

# Adhesion and Wetting of Nanoparticles on Soft Surfaces

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## SI: Simulation Details

We have performed coarse-grained molecular dynamics simulations of adhesion of spherical and cylindrical nanoparticles on soft substrates (see Figures 2). Nanoparticles were modeled by spherically and cylindrically shaped assembly of beads arranged into hexagonal closed-packed (HCP) lattice. The elastic substrates consisted of crosslinked bead-spring chains with the number of monomers  $N = 32$ . The elastic modulus of the substrate was controlled by changing degree of cross-linking between chains.

In our simulations, the interactions between all beads in a system were modeled by the truncated-shifted Lennard-Jones (LJ) potential<sup>1</sup>

$$U_{\text{LJ}} = \begin{cases} 4\varepsilon_{\text{LJ}} \left[ \left( \frac{\sigma}{r_{\text{ij}}} \right)^{12} - \left( \frac{\sigma}{r_{\text{ij}}} \right)^6 - \left( \frac{\sigma}{r_{\text{cut}}} \right)^{12} + \left( \frac{\sigma}{r_{\text{cut}}} \right)^6 \right] & r \leq r_{\text{cut}} \\ 0 & r > r_{\text{cut}} \end{cases} \quad (\text{SI.1})$$

where  $r_{\text{ij}}$  is the distance between the  $i$ th and  $j$ th beads and  $\sigma$  is the bead diameter. The values of the cutoff distance  $r_{\text{cut}}$  and the value of the Lennard-Jones interaction parameter  $\varepsilon_{\text{LJ}}$  are summarized in TableSI1. The connectivity of the beads into polymer chains, the cross-link bonds and bonds belonging to beads forming nanoparticles were modeled by the finite extension nonlinear elastic (FENE) potential<sup>2</sup>

$$U_{\text{FENE}}(r) = -\frac{1}{2} k_{\text{spring}} R_{\text{max}}^2 \ln \left( 1 - \frac{r^2}{R_{\text{max}}^2} \right) \quad (\text{SI.2})$$

with the spring constant  $k_{\text{spring}} = 30k_{\text{B}}T/\sigma^2$  and the maximum bond length  $R_{\text{max}} = 1.5\sigma$ . The repulsive part of the bond potential was modeled by the LJ-potential with  $r_{\text{cut}} = (2)^{1/6}\sigma$  and  $\varepsilon_{\text{LJ}} = 1.5k_{\text{B}}T$ .

The elastic substrate made of cross-linked polymer chains was placed on a solid substrate which was modeled by the external potential

$$U(z) = \epsilon_w \left[ \frac{2}{15} \left( \frac{\sigma}{z} \right)^9 - \left( \frac{\sigma}{z} \right)^3 \right] \quad (\text{SI.3})$$

where  $\epsilon_w$  was set to  $1.0k_B T$ . The long-range attractive part of the potential  $z^{-3}$  represents the effect of van der Waals interactions generated by the wall half-space.

**Table SI1 Interaction Parameters**

system	Spherical Nanoparticles		Cylindrical Nanoparticles	
	$\epsilon [k_B T]$	$r_{\text{cut}} [\sigma]$	$\epsilon [k_B T]$	$r_{\text{cut}} [\sigma]$
NP-NP	1.5	2.5	1.5	2.5
NP-Gel	1.5	2.5	1.5	2.5
Gel-Gel	1.5	2.5	1.5	2.5
Gel-Sub	1.0		1.0	
NP-Sub	1.0		1.0	

The system was periodic in  $x$  and  $y$  directions with system sizes listed in Table SI2.

**Table SI2 System Sizes**

Spherical Nanoparticles			Cylindrical Nanoparticles		
$R_p [\sigma]$	$L_x = L_y [\sigma]$	$L_z [\sigma]$	$R_{\text{cyl}} [\sigma]$	$L_x = L_y [\sigma]$	$L_z [\sigma]$
9.8	45.2	65.2	9.6	45.2	65.2
14.3	65.6	85.6	14.8	65.6	85.6
17.9	82.1	102.1	17.8	82.1	102.1
23.3	106.9	126.9	22.9	106.9	126.9
27.7	127.3	147.3	27.3	127.3	147.3
31.4	143.9	163.9	31.4	143.9	163.9

