Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information for: Structural transitions at the bilayer graphene–methanol interface from ab initio molecular dynamics

Flavio Siro Brigiano,[*,†,‡] Thomas Thevenet,[†] Alexis Markovits,[†] Julia Contreras-García,[†] Alfonso San Miguel,[¶] and Fabio Pietrucci[‡]

†*Sorbonne Universite, Laboratoire de Chimie Theorique, CNRS UMR 7616, Paris, 75005, France*

‡*Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, F-75005 Paris, France*

¶*Institut Lumiere Matiere, UMR5306 Universite Lyon 1-CNRS, Universite de Lyon, Villeurbanne, F-69622, cedex, France*

E-mail: Flavio.Siro_Brigiano@sorbonne-universite.fr

Stacking configurations along the dynamics

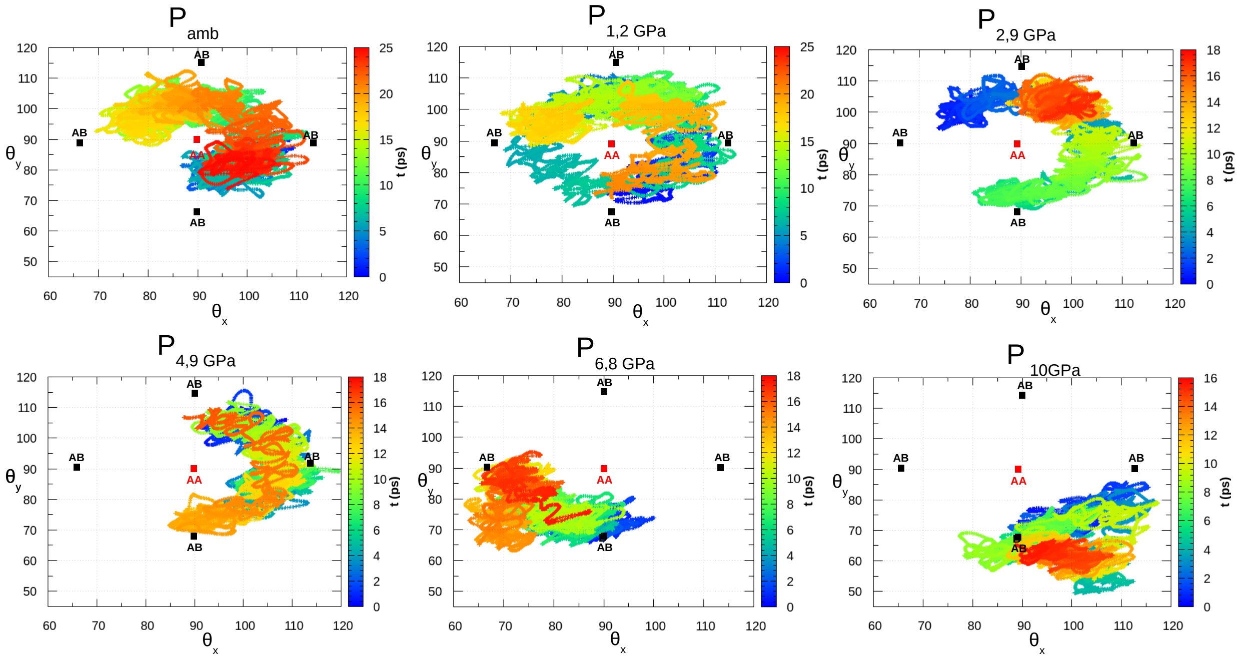

Figure S1. Distribution of the angles describing the relative displacement of the two BLG layers along the x (θ_x) and the y (θ_y) directions during the dynamics. The angles are formed between the vector parallel to the BLG layer (x, or y) and the vector connecting the closest interlayer carbon atoms. The position of the angles associated to the AA and AB stacking are indicated on the map.

