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Electronic supplementary information (ESI) for

Interfacial layering of hydrocarbons on pristine graphite surfaces immersed in water

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Supplementary Information Text

Free energy for transfer to the monolayer phase. Figure S1 illustrates the protocol used to calculate the free energy for transfer of an adsorbed molecule to the monolayer phase, as plotted in Figure 4d. The system contains 100 hexadecane molecules (or 200 octane molecules, not shown), which form a continuous aggregate along the y-axis (owing to periodic boundary conditions). The free energy is calculated as a function of the x-projected distance between the center of mass of the "tagged" hexadecane molecule and the center of mass of the aggregate. This transition coordinate is labeled as "Distance from center of aggregate". Because the form of the aggregate rapidly fluctuates, as is evidenced by the diverse structures in Figure S1, the plot in Figure 4d does not show a sharp transition in free energy between the isolated and monolayer regions. While the free energy profile in this transition region depends on the design of the simulation system, the difference in the free energy between the end points should be more universal, since the end points of the free energy profile correspond to an isolated "tagged" molecule (X > 7 nm) and a "tagged" molecule fully surrounded by other hexadecane molecules (X < 2 nm), For comparison, we converted these four coarse-grain structures into explicit-solvent atomistic models and performed an energy minimization and short equilibration (20 ps). Although the coarse-grain model does a relatively good job of representing feasible packing of the hexadecane molecules, there is a small discrepancy in the packing density and the coarse-grain model does not attempt to represent the tendency of the hexadecane molecules to align along the zigzag directions of the graphene sheet.

Diffusion coefficient of hexadecane in water. To obtain the diffusivity of hexadecane in bulk water for use in the Brownian dynamics simulations described below, we performed all-atom simulations of a single hexadecane molecule in a periodic box of 22320 water molecules. Because the self-diffusion of water is poorly represented by the TIP3P water model[1], we performed these simulations with the TIP4P-Ew water model[2], which has a self-diffusion coefficient much closer to the experimental value. The hexadecane molecule was represented by the CHARMM General Force Field[3]. The simulations were integrated with a 2 fs timestep and all atoms had their natural masses (no mass repartitioning was used). The system was first equilibrated for 100 ps in the NpT ensemble (with a barostat set to 1.01325 bar and thermostat set to 295 K). The mean volume of the system, $(8.8129 \text{ nm})^3$, was calculated over the last 90 ps of the equilibration and used for the subsequent simulations. Ten production simulations with different initial velocities were performed to track the motion of the center of mass of the hexadecane. To avoid biasing the rate of diffusion, which might occur with the Langevin thermostat, these simulations were performed with the momentum conserving Lowe-Andersen thermostat[4] at a temperature of 295 K. NAMD parameters loweAndersenCutoff and loweAndersenRate took the values 2.7 Å and 50 ps^{-1}. Each of the ten simulations was run for 10 ns and the diffusion coefficient was estimated from the mean square displacement over 0.2 ns subtrajectories by $D < r^2 > /(6t)$. We obtained the value D =0.65 nm^2.

Brownian dynamics simulations. To determine the adsorption kinetics on longer time scales and larger size scales than is feasible by atomistic molecular dynamics, we performed Brownian dynamics simulations of hexadecane molecules on the free energy landscape plotted in Figure 4b. The hexadecane molecules were treated as point particles subject to this free energy landscape similar to our approach in previous work[5,6]. Given that the concentration of molecules relative to their size is low in the air, water, and, initially, on graphene, we neglected hexadecane–hexadecane interactions. The simulations were performed using a special purpose C++ code. In the model used in the simulations, the graphene surface and air–water interface were parallel to the *xy*-plane. The size of the system was 1 μm × 1 μm in the *xy*-plane. Two simulations were performed with different thicknesses of the water layer. In the first simulation, the energy landscape along the *z*-axis was represented by the potential of mean force for hexadecane in Figure 4b, a graphene-to-air-distance of 3.7 nm. A second free energy landscape was created with an additional 2.0 nm of bulk water (a uniform energy corresponding to the value in bulk water) inserted at 1.9 nm, resulting in a total thickness of 5.7 nm. The diffusivity of hexadecane was chosen to be the constant value (0.65 nm^2/ns) calculated for bulk water as described above. The equation of overdamped Brownian motion was integrated with a 200 fs timestep to accurately capture the changes in free energy with position.

