H atoms, with $n = 1$ or 2. Periodic boundary conditions were assumed in the layer plane ($x, y$ coordinates) and free boundary conditions have been considered in the perpendicular $z$ direction. Chains of four Nosé-Hoover thermostats were coupled to each atomic degree of freedom to give the required temperature. Another chain of four thermostats was coupled to the barostat that controls the in-plane area of the simulation cell ($xy$ plane), yielding a constant pressure $P = 0.92$ atm. The equations of motion have been integrated by using the reversible reference system propagator algorithm (RESPA), which allows us to define different time steps for the integration of the fast and slow degrees of freedom. The time step $\Delta t$ corresponding to TB derived forces was taken as 0.5 fs, which yielded a good precision for the variables and temperatures considered here. For fast dynamical variables as the thermostats, we employed a time step $\delta t = \Delta t/4$.

The configuration space has been sampled at temperatures in the range from 300 to 1200 K. For a given temperature, a typical run consisted of $2 \times 10^5$ MD steps for system equilibration, followed by $2 \times 10^7$ steps (10 ns) for calculating average variables and analyzing the atom dynamics. In Fig. 1 we present a snapshot of an atomic configuration taken from a MD simulation of H close to a carbon vacancy in graphene. Yellow balls represent C atoms, whereas the small blue sphere represents the hydrogen atom. The simulation was carried out at $T = 300$ K.

B. DFT calculations

To check the precision of our TB procedure to describe hydrogenated defective graphene, we have carried out some state-of-the-art DFT calculations. We have calculated the adsorption energy and barriers for atomic hydrogen on a cluster of size similar to the supercell employed for the TB MD simulations. Dangling bonds of carbon atoms at the cluster borders were saturated by hydrogen atoms, whose $z$ coordinate was kept fixed on the graphene layer plane ($z = 0$) to have a reference for the atomic positions at the hydrogenic defect.

DFT calculations have been done with the Gaussian16 (Revision A.03) package using the B3LYP hybrid functional and Def2SV basis set. The Berny algorithm was employed for both minimizations (optimiza-
tions to a local minimum) and optimizations to transition states.\(^{68}\)

DFT-based ab-initio calculations have been carried out earlier to study various characteristics of atomic hydrogen on graphene, such as trapping of electrons,\(^{69}\) defect-induced magnetism,\(^{24,70}\) and opening of a gap in the electronic density of states.\(^{35}\) This computational procedure has been also applied to study the chemical activity of H on graphene,\(^{36}\) as well as the effect of an applied stress on hydrogen chemisorption.\(^{21}\) In our present context, DFT calculations have been applied to analyze the permeability of graphene for atomic species, with especial emphasis on hydrogen.\(^{31}\)

C. Vibrational frequencies

The harmonic vibrational frequencies for defective graphene with a carbon vacancy and a hydrogen atom were obtained by diagonalization of the dynamical matrix for the same simulation cell employed for the MD simulations. Interatomic force constants for the TB potential were calculated by numerical differentiation of the forces, using atom displacements of \(10^{-4}\) Å from the equilibrium positions. This gives us a \(HA\) for the vibrational modes.

To estimate anharmonic shifts of vibrational modes at finite temperatures we have used the so-called harmonic linear response (HLR) method, which was derived by considering the statistical mechanics of linear response within the framework of equilibrium quantum path-integral simulations.\(^{72,73}\) In the classical limit, the HLR approach is closely related to methods that analyze vibrational modes by studying spatial correlations of nuclear coordinates.\(^{74,75}\) In our procedure, vibrational frequencies are derived from the eigenvalues obtained by diagonalization of the covariance matrix of atomic displacements in thermal equilibrium. This matrix is readily calculated from spatial trajectories in the configuration space sampled by either MD or MC simulations.\(^{22}\) Quantum vibrational energies of molecules containing C–H bonds and several crystals have been investigated so far by the HLR method.\(^{59,61,77}\)

III. ZEROTEMPERATURE RESULTS

In this paper we focus on hydrogen in defective graphene. For comparison, we give some results obtained earlier for H on pristine graphene, in the absence of defects. In this case, the lowest-energy configuration corresponds to H bound to a C atom. This carbon atom relaxes out of the layer plane by 0.46 Å, and the C–H bond direction is perpendicular to the layer, with an interatomic length \(d_{\text{C–H}} = 1.17\) Å. This coordination is understood as the breaking of a \(\sigma\) bond and the creation of a \(\pi\) bond, thus modifying the hybridization of the C atom from \(sp^2\) to \(sp^3\).\(^{31,33,34}\) This chemisorption of hydrogen on pristine graphene gives rise to a defect-induced magnetic moment.\(^{33,34,70}\)