Simulations were carried out in a constant number of particles and temperature ensemble. The constant temperature was maintained by coupling the system to a Langevin thermostat<sup>1</sup> implemented in LAMMPS.<sup>3</sup> In this case, the equation of motion of the  $i$ th particle is

$$m \frac{d\vec{v}_i(t)}{dt} = \vec{F}_i(t) - \xi \vec{v}_i(t) + \vec{F}_i^R(t) \quad (\text{SI.4})$$

where  $m$  is the bead mass set to unity for all particles in a system,  $\vec{v}_i(t)$  is the bead velocity, and  $\vec{F}_i(t)$  denoted the net deterministic force acting on the  $i$ th bead. The stochastic force  $\vec{F}_i^R(t)$  had a zero

average value and  $\delta$ -functional correlations  $\langle \vec{F}_i^R(t) \vec{F}_i^R(t') \rangle = 6k_B T \xi(t - t')$ . The friction coefficient  $\xi$  was set to  $\xi = m/\tau_{LJ}$ , where  $\tau_{LJ}$  is the standard LJ-time  $\tau_{LJ} = \sigma(m/\epsilon_{LJ})^{1/2}$ . The velocity-Verlet algorithm with a time step  $\Delta t = 0.01\tau_{LJ}$  was used for integration of the equation of motion. All simulations were performed using LAMMPS.<sup>3</sup>

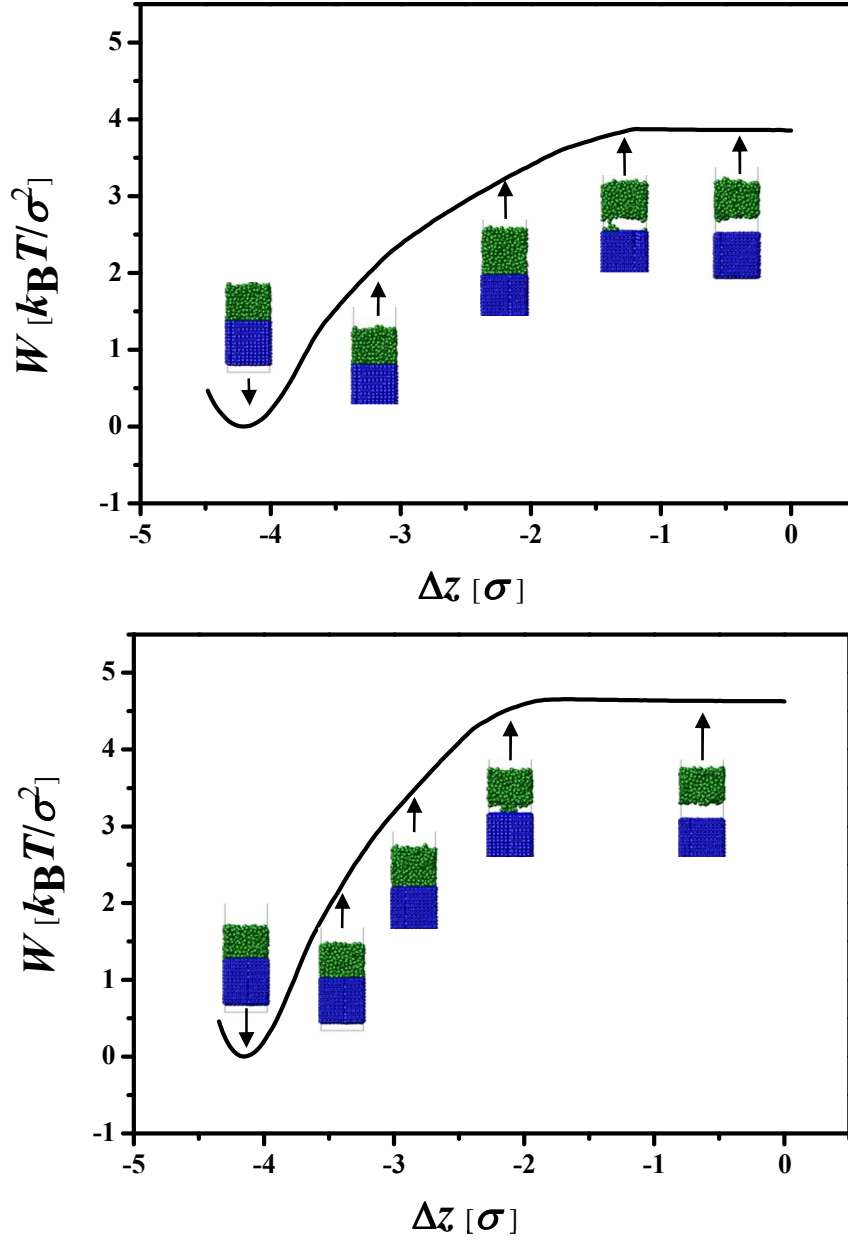
**Nanoparticles:** The crystal nanoparticles with cylindrical and spherical shapes were generated by arranging beads with diameter  $1.0\sigma$  into HCP lattice and connecting them by elastic bonds with twelve closest neighbors. Nanoparticles were relaxed by performing MD simulation runs lasting  $100\tau_{LJ}$ . After equilibration the bond length between beads forming nanoparticles is equal to  $0.97\sigma$ .

