Spontaneous Regeneration
of an Atomically Sharp Graphene/Graphane Interface
under Thermal Disordering

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ABSTRACT

The smearing of the graphene/graphane interface due to the thermally activated migration of hydrogen atoms is studied by the molecular dynamics method. Contrary to expectations, it is found that the fast spontaneous regeneration of this interface occurs even at a sufficiently high temperature $T \approx 1500$ K. As a result, the average width of the disordered region does not exceed the length of a C-C bond, i.e., the interface remains almost atomically sharp. The cause of this effect appears to be the specific shape of the potential relief of the system, namely, the significant difference between the heights of the energy barriers for the direct and inverse migrations of hydrogen atoms. A simple model that makes it possible to obtain the temperature dependence of the equilibrium distribution function of typical atomic configurations, to estimate the typical time of establishing the equilibrium state, and thereby to quantitatively describe the results of the computer experiment is presented.

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The existence of graphane, i.e., a graphene monolayer completely saturated by hydrogen from both sides, was recently predicted in theoretical work [1]. The experimental synthesis of graphane [2] put forth the problem of its possible applications. In contrast to graphene, graphane is an insulator and can be used in nanoelectronics in combination with graphene [3]. For example, various nanoelectronic devices can be manufactured by the selective sorption of hydrogen on graphene or graphene nanoribbons. At first glance, it seems that the operation temperatures of such devices should be very low, because the thermally activated migration of hydrogen atoms through graphene/graphane interfaces gives rise to the fast smearing of these interfaces and an uncontrolled change in the electrophysical characteristics of a device. Below, we show that this is not necessary: the computer experiment on the numerical simulation of the dynamics of the graphene/graphane system demonstrates that the interface resists thermal disordering and remains atomically sharp even at high temperatures. This effect is not only of fundamental interest, but also important for applications.

Our first aim was to determine the temperature dependence of the smearing rate of the graphene/graphane interface. The initial graphene sample was simulated by a 88-atom fragment of the hexagonal carbon monolayer with edges passivated by hydrogen in order to saturate the dangling bonds of sp-hybridized carbon atoms to weaken the effects of finite sizes (the number of passivating hydrogen atoms is 26). One half of this sample was transformed to graphane by alternating the bonding of one hydrogen atom to each of the 44 carbon atoms from both sides of the plane of the initial monolayer (i.e., the orientation of each hydrogen atom is determined by a graphene sublattice (of two equivalent sublattices) to which the nearest carbon atom belongs. As a result, we obtain the C_{88}H_{70} cluster presented in Fig. 1 (configuration “A” in Fig. 2).
To simulate the thermally activated migration of hydrogen through the graphene/graphane interface, we used the molecular dynamics method [4-6]. At the initial time, random velocities and displacements were assigned to all of the atoms so that the momentum and angular momentum of the cluster were zero. Then, the forces acting on the atoms were calculated. The classical Newtonian equations of motion were numerically integrated using the velocity Verlet method with a time step of $t_0 = 2.72 \times 10^{-16}$ s. The total energy of the system (the sum of the potential and kinetic energies) in the simulation process is conserved, which corresponds to a microcanonical ensemble (the system is thermally isolated from the environment) [4-6]. In this case, the “dynamic” temperature $T$ is a measure of the energy of the relative motion of atoms and is calculated from the formula

$$\langle E_{\text{kin}} \rangle = \frac{1}{2} k_B T (3n - 6),$$

where $\langle E_{\text{kin}} \rangle$ is the time-average kinetic energy of the system, $k_B$ is the Boltzmann constant, and $n$ is the number of atoms in the system ($n = 158$ in our case). To calculate the interatomic interaction forces, a nonorthogonal tight binding model [8] modified as compared to [7] was used. This model is a reasonable compromise between stricter ab initio methods and too simplified classical potentials of the interatomic interaction. It reasonably describes both small carbon (e.g., fullerenes [8]) and hydrocarbon (e.g., cubane $C_8H_8$ [9, 10]) clusters and macroscopic systems [8] and requires much less computer resources than ab initio methods; for this reason, it allows to study the evolution of the system of $\sim 100$ atoms for a time of $\sim 1$ ns sufficient for the collection of necessary statistics.

