

Supporting information: Solvent-mediated forces between ellipsoidal nanoparticles adsorbed at liquid-vapor interfaces

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1 The density profile

The density profile

$$\hat{\rho}(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v) \tanh\left(\frac{2(z - z_e)}{w}\right) \quad (\text{S.1})$$

was fitted to the simulation data by adjusting the liquid density ρ_l , the vapor density ρ_v , the Gibbs dividing surface z_e , and the thickness of the interface w . The simulation density profile $\rho(z)$ and the fitted density profile $\hat{\rho}(z)$, where z is the direction normal to the interface, are presented in figure S1 for an interface without the nanoparticle present.

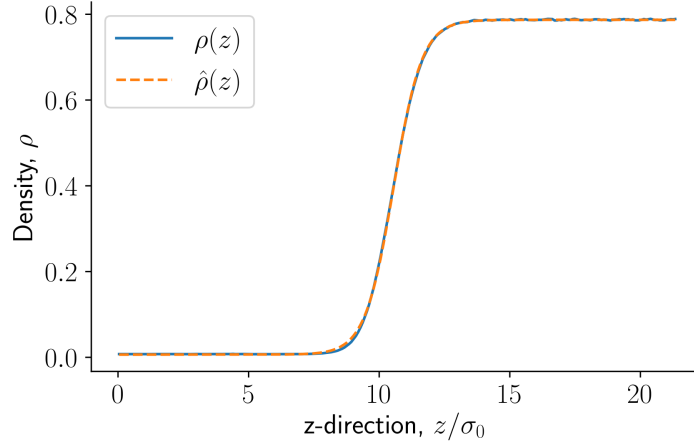


Figure S1: The density profile $\rho(z)$ and the fitted density profile $\hat{\rho}(z)$ as a function of the z -direction.

2 Interface deformation

When the nanoparticle is floating on the interface, the interface will be corrugated in the vicinity of the particle. The Gibbs dividing surface will then be a function of the lateral coordinates x and y , and therefore $z_e(x, y)$ was computed by fitting the density profile $\hat{\rho}(x, y, z)$ for a series of positions (x, y) . The MD results for the density profile, $\rho(x, y, z)$, were computed by counting particles in cubic bins of width $\Delta x = \Delta y = \Delta z = 0.2\sigma_0$.

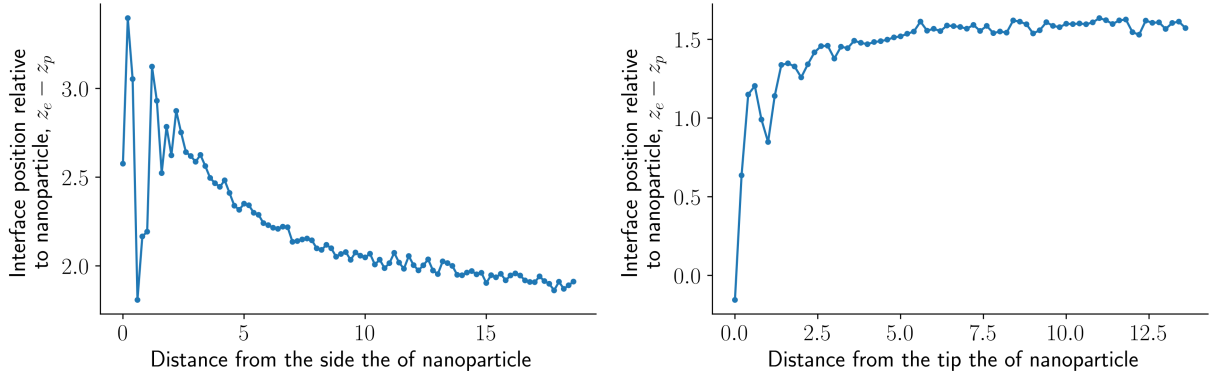


Figure S2: The Gibbs dividing surface relative to the center of mass position of the particle $z_e(x, y) - z_p$ (in units of σ_0) as a function of the distance from the surface of the nanoparticle for a prolate nanoparticle of radii $a = 7.5\sigma_0$ and $b = c = 2.5\sigma_0$ and well depth ratio $\kappa' = 5$. Interface deformation is shown as function of the distance from the side on the left and as a function of the distance from the tip on the right. A planar surface corresponds to $z_e(x, y) - z_p = 1.72\sigma_0$, which is the asymptotic value for large r .

