On the effect of particle morphology and interaction on near wall dynamics

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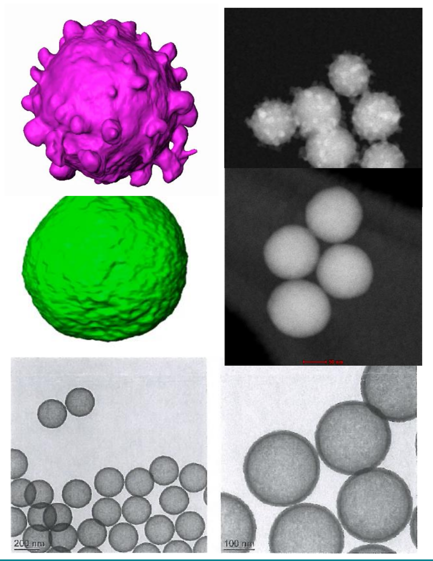
We employed evanescent wave dynamic light scattering [1] to study the near wall dynamics of different types of silica particles, i. e. full spheres, spherical shells and spheres with surface roughness, with the objective to investigate the effect of particle morphology on their near wall dynamics. While the dynamics of spherical particles and hollow shells is in agreement with theoretical predictions for hard sphere colloids [2] within experimental error, the rough particles show slower dynamics than expected for spheres. As the latter finding is at conflict with hydrodynamic theory, we further investigated the influence of static particle wall interaction on the dynamics. Our results indicate that the rough particles experience stronger van der Waals attraction than particles with a smooth surface, which may contribute to settle an open question in literature concerning the effect of particle roughness on interaction and adhesion [3, 4].

Colloidal systems

Particle type	R_H (nm)	$\langle R\rangle_{TEM}$ (nm)	σ
Rough	86	75	0.05
Smooth	73	75	0.05
Hollow	137	124	0.03



Evanescent wave

A laser beam that is totally reflected from a flat surface (of a material with refractive index n_1), which is in contact with a medium ($n_2 < n_1$), with incident angle $\alpha_i > \theta_{crit} = \sin^{-1}(n_2/n_1)$, creates an evanescent wave at the reflection spot that penetrates the medium of n_2 to a limited extent.

The electric field strength decays with the distance to the interface, z, as:

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp\left\{-\frac{\kappa}{2} z\right\}$$

where $\kappa/2 = \frac{2\pi}{\lambda}\sqrt{(n_1 \sin\alpha_i)^2 - n_2^2}$ is the inverse *penetration depth* of the evanescent field strength.

This electric field is scattered by dielectric particles that are sufficiently close to the interface.

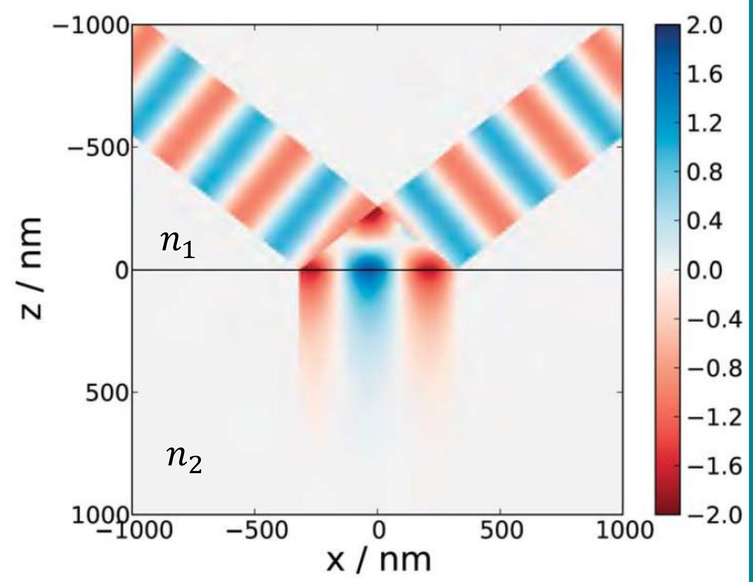


Figure 1. Incident, evanescent and reflected electric field at a glass/air interface. Image taken from Woods *et al.* (2014) *Soft Matter*, 10, 1071.