For hydrogen close to a carbon vacancy on a graphene sheet, we have calculated the minimum-energy configuration \((T = 0)\) by relaxing the position of H and C atoms, with the exception of the carbon atoms at the boundary of the simulation cell, whose motion was restricted to \(z = 0\). This gives a reference for the motion of hydrogen in the \(z\) direction, perpendicular to the layer plane. We found a lowest-energy arrangement with H bound to one of the three carbon atoms around the vacancy, and located off-plane with \(z_H = 0.77\) Å (we take \(z = 0\) for the graphene sheet). The C atom bound to H also moves off-plane to \(z_C = 0.40\) Å, and the C–H bond distance results to be 1.11 Å. Both C atoms near the vacancy and not connected to H, slightly relax off-plane in the opposite direction to hydrogen to \(z_C = -0.13\) Å. Our DFT calculations yield a desorption energy for hydrogen of 4.4 eV, which corresponds to the binding energy for a C–H bond appearing after passivation of one dangling bond close to the carbon vacancy. For this atom configuration in graphene, Casartelli et al.\(^{28}\) found from their DFT calculations a binding energy of 4.24 eV. This energy value contrasts with the much lower binding energy obtained for C–H bonds in defect-free graphene (about 0.8 eV).\(^{32,33,38}\) In this case, DFT calculations yield a small barrier of about 0.2 eV for hydrogen adsorption, as explained in the review by Bonfanti et al.\(^{78}\) For a single H atom at the carbon vacancy, we find that the adsorption is barrierless, in agreement with Ref.\(^{78}\)

An additional characterization of this point defect in graphene can be obtained from the vibrational frequencies of hydrogen. In Fig. 2 we display the vibrational density-of-states (DOS) for hydrogen, as derived from diagonalization of the dynamical matrix in a HA (dashed line). The peak at 3162 cm\(^{-1}\) corresponds to stretching of the C–H bond, which contrasts with a frequency of 2555 cm\(^{-1}\) for the C–H stretching vibration in nonde-
effective graphene. This is in line with a stronger C–H bond for hydrogen close to a carbon vacancy, as it passivates a “dangling bond” in this point defect, and is also confirmed by a shorter C–H bond length in defective graphene \((d_{C-H} = 1.11 \text{ Å})\), as compared with pure graphene \((d_{C-H} = 1.17 \text{ Å})\). The stretching frequency obtained here for the C–H bond in defective graphene lies between those found for \(A_1\) and \(T_2\) modes of methane in a \(\text{H}_2\) : \(3100\) and \(3242\text{ cm}^{-1}\), respectively.

Fig. 2 reveals a broad region between \(400\) and \(1500\text{ cm}^{-1}\), where H vibrations lie in the frequency range of modes associated to the graphene lattice. We observe two main peaks at \(854\) and \(1175\text{ cm}^{-1}\), which correspond to modes with H displacement perpendicular to the C–H bond direction.

To study the hydrogen dynamics around a carbon vacancy in graphene, an important question is the characterization of the saddle point for hydrogen jumps from one side of the graphene sheet (say \(z_H > 0\)) to the opposite side (\(z_H < 0\)). For the saddle point at \(z_H = 0\), our TB calculations give an atomic arrangement with a C–H bond distance of \(1.07\text{ Å}\), close to that of the minimum-energy configuration. The energy barrier for H crossing from the upper to the lower minimum is \(0.37\text{ eV}\), which turns out to be a relatively low barrier for hydrogen motion. For comparison, DFT calculations using the same graphene supercell yield for this process a barrier of \(0.42\text{ eV}\).

One can also think of H jumps from one C to a neighboring C atom close to the vacancy, breaking a C–H bond and building a new one. For this process we find from our TB calculations a barrier of \(1.54\text{ eV}\), clearly larger than that corresponding to up-down jumps for H connected to a single C atom. DFT calculations yield for this energy barrier a value of \(1.47\text{ eV}\), close to the TB result. From this relatively high barrier, we expect that this kind of H jumps will be rare events in our finite-temperature MD simulations, and their occurrence is expected to be much less likely than up-down H jumps preserving the bond of hydrogen with the same C atom.

