Electronic Supplementary Information

A microscopic view of graphene-oxide/poly(acrylic acid) physical hydrogels: effects of polymer charge and graphene oxide loading

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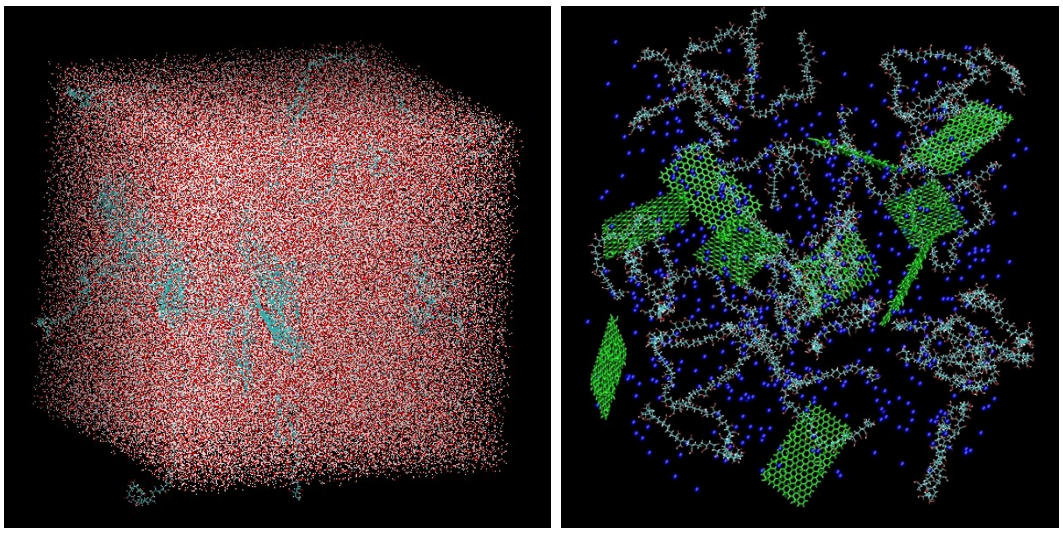
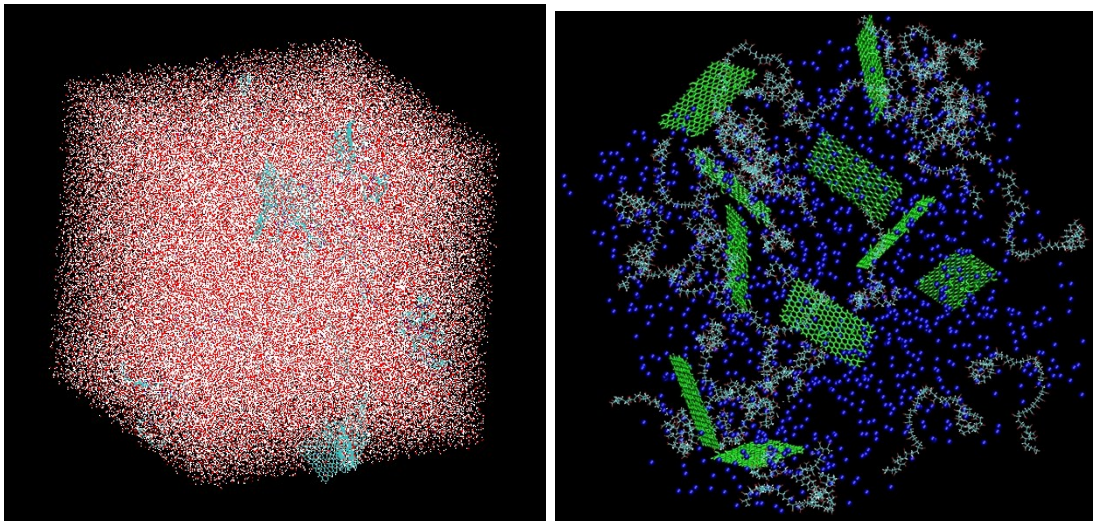
Initial structures of the composite hydrogels