In these simulations, we assumed that the number of hexadecane molecules at the air–water interface was in equilibrium with the concentration in the air, which is reasonable since the concentration and diffusivity in air[7] are higher than in water. The mean number at the air–water interface was calculated by:

$$\langle N_{aw} \rangle = A c_{air} \int_a^b dz \, exp[-\beta \omega(z)] \qquad (1)$$

where A = 1 μm^2 is the surface area, c_{air} = 500 $\mu\text{g/m}^3$ = 1.33 1018 molecules/m^3 is the chosen concentration of hexadecane in air, $w(z)$ is the potential of mean force shown in Figure 4b, β = $1/(k_B T)$ is the thermal energy, and a = 2.8 nm and b = 3.6 nm delineate the air–water interface. Every 100 Brownian dynamics steps, the number of molecules at the interface was chosen from a Poisson distribution consistent with N_{aw} = 2.7 molecules using the GNU Scientific Library[8]. The adsorption to the graphene–water interface was assumed to be quasi-irreversible and particles reaching z < 0.39 nm were counted as having been adsorbed and removed from the system.

In Brownian dynamics simulations of 31 and 295 billion steps, corresponding to 6.3 and 59.1 ms of simulated time, we counted 4 and 3 adsorption events for the thin (3.7 nm) and thick (5.7 nm) systems, respectively. Hence, we find rates of roughly 38 000 and 3000 molecules per minute for adsorption to a 1 μm^2 graphene–water interface. We compared this to the Kramers theory estimate[9] for the rate of transfer from the air–water interface to the graphite–water interface:

$$J = \sqrt{\kappa_{aw}\kappa_{barrier}}\frac{D}{2\pi k_B T}\exp(-\beta E_{barrier}) \tag{2}$$

where κ_{aw} is the harmonic force constant for the free energy well at the air–water interface, $\kappa_{barrier}$ is the harmonic force constant for the free energy barrier between the air–water and water–graphene wells, and $E_{barrier}$ is the height of this barrier. From Figure 4b, we estimated the values of κ_{aw} = 0.52 kcal/mol, $\kappa_{barrier}$ = 0.10 kcal/mol, and $E_{barrier}$ = 9.75 kcal/mol. For 2.7 molecules at the air–water interface, this gives a rate of 39 000 molecules/minute, which agrees well with the Brownian dynamics calculation of the same (thin) system. For the thick system, the barrier is much less parabolic in shape, so it is unclear how well this Kramers approximation would fare.

From atomistic simulations, we estimated a complete monolayer of hexadecane on graphene to be 361 pg/mm^2, which corresponds to 9.61 105 molecules on a 1 μm^2 graphite surface. Roughly, then, filling one third of a graphite surface would require 8 and 105 minutes for the thin and thick systems, respectively. In the experiments, the water layer is much thicker (1 mm); hence, transport by passive diffusion through the bulk water phase is unlikely to explain adsorption on the time scale seen in experiments.

