Near interface diffusion of various kinds of colloidal particles

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When suspended colloidal particles move in the ultimate vicinity of a flat solid interface, their mobility is smaller than in the bulk suspension due to a drag force caused by hydrodynamic interaction between the particle and the wall. Further, the friction acting on a particle depends on the direction of motion. Leading to different diffusion coefficients parallel, $D_{\parallel}$, and normal, $D_{\perp}$, to the interface. To expand the catalogue of particles being studied at interfaces [1-5], we are now investigating colloidal particles with controlled surface roughness and hollow shells. In this work, we show the anisotropic diffusion of these particles when they are close to a glass/dispersion interface by means of evanescent wave dynamic light scattering (EWDLS). By comparing the results from rough and hollow particles with data from smooth spherical particles and with theoretical predictions for hard sphere colloids [6,7] we assess the influence of particle shape on the particle-interface hydrodynamic interaction.

Colloidal systems

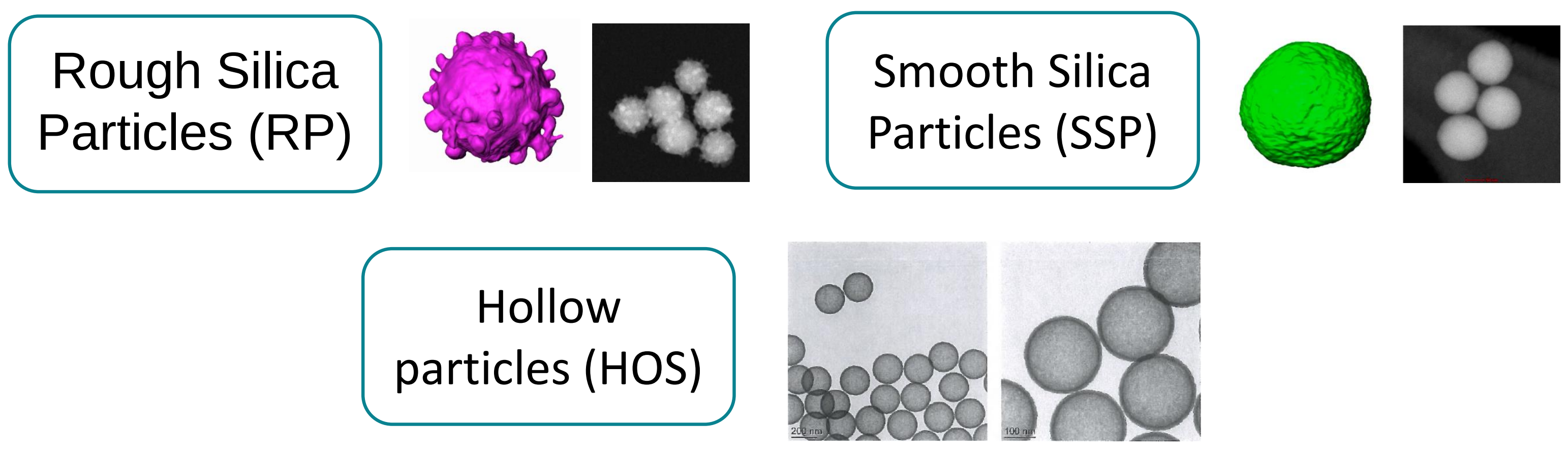

Figure 1. Colloidal particles used in this research

Particle type	R_H (nm)	$\langle R\rangle_{TEM}$ (nm)	λ_D^{-1} (nm)	$\zeta_{Potential}$ (mV)
Rough [8]	86	75	1000	-44
Smooth	73	75	1000	-
Polystyrene	106	-	30	-52
Hollow	137	124	1000	-

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 an 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.

