Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ordering of Lipid Membrane Altered by Boron Nitride Nanosheet

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SI-1. Orientations of lipid tails on the first layer of BNNS.

Interestingly, inspecting the climbing of lipid molecules, we find that lipid tails prefer the zigzag direction of BNNS (by 30° with respect to the z-axis) or perpendicular to z-axis (90° with respect to the z-axis) in the early extraction stage in most systems, as shown in Fig. S1b. To understand why the tails prefer such orientations, the van der Waals (VDW) interaction energies between the acyl chain (C2 to C14 of the sn1 tail in DMPC) and BNNS are calculated with the angle between the acyl chain and the z-axis varying from 20° to 100°. The energy profile shows two minimal wells at 30° and 90° as the energetic favorable orientations (Fig. S1a), suggesting that the zigzag directions is the energetically favorable orientation for the lipid tails. Similar phenomena have been observed in polymer/graphene systems.[1, 2]

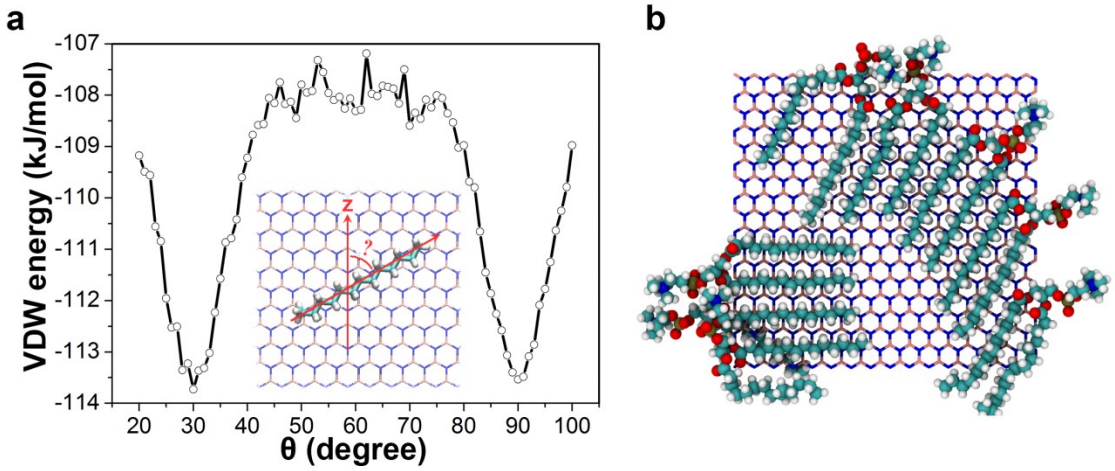

Figure S1. VDW interaction energies between BNNS and lipids with different tail orientations. (a) VDW energy profile. Orientation is defined by the angle between lipid tail and the z direction. (b) Representative orientated lipid conformations in the early extraction process. Only some of the lipid molecules are show for clarity.

SI-2. Mass density profiles calculation.

2D number-density maps were obtained using GROMACS built-in tools “gmx densmap” with a grid size of 0.02 nm in the x-y plane, averaged over the last 20 ns data from the simulations. Only heavy atoms are counted in this calculation. For bilayer with BNNS systems, the translational and rotational motion of BNNS are removed before this analysis.