We have also considered the case of two hydrogen atoms bound to different carbon atoms near the vacancy. In this case the minimum-energy arrangement corresponds to one H at \(z_H = 0.75\text{ Å}\) and the other at \(z_H = -0.75\text{ Å}\). The C atoms bound to H are located at \(z_C = 0.37\) and \(-0.37\text{ Å}\), respectively. The distance to the layer plane of both H and C is similar to the case of a single H atom at the vacancy, and the C–H bond distance is \(1.11\text{ Å}\). In Fig. 3 we present top and side views of the minimum-energy configuration with one H atom above the graphene layer plane and the other one below the layer. A configuration with both H atoms above or below the layer plane with \(|z_H| = 1.1\text{ Å}\) has an energy \(0.55\text{ eV}\) higher than the minimum-energy configuration. Such an atom disposition corresponds to a shallow local minimum of the energy surface, which turns out to be rather flat for small H displacements in that region. Thus, we have an effective repulsion between both H atoms, so that they prefer to stay at different sides of the graphene layer.

For hydrogen motion in this point defect, one can expect simultaneous jumps of both H atoms, interchanging its z coordinate (up-down jumps). For simultaneous crossing of the layer plane, we obtain a relatively large energy barrier of \(1.59\text{ eV}\). This barrier is higher than that obtained one H atom crosses the graphene layer to a z coordinate similar to the other one, and then the second H crosses the layer plane in the opposite direction. This process defines the saddle-point for the cooperative motion of both H atoms, yielding a barrier of \(0.57\text{ eV}\).

We have checked that the formation of molecular hydrogen \(\text{H}_2\) is unfavorable with respect to the creation of two C–H bonds near the vacancy. In fact, for an \(\text{H}_2\) molecule plus a vacancy our TB calculations give an energy of \(3.3\text{ eV}\) higher than that of the most stable disposition with two C–H bonds (DFT yields \(3.1\text{ eV}\)). Another possibility is that both H atoms link to a single carbon atom close to the vacancy, but this arrangement has an energy \(1.3\text{ eV}\) higher than the minimum-energy configuration.

Experimental data of the energy barrier for atomic hydrogen to cross the graphene layer are scarce. This is mainly due to the difficulty of obtaining samples with
well-characterized defects, through which the permeation process can take place. It has been observed that crossing a sheet of defect-free graphene may be enhanced by the presence of several H atoms clustering on the surface. Sun et al.\textsuperscript{12} have reported a barrier of 1.0 ± 0.1 eV for atomic hydrogen, obtained from dissociation of molecular H\textsubscript{2}. A similar barrier has been found by Bartolomei et al.\textsuperscript{13} from DFT calculations. For a specific arrangement of four neighboring H atoms in defect-free graphene, these authors found that crossing the sheet by one of them is the most probable event, with a barrier \(\Delta E = 0.82\) eV. These energy barriers are higher than those found here for hydrogen flipping through the sheet in the presence of a carbon vacancy.

**FIG. 4:** Probability density for the \(z\) coordinate of H (solid line) and C bound to H (dashed line) close to a vacancy, as derived from MD simulations at \(T = 1000\ K\).

**FIG. 5:** Mean-square displacement of H along the \(x\) and \(y\) directions. Symbols indicate results of MD simulations at several temperatures: circles for \((\Delta x)^2\) and squares for \((\Delta y)^2\). Dashed lines are guides to the eye. Error bars are less than the symbol size.

IV. FINITE-TEMPERATURE CONFIGURATIONS

We now turn to the results of our finite-temperature simulations for one hydrogen atom in defective graphene. From the calculations at \(T = 0\), we have two equivalent positions for H bound to a C atom with \(z_H = 0.77\) and -0.77 Å. In our MD simulations at finite temperatures (especially for \(T > 400\ K\)), we observe jumps of hydrogen from one equilibrium position to the other. Although the highest probability density for the presence of H occurs around these positions, we find that the mean position of hydrogen changes with temperature, as a consequence of thermal motion and anharmonicity of the C–H bond. Thus, at \(T = 500\ K\) we have a mean value \(\langle |z_H|\rangle = 1.01\) Å, which slightly decreases at higher temperature to \(\langle |z_H|\rangle = 0.97\) Å at 1200 K (angle brackets denote an ensemble average). Close to \(|z_H| = 1\) Å, the potential surface for H motion is "flatter" for decreasing \(|z_H|\), so at high temperature, \(\langle |z_H|\rangle\) slowly decreases. Accordingly, the mean value \(\langle |z_C|\rangle\) of the C atom bound to H takes values of 0.54 and 0.50 Å at \(T = 500\) and 1200 K, respectively. Thus, the difference between mean \(z\) coordinates of H and C atoms evolves from 0.37 to 0.47 Å in the temperature range from \(T = 0\) to 1200 K, and the mean angle between the C–H bond and the layer plane increases from 19.5 to 25.4 degrees. The mean length of the C–H bond, however, changes very slowly in this temperature range, increasing by about 0.01 Å from the low-temperature limit up to \(T = 1200\ K\).

