Supplementary information. Ballistic Diffusion in Poly-Aromatic Hydrocarbons on Graphite

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1 Experimental details

Sample preparation Papyex exfoliated graphite disks of 2.5 cm diameter were heated under vacuum in a pyrolytic furnace for 20 hours at 623 K. Afterwards, the discs were deposited in a cylindrical aluminum sample holder. In the case of benzene, the volume of liquid benzene (Merck 99.7 %), which is required to obtain a desired coverage, was dosed with a micro-pipette. In the case of pyrene, the amount of powder (Merck 99.7 %) required to reach a certain coverage, was weighted using a high precision balance. Finally, the alu-

minum sample holder was hermetically sealed using a lid with a steel knife edge. In the case of pyrene, the sample was introduced in a furnace at 160 C for one hour to sublime the powder and promote its adsorption uniformly in the whole volume of the sample. We need to mention that during this annealing process, the sample holder also contains air. However, to minimize the danger of oxidizing the pyrene, the temperature was carefully controlled not to go beyond 180 C.¹ We rely on the very high scattering cross section of pyrene for neutrons, 800 barns, to justify that the neutron scattering function is mainly sensitive to pyrene and not other species like water (168 barns). We also expect that the relatively high temperatures for which diffusion was measured (between 80 K and 350 K) prevent most of the chemical species (nitrogen or oxygen) present on air to adsorb on the graphite simultaneously to pyrene.

Analysis of the experimental scattering functions for benzene and pyrene In order to properly analyze the quasi-elastic intensity of the experimental scattering function, we remove the elastic part of the scattering. For benzene, we subtract the scattering function measured at 2 K, when we consider that the adsorbates are frozen on the surface and the scattered intensity is completely elastic. In the case of pyrene, we subtract the experimental scattering function for the clean graphite substrate (on which adsorption was performed afterwards). In addition, to make a valid comparison of the two scattering functions shown in Fig. 1 of the paper, we chose a temperature for which benzene and pyrene have the same mean square velocity $\langle v^2 \rangle$, as given by the equipartition theorem for two dimensions. The corresponding temperatures are 140 K for benzene and 320 K for pyrene.

The fit of the experimental data in Fig. 1 to Eq. 1 (of the paper) is achieved by truncating the sum at $n = 100$ (to allow the series expansion to converge), and seeking for the value of

χ which minimizes the goodness of the fit (GoF)¹ with the algorithm of minimum squares.

1.1 Molecular Dynamic Simulations

The molecular trajectories were calculated with the Forcite package of the commercial software Material Studio 6.0 (Accelrys, Inc./Biovia). The COMPASS forcefield² was used and the optimum parameters were taken from Ref.³ We choose the NVT ensemble (constant number of particle, volume and temperature). The time step was 1 fs time, which allowed us to include the fast hydrogen dynamics. The duration of the simulations was of 1 ns and the frequency with which the position of the atoms was recorded is 0.5 ps. Two different kinds of trajectories were calculated: i) thermalization trajectories where the Berendsen thermostat was chosen to quickly generate a thermally equilibrated distribution of positions and velocities, ii) trajectories whose starting point is the previously thermalized distribution of positions and velocities. In this second case the Nosé thermostat was used, to obtain a distribution of velocities fulfilling the Gibbs-Boltzmann distribution.⁴ For comparison with the experimental results, the scattering functions were calculated from the xy components of the MD trajectories using the nMoldyn 3 software package.⁵

1.2 Density Functional Theory Calculations

The DFT calculations were performed using CASTEP,⁶ a plane wave periodic boundary condition code. The Perdew Burke Ernzerhof⁷ exchange-correlation functional, with the dispersion force corrections developed by Tkatchenko and Scheffler (TS method),⁸ was em-

¹We take the typical definition of the goodness of fit: $\frac{1}{N-C} \sum_{i=1}^N \left(\frac{y_i^{exp} - y_i^{theo}}{\sigma_i} \right)^2$, where N is the number of data points which is typically of the order of 40, C is the number of free parameters which in this case are the global amplitude $A(Q)$, the mean square velocity $\langle v^2 \rangle$ and the friction parameter η . y_0 is fixed to the background of the vanadium SF. $y_i^{exp} - y_i^{theo}$ are the residuals and σ_i is the experimental uncertainty. Note that since we have subtracted the elastic signal from the experimental scattering functions, the intensity of the SF in the range between $[-0.2, 0.2]$ meV is altered. Therefore the deviations of the fit with respect to the experimental values should not be taken into account for the calculation of the GoF.