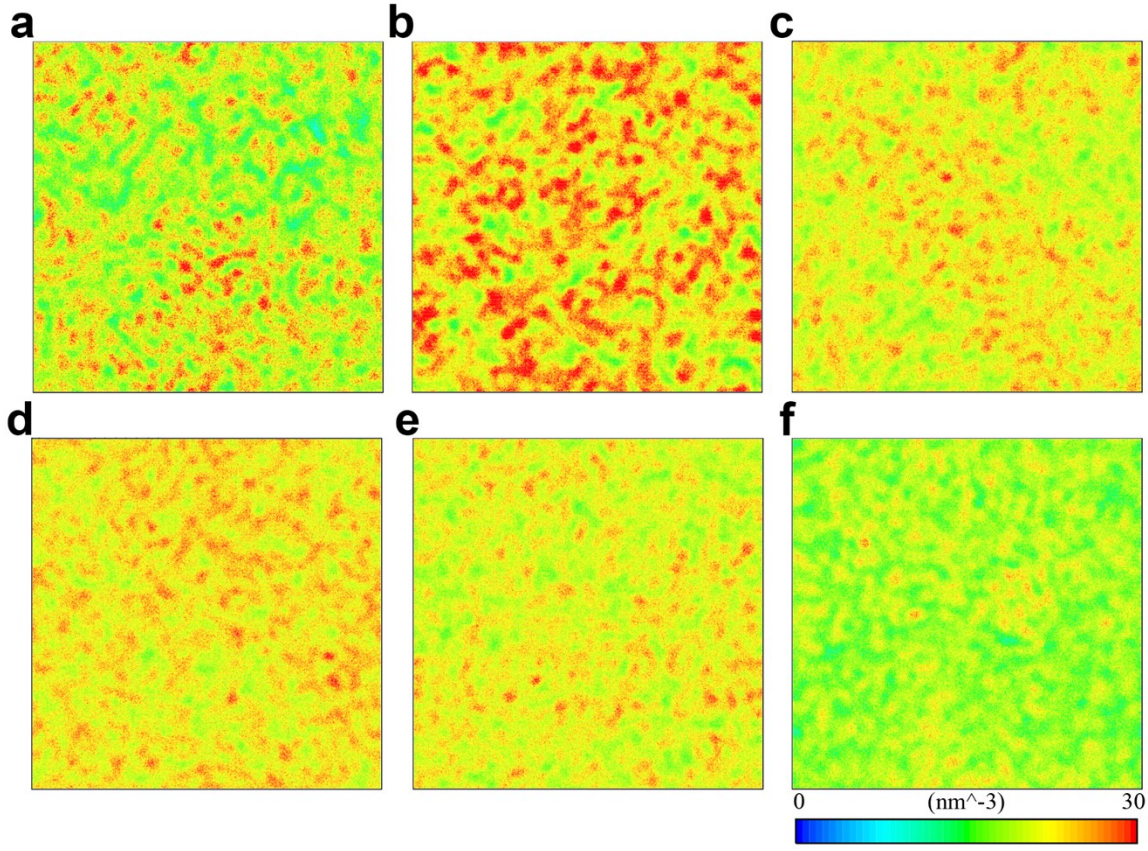

Figure S2. 2D density of lipid molecules in (a) DMPC, (b) POPS, (c) POPC, (d) SAPC, (e) DOPC, (f) DLPC systems without BNNS.

SI-3. Calculation of normalized atomic density in the normal direction of BNNS.

g(y) describes how density of lipids varies as a function of y coordinates, which can be expressed as:

$$g(\mathrm{y}) = \frac{1}{\rho}\left(\sum_i \delta(\mathrm{y} - \mathrm{y}_i)\right) \quad (1)$$

Bin size is set to be 0.01 nm. σ represents the average atomic density in the selected bin area. i iterates over the heavy atom in the counting region. For the membrane with BNNS systems, we first define a cuboid, that formed by moving the BNNS plan along y axis, to be the region affected by BNNS. Only the lipid in the upper layer with its center of mass located in the affected region will be counted. The hydrogen atoms are not considered in our calculation. For bilayer with BNNS systems, the translational and rotational motion of BNNS are removed before this analysis.