Evanescent wave DLS

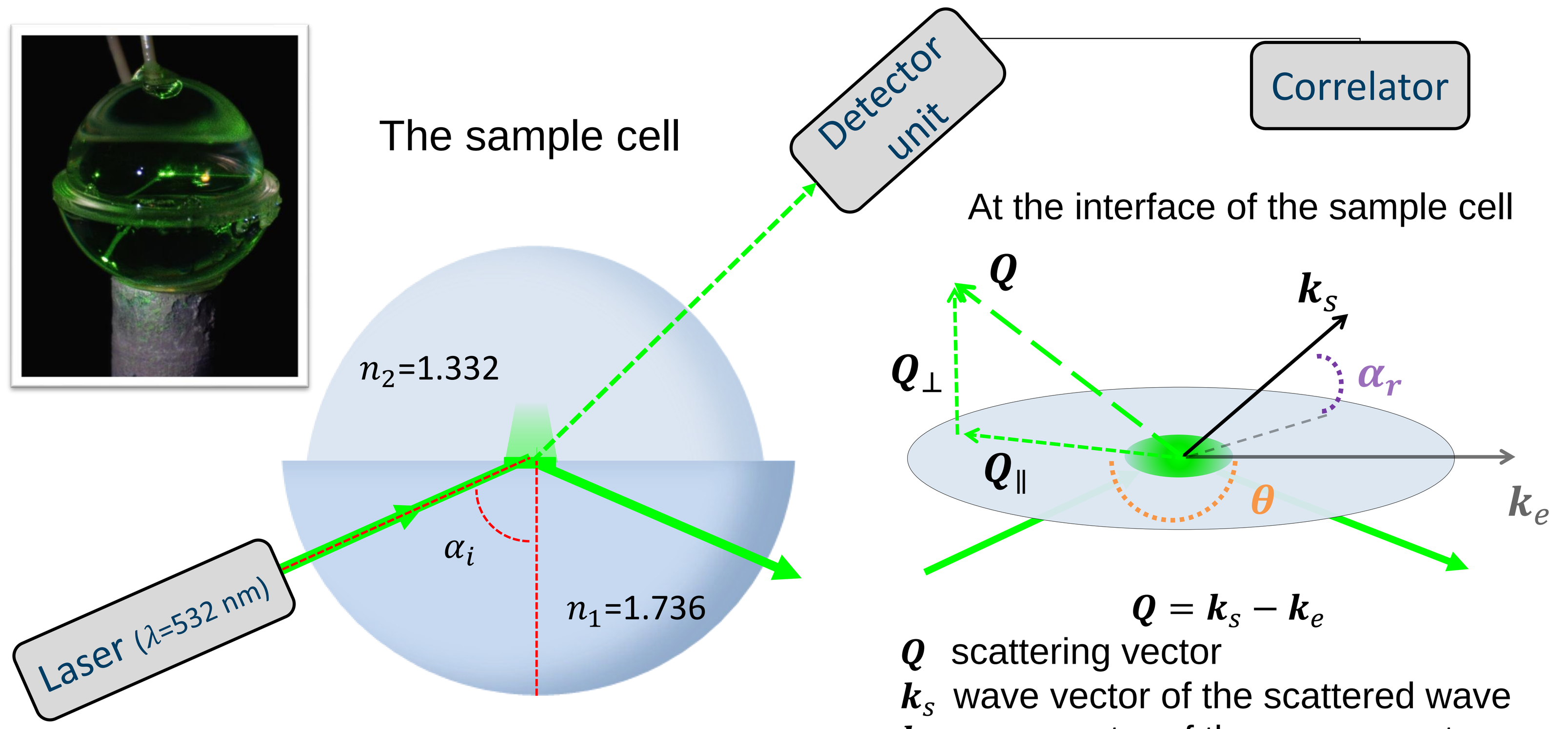


Figure 2. Sketch of the EWDLS set-up.

$\boldsymbol{Q} = \boldsymbol{k_s} - \boldsymbol{k_e}$

- $\boldsymbol{Q}$ scattering vector
- $\boldsymbol{k_s}$ wave vector of the scattered wave
- $\boldsymbol{k_e}$ wave vector of the evanescent wave
- $\boldsymbol{Q}_\perp$ normal component of $\boldsymbol{Q}$
- $\boldsymbol{Q}_\parallel$ parallel component of $\boldsymbol{Q}$

The initial slope of the field correlation function

When particles diffuse near a wall under the influence of an interacting potential $\Phi(z)$, the initial slope of EWDLS time correlation function is given by:

$$\Gamma = \frac{\int_R^\infty dz \exp\{-\beta\,\Phi(z)\}\exp\{-\kappa z\}\left[D_\parallel(z)\,Q_\parallel^2 + D_\perp(z)\,(Q_\perp^2 + \kappa^2/4)\right]}{\int_R^\infty dz \exp\{-\beta\,\Phi(z)\}\exp\{-\kappa z\}}$$

where z is the particle center to surface distance. With the average diffusion constants defined as

$$\langle D_{\parallel,\perp}\rangle_z(z) = \frac{\int_R^\infty dz \exp\{-\beta\,\Phi(z)\}\exp\{-\kappa\,z\}\,D_{\parallel,\perp}(z)}{\int_R^\infty dz \exp\{-\beta\,\Phi(z)\}\exp\{-\kappa\,z\}}$$