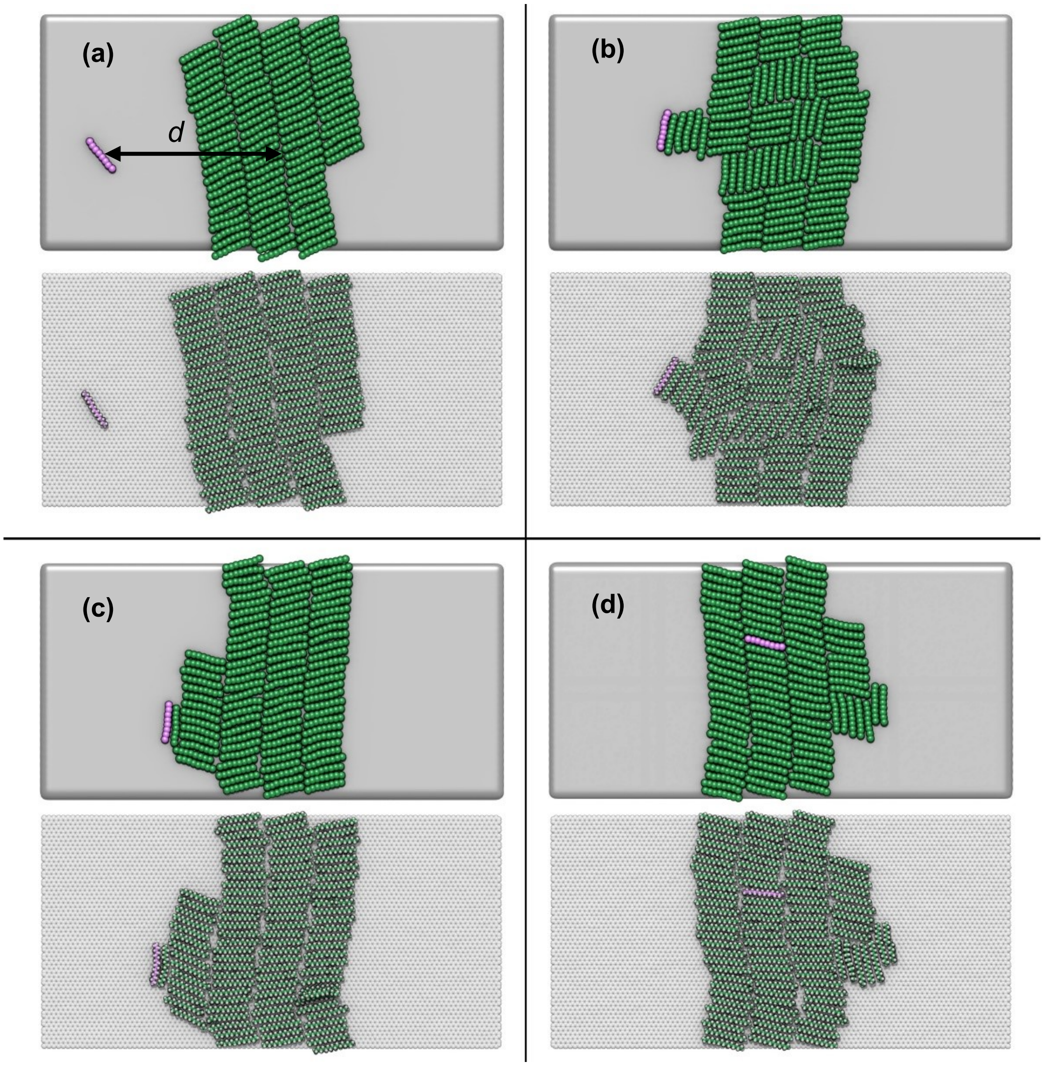

Figure S1. Images illustrating the protocol used to calculate the free energy for transfer of an adsorbed molecule to the monolayer phase, as plotted in Figure 4d (main text). The system contains 100 hexadecane molecules, which form a continuous aggregate along *y* axis (owing to periodic boundary conditions). The free energy is calculated as a function of *x*-projected distance between the center of mass of the "tagged" hexadecane molecule and the center of mass of the aggregate. This transition coordinate is referred to as "distance from center of aggregate". Figure S1 shows four exemplary structures of the aggregate (green molecules) and tagged molecule (magenta). The panels a, b, c, and d correspond to transition coordinates of 8.82, 6.03, 5.39, and 0.80 nm, respectively. The images of the atomistic structures are shown in the lower panels.