In Fig. 4 we display the probability density of the \(z\) coordinate for H (solid line) and C (dashed line), derived from MD simulations at \(T = 1000\ K\). As expected from the results mentioned above for the mean value \(\langle |z_H|\rangle\), the maximum probability for the presence of hydrogen occurs at \(z_H \approx 1\) and -1 Å. For the C atom bound to H, the maxima appear at \(z \approx 0.50\) and -0.50 Å. Note that the density at \(z = 0\) (energy barrier), even small, is not negligible for hydrogen, \(\rho_z(h) = 0.02\) Å\(^{-1}\), and is larger for carbon: \(\rho_z(c) = 0.10\) Å\(^{-1}\). The atomic dynamics associated to motion between both energy minima (maxima in the probability density shown in Fig. 4) is studied below in Sec. V.

To analyze the H displacements parallel to the layer plane we consider its mean-square displacement (MSD) in the \(x\) and \(y\) directions. In Fig. 5 we show the temperature dependence of these MSDs, as derived from MD simulations. In our coordinate system, the projection of the C–H bond on the layer plane is parallel to the \(y\) axis. This means that the \(y\) axis corresponds to the direction from the C bound to H to the center of the vacancy (missing C atom), which coincides with the so-called armchair direction in the graphene sheet. Then, the MSD in the \(x\) direction (parallel to the zigzag direction of graphene) is related to bending of the C–H bond (displacement perpendicular to the C–H axis). Within the precision of
our results, we find that \((\Delta x)^2\) increases linearly as the temperature is raised.

For the MSD in the \(y\) direction, however, we observe a clear deviation from linearity. The main reason for this behavior of \((\Delta y)^2\) is the onset of \(H\) jumps from one side to the other of the graphene layer at \(T > 400\) K in the course of the MD simulations. This means that during the jump process both bonded \(H\) and \(C\) atoms cross the plane \(z = 0\), where their \(y\) coordinates change with respect to those corresponding to the steady configurations at one or the other side (see Sec. V). The jump process does not appreciably affect the mean \(x\) coordinate of the linked \(H\) and \(C\) atoms. The change in the mean \(y\) coordinate of \(H\), \(\langle y_H\rangle\), amounts to 0.04 Å, which although not very large is enough to cause a superlinear increase in \((\Delta y)^2\) vs the temperature. In fact, we obtain in the region from 300 to 1200 K a dependence \((\Delta y)^2 \sim T^\alpha\) with an exponent \(\alpha = 1.24\).

We have calculated the vibrational DOS for \(H\) bound to a \(C\) atom close to a vacancy, using the HLR method described in Sec. II.C. The result obtained with this procedure for \(T = 300\) K is shown in Fig. 2 (continuous line). This DOS for \(H\) vibrations was derived from atomic displacements around their equilibrium positions in MD trajectories including \(1.2 \times 10^7\) steps. This length of the trajectories was necessary for a precise determination of the frequencies, with statistical error bars of less than 5 cm\(^{-1}\).

The clearest feature in the vibrational DOS of \(H\) is the \(C-H\) stretching mode, which appears at frequencies well above the rest of vibrations in the defective material. For this stretching vibration we find at 300 K a frequency of 2990 cm\(^{-1}\) (see Fig. 2), which means an anharmonic redshift of 172 cm\(^{-1}\) with respect to the harmonic calculation presented above in Sec. II (dashed line). Using the so-called forced vibrational method, Ishum et al.\(^{22}\) found a stretching frequency of about 2900 cm\(^{-1}\) for \(C-H\) stretching vibrations in defective graphene nanoribbons. For comparison, we mention that the HLR method has been previously applied to study vibrational modes in molecular systems. Thus, for \(C-H\) stretching modes in the ethyl radical (\(C_2H_5\)), it was found at \(T = 25\) K a redshift in the range from 270 to 310 cm\(^{-1}\).\(^{22}\) For the DOS of \(H\) in defective graphene we observe in the range between 400 and 1500 cm\(^{-1}\) changes in the position and intensity of the modes respect the harmonic result, with the most prominent peaks appearing now at 1005 and 1285 cm\(^{-1}\).

V. HYDROGEN DYNAMICS

We now present results of MD simulations for motion of one hydrogen atom in defective graphene at finite temperatures. From the calculations at zero temperature, we can expect jumps of \(H\) from one side to the opposite one of the graphene layer. In Fig. 6(a) we present the evolution of the \(z\) coordinate of hydrogen, \(z_H\), along a MD simulation run at \(T = 660\) K. The time interval displayed here amounts to 1 ns, i.e., \(2 \times 10^6\) MD steps. Even though \(z_H\) appreciably fluctuates due to thermal motion of \(H\), we clearly observe that the hydrogen atom resides most of the time around \(z_H = 1\) or \(-1\) Å. Around both plateaus we find fluctuations of \(z_H\) with a MSD \((\Delta z_H)^2 = 0.04\) Å\(^2\).