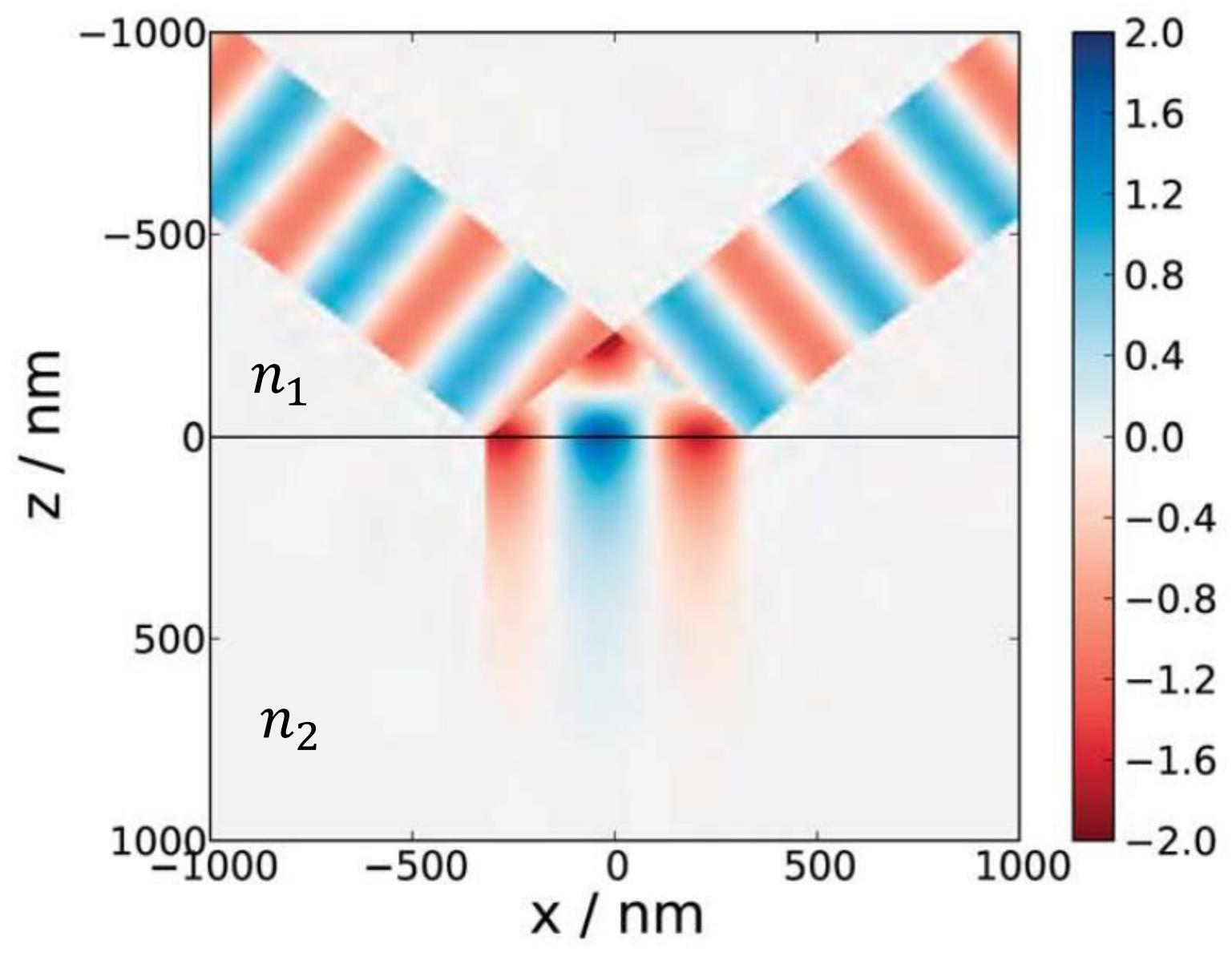

Figure 2. Incident, evanescent and reflected electric field at a glass/air interface. *Image taken from Ref. 9.*