ployed for all the calculations presented in this work. The plane wave basis set was truncated to a kinetic energy cutoff of 360 eV. The graphite surface was modelled by a three-layer (9×9) graphene slab. In this configuration, the distance that separates the adsorbates is close to 14 Å. The position of the carbon atoms within the graphite layers as well as the distance between the planes of the graphite single sheets was kept fixed during the structural optimizations of the adsorbed pyrene. We used Vanderbilt Ultrasoft Pseudopotentials⁹ for modelling the electron-nuclei interactions of both carbon and hydrogen atoms and the Brillouin zone was sampled at the gamma-point only. The electron energy was converged up to a tolerance of 10⁻⁸ eV while the force tolerance for structural optimizations was set to 0.05 eV.Å⁻¹. A vacuum layer of 20 Å was imposed above the graphite surface in order to avoid spurious interactions with the periodically repeated supercells.

2 Ballistic translations and rotations: a model for the incoherent scattering function

In this section, we develop the theoretical model to describe the incoherent scattering function arising from molecules which undergo simultaneously ballistic translations and uniaxial rotations. Therefore this formula is specially well suited to describe contribution of the pyrene protons to the scattering function, and contains information only about the self-diffusive regime.

Let us consider a collection of N identical molecules made of N_{at} atoms. The position of the j -th atom of the α -th molecule with respect to the laboratory frame is:

$$\mathbf{r}_j(t) = \mathbf{R}_\alpha(t) + \mathbf{u}_j^\alpha(t) \quad (1)$$

where $\mathbf{R}_\alpha(t)$ is the position of the center of mass (C.o.M) of the molecule and $\mathbf{u}_j^\alpha(t)$ is the

position of the the atom in the C.o.M reference frame. If we assume that translations and rotations are uncoupled, the resulting incoherent intermediate scattering function can be factorized into two terms:

$$I(\mathbf{Q}, t) = \sum_{\alpha}^N \underbrace{\langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_{\alpha}(t)) \exp(i\mathbf{Q} \cdot \mathbf{R}_{\alpha}(0)) \rangle}_{I_T(\mathbf{Q}, t)} \times \sum_j^{N_{at}} \underbrace{\langle \exp(-i\mathbf{Q} \cdot \mathbf{u}_j^{\alpha}(t)) \exp(i\mathbf{Q} \cdot \mathbf{u}_j^{\alpha}(0)) \rangle}_{I_R(\mathbf{Q}, t)}. \quad (2)$$

The first term depends only on the motion of the C.o.M and hence accounts for translations. This is the *translational ISF* $I_T(\mathbf{Q}, t)$. The second term depends on the motion of the atoms within the C.o.M reference frame. It is thus the rotational part of the ISF $I_R(\mathbf{Q}, t)$. The corresponding scattering function is the Fourier transformed from time to energy of Eq. 2, and consists in the convolution of the two terms:

$$S(\mathbf{Q}, \Delta E) = S_T(\mathbf{Q}, \Delta E) \otimes S_R(\mathbf{Q}, \Delta E). \quad (3)$$

2.1 Ballistic translations

The ballistic diffusive regime has been already described on the basis of the equipartition theorem and the relation between the mean square displacement and the mean square velocity:

$\langle \Delta r^2 \rangle = \langle v^2 \rangle t^2$.¹⁰ Its fingerprint is a Gaussian profile of the energy transfer:¹⁰

$$S_T(Q, \Delta E) = \frac{1}{\hbar \sqrt{\pi \langle v^2 \rangle} Q} \exp \left(-\frac{\Delta E^2}{2\hbar^2 \langle v^2 \rangle Q^2} \right). \quad (4)$$

where its HWHM follows a linear law of the momentum transfer:¹⁰

$$\Gamma(Q) = \hbar \sqrt{\ln(2) \langle v^2 \rangle} Q. \quad (5)$$

2.2 Uniaxial ballistic rotations

In this section we develop the exact form of the incoherent scattering function arising from uniaxial rotations around the symmetry axis of the molecule in the z direction (see Fig. 1). If molecules are rotating in the plane which contains the momentum transfer vector $\mathbf{Q}$,

Figure 1: In plane geometry: the momentum transfer $\mathbf{Q}$ between the incoming and the scattered neutron is contained in the same plane on which molecules are lying flat on the substrate. The in plane geometry is obtained setting the incoming beam direction parallel to the macroscopic surfaces of the graphite disks in the sample holder, and measuring the scattered neutrons in the same plane.