Bader Charge analysis

Table S1. Average charge on carbon atoms belonging to the BLG , obtained by Bader Charge analysis. The average charge for the bottom and upper BLG layers are also reported

P(GPa)	Charge-BLG	Charge$_{bottom}$	Charge$_{upper}$
0.0001	0.00 ± 0.16	0.0	0.0
1.2	0.00 ± 0.15	0.0	0.0
2.9	0.00 ± 0.12	0.0	0.0
4.9	0.00 ± 0.14	0.0	0.0
6.8	0.00 ± 0.13	0.0	0.0
10.0	0.00 ± 0.15	0.0	0.0

Enhanced sampling methods

Our strategy involved two distinct series of Metadynamics simulations using different collective variables (CVs): first, in order to discover transformation mechanisms without making any assumption about the pathways and products, we employed the social permutation invariant topological (SPRINT) coordinates; then, for selected reactions pathways identified through this approach, we applied the path-CVs for the bottleneck step of the reaction (single vacancy formation) to characterize the transition state more precisely and to estimate the corresponding free-energy barrier with higher accuracy.

SPRINT approach

The SPRINT coordinates are defined as:

$$S_i = \sqrt{N} * \lambda^{max} * v_i^{max,sorted}; i = 1, 2, ..., N \tag{1}$$

where N is the number of atoms, λ^{max} and v^{max}, sorted are the largest eigenvalue and corresponding eigenvector (with sorted entries) of the adjacency matrix of atoms

$$a_{i,j} = \frac{1-(r_{i,j}/r_0)^n}{1-(r_{i,j}/r_0)^m} \tag{2}$$

where r$_{ij}$ are interatomic distances and r$_0$, n, and m are parameters depending on the typical bond lengths of the system under consideration. Two sets of switching functions, characterized by different long range character, were adopted in distinct, indipendent SPRINT simulations.The r$_0$, n and m parameters are reported for all the couple of atoms in Tables S2 and S3. In both case the long tails of the switching functions C-C interactions, allowed the SPRINT variables to properly tracks the weak intermolecular interactions between the two BLG layers. No relevant difference in the reaction mechanism are observed between the simulations adopting the different switching functions parameters.

Thirty carbon atoms belonging to two large area of both the upper and lower BLG layers (see Fig.S2) and all the methanol molecules in the first interfacial layers (L1), entered the above definitions. We have benefited from the dimensional reduction allowed by the magnitude-ordering, which introduces correlations among the values of the S_i. Only eleven out of them were biased for each system. Fast preliminar Sprint metadynamics were repeated by adopting hills heights and width of respectively of 35 kJ/mol and 1.0 and a pace parameter for the hills deposition of 100 steps.

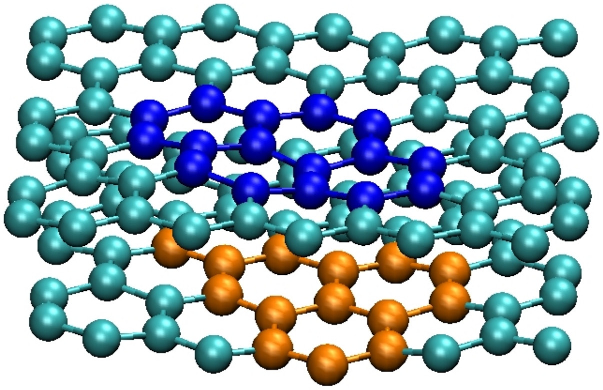

Figure S2. The carbon atoms of the upper and lower BLG layers included in the definition of the SPRINT coordinates are shown in dark blue and orange, respectively.

Table S2

Atoms	R_0 (Å)	N	M
C-C	2.4	4	16
C-H	1.1	8	16
C-O	1.5	8	16
H-H	0.74	8	16
H-O	0.95	8	16
O-O	1.4	8	16

Table S3

Atoms	R_0 (Å)	N	M
C-C	2.4	4	16
C-H	1.7	6	12
C-O	2.0	6	12
H-H	0.74	4	6
H-O	0.95	4	6
O-O	0.121	4	6

Path collective variables approach

The path collective variables method[1] was applied to refine the free energy associated with single vacancy formation, as obtained through SPRINT-based metadynamics (see Fig. 3 in the MT). The method involves defining a sequence of n reference configurations $x_{i i=1,\ldots,n}$ (where x represents the $3N$ Cartesian coordinates), corresponding to the initial state **I**,intermediate geometries, and the final state **III**. From this, two collective variables are defined; s, indicating the progression along the proposed reaction path, and z, indicating the deviation from it:

$$s = \frac{\sum_{k=1}^{n} k \, e^{-\lambda D[x(t),x_k]}}{\sum_{k=1}^{n} e^{-\lambda D[x(t),x_k]}} \tag{3}$$

$$z = -\frac{1}{\lambda} log \left[\sum_{k=1}^{n} e^{-\lambda D[x(t),x_k]} \right] \tag{4}$$