At $T = 2000 - 2500$ K in time $< 10$ ps, the interface is completely smeared due to the migration of a large number of hydrogen atoms from graphane to graphene and/or their desorption. However, as the temperature is decreased to $T = 1500 - 1800$ K, we observed the following picture. The migration of one hydrogen atom by the distance of a C-C bond
configuration “B” in Fig. 2 and similar configurations formed after the migration of other boundary hydrogen atoms by the distance of a C-C bond) is usually followed by a fast (in a time of $\sim 1$ ps) hop of this atom to the initial position (i.e., the return to configuration “A” occurs), whereas its repeated migration to the graphene region (configuration “C” in Fig. 2 and similar configurations) occurs very rarely. After the first elementary migration act, the liberated site is sometimes occupied by a hydrogen atom from the other sublattice (configuration “D” in Fig. 2 and similar configurations), which soon (in a time of $\sim 1$ ps) returns to its position, i.e., configuration “B” is recovered; then, it is transformed to configuration “A”. Sometimes, we observed the regeneration of the graphene/graphane interface even after a much more complex sequence of hops of several hydrogen atoms belonging to different sublattices. At $T = 1700 - 1800$ K, 10-15 complete recoveries of the disordered interface occurred during the simulation time ($\sim 0.1$ ns); after that, either the desorption of one hydrogen atom or molecule occurred or the width of the disordered region reached a length of several C-C bonds; i.e., the smearing of the interface became irreversible. A further decrease in the temperature results in a strong increase in the typical onset time of the disordering of the interface; as a result, the mean time interval between two successive recoveries and, therefore, the time required for the irreversible smearing of this interface, increased.

To determine the cause of the thermal stability of the graphene/graphane interface, we examine the form of the hypersurface of the potential energy of the system, $E_{\text{pot}}$, as a function of the coordinates of the constituent atoms and obtain the heights of the energy barriers separating atomic configurations “A”, “B”, “C”, and “D” shown in Fig. 2 (the calculation method was presented in more detail in [4, 5, 11, 12]). Figure 3 shows the profile of $E_{\text{pot}}$ along the reaction coordinate passing through configurations “A”, “B”,...
and “D”. It is seen that for the “A”↔“B” and “B”↔“D” transitions, the heights $U_{AB}$ and $U_{BD}$ of the barriers preventing disordering are larger than the heights $U_{BA}$ and $U_{DB}$, respectively, of the barriers preventing the return of the system to the initial state after the migration of one and two hydrogen atoms. For the transitions between configurations “B” and “C”, the barrier for the transition to configuration “C” that is farther from the initial configuration is also higher than the barrier for the inverse transition; i.e., $U_{BC} > U_{CB}$. The calculated heights of the barriers are $U_{AB} = 0.96$ eV, $U_{BA} = 0.35$ eV, $U_{BD} = 0.50$ eV, $U_{DB} = 0.39$ eV, $U_{BC} = 0.81$ eV, $U_{CB} = 0.62$ eV. According to the Arrhenius formula

$$P_{ij}(T) = A_{ij} \times \exp \left( -\frac{U_{ij}}{k_BT} \right),$$

where $P_{ij}$ is the probability of the $i \rightarrow j$ transition per unit time, $U_{ij}$ is the height of the barrier between two atomic configurations $i$ and $j$, and $A_{ij}$ is the frequency factor with the dimension $s^{-1}$; under the conditions $U_{ij} > U_{ji}$ and $k_BT << U_{ji}$, the system is more often in configuration $i$ than in configuration $j$ (if one of the frequency factors is not much smaller or much larger than the other).

