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The effect of particle shape and interaction on the near-wall dynamics

Yi Liu

Institute of Complex System (IBI-4)

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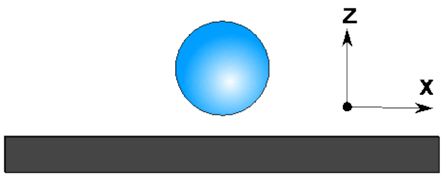
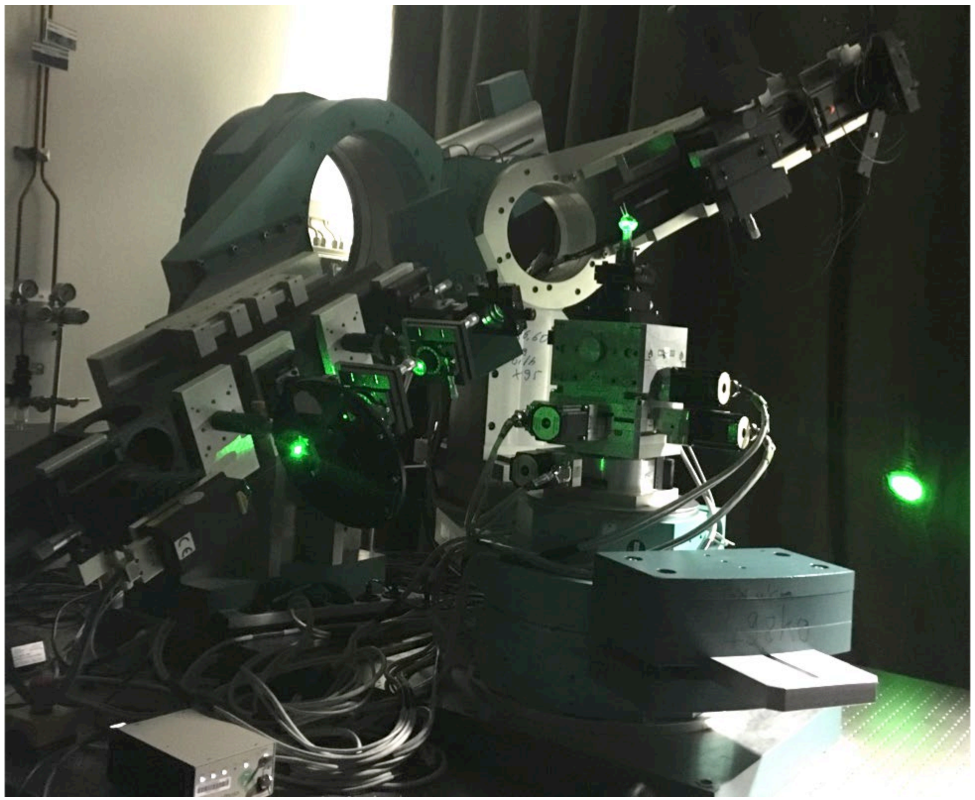
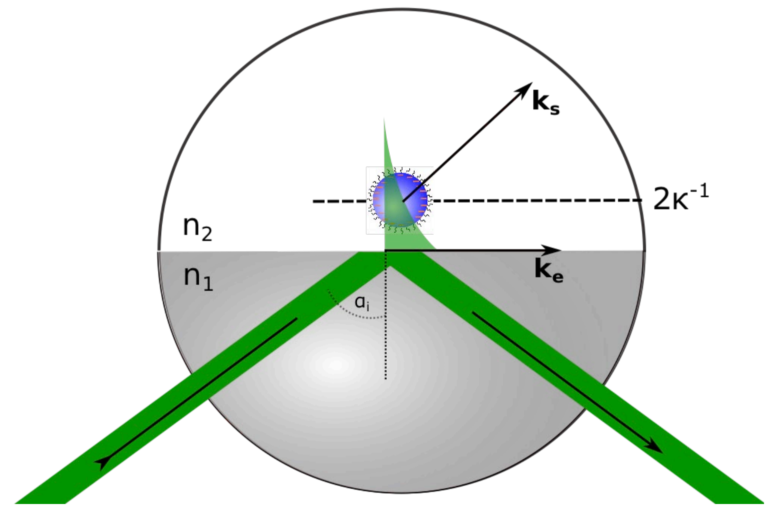
EWDLS for interface dynamics







