The Role of Water in the Electrophoretic Mobility of Hydrophobic Objects

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It is well established that hydrophobicity of an interface, droplet or a particle can be modulated by an external electric field. However, the provided explanations why these essentially uncharged objects like oil droplets exhibit a directional specific movement in the presence of electric fields remain controversial and continuously challenged. Here we study the static and the dynamic behaviour of a model hydrophobic object (Lennard-Jones particle) in water (SPC/E model), by performing extensive molecular dynamics simulations in the absence and the presence of electric fields using the GROMACS software package. We first combine simulations with the linear response theory to show that shear viscosity of water increases with the strength of the electric field. Furthermore, we identify a novel relaxation process in the water network. We then show that both the diffusion and the friction coefficient of the particle can be calculated independently, which allows us to demonstrate the validity of the Stokes-Einstein relation at the nanometer length scale, subject to clearly identified constraints on the mass and the size of the spherical particle, as well as the size of the system. After establishing a sound simulation protocol, we show that the electric field evokes on an average asymmetric distribution of the water molecules around the Lennard-Jones particle. This acts as a steady state density gradient, inducing a phoretic motion of the hydrophobic object towards the region of higher concentration of water. We interpret our data on a basis of Derjaguin theory for diffusiophoresis which predicts the steady state velocity of a colloidal particle as a function of the first moment of the concentration gradient, the effective hydrodynamic radius of the particle, and the shear viscosity of the solvent. This theoretically predicted driving velocity agrees exceptionally well with the results of the simulations.