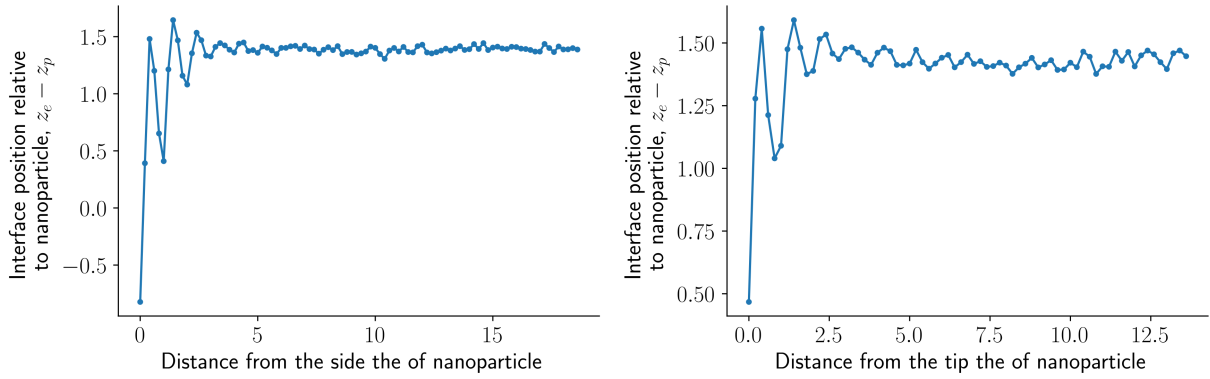


Figure S3: The Gibbs dividing surface relative to the center of mass position of the particle $z_e(x, y) - z_p$ as a function of the distance from the surface of the nanoparticle for a prolate nanoparticle of radii $a = 7.5\sigma_0$ and $b = c = 2.5\sigma_0$ and well depth ratio $\kappa' = 1$. Interface deformation is shown as function of the distance from the side on the left and as a function of the distance from the tip on the right. A planar surface corresponds to $z_e(x, y) - z_p = 1.41\sigma_0$.

