Effective temperatures and the breakdown of the Stokes-Einstein relation for particle suspensions

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The short- and long-time breakdown of the classical Stokes-Einstein relation for colloidal suspensions at arbitrary volume fractions is explained here by examining the role that confinement and attractive interactions play in the intra- and inter-cage dynamics executed by the colloidal particles. We show that the measured short-time diffusion coefficient is larger than the one predicted by the classical Stokes-Einstein relation due to a non-equilibrated energy transfer between kinetic and configuration degrees of freedom. This transfer can be incorporated in an effective kinetic temperature that is higher than the temperature of the heat bath. We propose a Generalized Stokes-Einstein relation (GSER) in which the effective temperature replaces the temperature of the heat bath [1]. This relation then allows to obtain the diffusion coefficient once the viscosity and the effective temperature are known. On the other hand, the temporary cluster formation induced by confinement and attractive interactions of hydrodynamic nature, makes the long-time diffusion coefficient to be smaller than the corresponding one obtained from the classical Stokes-Einstein relation. Then, the use of the GSER allows to obtain an effective temperature that is smaller than the temperature of the heat bath. Additionally, we provide a simple expression based on a differential effective medium theory (DEMT) that allows to calculate the diffusion coefficient at short and long times. Comparison of our results with experiments and simulations for suspensions of hard and porous spheres shows an excellent agreement in all cases.

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