30paa10gos



30paa10gof



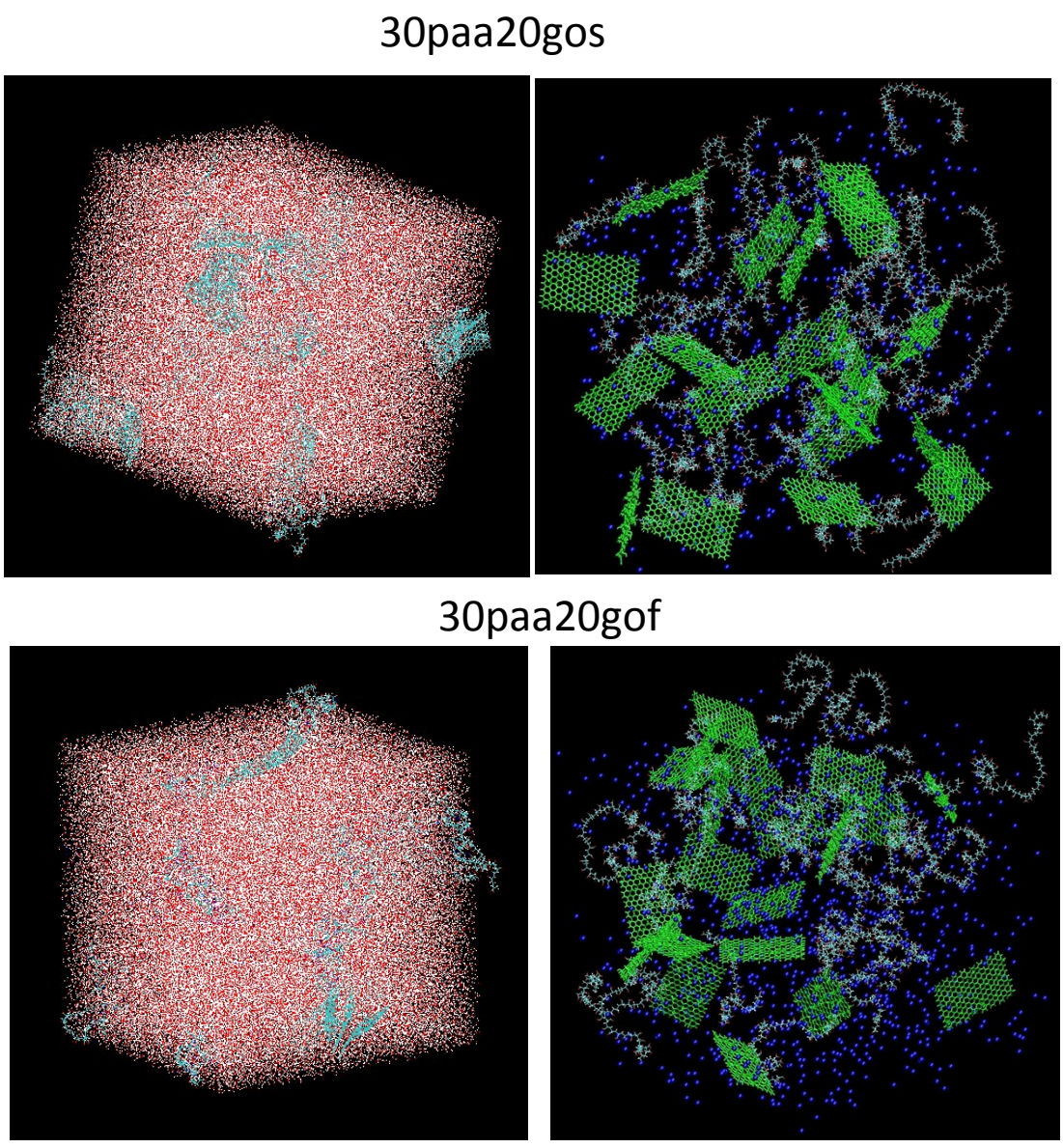


Figure S1. Snapshots of the simulated composite models as constructed, prior to equilibration. Left side: water molecules present. Right side: water molecules removed for clarity

