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## Supporting Information for: Molecular Structure and Multi-Body Interactions in Silica-Polystyrene Nanocomposites<sup>†</sup>

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### Hamaker theory

It is known that for objects containing a many atoms, the evaluation of the interactions between them has an high computational cost, since the calculation of a double sum over all interaction sites is required. For a pair of NPs, such a summation  $U_{sum}$  is written as<sup>1</sup>:

$$U_{sum} = \sum_{i \in NP_1} \sum_{j \in NP_2} U(r_{ij}) \quad (1)$$

where  $U(r_{ij})$  is the pairwise potential. If the particles have a simple geometrical shape, this relation can be generalized to a continuum approximation as:

$$U_{sum} = \int_{NP_1} \int_{NP_2} \rho_1(r) \rho_2(r') U(r-r') dV dV' \quad (2)$$

where  $\rho_i(r)$  is the number density of interaction sites belonging to particles 1 and 2 and  $V$  is the volume of the NP. For two spheres of radius  $r_1 \leq r_2$ , volume  $V_i = (4\pi/3)r_i^3$  placed at a distance  $r_{12} > r_1 + r_2$  and containing particles interacting via a Lennard-Jones potential, Eq. 2 can be solved by the Hamaker theory<sup>2</sup>. According to this approach, the attractive part of the interaction is written as:

$$U_A = -\frac{A_{12}}{6} \left[ \frac{2r_1 r_2}{r_{12}^2 - (r_1 + r_2)^2} + \frac{2r_1 r_2}{r_{12}^2 - (r_1 - r_2)^2} + \ln \left( \frac{r_{12}^2 - (r_1 + r_2)^2}{r_{12}^2 - (r_1 - r_2)^2} \right) \right] \quad (3)$$

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where  $A_{12}$  is the Hamaker constant and it takes the value  $A_{12} = 4\pi^2 \epsilon (\rho \sigma^3)^2$ . The repulsive contribution takes the form:

$$U_R = \frac{A_{12}}{37800} \frac{\sigma^6}{r_{12}} \left[ \frac{r_{12}^2 - 7r_{12}(r_1 + r_2) + 6(r_1^2 + 7r_1 r_2 + r_2^2)}{(r_{12} - r_1 - r_2)^7} + \frac{r_{12}^2 + 7r_{12}(r_1 + r_2) + 6(r_1^2 + 7r_1 r_2 + r_2^2)}{(r_{12} + r_1 + r_2)^7} - \frac{r_{12}^2 + 7r_{12}(r_1 - r_2) + 6(r_1^2 - 7r_1 r_2 + r_2^2)}{(r_{12} + r_1 - r_2)^7} - \frac{r_{12}^2 - 7r_{12}(r_1 - r_2) + 6(r_1^2 - 7r_1 r_2 + r_2^2)}{(r_{12} - r_1 + r_2)^7} \right] \quad (4)$$

By combining Eqs. 3- 4 one can obtain the total interaction. The Hamaker theory strictly holds for a pair of spherical particles interacting via a pure Lennard-Jones potential, however it constitutes a useful benchmark to test simulation results and can be applied to NPs of any size and interparticle separations.

### Atomistic simulations

We also simulate atomistic Silica NPs of the same size (4 nm of diameter) in order to calculate the PMF in the vacuum: the output of such simulations (using GROMACS 4.6.3<sup>3</sup>) has been used as interparticle PMF, to be added to the one calculated by averaging over forces due to polymer chains. A single atomistic Silica NP is constituted by 3189 atoms, of which 873 are silicons, 1936 are oxygens and 380 are hydrogens. In Tab. 1 we report the complete collection of potential parameters, including the non-bonded potential  $V_{nb}(r_{ij})$ , the bond stretching potential  $V_b(r)$  and the bond angle potential  $V_a(\theta)$ , defined as:

$$V_{nb}(r_{ij}) = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] + qi q_j / 4\pi \epsilon_0 r_{ij}^2 [1 + r_{ij}(\epsilon_{rf} - 1)(2\epsilon_{rf} + 1)(r_{ij}^2/r_{cut}^3)]; \quad (5)$$

$$V_b(r) = (k_r/2)(r - r_0)^2; \quad (6)$$

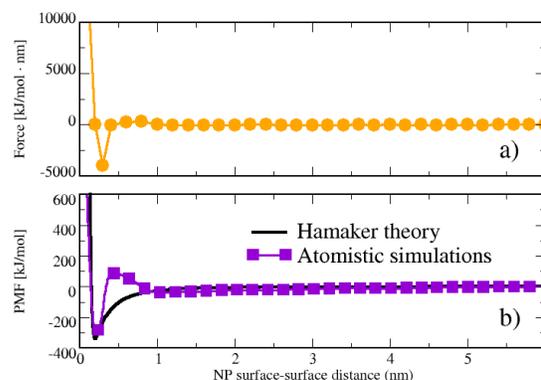
$$V_a(\theta) = (k_\theta/2)(\theta - \theta_0)^2. \quad (7)$$

