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Supplementary Information: Kinetic trapping of nanoparticles by solvent-induced interactions

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Supplementary Information

This supplementary information provides technical details of the molecular dynamics simulations performed in this work and determination of parameters employed in the theoretical model described in the main text.

Molecular Dynamics The fully atomistic MD simulations are performed with the open-source package LAMMPS[1]. The pairwise interatomic potential employed is the standard (12-6) LJ potential $U(r) = 4e_{ij}[(\sigma/r)^{12} - (\sigma/r)^6]$, which considers hard-core repulsion and non-retarded vdW attraction between the species $(i, j = l, p, w)$ modeling the liquid solvent, particle, and wall. To improve computational efficiency while accurately representing interatomic forces[2,3] the LJ potential is used with a cutoff distance $r_c = 2.5\sigma$ for liquid-liquid and liquid-solid interactions and $r_c = 4\sigma$ for particle-wall interactions. The MD simulations reported in Figs. 3-4 in the main text employ three particle-liquid interaction energies $e_{pl} =$ 0.5, 0.75, & 1 k_BT and wall-liquid interaction energies $e_{wl} =$ 0.5, 0.75, & 1 k_BT, particle-wall interactions $e_{pw} \simeq$ 0.5-2 k_BT, and the self-interaction energies are $e_{ii} = k_BT$ for all cases. The Hamaker constant for parameterizing vdW interactions in the particle PMF (Eq. 1 in the main text) is $A = \pi^2 4\sigma^6 n_p(n_w e_{pw} - n_l e_{pl})$, where $n_p = 1/\sigma^3$ is the particle number, density, n_w is the wall number density, e_{pw} is the (pairwise) particle-wall LJ energy, and $n_l = 0.8/\sigma^3$ is the (bulk) liquid number density. For the prescribed wall and fluid density, the (particle-wall) LJ energy is varied to produce the Hamaker constant values reported for the studied cases (cf. Figs. 3-4 in the main text).

All the MD simulations are performed in the NVT ensemble in a fully periodic domain (see Fig. 2a in the main text) with a Nose-Hoover thermostat to control the system temperature. For the modeled conditions the liquid has a bulk number density $n_l = 0.8/\sigma^3$ and a shear viscosity $\mu = 2.1\sqrt{mk_BT}/\sigma^2$ [4,5]. The free-space particle diffusivity in MD simulations is determined from linear fits to the mean square displacement of the modeled quasi-spherical nanoparticles ($R =$ 3 & 6 σ) in a fully periodic simulation box ($L_x = L_y = L_z = 80\sigma$) without solid walls. We find that the Stokes-Einstein relation $D = 6\pi\mu R_h/(k_BT)$ with a hydrodynamic radius $R_h = R + 2\sigma$ accounts for the particle diffusivity determined in free-space MD simulations within a 15% relative error for all studied cases and it is therefore used in the Smoluchwoski equation (Eq. 5 in the main text).

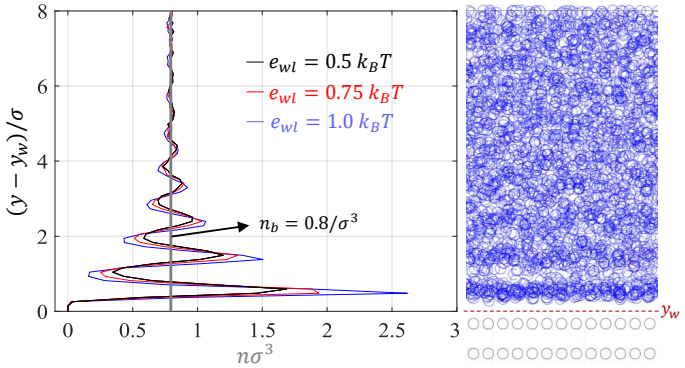

Fig. 1 Liquid number density profile $n(y)$ for three different solid-liquid interaction energies $e_{wl} =$ 0.5-1 k_BT. The right panel shows an orthographic side view of the liquid atoms near the modeled plane wall ($e_{wl} = k_BT$).

Interfacial energy To determine the solid-liquid interfacial energy for the modeled LJ interaction energies we perform a set of simulations with the quiescent liquid confined by the plane wall as reported in Fig. 2a in the main text with dimensions $L_x = L_z = 100\sigma$ and $L_y = 20\sigma$. As reported in Fig. 1, the modeled liquid form solvation layers with a thickness comparable to the liquid molecule diameter σ. We compute the equilibrium number density profile $n(y) = \iint n(x,y,z)dxdz/(L_xL_z)$ in the liquid (see Fig. 1) and determine the solid-liquid interfacial surface energy $\gamma = -k_BT\int_0^{Ly/2} n\log(n/n_l)dy$ from the energy required to remove the wetting liquid under equilibrium conditions[6,7]. The solid-liquid interfacial energies thus computed are $\gamma \simeq$ -0.23, -0.34, & -0.6 k_BT for the employed LJ interaction energies $e_{wl} =$ 0.5, 0.75, & 1 k_BT, respectively (cf. Fig. 1). The liquid-solid interfacial energies γ thus computed for a plane wall are employed to determine the wall-liquid and particle-liquid interfacial surface energies employed in analytical expressions and numerical solutions of the Smoluchowski equation reported in Figs. 3-4 in the main text.

Notes and references

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