Counterion charge distributions around a PAA chain

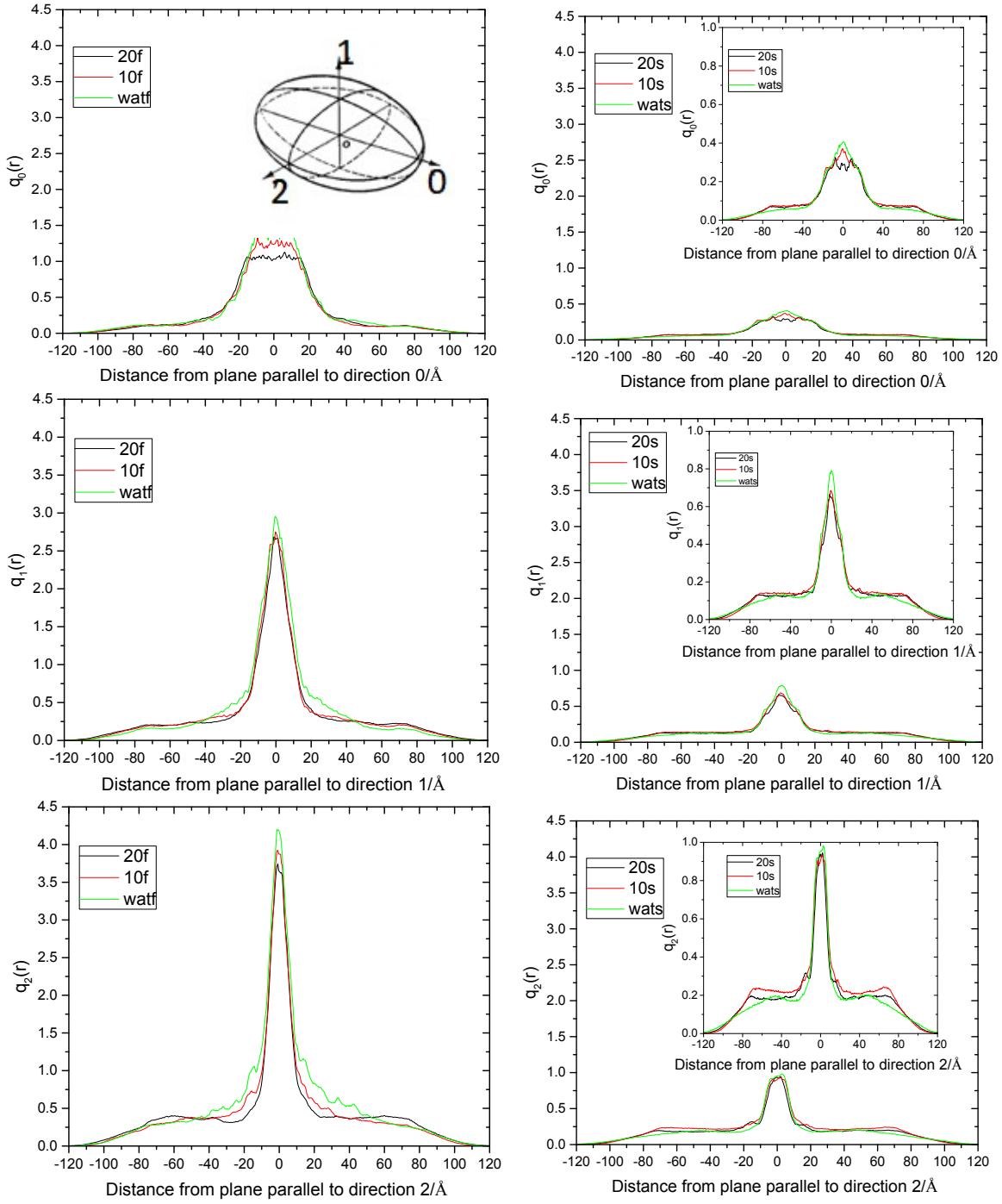


Figure S2. Charge distributions arising from the counterions, as a function of the distance from the plane defined by the center of mass of a chain and two of the directions of the eigenvectors of the inertia tensor (the 3 directions are denoted as 0,1 and 2 as identified in the top left plot). The left column of plots shows such charge distributions describing the models containing fully charged chains and the right column those corresponding to models bearing semicharged chains. The insets in the lower row graphs show zoomed-out pictures of the respective main plots. The abbreviations 10f, 20f, watf, 10s, 20s, wats, correspond to the 30paa10gof, 30paa20gof, 30paawatf, 30paa10gos, 30paa20gos, 30paawats models, respectively.