The evolution of the \(z\) coordinate of the \(C\) atom bound to \(H\), \(z_C\), is displayed in Fig 6(b) for the same time interval as in Fig 6(a) for \(H\). Jumps of this \(C\) atom between the upper and lower side of the graphene sheet occur in synchrony with those of \(H\), keeping a \(C-H\) distance of 1.11 Å. At 660 K, we find \(\langle |z_C|\rangle = 0.53\) Å.

At \(T \geq 500\) K we have observed up-down jumps of \(H\) and \(C\) atoms along the MD simulations similar to those presented in Fig. 6. At lower \(T\), we have not found any such event along our simulations, with a duration of 10 ns. This means that at room temperature \((T = 300\) K\) one expects a jump rate \(\nu \lesssim 1/(10\) ns\) = \(10^6\) s\(^{-1}\). At \(T \geq 500\) K the jump frequency \(\nu\) can be reliably estimated...
from the number of up-down jumps observed along the simulations.

For a number of atomic jumps $N_{+/-}$ in a simulation time $\Omega$, our estimation for the rate is $\nu = N_{+/-}/\Omega$. In this way, we have calculated the rate $\nu$ at several temperatures up to 1200 K from the jumps occurring in our MD simulations. In Fig. 7 we present an Arrhenius-type plot of the obtained jump rate vs the inverse temperature. Solid circles represent the frequency $\nu$ obtained from the observed number of jumps $N_{+/-}$ along simulation runs of $2 \times 10^7$ MDS ($\Omega = 10$ ns). These results can be well fitted to an expression $\nu \propto \exp(-\Delta E/k_B T)$, with an energy barrier $\Delta E = 0.40(1)$ eV. This effective barrier is close to that found for crossing the layer plane at $T = 0$, $\Delta E = 0.37$ eV (see Sec. III).

An alternative procedure to calculate the jump rate $\nu$ is based on the autocorrelation function $G(\tau)$ for the coordinate $z_H$. We define this time function as

$$G(\tau) = \frac{\langle z_H(t)z_H(t+\tau) \rangle}{\langle z_H(t)^2 \rangle}, \quad (1)$$

where the mean values are taken along a MD simulation run. Assuming that $z_H$ is a stochastic variable taking values $c$ and $-c$ with equal probability and a hopping frequency $\nu$, we have for a given initial condition $z_H(0)$ (see Appendix):

$$\frac{d\langle z_H(t) \rangle}{dt} = -2\nu \langle z_H(t) \rangle, \quad (2)$$

which yields

$$G(\tau) = \exp(-2\nu \tau). \quad (3)$$

The autocorrelation function $G(\tau)$ for a single hydrogen atom has been calculated from the $H$ trajectories obtained in our MD simulations at various temperatures, following the definition in Eq. (1). The results are presented in Fig. 8 at four temperatures in a logarithmic plot. From the slope of these lines we obtain the frequency $\nu$ using Eq. (3). Note that the lines displayed in Fig. 8 do not extrapolate to zero for $\tau \to 0$ (i.e., $G(\tau) \to 1$), due to thermal motion around the energy minima, which causes a fast decrease of $G(\tau)$ at short times to values $G(\tau) \sim 0.9$. Thus, we observe in fact $G(\tau) = C \exp(-2\nu \tau)$, with $C < 1$.

Open circles in Fig. 7 indicate the rate $\nu$ obtained from the autocorrelation function $G(\tau)$ at various temperatures. The results found with this procedure and those derived from direct enumeration of the $H$ jumps along the MD trajectories (solid circles) agree well, and yield the same effective energy barrier $\Delta E = 0.40(1)$ eV for this process. We have thus derived this effective barrier in two independent ways, which provides us with a consistency check for our calculations. From the data presented in Fig. 7, we can estimate the expected jump rate at room temperature from extrapolation of the results at higher temperatures. From the linear fit in the Arrhenius plot of Fig. 7, we find a ratio $\nu = 2 \times 10^6$ s$^{-1}$ at $T = 300$ K.