the exponential functions of Eq. 2 can be expanded as a summation of cylindrical Bessel functions² as done in Ref.:¹¹

$$\begin{aligned} \exp(i\mathbf{Q} \cdot \mathbf{u}_j^\alpha(0)) &= \exp[iQa_j \cos(\phi_j(0) - \gamma_{\mathbf{Q}})] = \sum_{n=-\infty}^{\infty} i^n J_n(Qa) e^{in(\phi_j(0) - \gamma_{\mathbf{Q}})} \\ \exp(-i\mathbf{Q} \cdot \mathbf{u}_j^\alpha(t)) &= \sum_{n=-\infty}^{\infty} (-i)^n J_n(Qa_j \exp[in(\phi_j(t) - \gamma_{\mathbf{Q}})] , \end{aligned} \quad (6)$$

$\gamma_{\mathbf{Q}}$ is the direction of the momentum transfer vector $\mathbf{Q}$ with respect to the laboratory frame, $\phi_j(t)$ is the orientation of the molecule at time t and a_j is the radius of the circle on which

²For the terms indexed with a negative n , we apply the Bessel function's symmetry property: $J_{-n}(x) = (-1)^n J_n(x)$

each atom moves when the molecule rotates. Introducing Eq. 6 into Eq. 2, yields an expression for the rotational incoherent ISF:

$$I_R(\mathbf{Q}, t) = \frac{1}{N_{at}} \sum_{j=1}^{N_{at}} \left\langle \sum_{n=-\infty}^{\infty} (-i)^n J_n(Qa_j) \exp[in(\phi_j(t) - \gamma_{\mathbf{Q}})] \times \sum_{n'=-\infty}^{\infty} i^{n'} J_{n'}(Q\rho) \exp[in'(\phi_j(0) - \gamma_{\mathbf{Q}})] \right\rangle. \quad (7)$$

We can further integrate Eq. 7 over all the possible directions $\gamma_{\mathbf{Q}}$ of the momentum transfer vector $\mathbf{Q}$. This last step is useful to obtain the ISF associated with the scattering of rotating adsorbates on a *Papayex* substrate, where the graphite crystallites do not present any preferential orientation in the xy plane.^{10,12} The integration on the angle $\gamma_{\mathbf{Q}}$ leads to³:

$$I_R(Q, t) = \frac{1}{N_{at}} \sum_{j=1}^{N_{at}} \sum_{n=-\infty}^{\infty} J_n^2(Qa_j) \langle \exp[in\Delta\phi_j(t)] \rangle \quad (8)$$

Note that in our case, the polar angle is fixed $\theta = \pi/2$ (see Fig. 1) and the Bessel function depends only on the product of the moduli $Q\rho$. $\Delta\phi_j(t) = \phi_j(t) - \phi_j(0)$ stands for the angular displacement of atom j .

In analogy with the case of ballistic translations, where the Van Hove correlation function is a Gaussian function of the mean square displacement,¹³ the Van Hove angular correlation function can be assumed to be a Gaussian function of the molecule angular displacement. Hence the cumulant expansion of the thermal average in Eq. 8 can be truncated in its quadratic term, by virtue of the Gaussian approximation. The resulting rotational ISF is a

³The integration over all the directions of $\mathbf{Q}$ gives rise to delta functions, defined in its integral form:

$$\int_0^{2\pi} d\gamma_{\mathbf{Q}} e^{i(n+n')\gamma_{\mathbf{Q}}} = \delta_{n,-n'}.$$

direct function of the mean square angular displacement $\langle \Delta\phi^2(t) \rangle$:

$$I_R(Q, t) \simeq \sum_{n=-\infty}^{\infty} \sum_{j=1}^{N_{at}} J_n^2(Qa_j) \exp \left[-\frac{n^2}{2} \langle \Delta\phi^2(t) \rangle \right]. \quad (9)$$

In the ballistic diffusive regime, the mean square angular displacement is: $\langle \Delta\phi^2(t) \rangle = \langle \omega^2 \rangle t^2$. Therefore, the ISF in Eq. 9 becomes a summation of Gaussian shaped decays:

$$I_R(Q, t) = \sum_{n=-\infty}^{\infty} \sum_{j=1}^{N_{at}} J_n^2(Qa_j) \exp \left[-\frac{\langle \omega^2 \rangle n^2}{2} t^2 \right]. \quad (10)$$