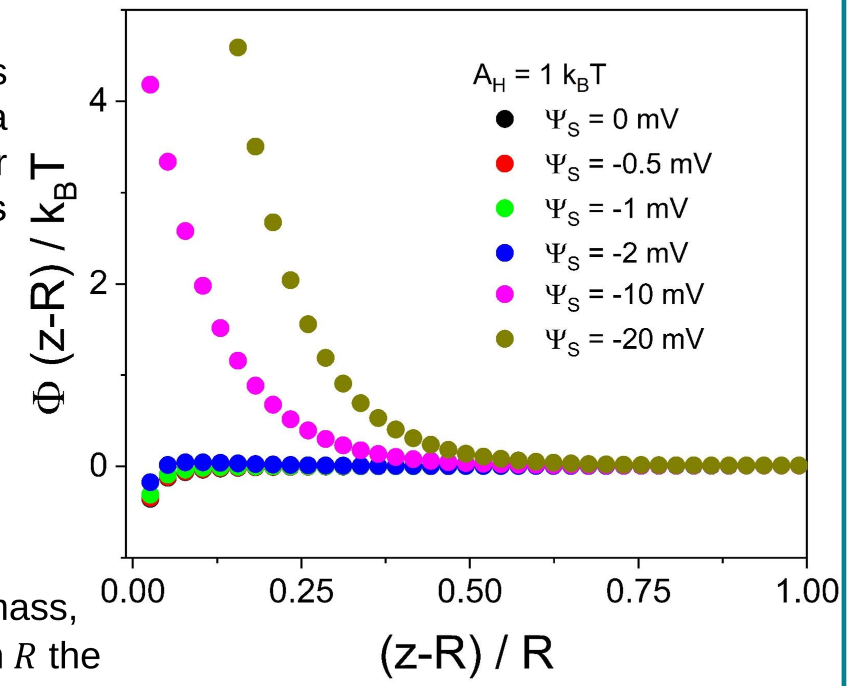
the following linear relation is obtained:

$$\Gamma = Q_\parallel^2\langle D_\parallel\rangle(\kappa) + \left(Q_\perp^2 + \frac{\kappa^2}{4}\right)\langle D_\perp\rangle(\kappa)$$

The interaction potential $\Phi(z)$

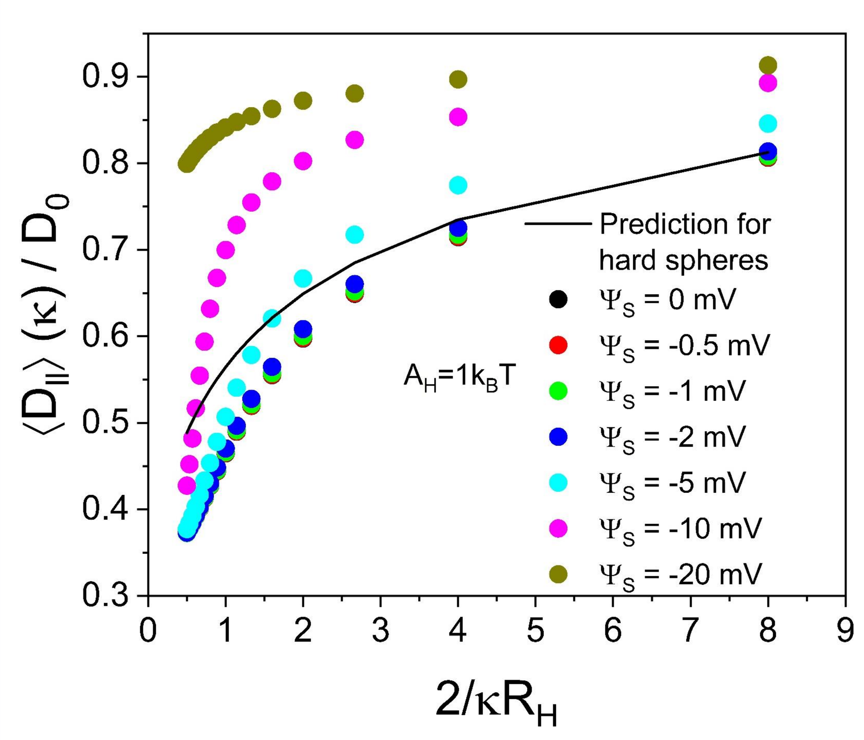
The potential between particle and wall is modelled as the superposition of a gravitational, an electrostatic and a van der Waals contribution in the Derjaguin's approximation:

$$\frac{\Phi(z)}{k_BT} = \frac{m_p}{k_BT}\,g\,z + B\,\exp\{-d\,\kappa_D\}$$
$$-\frac{A_H}{6}\left\{\frac{R}{d} + \frac{R}{d+2R} + ln\left(\frac{d}{d+2R}\right)\right\}$$



where m_p is the buoyancy corrected particle mass, g the gravitational acceleration, $d = z - R$ with R the particle radius and κ_D^{-1} the Debye screening length.
$B = B(\Psi_s)$ is the amplitude of the electrostatic interaction and A_H the Hamaker constant, both in thermal units, with the particles' electric surface potential Ψ_s.

The effect of DLVO particle-wall interaction on diffusion constants

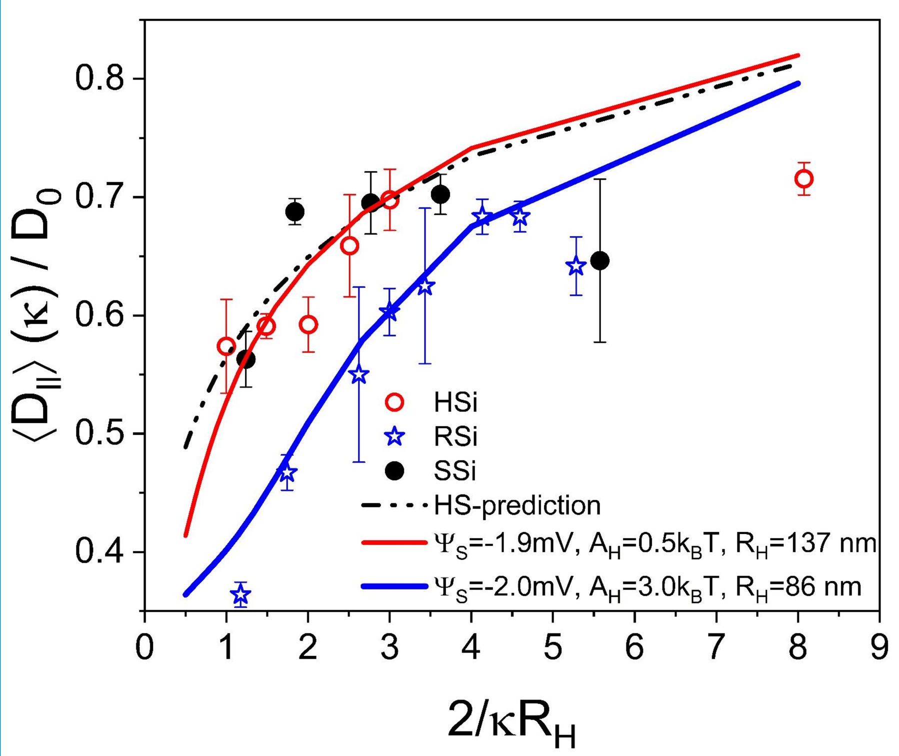


Normalized parallel diffusion constants of monodisperse particles, interacting with a wall. The interaction potentials are defined by the parameters indicated in the legend and R=100nm, κ_D^{-1}=100 nm. The effect of gravitation was found to be negligible.

Due to hydrodynamic interaction with the wall, the near wall diffusion of spheres is always smaller than the bulk value, D_0.

At high surface potentials, the diffusion is faster than expected for hard spheres, and vice versa, because the average separation distance between particle and wall increases $|\Psi_S|$ and consequently the hydrodynamic wall effect is reduced.

Results



The hollow (HSi) and smooth (SSi) spherical particles exhibit dynamics similar to hard sphere within experimental error. Taking into account an interaction potential with Ψ_S= -1.9 mV and A_H= 0.5 k_BT, slightly better agreement between experimental data and model prediction can be achieved for the hollow spheres.

The rough surface particles (RSi) show significantly slower dynamics than the hard sphere prediction. Acceptable agreement between experimental data and the model is achieved for Ψ_S= -2 mV and A_H= 3 k_BT.

Conclusions

There are conflicting predictions, based on theoretical and numerical approaches in literature concerning the effect of surface roughness on van der Waals interaction. While Bhattacharjee *et al.* find that van der Waals interaction is reduced by roughness [3], Walz *et al.* predict that the stabilizing barrier between two particles is reduced by roughness, keeping the surface charge unchanged.

Our experimental data for the near wall dynamics of rough particles indicate that they experience a more pronounced van der Wal attraction by a glass wall than smooth particles of the same material. This finding appears to support the second scenario.

References
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