D in equations (3) and (4) is a distance metric, whereas parameter λ is typically chosen such that $\lambda D(x_i, x_{i+1}) \approx 2.3$. Larger values of λ can result in steep gradients, while smaller values may cause the reference configurations to become numerically indistinguishable. The distance metric used in this work is taken from the previous work of Pietrucci.[2] It is defined as:

$$D[x(t), x_k] = \sum_{i\beta} \left[C_{i\beta}(t) - C_{i\beta}^{k} \right]^2 \tag{5}$$

$C_{i\beta}(t)$ is a coordination number which is a function of $x(t)$ and measures the number of atoms of type β coordinated to an i atom of α type. The parameter $C^k_{i\beta}$ is the corresponding value of $C_{i\beta}(t)$ for a reference k. The coordination number $C_{i\beta}(t)$ is a smooth switching function defined as:

$$C_{i\beta}(t) = \sum_{j \in \beta} \frac{1 - \left[\frac{r_{ij}(t)}{d_{\alpha\beta}}\right]^n}{1 - \left[\frac{r_{ij}(t)}{d_{\alpha\beta}}\right]^m} \tag{6}$$

where $r_{ij}(t)$ is an interatomic distance in a particular moment t, whereas $d_{\alpha\beta}$ is a typical bond distance between two atomic species. Note, that $d_{\alpha\beta}$ does not particularly correspond to the experimentally measured bond distance and should be viewed as a fine-tuned computational parameter. The $d_{\alpha\beta}$ for each kind of interatomic distances are reported in Table S2

A critical aspect of defining the path collective coordinates s and z is selecting the set of atoms for which $C_{i\beta}(t)$ will accurately describe the reaction progress. If the set is too small, it may not capture the entire reaction mechanism, while an overly large set may introduce excessive noise and lead to inefficient sampling of the reaction space.

Only two reference states were chosen to describe the reaction pathways of the SV formation at the BLG/methanol interface. Models **I** and **III** (Fig. 4 of the Main text) were employed respectively for k equal 1 and k equal 2 at the interface. Hence, the studied reaction mechanisms are not biased with a hypothesis on the path (no intermediates assumed). For both k states and reaction media, unbiased AIMD simulations were performed using the CP2K/Quickstep package[3] in combination with the PLUMED v.2.3 plug-in.[4,5] This allowed us to monitor changes of coordination number coordinates and to obtain final values of $C_{i\beta}(t)$ defined as time averages of 10 ps long trajectories collected with the time step of 0.5 fs. Trajectories as long as that were sufficient to equilibrate the system at 300 K. We chose $\lambda = 0.404$ which satisfies $\lambda D(x_i, x_{i+1}) \approx 2.3$ and maps the $k = 1$ and $k = 2$ references to $s \approx 1.1$ and $s \approx 1.9$, respectively.

Effect of pre-existing vacancies on the interface reactivity at ambient condition