Since $U_{BC} > U_{BD} > U_{BA}$, it is clear why at $k_BT << U_{BA}$, first, the system almost always returns to the initial state after the migration of one hydrogen atom; second, the subsequent migration of the hydrogen atom in the other sublattice occurs much more rarely; and, third, the displacement of an atom from the interface by the distance of two C-C bonds has a low probability. The same relations exist between the heights of the barriers separating the configurations formed after the migration of the other four boundary hydrogen atoms of our model system (see Fig. 2) and the subsequent migration of the corresponding atoms of the other sublattice. Thus, the physical cause of the thermal stability of the graphene/graphane interface is the specific shape of the potential relief of
the system, namely, the significant difference between the heights of the energy barriers for direct and inverse hops of the hydrogen atoms, see Figs. 2 and 3. It is worth noting that the potential relief for the simultaneous migration of several hydrogen atoms is much more complex and, at sufficiently strong disordering, the barrier for the inverse migration of a certain atom is sometimes higher than the barrier overcome by this atom in the path to a given configuration. In particular, this concerns migration along the interface. As a result, the system can be for a long time in a state strongly different from the initial state. However, the migration of one atom by the distance of two or more C-C bonds from the interface and the simultaneous migration of several atoms occur more rarely with a decreasing temperature. In our computer experiment for $T = 1500 \text{ K}$, such configurations do not appear in a time of about 1 ns, which corresponds to $3 \times 10^6$ steps of molecular dynamics. With a further decrease in temperature, an exponential increase is expected in the time interval in which only minimally disordered configurations “B” and “D” are formed (and rapidly “healed”).

To estimate the thermally equilibrium distribution function $f_i$ of configurations “A”, “B”, and “D” most often observed in the simulation, we used the chemical kinetic equations based on the following model. Let us consider the statistical ensemble of a large number of graphene/graphane systems ($C_{88}H_{70}$ clusters in our case). At the initial time, all of them are in configuration “A”. The probabilities $f_A(t)$, $f_B(t)$, and $f_D(t)$ of finding the system in configurations “A”, “B”, and “D”, respectively, at time $t$ satisfy the system of differential equations

$$\frac{df_A(t)}{dt} = P_{BA}f_B(t) - P_{AB}f_A(t) ,$$

$$\frac{df_B(t)}{dt} = P_{AB}f_A(t) - P_{BA}f_B(t) + 2P_{DB}f_D(t) - 2P_{BD}f_B(t) ,$$

$$2\frac{df_D(t)}{dt} = 2P_{BD}f_B(t) - 2P_{DB}f_D(t) \quad (2)$$
with the initial condition

\[ f_A(0) = 1, \quad f_B(0) = 0, \quad f_D(0) = 0, \quad (3) \]

Here, the conditional transition probabilities \( P_{ij} \) are given by Eq. (1) and we take into account only the “A” \( \leftrightarrow \) “B” and “B” \( \leftrightarrow \) “D” transitions (i.e., neglect the transitions to more disordered configurations) and the existence of two equivalent “D” configurations, see Fig. 2. Note that \( f_A(t) + f_B(t) + 2f_D(t) = 1 \) at any time according to Eqs. (2) and (3). In the steady (thermodynamically equilibrium) state, \( df_i(t)/dt = 0 \) for all of the configurations \( i = A, B, \) and \( D; \) for this reason, we obtain the system of linear homogeneous equations for equilibrium (at \( t \to \infty \)) values \( f_i \) from Eqs. (2) and (3); the solution of this system has the form

\[
\begin{align*}
  f_A &= 1 - \frac{P_{AB}(P_{DB} + 2P_{BD})}{P_{AB}(P_{DB} + 2P_{BD}) + P_{BA}P_{DB}}, \\
  f_B &= \frac{P_{AB}P_{DB}}{P_{AB}(P_{DB} + 2P_{BD}) + P_{BA}P_{DB}}, \\
  f_D &= \frac{P_{AB}P_{BD}}{P_{AB}(P_{DB} + 2P_{BD}) + P_{BA}P_{BD}}. \quad (4)
\end{align*}
\]

Since the height \( U_{AB} \) is much larger than the heights of all other barriers, according to Eqs. (1) and (4), \( f_A \) at \( T < 2000 \) K is close to unity, while \( f_B \ll 1 \quad f_D \ll 1. \)