Evanescent Wave DLS: Experimental set-up

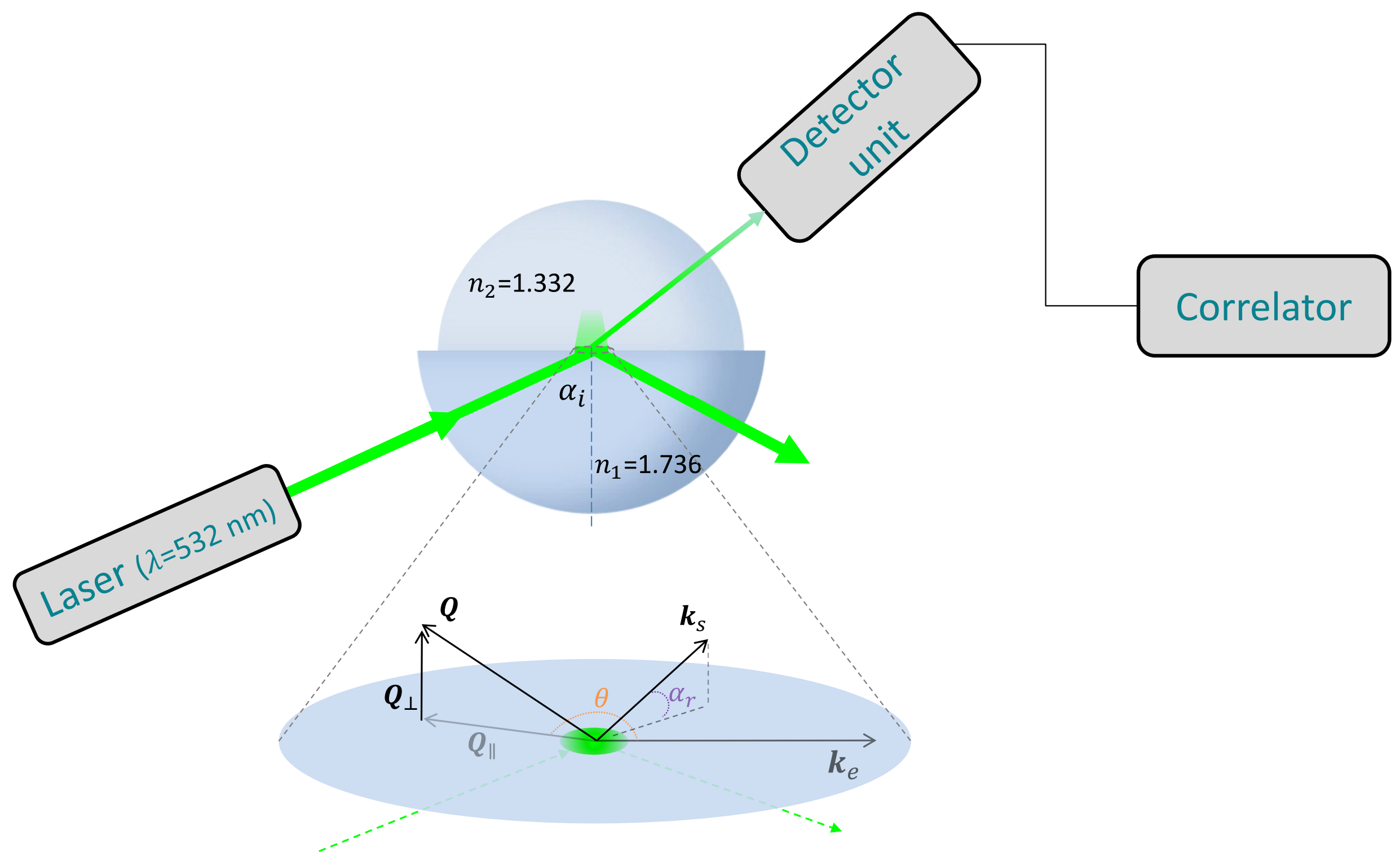

Figure 3. Sketch of the EWDLS set-up

Evanescent Wave DLS: Data analysis

At *short times*, the time correlation function of the scattered field:

$$g_1(t) = \exp\{-\Gamma t + \mathcal{O}(t^2)\}.$$

Here Γ is the initial relaxation rate that can be re-written as:

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

and $\langle D_{\parallel,\perp}\rangle(\kappa)$ are the κ-dependent mean diffusivities, parallel and normal to the interface. The pointed brackets indicate an average over the illuminated volume .