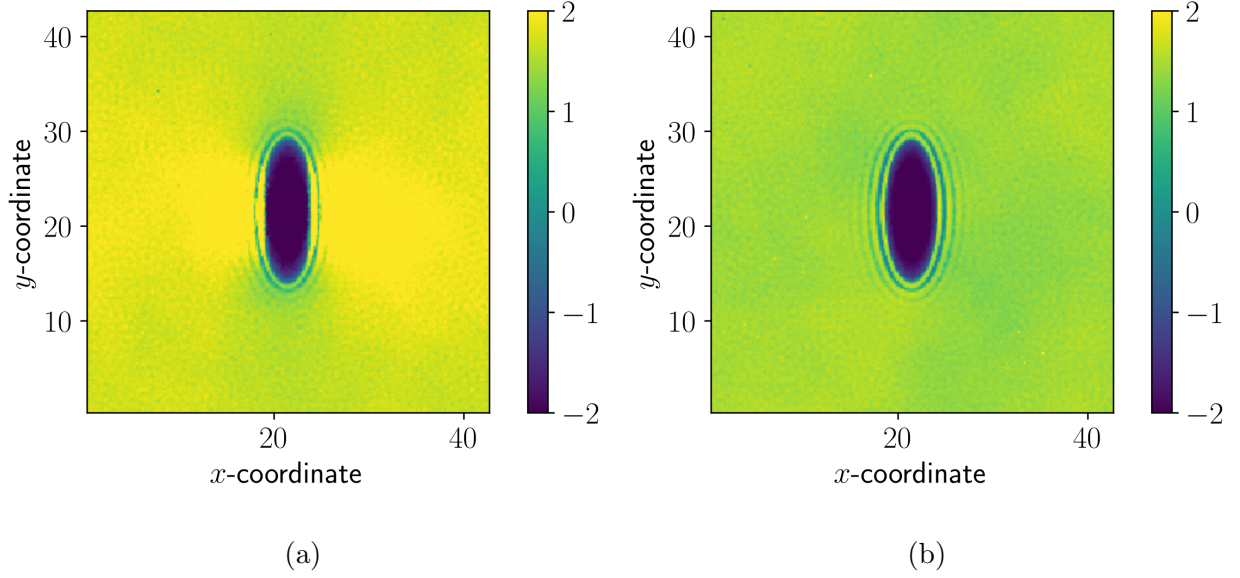


Figure S4: The Gibbs dividing surface relative to the center of mass position of the particle $z_e(x, y) - z_p$ for a prolate nanoparticle of radii $a = 7.5\sigma_0$ and $b = c = 2.5\sigma_0$ and well depth ratio **(a)** $\kappa' = 5$ and **(b)** $\kappa' = 1$.

The Gibbs dividing surface relative to the center of mass position of the particle $z_e(x, y) - z_p$, where z_p is the center of mass of the nanoparticle, is plotted as a function of the distance from the side and the tip of the nanoparticle in figure S2 for the case $\kappa' = 5$ and in figure S3 for the case $\kappa' = 1$. The full function $z_e(x, y) - z_p$ is shown as a heat map in figure S4. The prolate nanoparticles are of radii $a = 7.5\sigma_0$ and $b = c = 2.5\sigma_0$.

3 Nanoparticle-nanoparticle interaction

The direct nanoparticle-nanoparticle force between two prolate nanoparticles of radii $a = 7.19\sigma_0$ and $b = c = 2.53\sigma_0$ has been investigated by constructing two nanoparticles by placing Lennard-Jones atoms in a prolate ellipsoidal shape and calculating the force between them in vacuum. The Lennard-Jones particles are placed in an face-centered cubic lattice of number density $\rho = 1\sigma_0^{-3}$, see figure S5. At this number density the distance between the closest pairs of particles in the face-centered cubic lattice is $2^{1/6}\sigma_0$, at which point the Lennard-Jones force between the particles is zero. The Lennard-Jones particles in a nanoparticle only

interact with Lennard-Jones particles in the other nanoparticle. They interact according to the Lennard-Jones potential described in equation S.2. The interaction strength was set to $\varepsilon_{np} = 0.7\varepsilon_0$ and the diameter of the Lennard-Jones particles to $\sigma_{np} = \sigma_0$. At 300 K this interaction strength is of the order of $k_B T$, which is a typical interaction strength between methyl groups in aliphatic chains coating *e.g.* gold nanoparticles.¹ We did not cut-off the pair interactions, and hence we used the full Lennard-Jones potential in our calculations the calculations reported in figure S6.

$$u^{\text{lj},s}(r) = 4\varepsilon_{np} \left[\left(\frac{\sigma_{np}}{r} \right)^{12} - \left(\frac{\sigma_{np}}{r} \right)^6 \right] \quad (\text{S.2})$$

The nanoparticles do not have smooth surfaces due to the fact that they are a collection of Lennard-Jones atoms as illustrated in figure S5. In order to compare with the smooth Gay-Berne potential, the force was averaged over the rotational angle ϕ around the long axis of the prolate ellipsoid. The force between the two nanoparticles in the three orientations side-by-side (SS), side-to-tip (ST) and tip-to-tip (TT) is given as a function of the surface-to-surface distance d in figure S6. The surface-to-surface distance is defined to be zero at the point where the potential energy is zero. The sum of the solvent-mediated force, capillary force and the direct nanoparticle-nanoparticle force is presented in figure S8.

Table S1: The minimum direct nanoparticle-nanoparticle force and the surface-to-surface distance where the direct force is minimum for three orientations side-by-side, side-to-tip and tip-to-tip. The solvent-mediated force is given for the distance where the direct force is at a minimum.

