



Correlated dynamics of weakly charged silica spheres at an aqueous interface

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Optical microscopy and multi-particle tracking are used to investigate the spatially correlated motion of weakly charged silica spheres at an air-water interface for different area fraction n occupied by the particles. With the increase of n , the cross-correlation enhances for the Coulomb interaction increases. The Coulomb interaction between colloidal particles should serve as an effective surface viscoelastic role in our system. The correlated motions for various values of n and different particles can be scaled onto a single master curve with the scale factor $\frac{R}{d} \left(\frac{\eta_w d}{\eta_{es,2p}} \right)^{3/2}$, where R and d is particles'

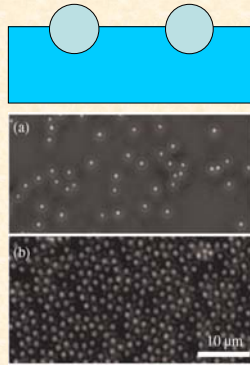
separation and diameter, η_w is the viscosity of the water, and $\eta_{es,2p}$ is the effective surface viscosity whose measurements agree well with that of one-particle surface viscosity $\eta_{es,1p}$.

Motivation

The cross correlation of bulk suspensions is long-ranged and decays with inter-particle distance R as $1/R$. In many real circumstances, particles are not completely free, but spatially confined in some special environments, such as fluid interface and cell membrane. The cross correlation of confined colloidal suspensions are one of the current investigation focus. The cross correlation of hard-spheres at the interface with polymers has been investigated. The effects of the electrostatic interaction between particles at pure interface on the cross correlation are not clear present, which need systematical investigation.

Experiment

We put the silica spheres at the clean air-water interface. All the position and velocity of particles at air-water interface were recorded by a CCD connect to PC. Using homemade software we construct particle trajectories from the consecutive images.



In the experiment, we measure the mean cross-correlated particle motion

$$D_{rr}(r, \tau) = \langle \Delta r_r^i(t, \tau) \Delta r_r^j(t, \tau) \delta(r - R^{i,j}(t)) \rangle_{i \neq j}$$

$$D_{\theta\theta}(r, \tau) = \langle \Delta r_\theta^i(t, \tau) \Delta r_\theta^j(t, \tau) \delta(r - R^{i,j}(t)) \rangle_{i \neq j}$$

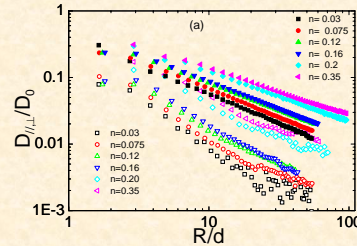
D_{rr} indicates the correlated motion along the line joining the centers of particles, and $D_{\theta\theta}$ represents the correlated motion perpendicular to this line. The τ -independent quantities

$$D_{||} = \langle D_{rr} / \tau \rangle, D_{\perp} = \langle D_{\theta\theta} / \tau \rangle$$

References

- [1] V. Prasad, S. A. Koehler, and Eric R. Weeks, Phys. Rev. Lett., **97**, 176001 (2006).
- [2] T. M. Fischer, P. Dhar and P. Heinig, J. Fluid Mech., **558**, 451 (2006).
- [3] W. Chen and P. Tong, Europhys. Lett., **84**, 28003 (2008).
- [4] M. H. Lee, P. C. Steven, H. R. Daniel, J. S. Kathleen and L. L. Robert, Soft Matter, **7**, 7635 (2011).

Experiment results and data analysis

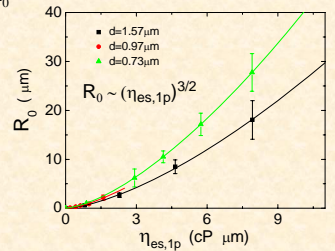
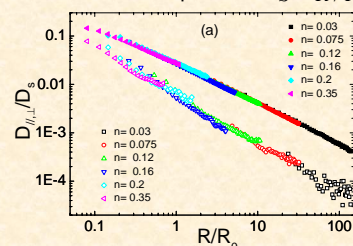


Correlation function $D_{||}$ (solid symbols) and D_{\perp} (open symbols) (scaled by D_0) as a function of inter-particle distance R (scaled by d) with various values of area fraction n . Different symbols represent the data for different area fraction n . The samples are silica $d = 1.57(0.06 \mu\text{m})$.

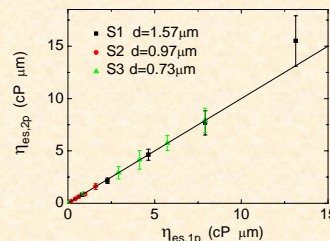
According to Fischer's theory [2], the reverse of self-diffusion coefficient

$$\frac{1}{D_s} = \frac{k^{(0)} \eta_w a}{k_B T} + \frac{k^{(1)} \eta_s}{k_B T} \quad \frac{1}{D_s} = \frac{k^{(1)} \eta_s}{k_B T} = \frac{1}{D_s^s} \frac{k^{(0)} \eta_w a}{k_B T}$$

After scaling the horizontal axis by D_s , we create a master curve with a reduced separation $S = R / R_0$



$$\eta_{es,1p} = \left(\frac{6\pi}{\alpha(1-\beta n - \gamma n^2)} - k^{(0)} \right) \frac{\eta_w a}{k^{(1)}}$$



If we define the scale factor R_0 as $\eta_{es,2p} / \eta_w$ following the definition of Prasad *et al.* [1], we would obtain the relationship

$$\eta_{es,2p} = (\eta_{es,1p})^{3/2}$$

This is not reasonable in physics for their dimensions are non-uniform. Referring to the relationship of R_0 to $\eta_{es,1p}$, we present a new definition of the separation scale factor:

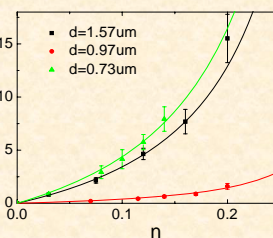
$$R_0 = d \left(\frac{\eta_{es,2p}}{\eta_w d} \right)^{3/2}$$

Using this new definition, the measurements of effective surface viscosity $\eta_{es,2p}$ agree well with $\eta_{es,1p}$ for particles S1, S2 and S3.

Referring to the Vogel-Fulcher law and free volume theory the effective surface viscosity $\eta_{es,2p}$ could be written as:

$$\eta_{es,2p} = \eta_0 \left[\exp \left(\frac{bn}{1-bn} \right) - 1 \right]^{-1}$$

$$b = 2.25$$



samples	d (cP \mu m)	\eta_0 (cP \mu m)
S1 silica	1.57(0.06)	10.18(0.10)
S2 silica	0.97(0.05)	1.15(0.05)
S3 silica	0.73(0.04)	13.01(0.26)