Supplementary Material
Computational investigation of the effects of polymer grafting on the effective interaction between silica nanoparticles in water

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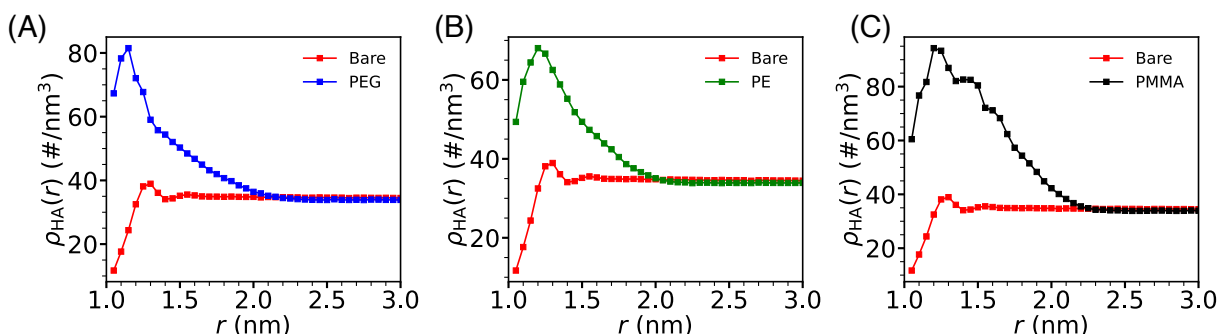Research (IISER) Tirupati, Tirupati, Andhra Pradesh 517619, India*

FIG. S1. The heavy-atom (atoms excluding hydrogen) number density profile ($\rho_{\mathrm{HA}}(r)$) in the radially outward direction from the center-of-mass of the PEG (A), PE (B), and PMMA (C) grafted Si-NP. The red line with filled squares shows the $\rho_{\mathrm{HA}}(r)$ for the bare Si-NP. It is evident from the figure that the density of the total number of heavy atoms near the Si-NP interface is higher for grafted Si-NPs compared to the bare Si-NP. This suggests that the decrease in water density around a single nanoparticle (Fig. 3 of the main text) is due to the interfacial region being occupied by the grafting polymer atoms.
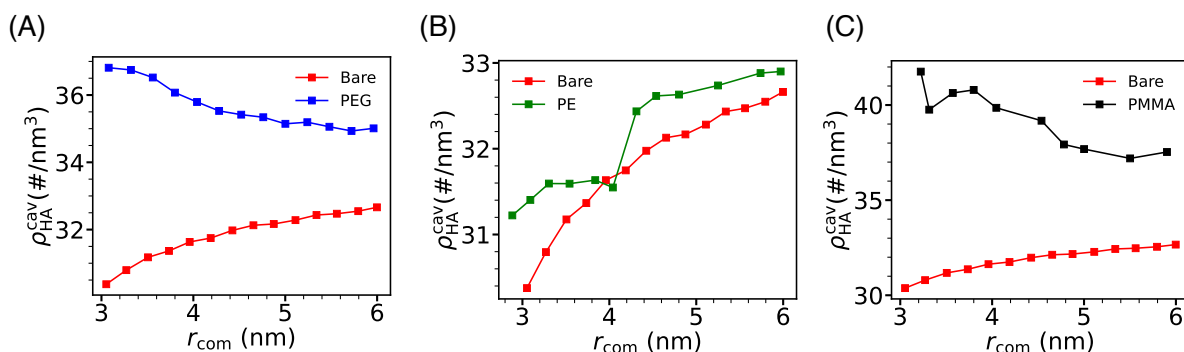

FIG. S2. The dependence of the heavy-atom number density of the confined region ($\rho_{\mathrm{HA}}^{\mathrm{cav}}$) surrounded by two Si-NPs on the inter-particle center-of-mass separation (r_{com}) for the PEG (A), PE (B), and PMMA (C) grafted Si-NP cases. The red line with filled squares shows the same for the bare Si-NP. We note that the $\rho_{\mathrm{HA}}^{\mathrm{cav}}$ increases monotonically for the case of PEG- and PMMA-grafted Si-NPs, and decreases for the case of the PE-grafted Si-NP with an abrupt change near $r_{\mathrm{com}} = 4$ nm. This abrupt change in $\rho_{\mathrm{HA}}^{\mathrm{cav}}$ is consequence of the partial dewetting of the confined region (see Fig. 4 in the main text). At lower inter-particle separations the heavy atoms of the grafting polymer chains contribute dominantly to $\rho_{\mathrm{HA}}^{\mathrm{cav}}$.
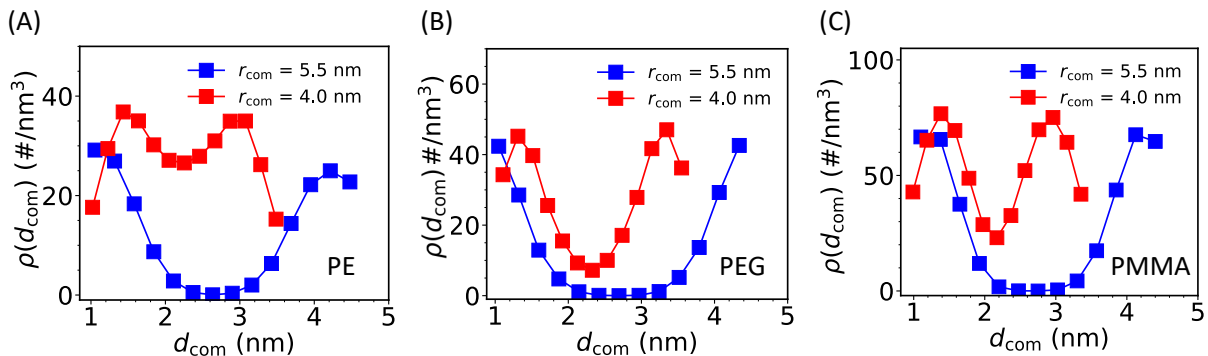
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FIG. S3. The polymer atom number density profile inside the cylindrical cavity formed by two Si-NPs (see Fig. 4A) fixed at a center-to-center separation of 5.5 nm (blue) and 4.0 nm (red). Here, d_{com} represents the distance from the centre of the Si-NP along the direction connecting the centres of the two Si-NPs. The diameter of the Si-NP is 2 nm. At a smaller inter-particle separation (4 nm), the grafting polymer atoms number density is higher. This gives rise to a hindered translation dynamics of the confined (cavity) water molecules.