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

$$2\kappa^{-1} = \frac{\lambda_0}{2\pi\sqrt{(n_1 \sin\alpha_i)^2 - n_2^2}}$$

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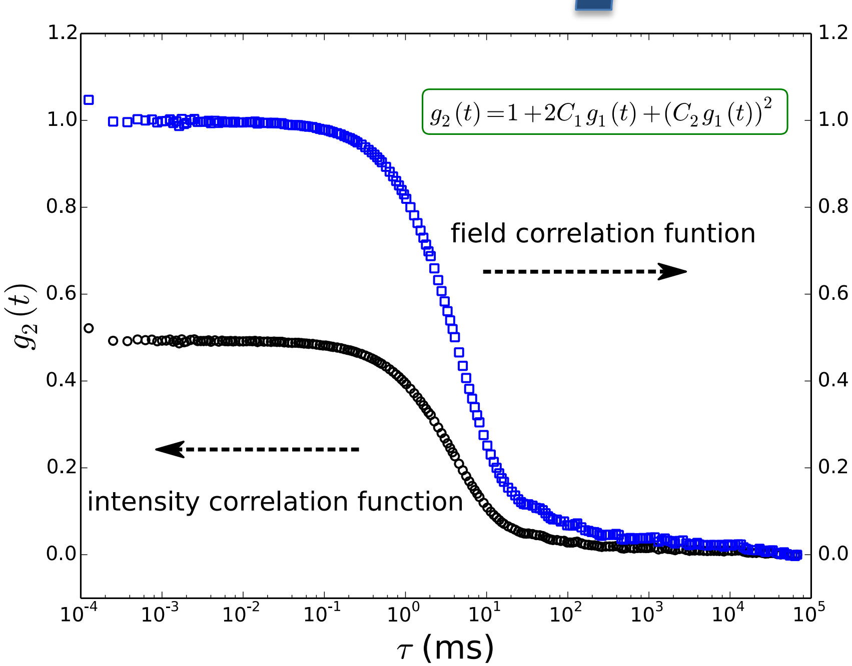
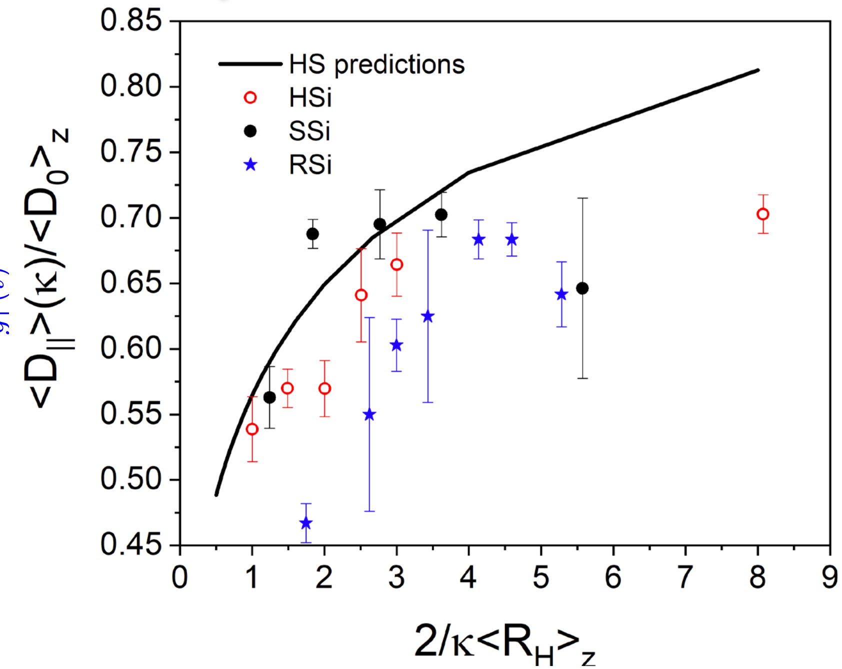
$\Gamma(Q)$





Generality

- Particles are slowed down at interface due to hydrodynamic interaction.
- The larger the penetration depth, the weaker the slow-down effect.

Limitation

- The correlation function is the only source of information
- Dynamic behavior is impacted by static properties
- Static information cannot can not be directly discerned from dynamic information.

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Nothing in life is a hard sphere

- Static interaction with the wall
  - van der Waals attraction
  - electrostatic repulsion
  - gravitational contribution
- Polydispersity
  - happens in synthesis of model systems
  - inevitable and non-negligible in biological samples
- the devil is in Aggregation
  - size of aggregates
  - percentage of aggregates
- Particle shape and morphology
  - e.g. core/shell

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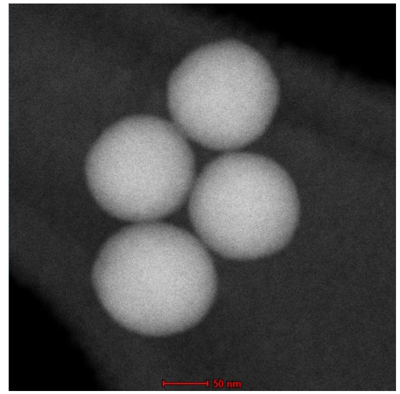
Three systems under investigation

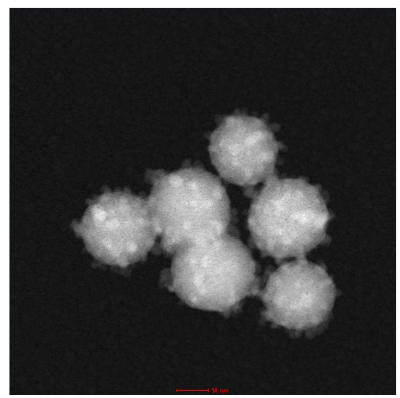
SSi - Smooth silica particle

$_H$=77 nm

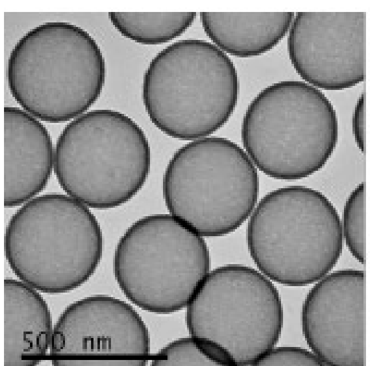


rticle.

$_H$=86 nm



HSi -- Hollow silica particle.