The resulting ballistic rotational SF is a summation of terms:

$$S_R(Q, \Delta E) = \sum_{n=-\infty}^{\infty} \sum_{j=1}^{N_{at}} J_n^2(Qa_j) S_n(\Delta E). \quad (11)$$

where $S_n(\Delta E)$ are Gaussian functions of the form:

$$S_n(\Delta E) = \frac{1}{\hbar \sqrt{\langle \omega^2 \rangle n^2}} \exp \left[-\frac{\Delta E^2}{2\hbar^2 \langle \omega^2 \rangle n^2} \right], \quad (12)$$

whose HWHM is:

$$\Gamma_n = \hbar \sqrt{2 \ln 2 \langle \omega^2 \rangle n}. \quad (13)$$

The scattering function in the case of hydrogenated pyrene is dominated by the incoherent scattering of the protons within the molecule. Therefore, the summation over the scatterers in Eq. 11 can be reduced to a summation over the protons of the molecule. We can further simplify it by considering the geometry of the molecule: we can regroup the protons of pyrene into three groups, depending on their distance with respect to the center of mass of the molecule (see Fig. 1). Therefore the scattering function adapted to pyrene rotations reads:

$$S_R(Q, \Delta E) = \sum_{n=-\infty}^{\infty} \sum_{j=1}^3 N_j J_n^2(Qa_j) S_n(\Delta E). \quad (14)$$

where $N_j = (4, 4, 2)$ is the number of protons per circle and a_j is the radius of each circle.

2.3 Ballistic translational-rotational (BTR) model: Combination of translations and rotations

In the last step, we combine the SFs for translations (Eq. 4) and uniaxial rotations (Eq. 14) via a convolution leading to:

$$S_{BTR}(\mathbf{Q}, \Delta E) = J_0^2(Qa)S_T(Q, \Delta E) + 2 \sum_{n=1}^{\infty} J_n^2(Qa)S_T(Q, \Delta E) \otimes S_n(\Delta E). \quad (15)$$

The convolution of two Gaussian functions such as $S_T(Q, \Delta E)$ and $S_n(\Delta E)$ leads to a Gaussian function. As a result, the ballistic translational-rotational (BTR) scattering function $S_{BTR}(\mathbf{Q}, \Delta E)$ is a summation of Gaussian functions of the form

$$S_T(Q, \Delta E) \otimes S_n(\Delta E) \propto \exp \left[-\frac{\Delta E^2}{2\hbar^2(\langle \omega^2 \rangle n^2 + \langle v^2 \rangle Q^2)} \right] \quad (16)$$

whose HWHM is:

$$\Gamma_n = \hbar \sqrt{2 \ln 2 (\langle \omega^2 \rangle n^2 + \langle v^2 \rangle Q^2)}. \quad (17)$$

Fig. 2 represents the ballistic translational (Eq. 4), rotational (Eq. 14) and translational-rotational (Eq. 15) scattering functions as a function of the momentum and energy exchange. The corresponding half-width-half-maximum is also included as a black line on the contour plot of the scattering functions. $S_T(\mathbf{Q}, \Delta E)$ displays a HWHM which increases linearly with Q , as expected from ballistic translations.¹⁰ On the contrary, $S_R(\mathbf{Q}, \Delta E)$ presents a HWHM with oscillations which are related to the geometry of the molecule.¹¹ There are three maxima which are related to the three different distances of the pyrene's protons with respect to the center of mass of the molecule (see Fig. 1). Furthermore, it doesn't decay to zero for very small momentum transfers, but it has an offset. This is a typical feature from confined

motion.^{10,11,14} As a result, $S_{BTR}(\mathbf{Q}, \Delta E)$ has a HWHM which increases with the momentum transfer (due to the translational part) in a non-linear way (because of rotations). Note that we cannot derive an analytical formula for the total HWHM of Eq. 15.

Figure 2: Theoretical scattering functions $S(Q, \Delta E)$ (contour plot) and quasi-elastic broadenings $\Gamma(Q)$ (black solid line) for ballistic translations (Eq. 4), ballistic rotations (Eq. 14) and the ballistic translational-rotational model, BTR, which is the convolution of the two previous models (Eq. 15).

2.4 Fitting of the experimental and simulated data to the ballistic translational-rotational (BTR) model

Figs. 3 and 4 show the result of the fit of the experimental and the simulated data to Eq. 2 (of the main paper) at different temperatures and these momentum transfers which are represented in panels A, B and C of Fig. 3 of the paper. We include the profiles of translations, rotations and its convolution, the so-called BTR model.

The fits are achieved by truncating the summation in the translational-rotational term (Eq. 3) for $l = 10$. In the case of the MD simulations, we have performed a global fit where the SF of the C.o.M has been fitted to Eq. 4 of this appendix (ballistic translations) and an inelastic term, while the SF of the full molecule has been fitted to Eq. 2 of the main paper. The idea is to obtain a value for the mean square velocity from the fit of the C.o.M SF which is introduced as a fixed parameter in the fit of the full molecule SF and from where we can extract a value for the the mean square angular velocity.

