

Supporting Information: A colloid model system for interfacial sorption kinetics

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Charged depletant interaction potential

The interaction energy from charged depletants, U_{dep} , is found by integrating the force on the particle by the surround depletants. This force is found by,

$$\mathbf{F} = \int_V \rho(\mathbf{x}) \nabla U_{d-p}(\mathbf{x}) d\mathbf{x}, \quad (1)$$

where U_{d-p} is the energy between depletant and particle and $\rho(\mathbf{x})$ is the probability of finding a depletant molecule at \mathbf{x} . The long range interaction between depletant particles are taken into account using a virial expansion for the depletant density,

$$\rho(\mathbf{x}) = \rho_\infty \exp\left(\frac{-U_{d-p}(\mathbf{x})}{k_B T}\right) \left[1 + b_1(\mathbf{x})\rho_\infty + O(\rho_\infty^2)\right], \quad (2)$$

where $b_1(\mathbf{x})$ is the second virial coefficient. This coefficient is calculated by considering the depletant-particle interaction as well as the depletant-depletant interactions,

$$b_1(\mathbf{x}) = \left[\exp\left(\frac{-U_{d-p}(\mathbf{x} + \mathbf{r})}{k_B T}\right) - 1 \right] \left[\exp\left(\frac{-U_{d-d}(\mathbf{r})}{k_B T}\right) - 1 \right] d\mathbf{r}, \quad (3)$$

where $U_{d-d}(\mathbf{r})$ is the interaction energy between depletant particles. The virial coefficient and force expression are integrated over all space where U_{d-d} and U_{d-p} are non-negligible.

The electrostatic interaction between two particles with radii a_i and a_j is computed as^{1,2}

$$U_{i-j}(r) = 4\pi\epsilon_r\epsilon_0(k_bT/e)^2 \frac{a_i a_j Y_i Y_j}{r} \exp(-\kappa(r - a_i - a_j)), \quad (4)$$

where r is the center-to-center distance between particles, κ^{-1} is the Debye length, and Y_i and Y_j are the effective surface potentials. The full expression for the effective surface potential is given in Bell et al., however when $\kappa a > 1$ the expression can be approximated by $Y_i = 4 \tanh(e\phi_i/4k_bT)$, where ϕ_i is the Stern surface potential.

Colloid diffusion

The diffusive properties of the particles are investigated from measured trajectories. The mean squared displacement (MSD) in both parallel (XY) and perpendicular (Z) to the surface is shown in Figure 1. The parallel direction shows Fickian diffusion, while the perpendicular diffusion quickly transitions to a constant mean squared displacement due to the confinement induced by the interaction potential, i.e. from the downward pressure of gravity and the upward pressure of repulsion from the surface.

The MSD parallel to the wall is calculated separately for periods when the particle is in the “on” well and when it is in the “off” well. The diffusion is found to have the expected linear time dependence in both cases but is greater in the “off” well compared to when it is in the “on” well. The diffusivity is compared to theoretical diffusivity values at a given distance from the wall.³ The diffusivity in the “on” well is found to be similar for all experimental systems. The diffusivity is found to correspond to a height of $0.087 \pm 0.05 \mu\text{m}$ while the diffusivity in the “off” well is found correspond to a height of $0.74 \pm 0.07 \mu\text{m}$. The height in the “off” well is used to estimate the “off” well perpendicular diffusion coefficient used in the main text.

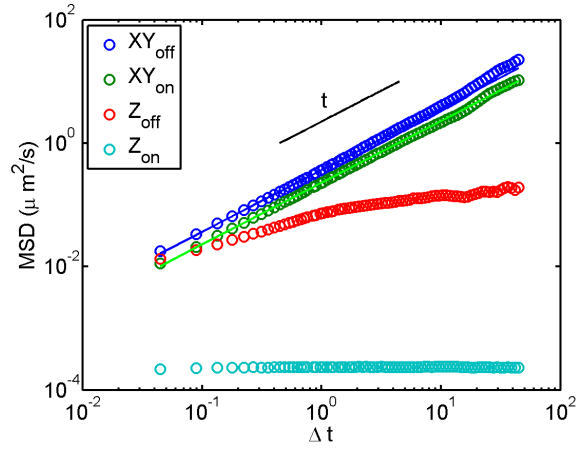


Figure 1: Mean squared displacement for 0.4 vol % and 0.5 mmol/L NaCl parallel to the wall (XY) and perpendicular to the wall (Z). The data are separated into MSD for particles that are in the “on” and “off” wells for both parallel and perpendicular directions.

References

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- (2) Weroński, P.; Walz, J. Y. An approximate method for calculating depletion and structural interactions between colloidal particles. *Journal of colloid and interface science* **2003**, *263*, 327–332.
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