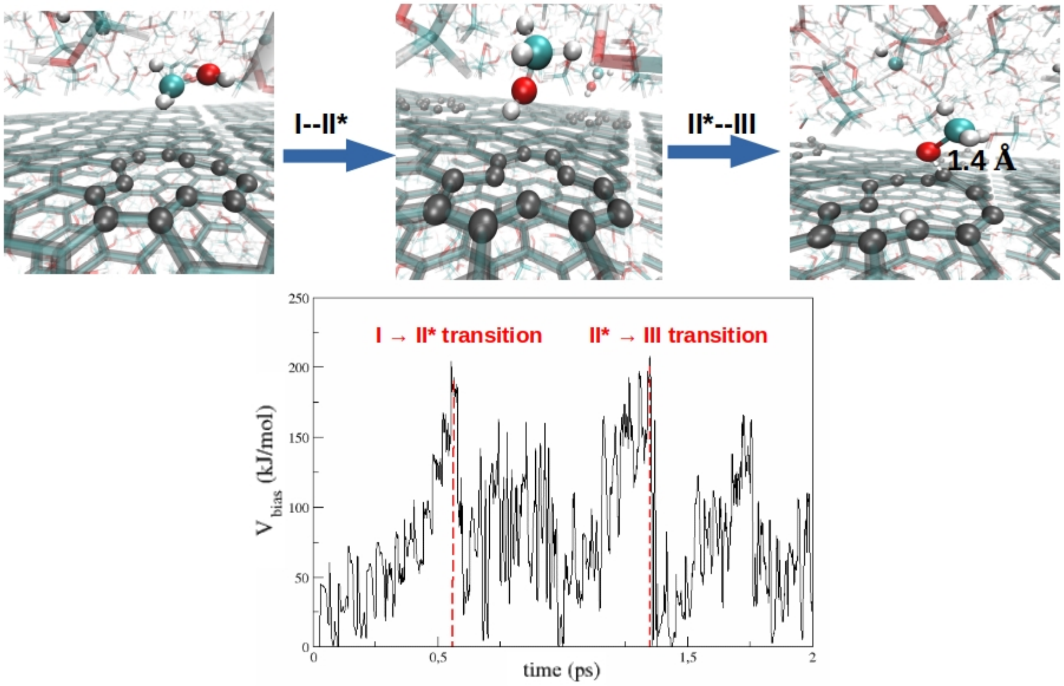

Figure S3. Snapshots for SV-BLG/methanol functionalization explored by SPRINT metadynamics at ambient pressure. b) Metadynamics bias as a function of simulation time; the I→II*, II*→III transitions, corresponding to a drop in the bias due to the jump to a new, unexplored free-energy basins, is indicated by a red dashed line.

Methanol Carbon Density profile

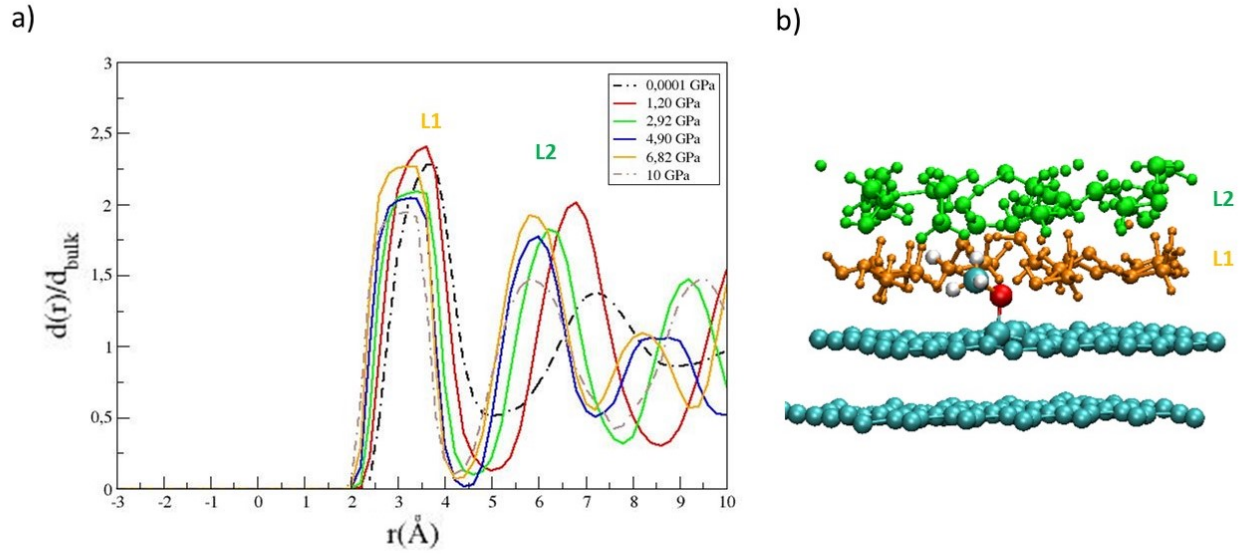

Figure S4. a): Time-averaged Carbon-methanol density profiles for BLG/methanol interfaces simulated under various pressure conditions ranging from 10^{-4} to 10 GPa. Each profile is normalized with respect to the bulk methanol density. The two peaks associated to the first (L1 in orange) and second (L2 in green) interface layers are reported. b): Snapshot of -OCH_3 functionalized BLG immersed in methanol at 6.8 GPa. Methanol molecules within the L1 and L2 layers are highlighted in orange and green, respectively. The BLG carbon atoms are displayed in grey, while the functional group's carbon, oxygen, and hydrogen atoms are shown in grey, red, and white, respectively.