Orientation	Surface-to-surface distance at minimum force, d_{min}/σ_0	Force at the minimum, $f_{\text{min}}^{np}\sigma_0/\epsilon_0$	Solvent-mediated force, $f\sigma_0/\epsilon_0$
Side-by-side (SS)	0.28	-51.53	48.44
Side-to-tip (ST)	0.29	-8.37	9.71
Tip-to-tip (TT)	0.27	-5.97	0.19

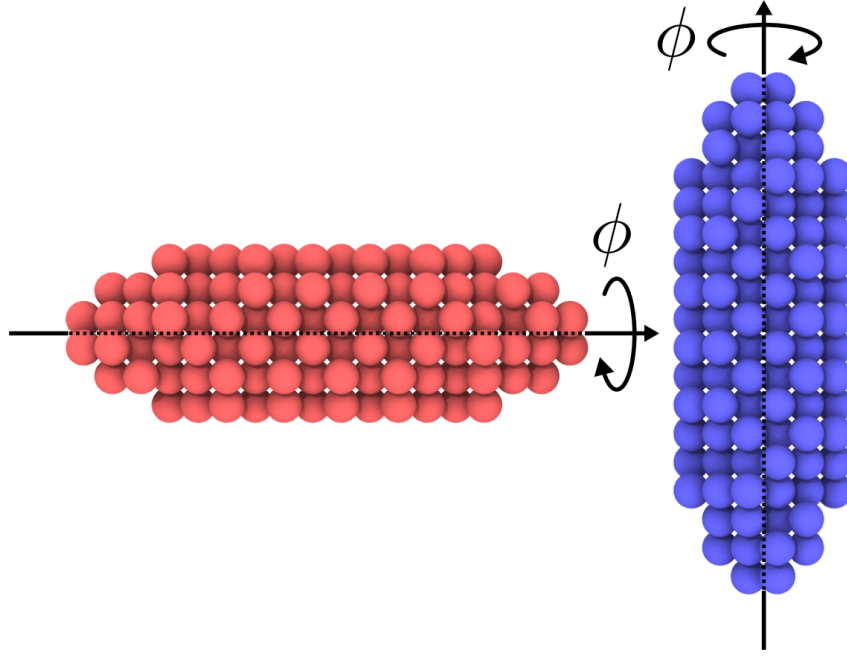


Figure S5: Two collections of Lennard-Jones atoms arranged in a face-centered cubic lattice at density $\rho^* = 1$ in the shape of prolate ellipsoids of radii $a = 7.5\sigma_0$ and $b = 2.5\sigma_0$ in the side-to-tip orientation. The nanoparticles are rotated around the long axis.

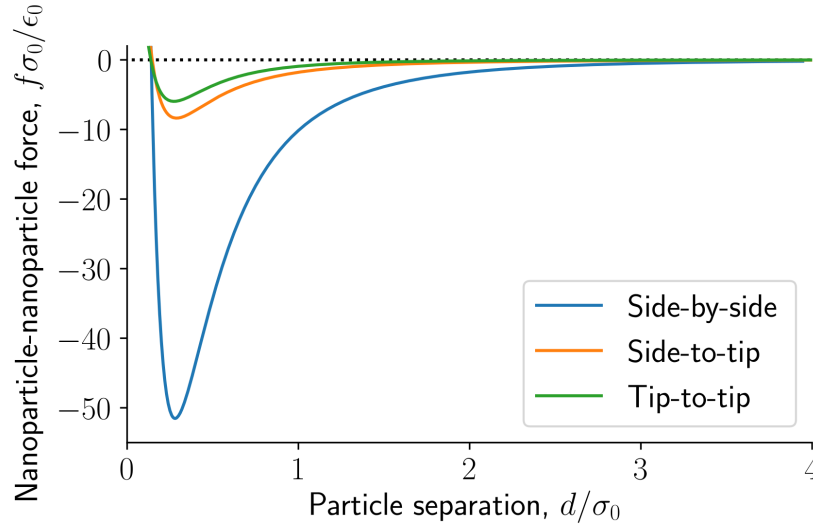


Figure S6: The direct nanoparticle-nanoparticle force between two prolate ellipsoidal nanoparticles constructed by a collection of Lennard-Jones particles in a face-centered cubic lattice. The nanoparticles are in three orientations, side-by-side (SS), side-to-tip (ST) and tip-to-tip (TT).