R_H=154 nm

All samples are dispersed in pure water
Debye length 100 nm
Samples are gently centrifuged (800 rpm for 16 hours)
before measurements to spin down potential aggregates

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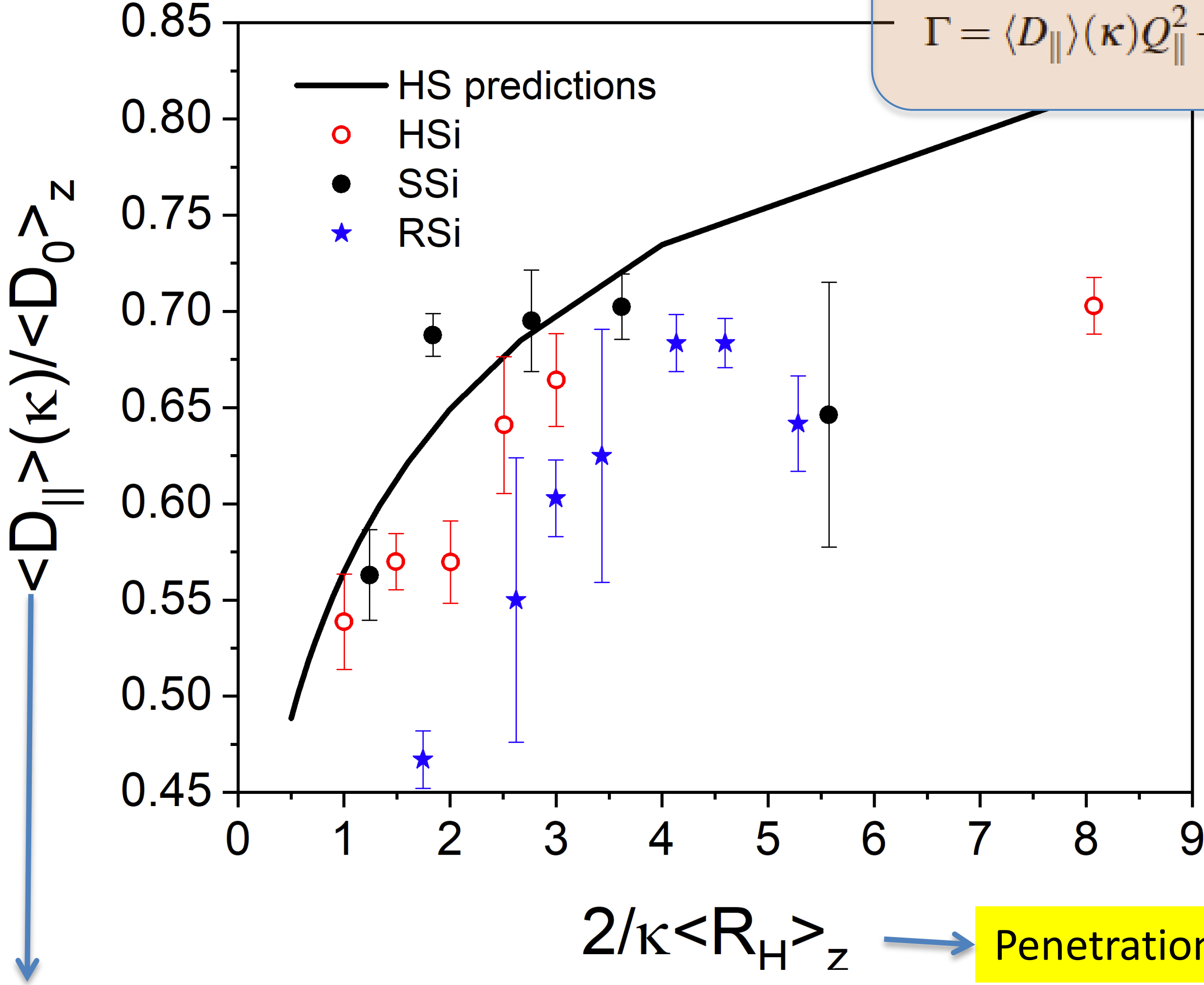
Experimental EWDLS data

$$\langle D_{\parallel,\perp}\rangle(\kappa) = \kappa \int_R^\infty dz\, D_{\parallel,\perp}(z)\exp\{-\kappa(z-R)\}$$

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



Penetration normalized by radius

interfacial diffusion is normalized with bulk diffusion D_0
unitless

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Experimental EWDLS data

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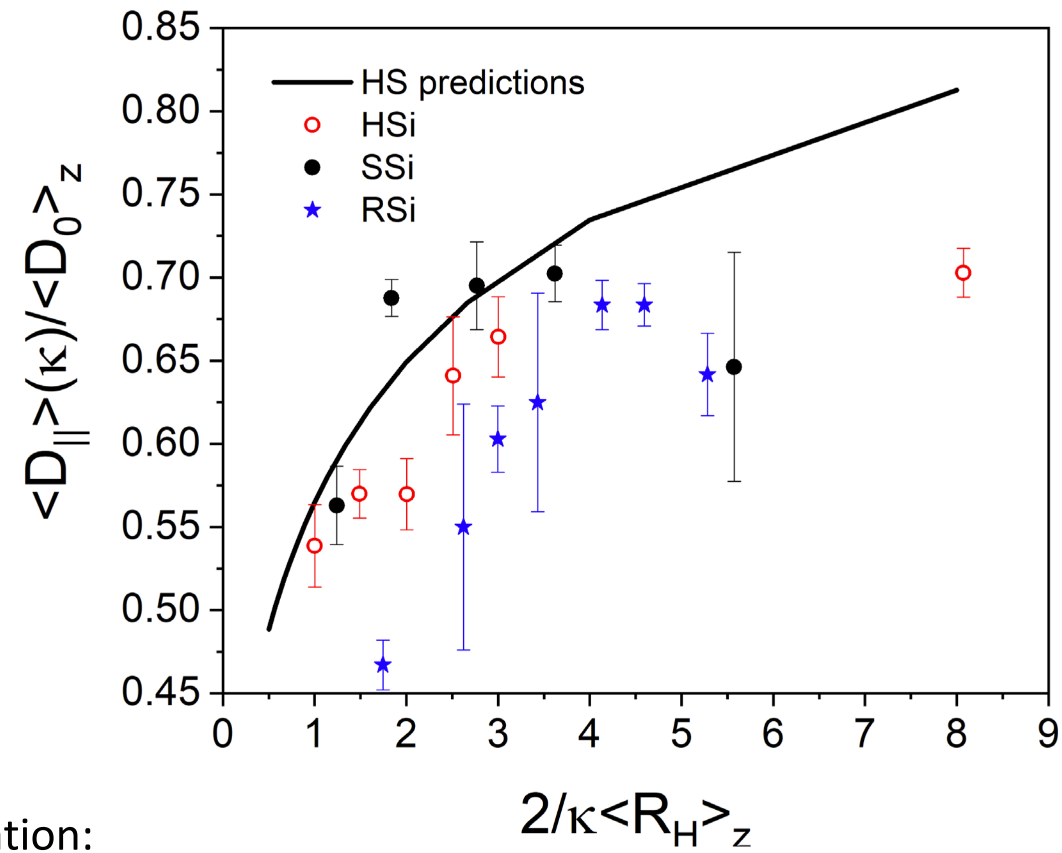