At this point, one may ask if the hydrogen jumps are uncorrelated or there is some correlation between them, in the sense that the atomic arrangement after a jump “remembers” in some way the configuration before the jump. This could favor a return to the old configuration. The presence or lack of correlations between $H$ jumps can be analyzed by studying the distribution of the number of jumps for time intervals of a given length $\Pi$. For uncorrelated stochastic events, their num-
The number of jumps in a time interval follows a Poisson distribution. In our case, this means that for uncorrelated jumps with jump rate \( \nu \) (mean time between events equal to \( 1/\nu \)), the probability \( P(n) \) for the number \( n \) of jumps in a time interval \( \Pi \) should be given by:

\[
P(n) = e^{-\nu \Pi} \frac{(\nu \Pi)^n}{n!}.
\]  

(4)

The mean value for this probability distribution is \( \mu = \nu \Pi \), i.e., the average number of hydrogen jumps in a time interval \( \Pi \) is \( \nu \Pi \). Note that for low temperature and small \( \nu \), i.e. \( \nu \Pi \ll 1 \), only \( n = 0 \) and \( 1 \) will have an appreciable probability.

We have split our MD trajectories at several temperatures in time intervals of length \( \Pi = 5 \) ps (\( 10^4 \) MD steps), and obtained frequencies for the number of jumps \( n \) in those intervals, from where we derived the corresponding probability distribution. This is shown in Fig. 9, where solid symbols represent results yielded by MD simulations at \( T = 660 \) K, \( 750 \) K, \( 1000 \) K, \( 1200 \) K, and \( 1200 \) K (triangles). Open circles joined with dashed lines indicate the expected Poisson distribution corresponding to the same time window \( \Pi \). Error bars of the simulation results, when not shown, are in the order or less than the symbol size.

In Fig. 9: Probability distribution for the number of H jumps in a time window \( \Pi = 5 \) ps. Solid symbols represent results derived from MD simulations at \( T = 660 \) (circles), \( 750 \) (squares), \( 1000 \) (diamonds), and \( 1200 \) K (triangles). Open circles joined with dashed lines indicate the expected Poisson distribution corresponding to the same time window \( \Pi \). Error bars of the simulation results, when not shown, are in the order or less than the symbol size.

VI. TWO HYDROGEN ATOMS IN A CARBON VACANCY

We have also carried out MD simulations for two H atoms bound to two different C atoms close to a vacancy in graphene. In this case, two dangling bonds are passivated by hydrogen. According to the calculations at \( T = 0 \) presented in Sec. III, the minimum-energy state corresponds to the H atoms (which we will label 1 and 2) located at opposite sides of the graphene layer, each one at a distance of 0.75 Å to the layer plane.

As in the case of a single H at the vacancy, for two H atoms one expects appreciable motion of H at finite temperatures, and in particular crossing of the graphene plane. In Fig. 10 we show the coordinates \( z_H^{(1)} \) and \( z_H^{(2)} \) of both hydrogen atoms at \( T = 850 \) K, along a MD trajectory in a time interval of \( 1 \) ns (\( 2 \times 10^6 \) MD steps). Panels (a) and (b) correspond to hydrogen atoms 1 and 2, respectively. One observes the correlation in the jumps of both atoms: they are located at opposite sides of the graphene layer, and simultaneously (as seen at the scale of the plot) cross the layer plane interchanging their coordinate \( z_H \). At this temperature, the mean distance of the H atoms to the plane is \( \langle |z_H| \rangle = 0.81 \) Å, somewhat higher than in the minimum-energy configuration, with a MSD \( (\Delta z_H)^2 = 0.07 \) Å².

We have calculated the jump rate of the H atoms using the same procedures as in the case of a single hydrogen. The results are presented in Fig. 7 along with the data corresponding to a single H, discussed above in Sec. V. For two H atoms, solid squares correspond to the mean jump rate \( \nu \) obtained from the statistics of jumps observed along the simulations (\( \nu = N_{+-}/\Omega \)), whereas open squares were derived from the correlation function \( G(\tau) \) for each H atom. The results of both methods are close one to the other, and we observe that the solid symbols lie somewhat above the open ones, especially at the lowest temperatures considered here. This does not seem to be fortuitous, and may be due (apart from the poorer statistics at lower temperature) to additional correlations in the jump process, not taken into account in
The statistics used in our procedures. In any case, the whole ensemble of data can be well fitted to an expression of the form \( \nu \propto \exp(-\Delta E/k_B T) \), with an activation barrier \( \Delta E = 0.61(3) \text{ eV} \). This effective energy barrier is close to that obtained at \( T = 850 \text{ K} \). The data shown in Fig. 11 presents the temperature dependence of the correlation functions \( A_{\text{H-H}} \) and \( B_{\text{H-H}} \) for the \( z \) coordinate of both H atoms close to a carbon vacancy. These functions are defined in Eqs. (4) and (6). Symbols are data points derived from MD simulations. Dashed lines are guides to the eye.