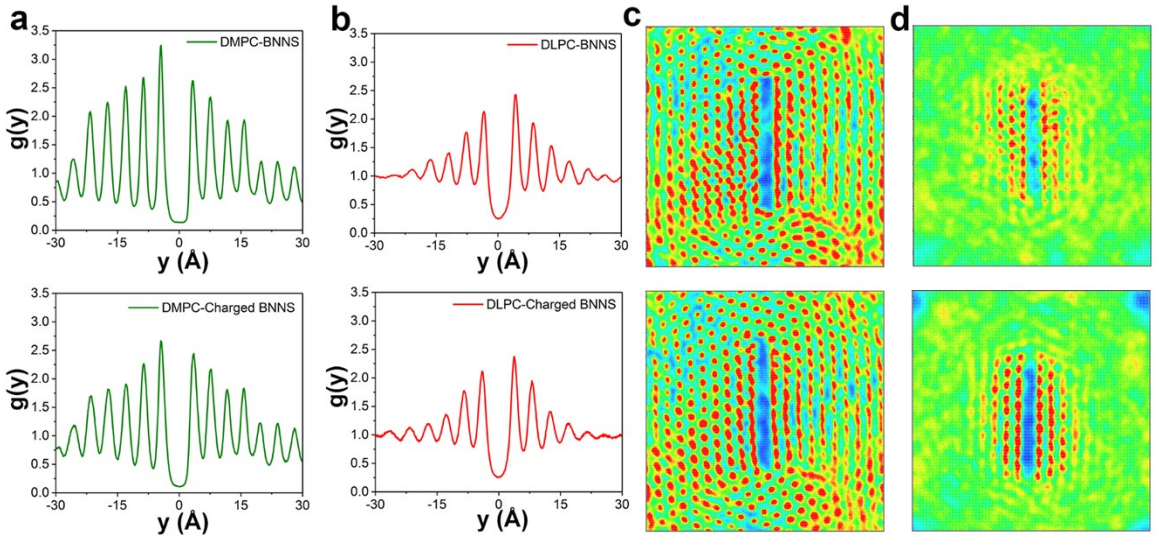

Figure S3. Comparison of the results with BNNS treated as uncharged/ partial charged particles. (a) g(y) of DMPC-BNNS systems. (b) g(y) of DLPC-BNNS systems. (c) 2D density of lipid molecules in DMPC-BNNS systems. (d) 2D density of lipid molecules in DLPC-BNNS systems. The upper panel are results calculated from systems with uncharged BNNS, the lower panel are results calculated from systems with partial charged BNNS.

SI-4. Orientation of Lipid molecules.

Orientation angle (θ) of lipid molecule is defined as the angle between V_{lip} and the Z direction (Fig. S3a), where V_{lip} is point form the COM (blue bead) of the head group (C2, P atom) (orange beads) to the COM (blue bead) of its tail group (last three C atoms of each tail) (orange beads).