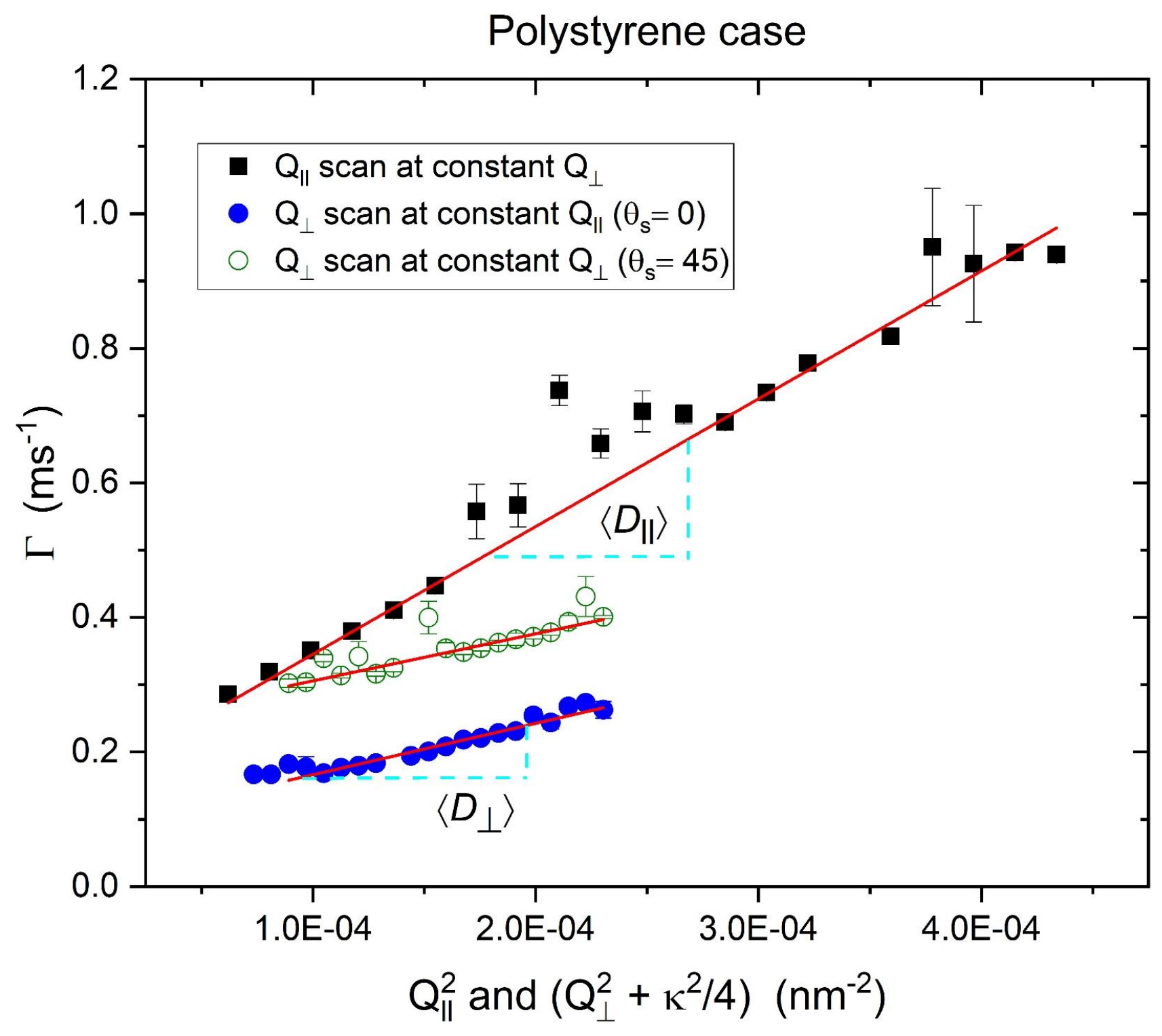

Figure 4. Relaxation rates from a $Q_\parallel^2$-scan at constant $Q_\perp^2$and from $Q_\perp^2$-scans at constant $Q_\parallel^2$.