**Gel Substrate:** To create an elastic substrate, polymer chains were placed inside a slab with thickness  $H_0$ . After cross-linking, the system was equilibrated for  $10^4\tau_{LJ}$  on the top of a rigid wall interacting with beads belonging to polymer chains through potential eq SI.3. The equilibrium thickness,  $H$ , of the elastic substrate is given in Table SI3. It was calculated using the height distribution function of the gel.

**Table SI3 Equilibrium Thickness  $H$  [ $\sigma$ ] of the Elastic Substrate**

$R_p$ [ $\sigma$ ]	$G$ [ $k_B T/\sigma^3$ ]					
	0.024	0.072	0.162	0.254	0.501	0.842
9.8	22.2	22.0	21.8	21.7	21.4	21.1
14.3	33.1	22.1	21.9	21.8	21.5	21.2
17.9	45.3	22.1	21.9	21.8	21.5	21.2
23.2	45.3	22.1	21.9	21.8	21.5	21.2
27.7	66.5	22.1	21.9	21.8	21.5	21.2
31.4	--	22.1	21.9	21.8	21.5	21.2

Simulation of nanoparticle adhesion to the elastic substrate started with placing a nanoparticle at a distance of  $2.0\sigma$  from the substrate. A harmonic spring with the spring constant  $K_{sp} = 100k_B T/\sigma^2$  was applied to nanoparticle center of mass for  $100\tau_{LJ}$  to bring nanoparticle into contact with the gel substrate then the spring was removed. The system was equilibrated for  $4 \times 10^4\tau_{LJ}$  followed by production run lasting  $10^4\tau_{LJ}$ .



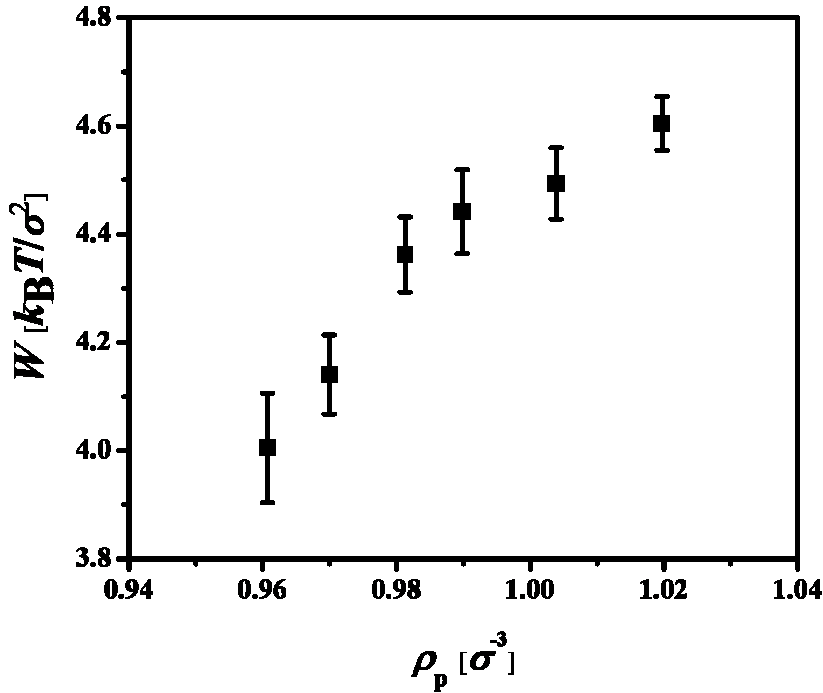
**Figure S11** Potential of mean force as a function of the center of mass displacement along z-axis for soft ( $G = 0.023 k_B T / \sigma^2$ ) (top figure) and hard ( $G = 0.857 k_B T / \sigma^2$ ) (bottom figure) elastic substrate and LJ-interaction parameter  $\varepsilon_{\text{LJ}} = 1.5 k_B T$ . The insets show typical system configurations during simulation runs.