Pair distribution functions between hydrogen-bonding forming atom pairs belonging to a GO flake and to a PAA chain

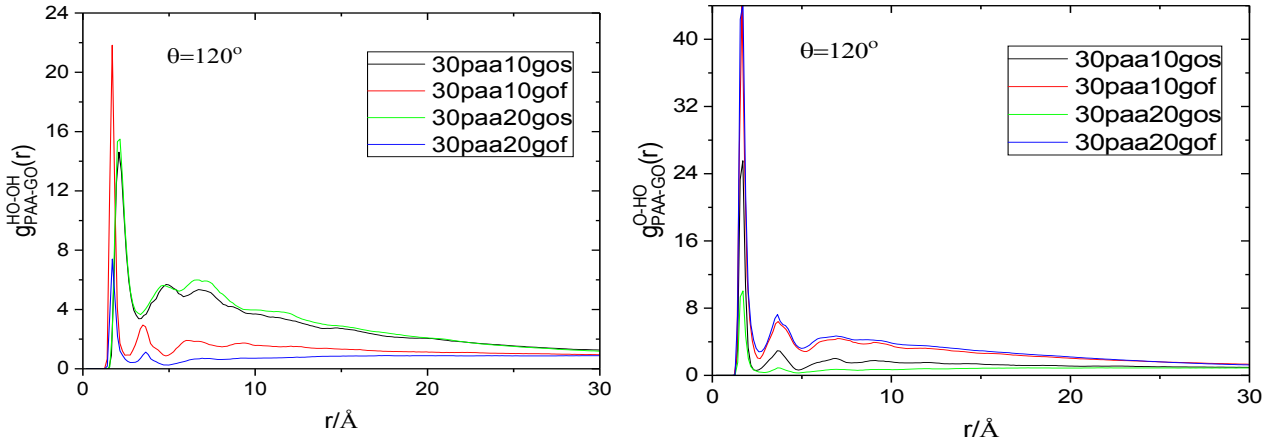


Figure S3:pair distribution functions used for the identification of HO-OH and O-HO GO-PAA pairs.

Static structure factor arising from the centers of mass of the PAA chains

To minimize a possible bias arising from an anisotropic arrangement of PAA chains, we have calculated the structure factor by averaging over 20 directions uniformly distributed on the surface of a sphere for each magnitude of the scattering vector $\left|\vec{q}\right| \equiv q$, as described in eq. S1

$$S_{cm}(q) = \left\langle \left\langle \frac{1}{N} \left| \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{r}_i} \right|^2 \right\rangle_{|\vec{q}|} \right\rangle_{directions} \quad \text{(S1)}$$

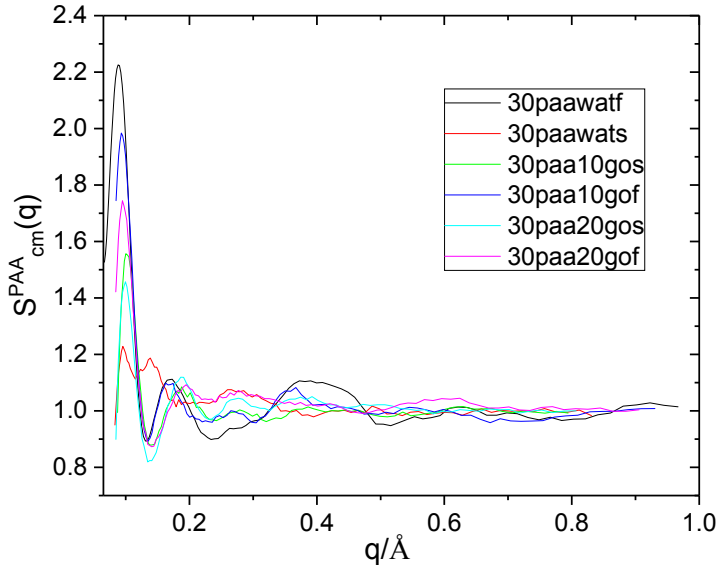


Figure S4: Static structure factor arising from the center of mass of the PAA chains of the simulated systems.