**Table 1** Parameters of atomistic Silica NPs

Atom	$\sigma$ (nm)	$\epsilon$ (kJ mol <sup>-1</sup> )	$q$ (e)
Si	0.392400	2.510400	1.020
O	0.315400	0.636840	-0.510
H	0.235200	0.092000	0.255
Bond	$r_0$ (nm)	$k_r$ (kJ mol <sup>-1</sup> nm <sup>-2</sup> )	
Si-O	0.1630	$1 \cdot 10^7$	
O-H	0.0950	$1 \cdot 10^7$	
Bond angle	$\theta_0$ (degrees)	$k_\theta$ (kJ mol <sup>-1</sup> rad <sup>-2</sup> )	
O-Si-O	109.47	469.716	
Si-O-Si	144.00	209.598	
Si-O-H	119.52	228.836	

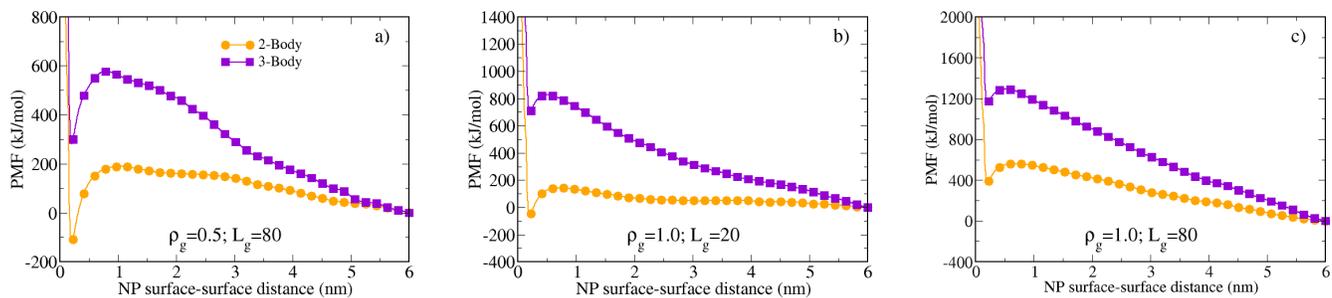
The non bonded potential defined in Eq. 5 is given by two different contributions: the first one is the standard Lennard-Jones potential, determined by the interaction energy  $\epsilon$  and the close-contact distance  $\sigma$ . The second term is a combination of the Coulombic interaction between two atoms with charges  $q_i$  and  $q_j$  ( $\epsilon_0$  being the vacuum permittivity) and a reaction field<sup>4</sup> with a dielectric constant  $\epsilon_{rf}$  which, after the cutoff length  $r_{cut}$ , is modeled by using the Kirkwood approximation<sup>5</sup>. The bond stretching potential  $V_b(r)$  (Eq. 6) is defined through the elastic constant  $k_r$  of the material and the elongation  $r$  respect to the equilibrium position  $r_0$ . A similar expression holds for the bond angle potential  $V_a(\theta)$ , defined by Eq. 7, where  $\theta$  and  $\theta_0$  are the angular counterparts of  $r$  and  $r_0$  and  $k_\theta$  is a constant still dependent on the material properties. Atomistic simulations have been performed by using the GROMACS 4.6.3 package<sup>3</sup>, employing a cubic simulation box of side  $L_b = 22$  nm with periodic boundary conditions. In all simulations we have used a time step of 1 fs and a cutoff of 1.0 nm, while the Coulomb long-range electrostatic interactions have been treated by means of a generalized reaction field<sup>4</sup> with a dielectric constant  $\epsilon_{rf} = 6.23$  and a cutoff of 1.0 nm. The temperature of the systems has been kept constant at  $T = 590$  K by using a Berendsen thermostat<sup>6</sup> with a time coupling  $\tau = 0.1$  ps. The procedure for calculating the PMF is similar to that previously described: a collection of different starting configuration is built by using the Packmol program. Values of  $r_{min}$  and  $r_{max}$  are assumed equal to those implemented for the CG models, hence  $r_{min} = 4$  nm and  $r_{max} = 10$  nm. Then, after a minimization of 15 ps, equilibration runs of 10 ns have been preliminarily produced, finally averaging the forces over the next 20 ns.