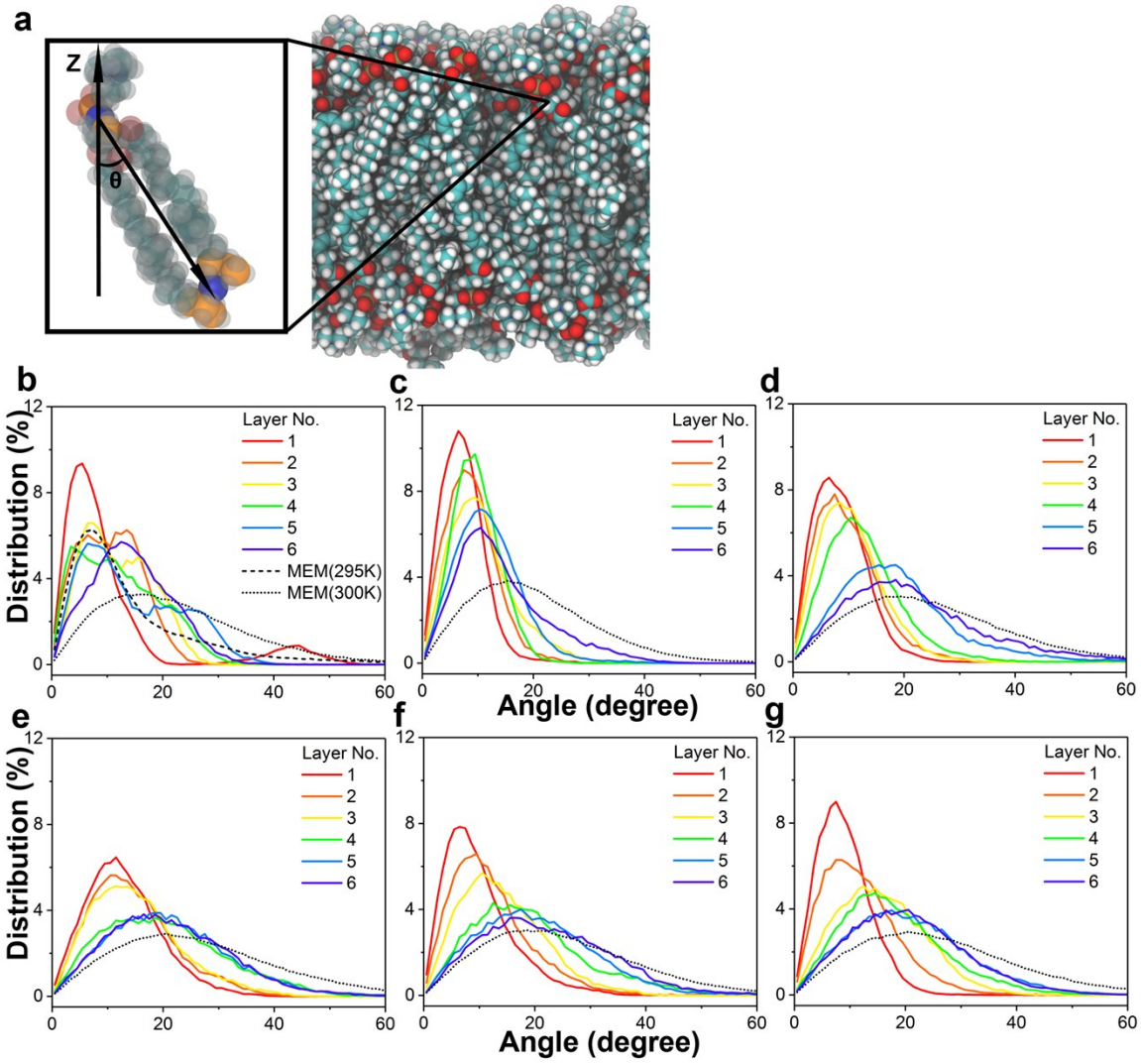

Figure S4. Lipid orientation distributions. (a) Orientation of a lipid molecule. (b-g) Angular distribution of lipid tails in DMPC, POPS, POPC, SAPC, DOPC, DLPC systems. Different colored lines correspond to lipid layers, with 1 closest and 6 furthest to BNNS. Black dotted lines represent lipid tail orientation in membrane system without BNNS. The line of distribution is much sharp when lipids are closer to BNNS and become boarder when further apart.

SI-5. Order parameter analysis.

Order parameter is a sensitive measure of structural orientation or dynamics of lipids in a bilayer. From simulations, when averaging by fast axial rotation is assumed, lipid order parameter characterizes the orientational mobility of the C–D bond and is defined as

$$S_{CD} = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle \qquad (2)$$

where θ is the angle between the C–D bond vector and a reference axis. In our case it is the z axis which is perpendicular to the membrane plane. In this study S_{CD} of C4 atom of the sn1 tails is calculated and compared unless otherwise stated.

SI-6. MSD calculation.

Mean square displacement is calculated by "gmx msd", a built-in tool of GROMACS. We simplified the case by represent each lipid with its phosphorus atom. And only the lateral (in x-y plane) displacement is considered. The time between reference points was set to be 10 ps.

The diffusion constant is calculated by least squares fitting a straight line (D×t + c) through the MSD(t) from 10 ns to 60 ns data, where D is the diffusion constant, t is the diffusion time and c is the y-intercept. Error estimate is calculated as the difference of the diffusion coefficients obtained from fits over the two halves of the fit interval.

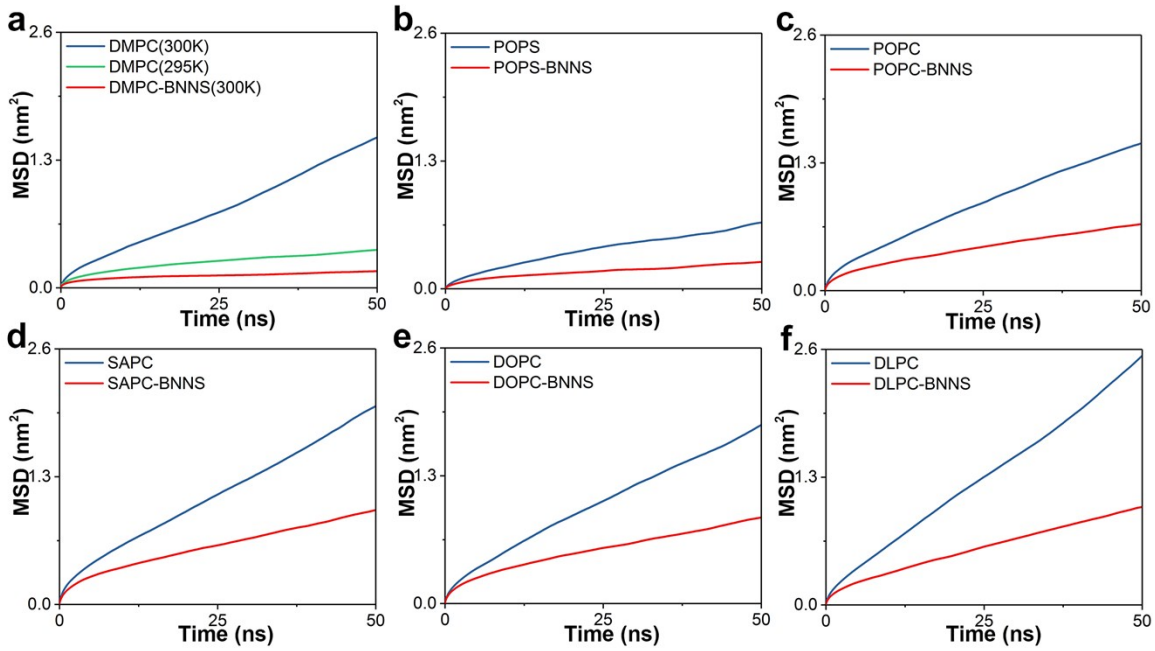

Figure S5. Mean square displacement of lipid molecules in (a) DMPC, (b) POPS, (c) POPC, (d) SAPC, (e) DOPC, (f) DLPC systems with/without BNNS.