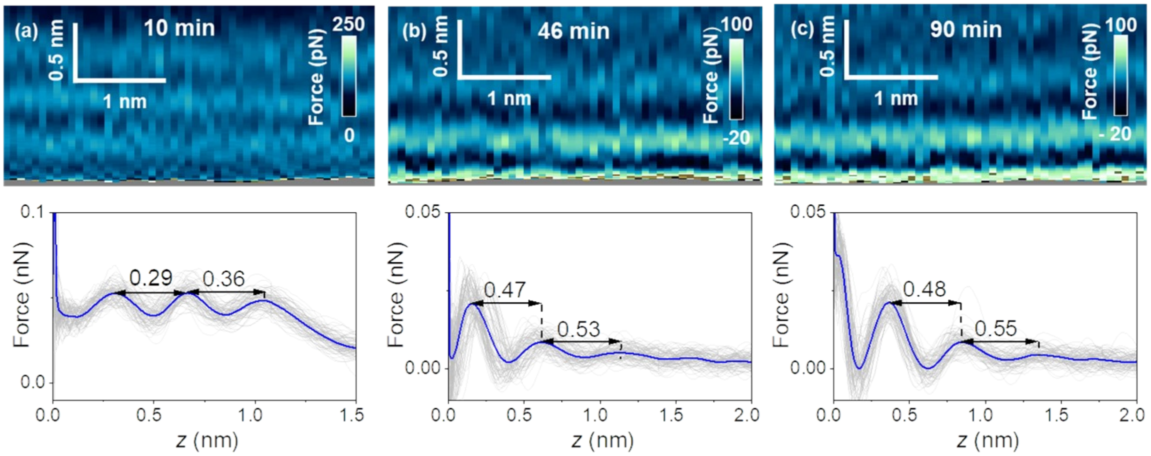

Figure S2. 2D force (*x*, *z*) maps and force-distance curves of graphite-water interfaces. The temperature of the cell was held constant at 38.0 ± 0.1°C The maps were extracted from 3D AFM volume images. (a) 2D force (*x*, *z*) map (top) and corresponding force-distance curves (bottom) for an immersion time of t = 10 minutes. (b) 2D force (*x*, *z*) map (top) and force-distance curves (bottom) for an immersion time of t = 46 minutes. (c) 2D force (*x*, *z*) map (top) and force-distance curves (bottom) for an immersion time of t = 90 minutes. The average force-distance curve is highlighted by a thick continuous line. Additional experimental parameters: f_1 = 799.463 kHz, k_1 = 9.8 N/m, Q_1 = 4.0, A_0= 400 pm, A_{sp} =300 pm.

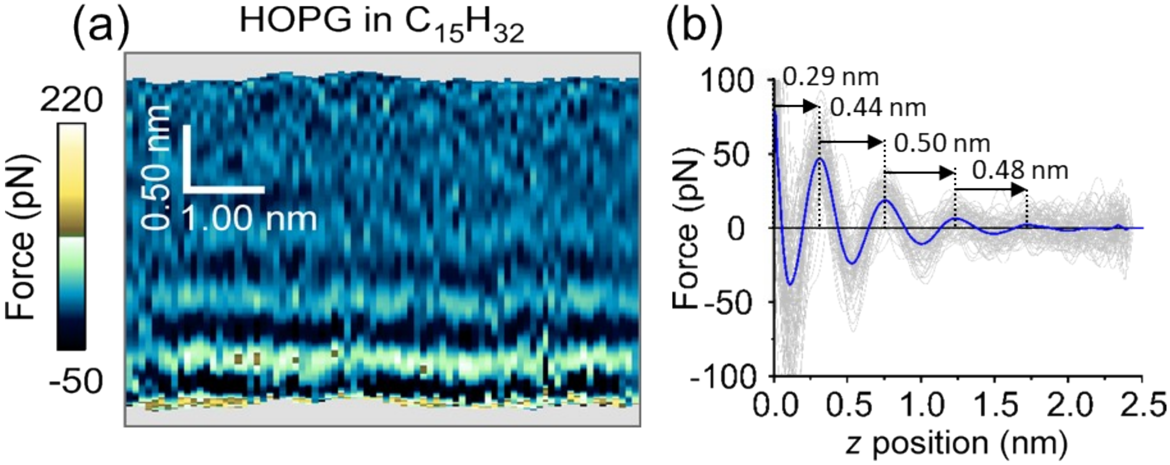

Figure S3. *n*-pentadecane on HOPG. (a) Two-dimensional (2D)-AFM *xz* force map of the HOPG-$C_{15}H_{32}$ interface. (b) Force–distance curves (FDC) corresponding to panel (a). The averaged curve is highlighted in blue. Data from ref.10.

3D-AFM experiments were performed by immersing HOPG in *n*-pentadecane[10]. Figure S3a shows a representative 2D-AFM *xz* force map of the HOPG-$C_{15}H_{32}$ interface. The interlayer spacing (Fig. S3b) is 0.47 ± 0.03 nm. This value indicates that the linear hydrocarbon chains are oriented in parallel to the HOPG surface. No ordering of the liquid was detected for tip-sample distances of $\gtrsim$2.0 nm.

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