PAA chain dynamics close to the PAA/GO interface

To check the effect of PAA physical adsorption onto GO on chain dynamics along the interface and perpendicular to it, we monitored the incoherent dynamics structure factor (eq. 7) at q=0.1Å^{-1} (which practically coincides with q* as shown in fig. S4) arising from chains with a center of mass within the first adsorption layer, as defined by the first peak (approximately at 5Å) of the polymer density profile shown in fig. 7 of the main text; for consistency we have considered the same definition of the 1st layer for the models based on the fully charged chains, as well. Figure S5 compares the calculated spectra with those corresponding to the average behavior.

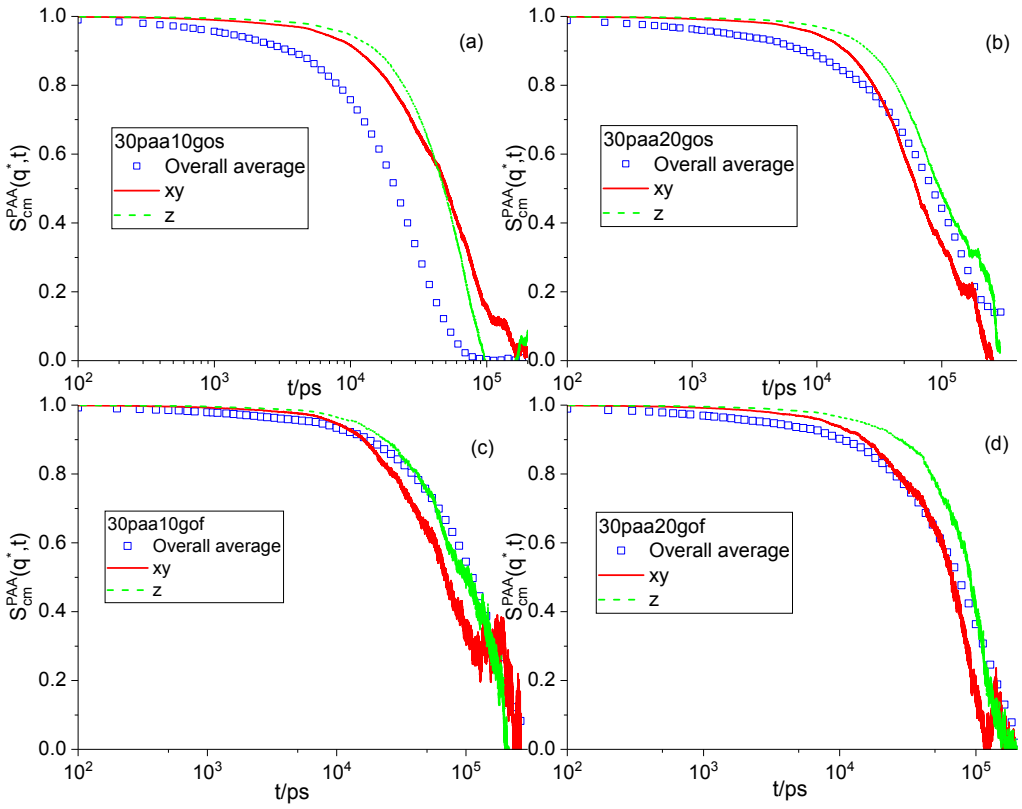


Figure S5: The dynamic structure factor arising from chains with a center of mass within the first adsorption layer, along a GO plane (denoted as xy) and normal to it (denoted as z). Spectra characterizing the overall average are also shown for visual comparison.

PAA bond reorientational motion close to the PAA/GO interface

Local dynamics at the 1st adsorption layer was examined by calculating the bond reorientational motion (eq. 6 in the main text) for C-C and C-O bonds (we focused on the models based on the semicharged chains). As a visual aid for comparison purposes, respective correlation functions describing the overall average behavior shown in fig. 12 of the main text, are also included.