Observation:

- SSi agrees with HS prediction except for the outlier at high penetration depth;
- HSi is systematically slightly slower than the HS prediction;
- RSi is significantly slower than HS prediction.
- The observation is contrary to hydrodynamic theories.
- The observed effect is likely to come from static interaction.

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Model calculation

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Hard sphere

$$\langle D_{\parallel,\perp}\rangle(\kappa) = \kappa \int_R^{\infty} dz\, D_{\parallel,\perp}(z) \exp\{-\kappa(z-R)\}$$

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

Static particle-wall interaction

$$\Phi(z) = \Phi_{vdW}(z) + \Phi_{er}(z) + \Phi_g(z)$$

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

the number density becomes a function of z when particle interacts with wall

Polydispersity and aggregation plus potential

$$\langle\Gamma\rangle_R = \frac{\int_0^{\infty} dR \boxed{B_{nw}^2(Q,\kappa,R) P(R)} \int_R^{\infty} dz \boxed{\exp\{-\beta\Phi(z)\}} \exp\{-\kappa z\} D(Q,\kappa,R)}{\int_0^{\infty} dR \boxed{B_{nw}^2(Q,\kappa,R) P(R)} \int_R^{\infty} dz \boxed{\exp\{-\beta\Phi(z)\}} \exp\{-\kappa z\}}$$

the near wall form factor does not cancel for the expression of Gamma.

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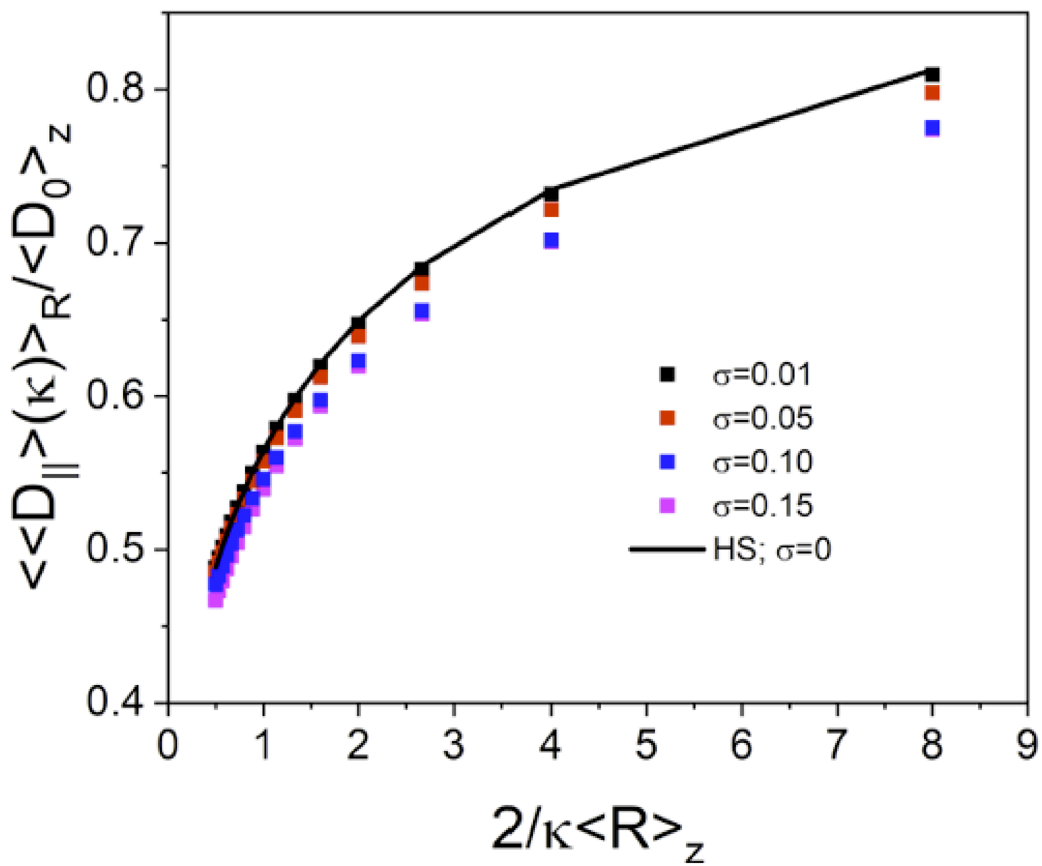
Model calculation: Polydispersity

- Polydispersity is modeled by a Gaussian distribution
- μ: mean value. σ: relative standard deviation
- Spherical particles with Gaussian size distribution, interacting only with excluded volume
- Polydispersity less than 10% has a negligible influence on near-wall dynamics.
- The silica particles under study have a polydispersity far blow 10%



