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Near-wall dynamics of spherical colloids: Translational and rotational diffusion

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In this work, we employ Evanescent Wave Dynamic Light Scattering (EWDLS) to infer information on diffusion in a dilute suspension of Brownian particles bounded by hard planar wall, and support it by a full theoretical analysis, followed by Brownian Dynamics simulations. EWDLS is an experimental technique giving an insight into near-wall diffusion of submicron-sized particles. In such experiments, the light is scattered on colloidal particles diffusing in the presence of a wall and the scattered light intensity time autocorrelation function is measured in order to trace near-wall dynamics of a suspension. The evanescent wave which enters the sample decays as $exp(-kz/2)$ with the distance z from the wall, and restricts the scattering volume to a region characterized by the penetration depth k^{-1}. Compared to standard Dynamic Light Scattering technique, EWDLS has some inherent features, including the effects of non-uniform illumination of the sample, and the hindrance of particles' diffusivity near a hard boundary. As hydrodynamic interactions with the wall have a pronounced effect on the dynamics of the particles on top of their direct and mutual hydrodynamic interactions, it has a reflection in the structure of scattered electric field correlation function, rendering the interpretation of experimental data much more involved.

In a dilute suspension of spherical particles, the system is fully characterised by one-particle properties. Using the Smoluchowski equation formalism, we provide a suitable theoretical framework for the derivation of exact theoretical expression for the initial decay rate (first cumulant) of the measured correlation function and relate it to the diffusive properties of the system. By using optically anisotropic spherical colloids in EWDLS experiments, and employing measurements on differently polarized light (VV- and VH-geometry) we are able to trace both the translational and rotational diffusion of spherical colloids near a wall. Moreover, our setup allows independent variation of the components of the scattering vector parallel and perpendicular to the wall, hence allowing to extract the diffusion coefficients of particles in these directions and to investigate the anisotropy of their motion in more detail.

We also present a comparison of experiments, theoretical results, and Brownian Dynamic simulations. In order to interpret the measured data, we suggest a new way of analysis to account for the long-time decay of measured correlation functions. Applying this procedure to the data, we find very good agreement between theoretical predictions and experimental results, free of adjustable parameters. This in turn gives us the possibility to measure the averaged diffusion coefficients, either translational, or rotational, and opens a new way of determining the effects of confinement on colloidal dynamics experimentally. We also develop some practical tools for experimentalists, providing them with a convenient way to calculate the first cumulant, using the expressions we have developed. The results can be directly compared with the measured initial decay rates. EWDLS seems to be the first experimental technique available to probe spatially-resolved rotational diffusion of nanoparticles in the vicinity of the wall.

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