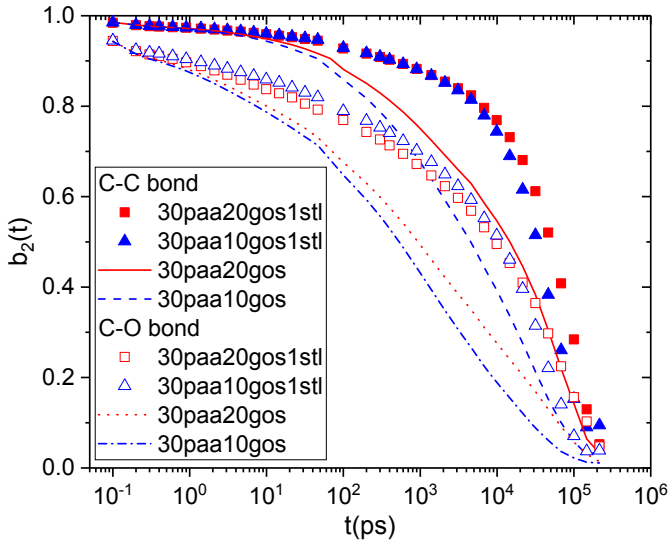


Figure S6: Comparison between the bond reorientational correlation functions of the C-C and the C-O PAA bonds located within the adsorption layer and those describing the corresponding average behavior.

The estimated degree of slowing down of bonds in the adsorbed layer amounts to a factor between 2 and 3 in our case.

Self van Hove correlation functions of the counterions at different time intervals.

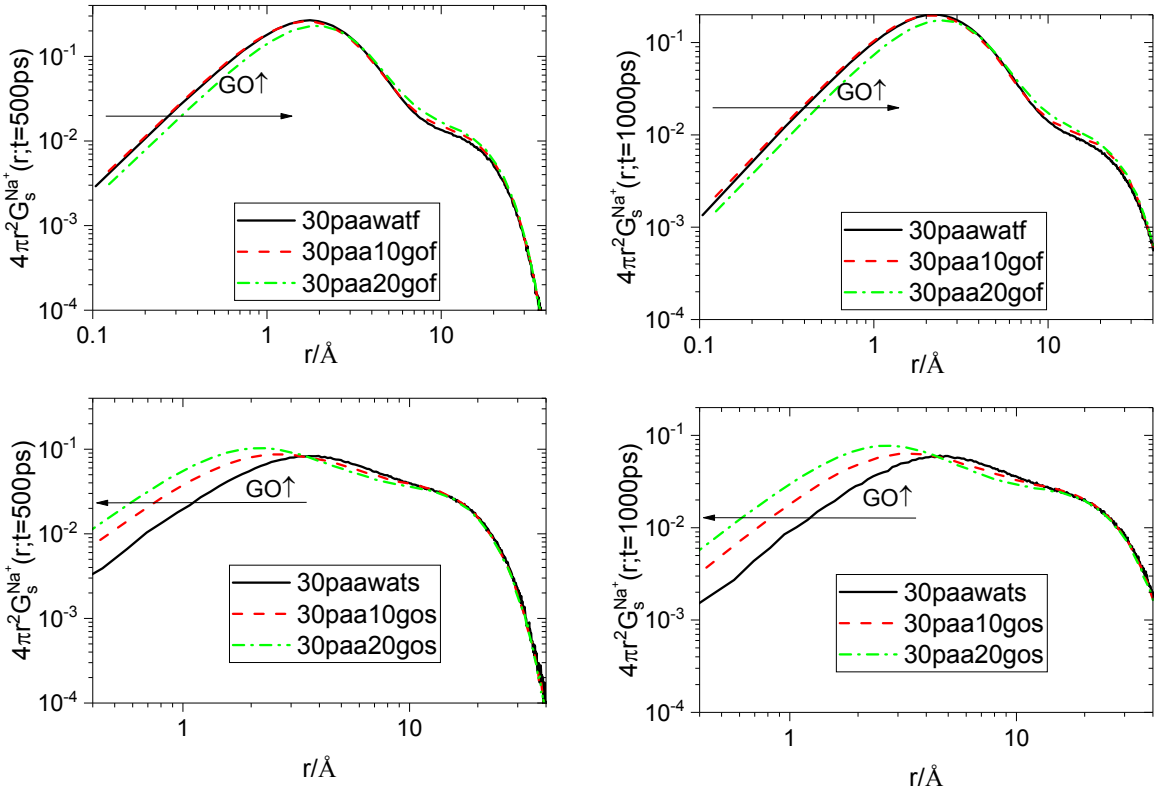


Figure S7: Self van Hove correlation functions describing the mobility of Na^+ counterions for the examined models, at t=500ps (left) and t=1000ps (right)