π electron pair delocalization

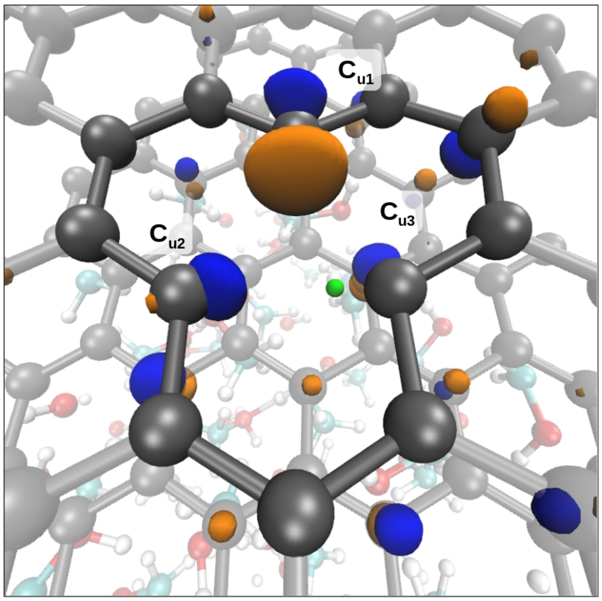

Figure S5. Maximally localized Wannier function and center associated to the π electron pair delocalized between the SV and the bottom layer. The Wannier center is represented with a green ball. The associated Wannier function is represented with an isosurface of value 0.05 for both the orange and blue lobes. The delocalized character of the orbital is evidenced by the presence of multiple lobes on different atomic positions of both the upper and lower Graphene layers.

C···O interaction and C–C bond ELF shapes

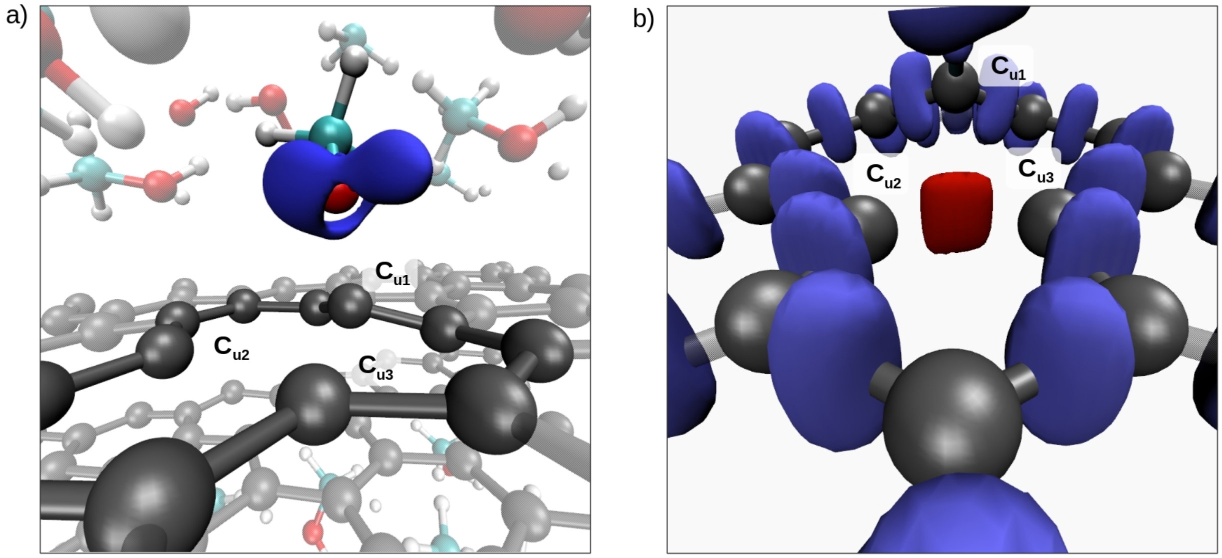

Figure S6. a): Deformation of the ELF lone pair shape around the oxygen atom of the methanol molecule approaching the BLG, revealing the intermolecular interaction with the C$_{u1}$ atom (structure II). Isosurface of 0.83 ELF value is used for the surface visualization. b) The ELF isosurface (0.83) centered on the SV of BLG (structure IV) is represented. The ELF basin related to the C$_{u2}$-C$_{u3}$ bond is highlighted in red.

References

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