where the brackets indicate averages over the MD trajectories. In Fig. 11 we present the temperature dependence of \( A_{\text{H-H}} \) (solid circles), as derived from our simulations. For the ideal disposition of H atoms fixed on their minimum-energy positions (classical \( T = 0 \) limit), one has \( A_{\text{H-H}} = -1 \). At finite temperatures, thermal motion causes an increase in \( A_{\text{H-H}} \) (a reduction of its absolute value), as shown in Fig. 11. \( A_{\text{H-H}} \) grows linearly with temperature up to about 800 K, and increases faster at higher \( T \). The main reason for this increase in \( A_{\text{H-H}} \) is the rise of the numerator in Eq. (5), since thermal fluctuations in the atomic positions cause uncorrelated motion of both H atoms around their equilibrium positions.

The second (apparently simpler) function considered here to analyze correlations in the \( z \) coordinates of both H atoms is defined as

\[
B_{\text{H-H}} = \frac{\langle z_{1H}^{(1)} z_{2H}^{(2)} \rangle}{\langle z_{1H}^{(1)} \rangle \langle z_{2H}^{(2)} \rangle},
\]

where “sgn” denotes the sign function, i.e., sgn \( z \) = 1 or -1 for \( z > 0 \) and \( z < 0 \), respectively. Results for \( B_{\text{H-H}} \) derived from our MD simulations are shown in Fig. 11 as solid squares.

The product of both terms inside the brackets in Eq. (6) takes values 1 or -1, the former when both H atoms are at the same side of the graphene layer and the latter when they are at opposite sites of the layer plane. Thus, at \( T < 700 \text{ K} \) the probability for having simultaneously both H atoms at the same side is very low, and \( B_{\text{H-H}} \approx -1 \). At higher temperatures, this probability grows, mainly due to thermal fluctuations of the atomic position during the up-down jumps. Looking together at both functions in Fig. 11, \( A_{\text{H-H}} \) and \( B_{\text{H-H}} \), it turns out that the former is more sensitive to thermal motion than the latter, especially at temperatures lower than 800 K.
where $B_{H-H}$ is nearly constant and $A_{H-H}$ grows linearly as the temperature is raised.

The function $B_{H-H}$ is directly related to the probability for finding both H atoms on the same side of the graphene layer. Calling $Q$ this probability, one has

$$Q = \frac{1}{2} \left( 1 + B_{H-H} \right). \quad (7)$$

In the low-$T$ classical limit one has $Q = 0$. At $T = 1000$ K, we obtain $B_{H-H} = -0.972$ and $Q = 0.014$, still a rather small probability at this high temperature.

We note that at low $T$, the treatment of H atoms as distinguishable entities is no longer possible, as they have to be considered as quantum identical atoms, and classical trajectories for both of them are not realistic. At $T \gtrsim 300$ K, however, the quantum exchange probability is very low, so that such trajectories are a reliable description of this system. A classical treatment at these temperatures is favored by the fact that the defect complexes that really hop include not only hydrogen atoms, but also the heavier carbon atoms bound to them.

VII. SUMMARY

We have studied the dynamics of atomic hydrogen in defective graphene. In particular, we considered crossing of a graphene layer by H atoms in the presence of carbon vacancies. This provides us with essential information on a relevant part of the dynamical process leading to hydrogen permeation in graphene.

It has been shown that TB MD simulations of hydrogen in defective graphene constitute a reliable tool to study the atomic motion in a wide range of temperatures, employing an interatomic potential fitted to ab-initio calculations. As a consequence of the large relaxation of the nearest C atoms, the hydrogen dynamics in graphene requires a concomitant motion of these atoms. Thus, H jumps from one side of the layer plane to the other are in fact a cooperative process engaging the impurity and the nearest host atoms.

For an H atom near a vacancy, the minimum-energy configuration corresponds to the impurity located off-plane at a distance of 0.77 Å from the graphene layer. The C atom attached to H also relaxes off-plane to $z_C = 0.40$ Å. The C–H bond forms an angle of 19.5 degrees with the graphene plane. Our results at $T = 0$ derived from the TB Hamiltonian display good agreement with those obtained from ab-initio DFT calculations.