All-atom MD simulation in the vacuum have been assessed against predictions obtained by using the Hamaker theory. In this framework the total interaction between two NPs constituted by a large number of beads is given by a proper summation of the bead-bead Lennard-Jones interactions. The latter have been calculated by averaging the atomistic Lennard-Jones parameters for oxygen and silicon (see Tab. 1) and then using the Lorentz-Berthelot mixing rules. Results for these atomistic simulations and the comparison with the theory are reported in Fig. 1: the force (panel a) is strongly positive for NPs in close contact, then showing a deep minimum before going to zero for interparticle distances larger than 1 nm. Simulation results for the PMF (panel

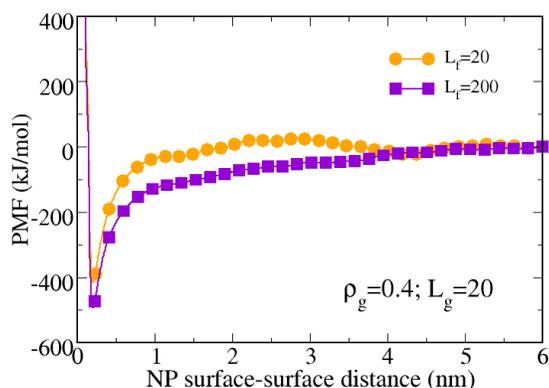


**Fig. 1** Force (a) and PMF (b) between a pair of ungrafted atomistic NPs in the vacuum obtained from atomistic simulations (symbols). In panel (b) a comparison with the Hamaker theory (full line) is reported.

b) provide the existence of a short-range attractive region with a well defined minimum of  $\simeq -330$  kJ/mol for a NP surface-surface distance of  $\simeq 0.2$  nm. In addition, we also observe a small maximum for an interparticle separation of  $\simeq 0.45$  nm: this feature can be explained by taking into account the repulsive contribution coming from the coulombic potential: due to the presence of hydrogen atoms on the most external shells, two NPs placed at a short distance experience a significant electrostatic repulsion. This effect is partially offset by the formation of hydrogen bonds between oxygen and hydrogen atoms belonging to the different NPs. However, for interparticle separations higher than 0.3 nm (see Ref.<sup>7</sup>), hydrogen bonds can not develop, this giving rise to the shoulder observed in the PMF. When compared to the Hamaker theory, the agreement is remarkably good, except for the presence of the above said shoulder; in particular, the two approaches quantitatively agree in providing the estimate of the minimum of the PMF. In order to focus our investigation on the global behavior of the PMF rather than on surface effects, we shall henceforth adopt the so obtained Hamaker potential energy to describe the interaction between two Silica NPs cores.



**Fig. 2** Comparison between two-body and three-body PMF between grafted NPs as a function of their mutual distance for  $D_3 = 4$  nm and  $L_f = 1000$ . Values of  $\rho_g$  and  $L_g$  are in the legends.



**Fig. 3** Effect of increasing  $L_f$  on the two-body PMF between grafted NPs as a function of their mutual distance for  $\rho_g = 0.4$  chains/nm<sup>2</sup> and  $L_g = 20$ . Specific values of  $L_f$  are in the legends.

## Two and three-body potentials of mean force

In Fig. 2 we show the comparison between two and three-body PMF between grafted NPs with  $D_3 = 4$  nm and  $L_f = 1000$ . As already observed for  $L_f = 20$ , the three-body PMF is increasingly repulsive for all grafting densities and grafted chain lengths. Hence, provided that  $\rho_g \geq 0.5$ , the three-body contribution to the total PMF is significantly repulsive for both low ( $L_f = 20$ ) and high

( $L_f = 1000$ ) molecular weights of the free chains.

In Fig. 3 we investigate the effect of increasing the free chain length on the two-body PMF between grafted NPs with  $\rho_g = 0.4$  chains/nm<sup>2</sup> and  $L_g = 20$ . As already observed for the ungrafted case (see Fig.6a of the main text),  $L_f$  does not qualitatively influence the behavior of the PMF, even if some quantitative differences appear: in particular, in the regime of low interparticle separations (from 0.5 to 3 nm) long free chains ( $L_f = 200$ ) increase the attraction between the NPs, in comparison with short chains ( $L_f = 20$ ). In both cases the PMF is negative in the almost whole regime of NP-NP surface distances, suggesting that a phase separation is expected under these conditions.

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