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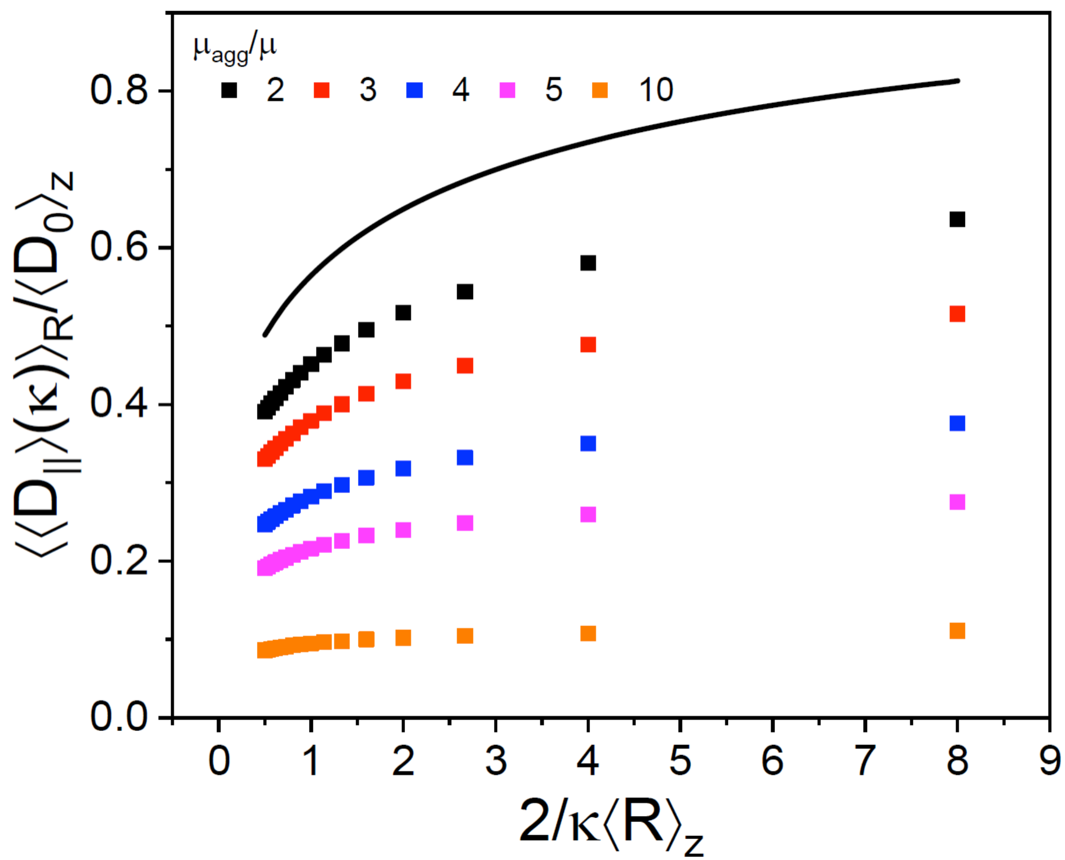
Model calculation: Aggregation

- Aggregation is modeled by a bimodal Gaussian distribution: $\mu + \mu_{agg}$
- Variation of aggregate size, μ_{agg}, at fixed volume fraction 5%.
- Presence of small aggregates (μ_{agg}=2μ) greatly slows down near-wall dynamics.



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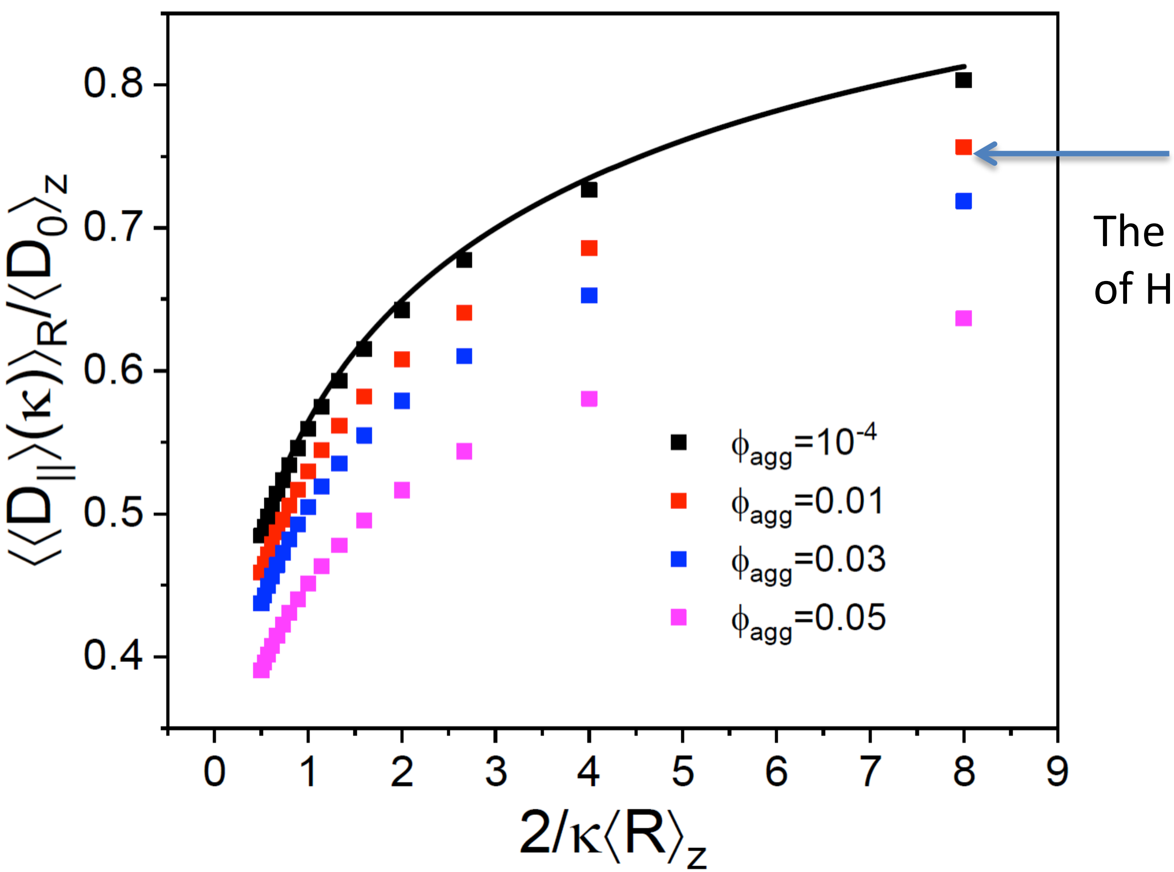
Model calculation: Aggregation