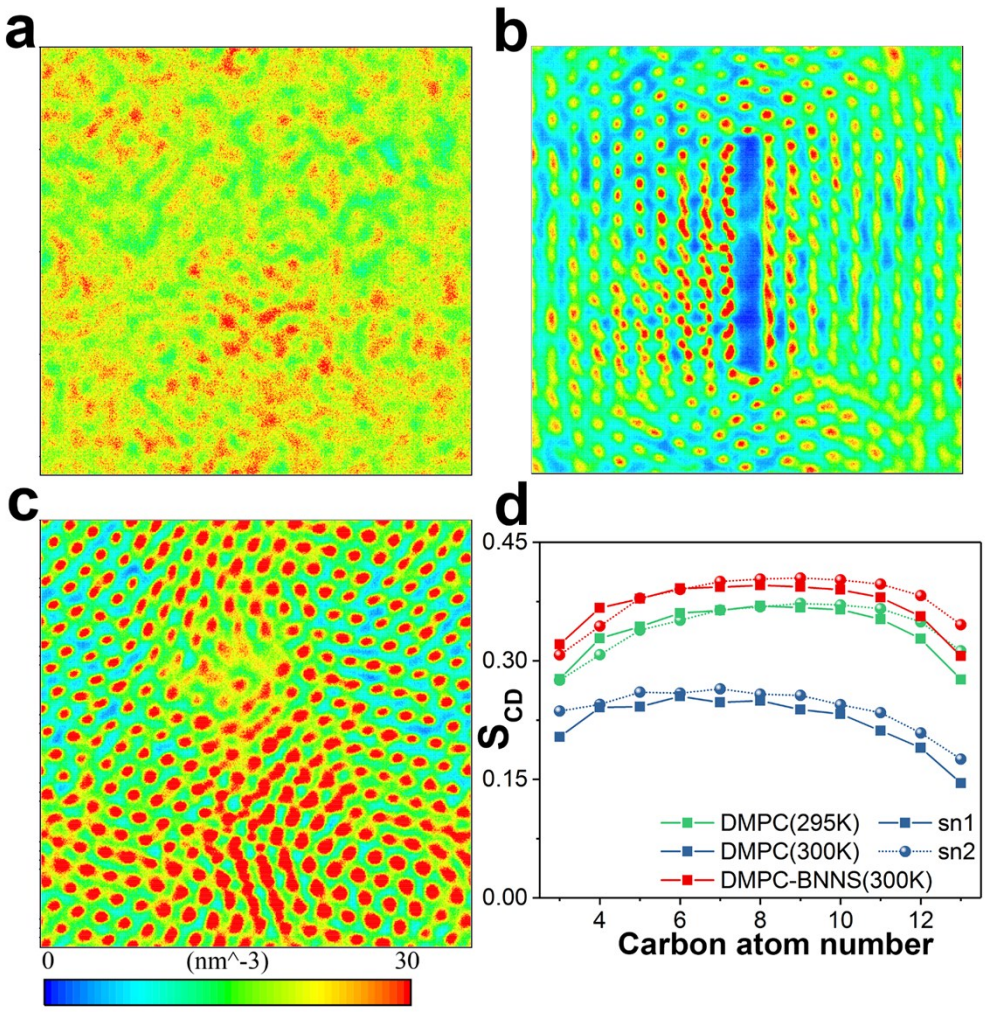

Figure S6. Comparison of three DMPC systems. 2D density of lipid molecules in (a) DMPC (300 K) (b) DMPC-BNNS (300 K) (c) DMPC (295 K). (d) Comparison of S_{CD} in the above systems.

Table S1. Information of equilibrated bilayers.

Lipid Name	Equilibrated box length in x/y-direction (nm)	Equilibrated box length in z-direction (nm)	No. of solvent per lipid
DLPC	8.750±0.064	12.640±0.185	95.5
DMPC	8.264±0.027	13.540±0.088	87.7
POPC	8.802±0.056	12.877±0.161	90.7
POPS	8.198±0.031	13.703±0.102	81.8
DOPC	9.156±0.048	13.064±0.135	101.6
SAPC	9.239±0.057	12.191±0.151	93.5

References

1. W. Chenyu, *Nano Lett*, 2006, **6**, 1627-1631.
2. M. Gulde, A. N. Rissanou, V. Harmandaris, M. Muller, S. Schafer and C. Ropers, *Nano Lett*, 2016, **16**, 6994-7000.