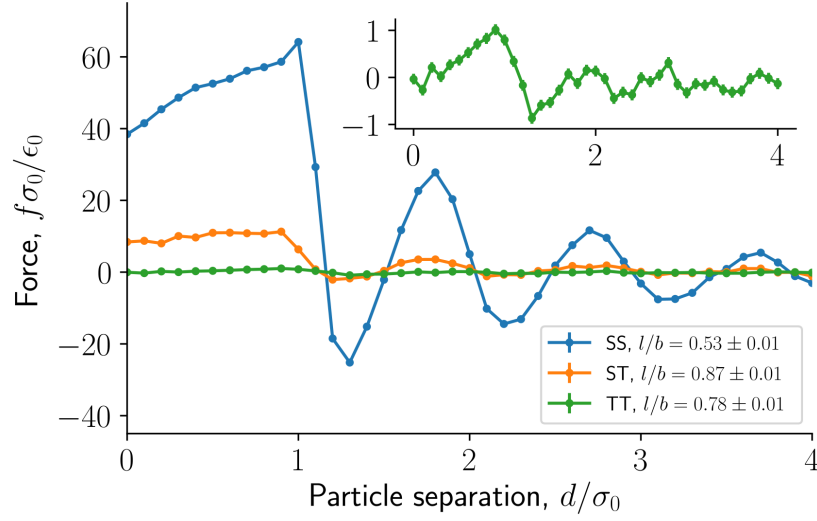


Figure S7: Solvent-mediated and capillary force between two prolate nanoparticles with well depth ratio $\kappa' = 5$ as function of surface-to-surface separation d . The three graphs represent side-by-side (SS), side-to-tip (ST) and tip-to-tip (TT) orientations. The tip-to-tip (TT) configuration is shown in the inset.

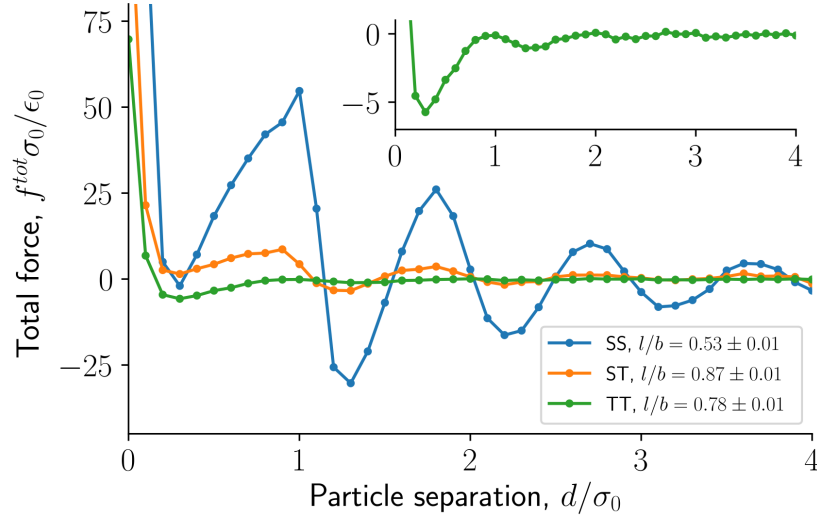


Figure S8: The direct nanoparticle-nanoparticle force in figure S6 plus the solvent-mediated and capillary force in figure S7 as a function of surface-to-surface separation d . The three graphs represent side-by-side (SS), side-to-tip (ST) and tip-to-tip (TT) orientations. The tip-to-tip (TT) configuration is shown in the inset.

References

- (1) Reguera, J.; Ponomarev, E.; Geue, T.; Stellacci, F.; Bresme, F.; Moglianetti, M. Contact angle and adsorption energies of nanoparticles at the air–liquid interface determined by neutron reflectivity and molecular dynamics. *Nanoscale* **2015**, 7, 5665–5673.