- Aggregation is modeled by a bimodal Gaussian distribution: $\mu + \mu_{agg}$
- Variation of volume fraction of aggregates at fixed size $\mu_{agg}=2\mu$.
- 1% of aggregates will slow down dynamic significantly.



The red symbols is reminiscient of HSi data

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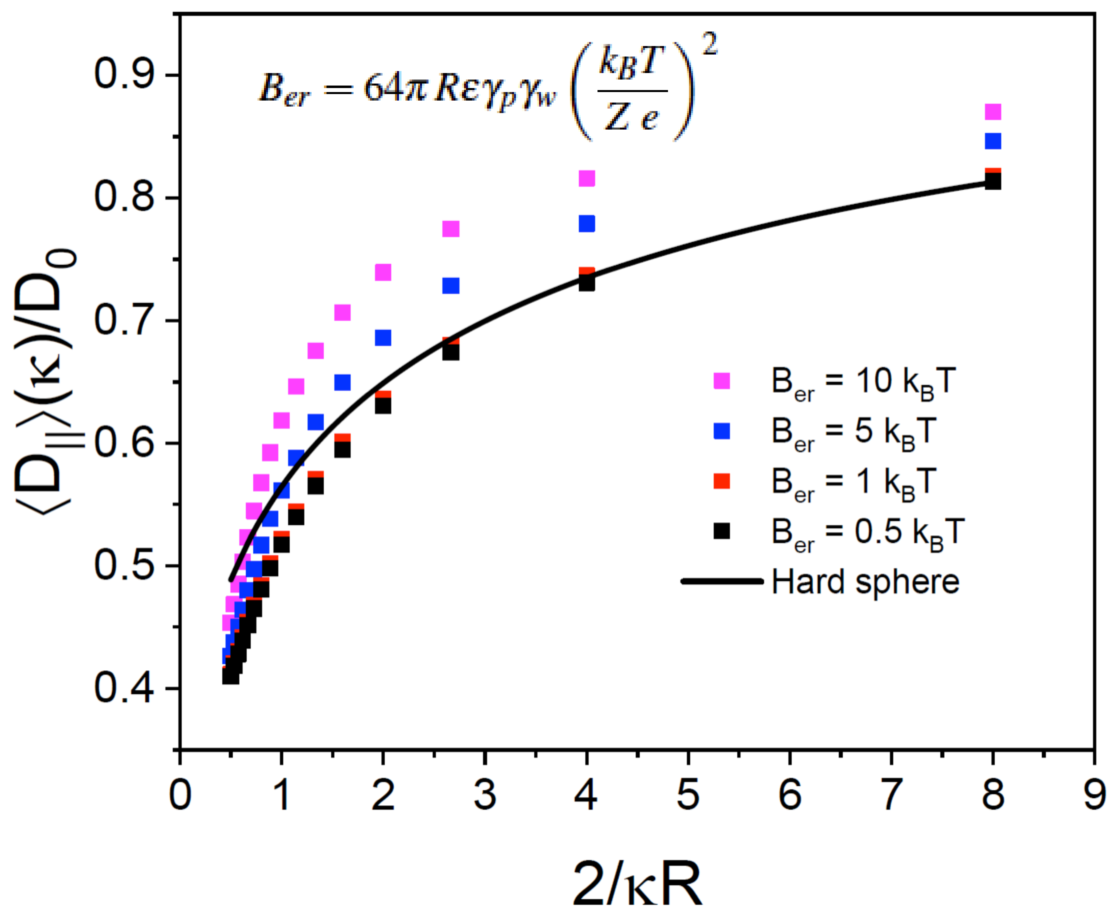
Model calculation: static interaction

$$\Phi(z) = \Phi_{vdW}(z) + \Phi_{er}(z) + \Phi_g(z)$$

fixed van der Waals and gravitation, various electrostatic interaction, monodisperse
R=100 nm, A_H=0.5 k_BT, $\Delta\rho$=1g/mL
Electrostatic repulsion accelerates near-wall dynamics.



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Model calculation: static interaction