**Work of Adhesion:** In order to evaluate the work of adhesion between nanoparticle and gel we have calculated the potential of mean force between a crystal slab and elastic substrate by using the weighted

histogram analysis method (WHAM) <sup>4</sup>. In these simulations, two slabs of crystal and gel with dimensions  $10\sigma \times 10\sigma \times 10\sigma$  were pushed toward each other. In these simulations we set  $z$ - component of the velocity of the crystal slab was set to zero thus fixing its location at the origin  $z = 0\sigma$ . The center of mass of the gel slab,  $z_{\text{cm}}$ , was tethered to location  $z^*$  by a harmonic spring

$$U(z_{\text{cm}}, z^*) = \frac{1}{2} K_{\text{sp}} (z_{\text{cm}} - z^*)^2 \quad (\text{SI.5})$$

with the value of the spring constant  $K_{\text{sp}}$  varying between  $200k_{\text{B}}T/\sigma^2$  and  $500k_{\text{B}}T/\sigma^2$ . We have moved location of the tethering point with increment  $\Delta z^* = 0.1\sigma$ . For each location of the tethering point, we have performed the simulation runs lasting  $5 \times 10^3 \tau_{\text{LJ}}$ , during which we have calculated distribution of the center of mass of the gel. WHAM method was applied to calculate potential of the mean force between a crystal slab and elastic substrate from distribution function of the center of mass. Figure SI1 shows the potential of mean force between a gel and a crystal slab calculated from simulations with the spring constant  $K_{\text{sp}} = 400k_{\text{B}}T/\sigma^2$ . Figure SI2 summarizes our results for work of adhesion,  $W = \Delta F/A$ , as a



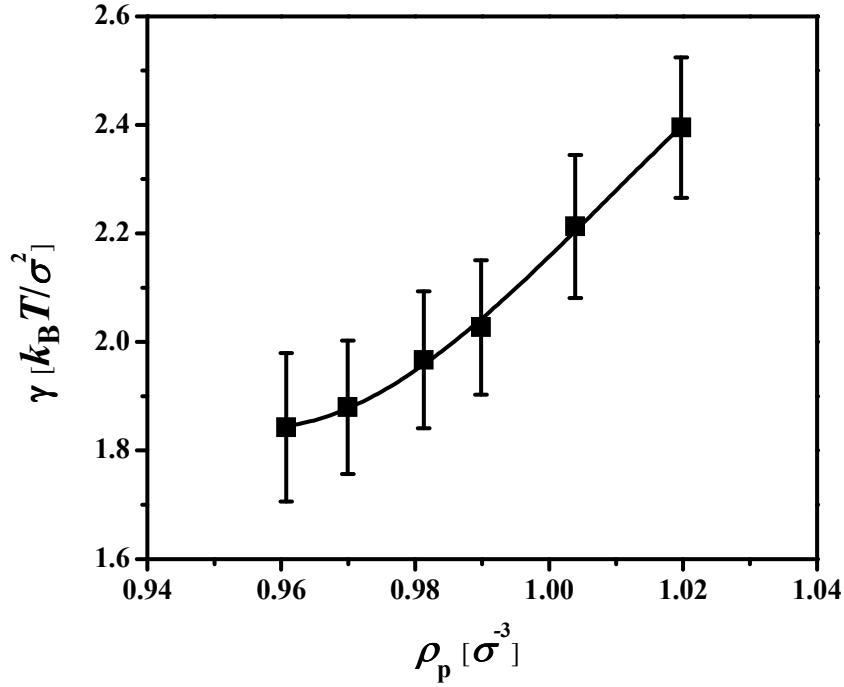
**Figure SI2** Dependence of the work of adhesion  $W$  between crystalline slab and elastic substrate on the substrate bulk density.

function of gel density,  $\rho_p$ .

