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Breakdown of the Stokes-Einstein relation for nanoparticles

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The Stokes-Einstein (SE) relation [1,2] is one of the most fundamental equations for diffusive transport of particles dissolved in fluid media. While derived and verified on the macroscale with large particles like gamboge granules [3], experiments show the failure of the application on the nanoscale for small molecules such as sucrose and urea [4]. This raises the question, which conditions need to be satisfied for the SE relation to hold. While one central aspect is the mass ratio of the particle to the solute molecules, surface interactions and solvent ordering might play important roles, leading to a critical particle size [5]. On the nanoscale, molecular dynamics (MD) simulations gained popularity to tackle such issues, even though further issues arise. Most prominent are finite system size effects [6] and the correct calculation of transport coefficients using Green-Kubo relations [7,8].

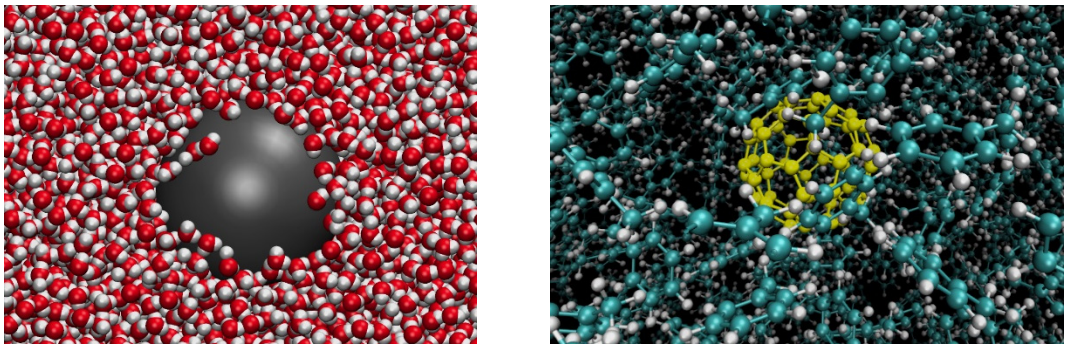

Figure 1: Snapshots of two simulated systems: (left) partially realistic system of a Lennard-Jones sphere in water, (right) full realistic system of a fullerene C60 in toluene.

We run extensive MD simulations of all-atom, coarse-grained and toy model systems (Fig. 1) to tackle physical aspects like the mass ratio and simulation aspects like the system size systematically. This allows us to estimate the range of applicability of the SE relation to systems of dissolved nanoparticles and the requirements for accurate simulation and analysis of transport coefficients like the diffusion and friction coefficient over a wide set of parameters [9].

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