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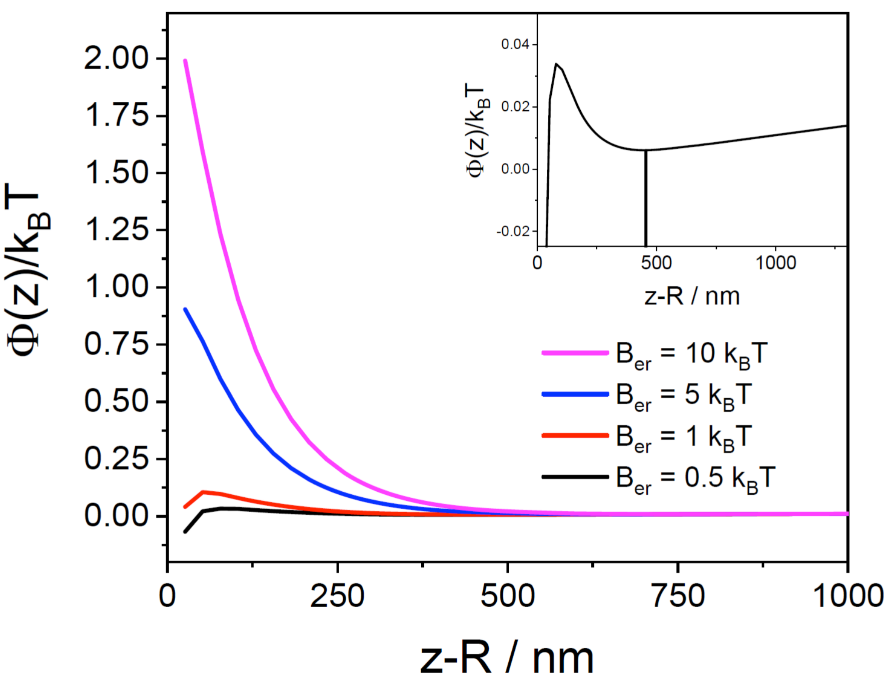
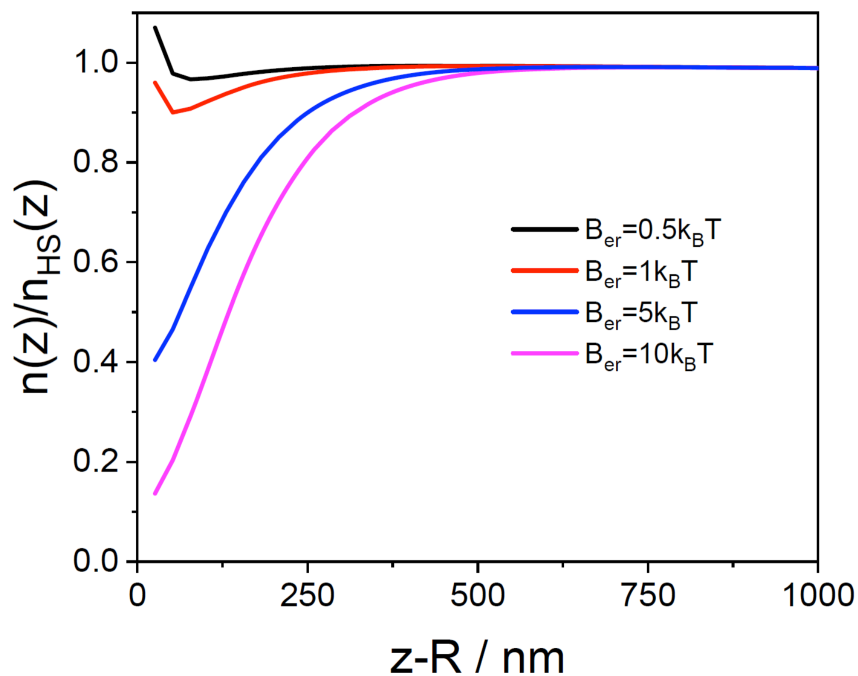
$$\Phi(z) = \Phi_{vdW}(z) + \Phi_{er}(z) + \Phi_{g}(z)$$

$R=100$ nm, $A_H=0.5\ K_BT$, $\Delta\rho=1$g/mL

- Particle number density is no longer homogeneous at wall, due to static interaction.
- At higher B_{er} , the near wall area (3*R) is depleted of particles.
- If the B_{er} is smaller than A_H, an enrichment of particles occurs near the wall.





- Static interaction changes the number density of particles at wall
- Particles closer to the wall are slowed down more strongly

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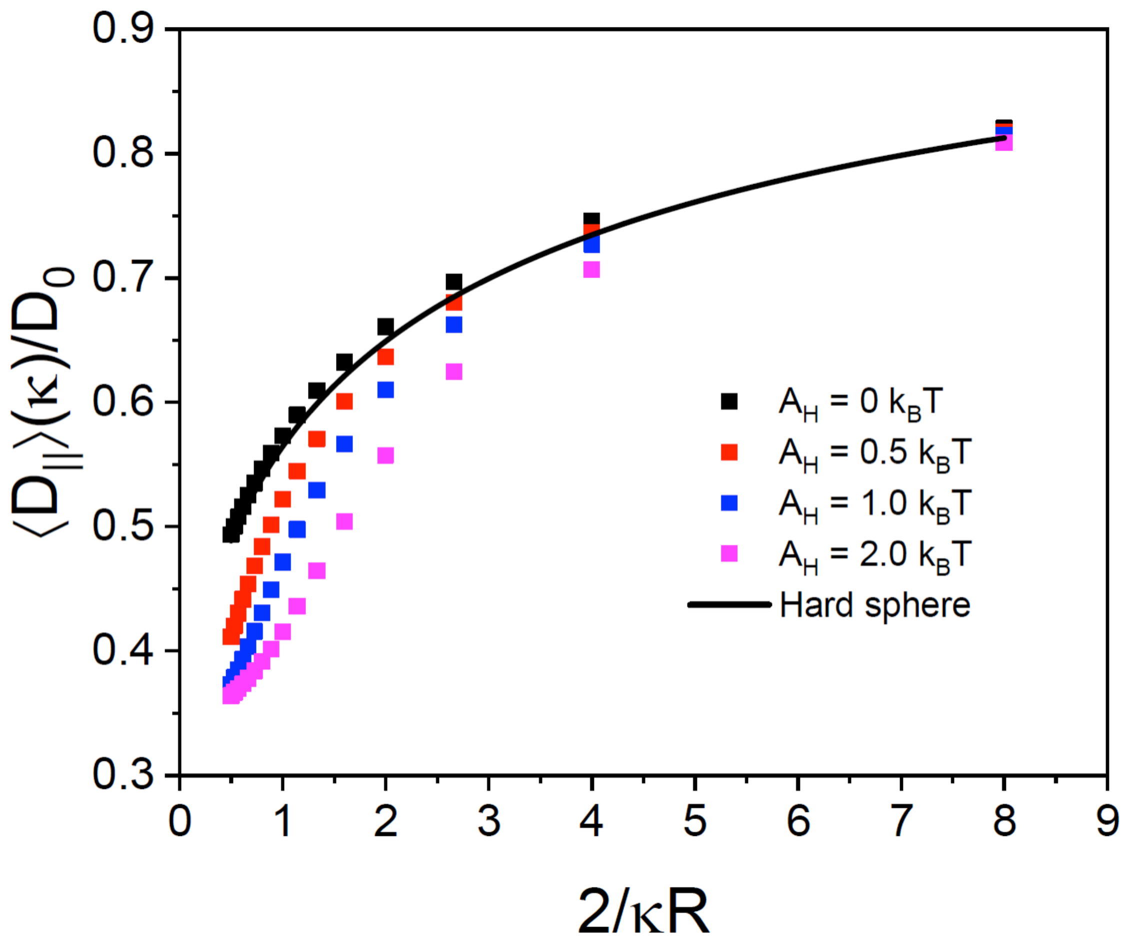
Model calculation: static interaction