Figure 3: Fitting of the simulated scattering functions $S(Q, \Delta E)$ to Eq. 4 (ballistic translations in the case of the CoM of the molecule) and Eq. 2 of the main publication at 320 K for different values of the momentum transfer. The resulting dependence of the quasi-elastic broadening on the momentum transfer at 320 K is displayed in the panels B of Fig. 3 in the paper.

Figure 4: Fitting of the 0.1 ML (top) and 0.2 ML (bottom) experimental scattering functions $S(Q, \Delta E)$ to Eq.2 of the paper at different temperatures and momentum transfer values: $0.6 \text{ \AA}^{-1}$ (left), $1.2 \text{ \AA}^{-1}$ (right).

3 Density functional theory

In this section we summarize our results for the DFT calculations on the systems pyrene/graphite and benzene/graphite.

3.1 Pyrene adsorption

We have optimized the geometry of adsorbed pyrene in several different positions on top of graphite, and at several rotational angles. Since it was suggested that pyrene could sit in an AB stacking on top of graphite (one of the central carbon atoms on top of a graphitic carbon, with the molecule aligned parallel to the graphite basal plane), we started the geometry optimizations considering both rotations around the centre of the molecule and around one of the central carbon atoms. Fig. 5 displays the different geometries and compares their energy difference with respect to the minimum energy configuration. The minimum energy configuration has an energy of -1.56 eV. The closest minimal energy configuration has only +2 meV of difference while the third most favorable configuration has an energy difference of +11 meV. Both of them are achieved by translating the molecule from the absolute minima. Therefore an estimation for the upper limit of the lateral diffusion energy barrier is 11 meV. This value is very close to the energy barrier for benzene lateral diffusion on graphite.¹⁵

Figure 5: Summary of the different geometry configurations that the pyrene can adopt on the graphite basal plane. The difference of energy with respect to the optimum geometry is indicated in each figure in (eV). The optimal configuration is marked with a red square. The two closest configuration are marked with an orange and a green square respectively.

3.2 The tumbling of pyrene and benzene

We have calculated the potential well to estimate the frequency of tumbling (librations of the whole molecule around the x and the y axis) of pyrene and benzene with respect to the substrate plane. Fig. 6) represents the potential energy as a function of the tilting angle. From the fit of the well to a quadratic law, we estimate the strength of the restoring force k , and therefore, the frequency of the tumbling $\omega_{x,y} = \sqrt{\frac{k_{x,y}}{I_{x,y}}}$, where $I_{x,y}$ is the moment of inertia of the molecule with respect to the x and y axis respectively. The energy associated with the tumbling frequency is given by the ground level of the quantum harmonic oscillator:

$E = \hbar\omega_{x,y}/2$. The results are summarized in Tab. 1. Note that the benzene energy potential behaves quadratically over angles between [0,6] degrees. On the contrary, the pyrene energy potential is quadratic only for angles between [0,1] degrees. This is due to the coupling of the tumbling with the remaining internal degrees of freedom of the molecule (reported in Ref.¹⁶). Therefore the fit at very small angles gives a good indication for the energy required to initiate the tumbling motion of the molecule.

Table 1: Summary of the DFT calculations for pyrene and benzene.

	C ₆ H ₆	C ₁₆ H ₁₀
Temperature (K)/Thermal energy (meV)	140 / 12	320 / 27
C-H bond angle (degree)	2.028	2.186
Distance carbon ring-surface (Å)	3.117	3.258
$I_{x,y}$ ¹ ($\times 10^{-46}$ kg.m ²) (x -axis/ y -axis)	14.45	82.5/ 150.05
Energy barrier for upright reorientation (meV) (x -axis/ y -axis)	300 /330	1250 /1350
k (meV.degree ⁻²) ²	1.60 $\pm$ 0.02	68 $\pm$ 4/41 $\pm$ 1
ω ($\times 10^{12}$ rad.Hz) ²	0.41 $\pm$ 0.04	1.15 $\pm$ 0.04/0.659 $\pm$ 0.008
Energy of tumbling $\hbar\omega/2$ (meV)	0.1385 $\pm$ 0.005	0.38 $\pm$ 0.01/0.217 $\pm$ 0.003

¹ Taken from Ref¹⁶ for pyrene and from Ref.¹⁷ for benzene.

² Obtained from the fitting of the DFT potential well to a quadratic law of the tilting angle.

Figure 6: DFT calculated potential energy versus the tilting angle of the molecular plane with respect to the surface plane for pyrene and benzene. The colored areas mark the thermal energy at the two measurement temperatures and the parabolas show the fit of the potential energy to a quadratic law of the tilting angle.

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