To determine \( f_A, f_B, \) and \( f_D, \) it is necessary to know all of the frequency factors \( A_{ij} \) in Eqs. (4). Their calculation is a difficult problem. Since numerous (about 100) transitions between configurations “A” and “B” were observed in the simulation of the dynamics of the disordering of the graphene/graphane interface, we collected a lot of statistics and directly determined the frequency factors of these transitions from the straight line approximation of the calculated dependences of the transition times \( \tau_{AB} = P_{BA}^{-1} \) and \( \tau_{BA} = P_{BA}^{-1} \) on the inverse temperature using Eq. (1). We obtain \( A_{AB} \approx 2 \times 10^{14} \) s\(^{-1}\) and \( A_{BA} \approx 5 \times 10^{13} \) s\(^{-1}\) (the \( U_{AB} \) and \( U_{BA} \) values also determined in these calculations.
coincide within the statistical errors with the values presented above, which were obtained by a fundamentally different method). Estimating the frequency factors $A_{BD}$ and $A_{DB}$ as $10^{14}$ s$^{-1}$, we calculated the distribution function over the configurations for several temperatures for which the simulation was performed. For example, for $T = 1800$ K, we obtained $f_A = 0.866$, $f_B = 0.068$, and $f_D = 0.033$. These values are in good agreement (taking into account rough approximations) with the values $f_A = 0.814$, $f_B = 0.119$, and $f_D = 0.032$, which were determined as the relative time intervals during which the system was in the corresponding states in the simulation of its time evolution (the total number of molecular dynamics steps was more than 200 000; the relative weight of other, more disordered configurations was 0.003). This agreement between the statistical and dynamic data is a consequence of ergodicity (the mean value over the ensemble of the systems is equal to the average value over the trajectory of one system). The typical time $\tau$ of establishing the equilibrium state can be determined exactly from Eqs. (2) and (3), but the analytical solution is lengthy and we present only the estimate of $\tau^{-1} \sim \text{max}\{P_{AB}, P_{BA}, P_{BD}, P_{DB}\}$. In view of the relation $P_{BA}, P_{DB} \gg P_{AB}, P_{BD}$ at a fixed temperature, this time is primarily determined by the “B”→A and “D”→B transition rates. For example, for room temperature, we obtain $\tau \sim 10$ ns.

To conclude, we emphasize that the frequency factor $A_{AB}$ was numerically determined for a small model system with the length of the graphene/graphane interface $L \approx 1$ nm and the migration processes of only five boundary hydrogen atoms contribute to this factor. An increase in $L$ leads to the corresponding (proportional to the number of boundary atoms, i.e., to $L$) increase in $A_{AB}$ and, hence, to the increase in the probability of the formation of disordered configurations at a given temperature and to the decrease in the onset time of their formation. However, the statistical weight of these configurations
remains small, about $10^{-7}$ at room temperature even at $L \sim 1 \mu m$. Thus, the interface (if it is a straight line) is very stable against thermal disordering; for this reason, hybrid graphene/graphane systems are promising for nanoelectronics.

Finally, note that only a zigzag graphene/graphane interface has been considered in this work. It is also of interest to examine the thermal stability of an armchair interface.

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Figure captions

Fig. 1. \( \text{C}_{88}\text{H}_{70} \) cluster as a model of the graphene/graphane system. The large and small balls are carbon and hydrogen atoms, respectively.

Fig. 2. Typical configurations of the \( \text{C}_{88}\text{H}_{70} \) cluster most often observed in the simulation of the thermal stability of the graphene/graphane interface. The closed circles are carbon atoms. The small open circles are passivating hydrogen atoms. The large open circles and squares are hydrogen atoms located in different sublattices (above and below the cluster plane, respectively): (A) the initial state, (B) the configuration formed after the migration of one hydrogen atom from graphane to graphene by the distance of a C-C bond, (C) the configuration formed after the migration of one hydrogen atom from graphane to graphene by the distance of two C-C bonds, and (D) the configuration formed after the migration of each of the two hydrogen atoms belonging to different sublattices from graphane to graphene by the distance of a C-C bond.

Fig. 3. Schematic profile of the potential energy \( E_{\text{pot}} \) of the \( \text{C}_{88}\text{H}_{70} \) cluster near configurations “A”, “B”, and “D” (see Fig. 2); S1 and S2 are the saddle points. The energies are measured from the energy of configuration “A”. The heights of the energy barriers are \( U_{AB} = E_{S1} - E_{A} \), \( U_{BA} = E_{S1} - E_{B} \), \( U_{BD} = E_{S2} - E_{B} \), and \( U_{DB} = E_{S2} - E_{D} \).
Fig. 2
Fig. 3