I.   COARSE-GRAINED MODELLING OF POLYMER-GRAFTED SILICA NANOPARTICLES DISPERSED IN WATER

In our coarse-grained model of the Si-NP system, the Si-NPs interact through a simplified two-body (solvent-mediated) effective interaction in the absence of solvent (water). We first fitted the PMFs (see Fig. 2 in the main text) using appropriate mathematical functions given below (see Table I for the fitting parameters).

$$U_{\text{eff}}(r) = \epsilon \left[\left(\frac{A}{r - r_a} \right)^\alpha + \left(\frac{B}{r} \right)^\beta + C \exp\left(-D(r - r_b) \right) + E \exp\left(-F(r - r_b)^2 \right) \right]. \tag{1}$$

Subsequently, we generated tabulated potentials for the non-bonded interactions based on these parameters derived from the PMF fitting. Initially, we used the *insert-molecules* tool within GROMACS to randomly place 1000 spheres representing Si-NPs, encompassing both bare and grafted variants, into a simulation box measuring 20 nm in length. We then performed energy minimization to resolve any potential overlaps among the spheres. Following this, we conducted MD simulations for minimum of 1 microsecond in the (NPT) ensemble at $T = 300$ K and $P = 1$ bar. We set a potential cutoff distance of 4.0 nm for the non-bonded interactions (beyond this distance, the PMF for all the Si-NPs exhibit saturation). We employed GROMACS version 2018.8 to conduct the simulations of our coarse-grained Si-NP systems. The Nose-Hoover thermostat was used to maintain a constant temperature and constant pressure was maintained using Berendsen barostat. The mass of the bare, PE, PEG and PMMA-grafted Si-NPs are 7101.6, 10187.5, 12343.8, and 18114.5 amu, respectively.

TABLE I. The PMF fitting parameters using Eq. 1 for the bare, PE, PEG and PMMA-grafted Si-NPs.

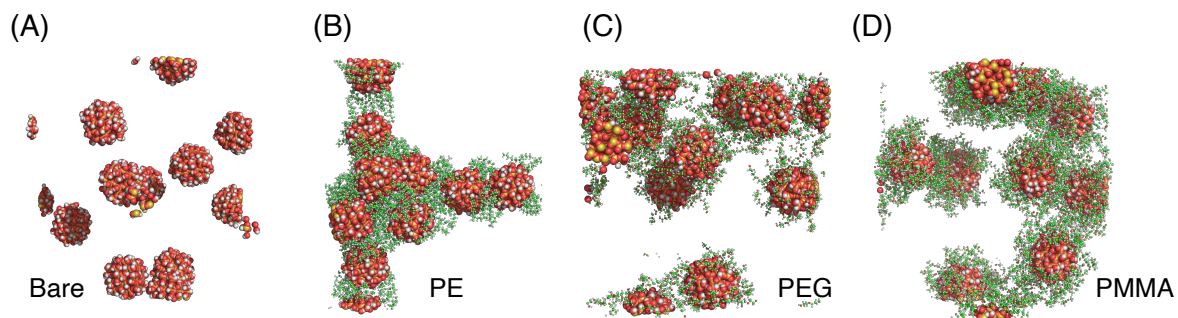|	Bare	PE	PEG	PMMA
α	6	6	6	6
β	20	20	48	36
ϵ	0.577038	1.6182	20.5482	49.3963
r_a	1.7508	1.88953	0.359607	-0.621649
r_b	0.95675	2.843	1.19935	0.93812
A	0.297769	0.10667	2.21065	3.35146
B	-0.02549	2.43209	2.0887	1.66921
C	-8.8043	-9.82162	-37.8223	-68.2121
D	1.382692	2.36867	2.2554	1.81971
E	-127.128	-30.6766	3.53365	14.581
F	2.668890	1.83014	0.933275	0.705895

FIG. S4. A snapshot of the bare (A), PE (B), PEG (C), and PMMA (D) grafted Si-NP system containing 10 Si-NPs dispersed in TIP3P water after 100 ns equilibration of the system in the NPT ensemble at $T = 300$K and $P = 1$ bar. For the sake of clarity, we have removed the water molecules and only shown the Si-NPs. We note that the PE-grafted Si-NPs show a much higher propensity to aggregate compared to the bare and other (PEG and PMMA) grafted Si-NPs. The PE-grafted system formed an aggregate within 40 ns, whereas the other Si-NPs did not aggregate even after 100 ns of simulation.