At finite temperatures, the coordinate $z_H$ presents plateaus along trajectories generated by MD simulations, with jumps from one plateau to the other corresponding to hydrogen crossing the layer plane (interchange between $z_H > 0$ and $z_H < 0$). Jump rates at different temperatures were obtained using two methods based on the jump statistics along the MD trajectories and the autocorrelation function $G(\tau)$. Both procedures give results consistent with one another. Analysis of the impurity jump rate as a function of the inverse temperature allowed us to calculate an effective energy barrier for traversing the layer plane at finite temperatures. For an H atom near a vacancy, we found a barrier of 0.40 eV, with a jump frequency $\nu = 2 \times 10^6$ s$^{-1}$ at room temperature.

For two H atoms, we observe a concerted motion with concurrent passage through the vacancy. In this case, the effective barrier is found to be 0.61 eV, with $\nu = 7 \times 10^2$ s$^{-1}$ at 300 K. The C atoms linked to H atoms equally move from one to the other side of the graphene layer, thus preserving the C–H bonds along this dynamic process.

In this paper, we have focused on the crossing mechanism for atomic hydrogen. The whole process of hydrogen permeation through carbon vacancies in graphene would include also H$_2$ dissociation and atomic diffusion on the surface, prior to the layer crossing, as well as subsequent recombination and desorption.

An interesting extension of this work could be the consideration of quantum effects in the hydrogen dynamics. In particular, application of transition-state theory, based on Feynman path integrals may be employed to study the renormalization of the classical energy barriers and the jump rates at $T$ lower than room temperature.

CRediT author contribution statement

Carlos P. Herrero: Data curation, Investigation, Validation, Original draft
José A. Vergés: Methodology, Investigation, Validation
Rafael Ramírez: Methodology, Software, Investigation, Validation

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A: Autocorrelation function

The autocorrelation function for the coordinate $z_H$ of hydrogen is defined as

$$G(\tau) = \frac{\langle z_H(t)z_H(t+\tau) \rangle}{\langle z_H(t)^2 \rangle} \quad (A1)$$
with
\[ \langle z_H(t)z_H(t + \tau) \rangle = \frac{1}{Ω} \int_0^Ω z_H(t)z_H(t + \tau) dt. \]  \hspace{0.5cm} (A2)

To derive an analytical expression for the autocorrelation function, we consider a random variable \( z_H \) taking values \( c \) and \( -c \) with equal probability, and a time sequence controlled by a stochastic process with a rate \( \nu \) for jumps between \( c \) and \( -c \). We will call \( P_+(t) \) and \( P_-(t) \) the probabilities of having \( z_H = c \) or \( -c \) at time \( t \), respectively, with \( P_+(t) + P_-(t) = 1 \). Given an initial condition \( z_H(0) \), we have for time \( t \):
\[ \langle z_H(t) \rangle = cP_+(t) - cP_-(t) = c[2P_+(t) - 1], \]  \hspace{0.5cm} (A3)
and
\[ \frac{d\langle z_H(t) \rangle}{dt} = 2c \frac{dP_+(t)}{dt}. \]  \hspace{0.5cm} (A4)

Here \( \langle z_H(t) \rangle \) indicates the mean value of \( z_H \) at time \( t \) for all stochastic trajectories starting at \( z_H(0) \).

For a time interval \( \Delta t \), the mean number of jumps is \( \nu \Delta t \). Then, for small \( \Delta t \) (i.e., \( \nu \Delta t \ll 1 \)) the probability \( P_+(t + \Delta t) \) can be written as
\[ P_+(t + \Delta t) = P_+(t) + [P_-(t) - P_+(t)] \nu \Delta t, \]  \hspace{0.5cm} (A5)
and a similar expression holds for \( P_-(t + \Delta t) \). This means that the time derivative of \( P_+(t) \) is given by
\[ \frac{dP_+(t)}{dt} = [P_-(t) - P_+(t)] \nu, \]  \hspace{0.5cm} (A6)
or
\[ \frac{dP_+(t)}{dt} = [1 - 2P_+(t)] \nu. \]  \hspace{0.5cm} (A7)

Then, from Eqs. (A4) and (A7) one finds
\[ \frac{d\langle z_H(t) \rangle}{dt} = -2\nu \langle z_H(t) \rangle \]  \hspace{0.5cm} (A8)
and
\[ \langle z_H(t) \rangle = z_H(0) \exp(-2\nu t). \]  \hspace{0.5cm} (A9)

Note that for long \( t \) (\( \nu t \gg 1 \)), both \( P_+ \) and \( P_- \) converge to 0.5, and \( \langle z_H(t) \rangle \to 0 \).

Finally, we find for the autocorrelation function
\[ \langle z_H(t)z_H(t + \tau) \rangle = \langle z_H(0)z_H(\tau) \rangle = \exp(-2\nu \tau), \]  \hspace{0.5cm} (A10)
where we have used the time translation invariance for the origin of the stochastic trajectories.

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