Molecular Dynamics Simulations of Nanoparticle Interactions with a Planar Wall: Does Shape Matter?

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Abstract. We investigate the hydrodynamic interactions of spherical colloidal nano particles and nano tetrahedra near a planar wall by means of molecular dynamics (MD) simulations of rigid particles within an all-atom solvent. For both spherical and nano-tetrahedral particles, we find that the parallel and perpendicular components of the local diffusion coefficient and viscosity, show good agreement with hydrodynamic theory of Faxén and Brenner. This provides further evidence that low perturbations from sphericality of a nanoparticle's shape has little influence on its local diffusive behaviour, and that for this particular case, the continuum theory fluid dynamics is valid even down to molecular scales.

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1 Introduction

The diffusion of suspended particles in liquids is one of the most fundamental transport processes in physical chemistry, with many applications in material science, chemical engineering, and biology. Indeed, such diffusion processes may significantly affect the properties of the liquid suspension; for instance, it is known that particle diffusion sets the rate-limiting step to many chemical reactions in liquids [1], and that the addition of

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particles to liquids leads to an increase of the viscosity, as predicted by Einstein nearly a century ago [2]. The diffusion of a suspended particle within a liquid is inversely related to the dynamic viscosity of the liquid, according to the Fluctuation-Dissipation-Theorem (FDT) [3], as combined with Stoke's law for the drag experienced by a colloidal particle within a fluid solvent [4]. The mathematical expressions associated with these two conceptual pillars are typically derived in free-space, where long-range hydrodynamic correlations can develop without hindrance. However, in the presence of solid walls (confined flows), or other colloidal particles (dense suspensions), it is known that both particle diffusivity and liquid viscosity acquire significant corrections, due to the distortions experienced by hydrodynamic correlations as compared to the ideal case of a single particle within an infinite fluid domain. Such finite-size and finite-concentration effects are paramount to most practical applications, typically involving colloidal suspensions of nano-particles of assorted shapes [5, 6]. In this paper, we shall focus on finite-size effects in confined nanofluids. Several experimental [7–11] as well as theoretical [12] studies have focussed on these effects for colloidal particles. More specifically, we compute the local diffusion coefficients of a suspended nanoparticle as a function of its distance from a planar wall, along both parallel and perpendicular directions to the wall. To this purpose, extensive molecular dynamics (MD) simulations are performed, and compared against the analytical results, as provided by Faxén's and Brenner's continuum hydrodynamics theories [13–15]. Two basic shapes are explored, spherical and tetrahedral, the latter being of special interest to the growth of optical crystals through self-assembly of silicon nano-particles [16, 17].

Deviations from continuum hydrodynamics in the vicinity of the wall have made the object of basic molecular dynamics investigations in the past. Vergeles et al. performed molecular dynamics simulations of a single sphere approaching a planar wall at constant velocity u [18]. These authors confirmed the validity of hydrodynamics sufficiently away from the wall, and showed that the near-wall divergence disappears in the atomistic treatment due to a depletion of the fluid layer. More recently, Challa and van Swol [19], alluded to the importance of solvation forces, namely the conservative forces experienced by the sphere independently of its speed.

Since we aim at a realistic model of a nanoparticle immersed in a liquid and ask for the validity of Faxén's and Brenner's hydrodynamic theories in this case, our simulation setup will differ from the one used in the aforementioned works in several aspects. i) Instead of assigning a constant velocity to the nanoparticle, requiring the assumption that its mass is infinite, we track its thermal equilibrium fluctuating motion and apply statistical mechanical theory (Green-Kubo relations) and the Stokes-Einstein relation to compute transport coefficients from velocity autocorrelation functions (VACFs). ii) As a consequence, our nanoparticle is not just small in terms of length scales, but in addition, it will not have infinite mass. On the other hand, we aim at approximately Brownian behaviour, i.e. an exponentially decaying VACF. For this, we require a mass density for the nanoparticle which is considerably larger than the fluid density. It will turn out that Brownian behaviour is already sufficiently achieved for a mass density ratio of 10. iii) Investigating