Results

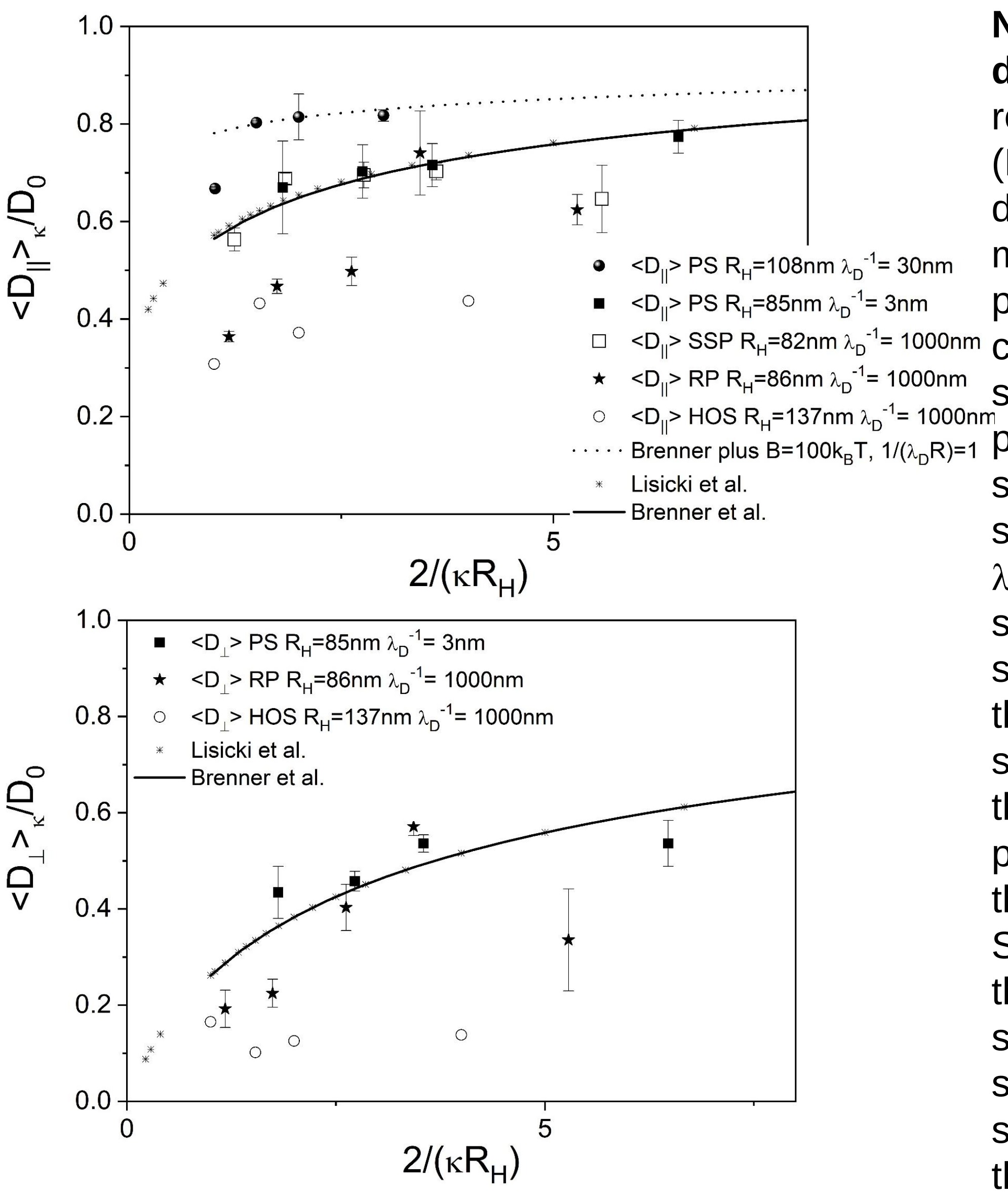

Figure 5. Normalized diffusion coefficients parallel (top) and normal (bottom) to the interface in dependence of the normalized penetration depth.

Normalized near wall diffusion coefficients. Both, rough (RP) and hollow particles (HOS) exhibit a significant decrease of their normalized mean diffusion constant parallel to the surface, as compared to solid particles with smooth surface, i.e. polystyrene (PS) and smooth silica (SSP). At sufficiently small Debye screening length, λ_D^{-1}, the parallel diffusion of the smooth particles show satisfactory agreement with theoretical prediction for hard sphere (HS) colloids [6,7]. Note that the dynamics of PS particles at large λ_D^{-1} are faster than the HS prediction.
Similar behavior is observed for the diffusion normal to the surface. While the dynamics of smooth polystyrene particles at small λ_D^{-1} follow the predictions, the dynamics of the rough and the hollow particles are slower than expected for hard spheres.

Conclusion

Here we show experimental evidence of how particle morphology affects the dynamics of colloids near to a glass/aqueous interface. It is shown that rough and hollow particles show slower near wall dynamics as compared to the simple case of full body hard sphere like particles with smooth surface. As the measurements on the rough and the hollow particles were performed at large screening lengths, we would expect an acceleration of their dynamics, if the deviation from hard sphere behavior was caused by static particle wall interactions. However, we are observing the opposite behavior. van der Waals attraction, which might lead to a slowing down of the near wall dynamics, can be ruled out for rough particle [10]. This leads us to conclude that the observed slowing down of the rough and hollow particles is very likely due do a different hydrodynamic interaction with the wall as compared to full body hard sphere like particles.

References

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