$$\Phi(z) = \Phi_{vdW}(z) + \Phi_{er}(z) + \Phi_{g}(z)$$

- fixed electrostatics and gravitation, various van der Waals interaction, monodisperse
- R=100 nm, B_{er}=1 k_BT, $\Delta\rho$=1g/mL
- Van der Waals attraction slows near-wall dynamics.



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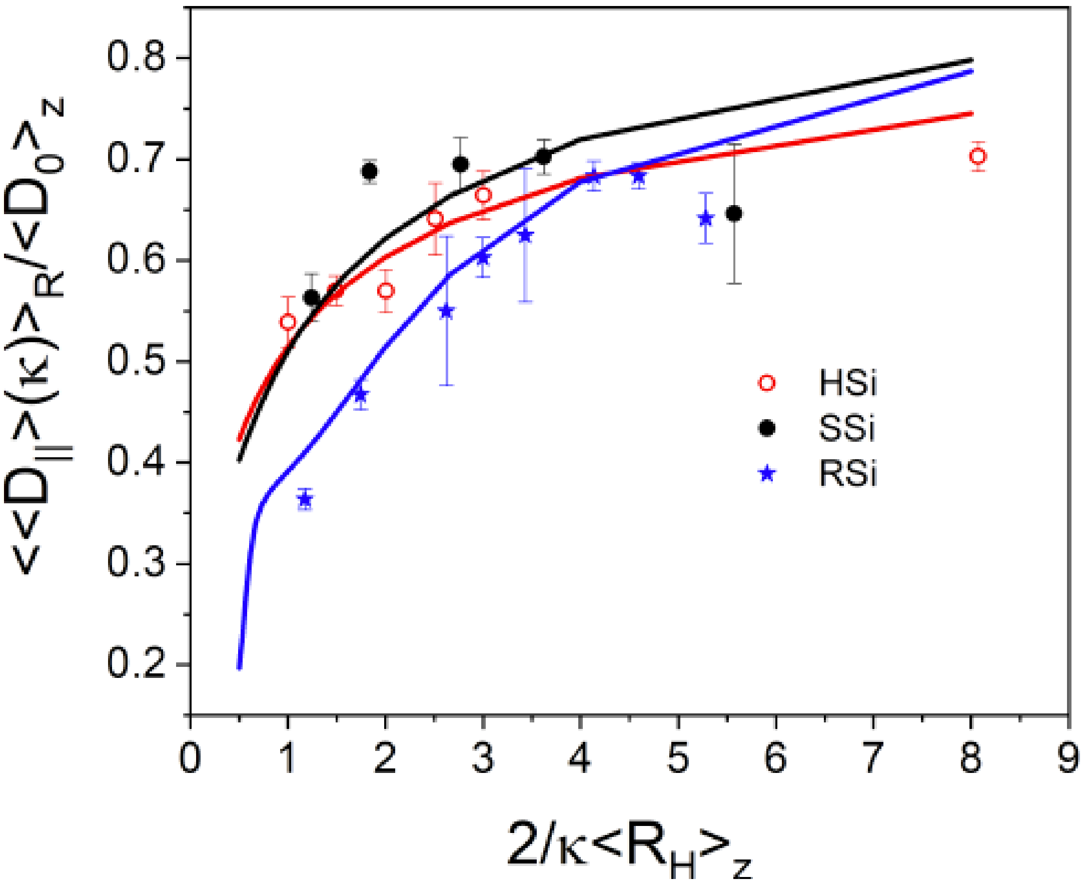
Comparison to experimental data



Particle type	$< R_H >_z$ nm	σ	$\frac{B_{er}}{k_BT}$	$\frac{A_H}{k_BT}$	ϕ_{agg}
SSi	71	0.05	1.5	0.5	5×10^{-3}
HSi	154	0.05	1.0	0.25	0.03
RSi	80	0.05	1.5	2.75	5×10^{-3}

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Conclusion

- Model calculation:
  - Effect of polydispersity less than 10% is negligible
  - Aggregates have a major effect on the data interpretation
- In comparison with experiments
  - For the SSi and HSi system, very good agreement can be obtained by including a small fraction of aggregates and a particle-wall DLVO interaction
  - For the RSi system, at least a five times higher Hamaker constant needs to be taken into account to match the calculated data to the experimental results
-

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