**Surface Tension:** The surface tension of an elastic substrate was evaluated by integrating the difference of the normal  $P_N(z)$  and tangential  $P_T(z)$  to the interface components of the pressure tensor.<sup>5</sup> Note that in our simulations, the  $z$  direction was normal to the interface.

$$\gamma = \int_{-\xi}^{\xi} (P_N(z) - P_T(z)) dz \quad (\text{SI.6})$$

where  $2\xi$  is the thickness of the interface that was determined from the monomer density profile as an interval within which the monomer density changes from zero to its bulk value. The simulation results for surface tension of the elastic substrate are summarized in Figure SI3.



**Figure SI3** Dependence of the gel surface tension on the bulk density.

## SI: Derivation of Eqs 1 and 12.

Consider a rigid spherical nanoparticle in contact with soft substrate (see Figure 4). The surface free energy of this nanoparticle/substrate configuration can be written as follows

$$F_{surf}(a, \Delta h) = (A - \pi a^2) \gamma_s + 2\pi R_p (2R_p - \Delta h) \gamma_p + 2\pi R_p \Delta h \gamma_{ps} \quad (\text{SI.7})$$

where  $\gamma_p$  is the surface energy of the particle,  $\gamma_s$  is the surface tension of a substrate and  $\gamma_{sp}$  is the surface tension nanoparticle/substrate interface, and  $A$  is the area of the substrate. In obtaining eq SI.7 we used the expression for surface area of a spherical cup with height  $h$ ,  $A_{sp}(h) = 2\pi R_p h$ . The change of the surface free energy due to nanoparticle adsorption is equal to

$$\Delta F(a, \Delta h) = F_{surf}(a, \Delta h) - F_{surf}(0, 0) = -\pi a^2 \gamma_s - 2\pi R_p \Delta h \gamma_p + 2\pi R_p \Delta h \gamma_{ps} \quad (\text{SI.8})$$

Substituting into eq SI.8 relationship between contact radius  $a$  and indentation depth  $\Delta h$ :

$a^2 = 2R_p \Delta h - \Delta h^2$ , we arrive at

$$\Delta F(\Delta h) = \pi \gamma_s \Delta h^2 - 2\pi R_p \Delta h \gamma_s - 2\pi R_p \Delta h \gamma_p + 2\pi R_p \Delta h \gamma_{ps} \quad (\text{SI.9})$$

Introducing work of adhesion,  $W = \gamma_p + \gamma_s - \gamma_{ps}$ , we obtain eq 1

$$\Delta F(\Delta h) = \pi \gamma_s \Delta h^2 - 2\pi W R_p \Delta h \quad (\text{SI.10})$$

In the case of the cylindrical nanoparticle the free energy per unit length of the cylindrical nanoparticle in contact with substrate is written as

$$F_{surf}(\alpha) = (L - 2 \sin(\alpha) R_p) \gamma_s + (2\pi R_p - 2\alpha R_p) \gamma_p + 2R_p \alpha \gamma_{ps} \quad (\text{SI.11})$$

where  $L$  is the length of the substrate. The change in the surface free energy due to adsorption of the cylindrical nanoparticle is equal to

$$\Delta F_{surf}(\alpha) = F_{surf}(\alpha) - F_{surf}(0) = -2 \sin(\alpha) R_p \gamma_s - 2\alpha R_p \gamma_p + 2R_p \alpha \gamma_{ps} \quad (\text{SI.12})$$

Expanding  $\sin(\alpha) \approx \alpha - \alpha^3 / 6$  and using expression for the work of adhesion  $W$  we obtain eq 12

$$\Delta F_{surf}(\alpha) \approx -2W \alpha R_p + \frac{1}{3} \gamma_s R_p \alpha^3 \quad (\text{SI.13})$$

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