Translational and rotational diffusion coefficients in nanofluids from polarized dynamic light scattering

Francisco E. Bioucas*[1], Cornelia Damm[2], Wolfgang Peukert[2], Michael H. Rausch[1], Thomas M. Koller[1], Cédric Giraudet[1], Andreas P. Fröba[1]

[1]Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany
[2]Institute of Particle Technology (LFG), FAU, Erlangen, Germany
*francisco.bioucas@fau.de

Nanofluids representing nanometer-sized solid particles dispersed in liquids are of interest in many fields of process and energy engineering, e.g., heat transfer, catalysis, and the design of functionalized materials [1]. The physical, chemical, optical, and electronic properties of nanofluids are strongly driven by the size, shape, surface potential, and concentration of the nanoparticles. For the analysis of diffusive processes in nanofluids allowing access to, e.g., particle size and its distribution, dynamic light scattering (DLS) is the state-of-the-art technique. It is based on the analysis of microscopic fluctuations originating from the random thermal movement of particles in the continuous liquid phase at macroscopic thermodynamic equilibrium. For anisotropic particles or particle aggregates, besides translational diffusion also rotational diffusion occurs. To obtain the sum of the orientation-averaged translational (D_T) and rotational (D_R) diffusivities by depolarized DLS [2], a homodyne detection scheme is usually applied which can hardly be fulfilled in the experimental realization. Furthermore, the experiments are restricted to limited ranges for temperature, particle concentration, and viscosity.

The objective of this work is to show the applicability of polarized DLS for the simultaneous study of translational and rotational diffusion in nanofluids. For this, the polarized component of the scattered light modulated by the random motion of anisotropic particles was studied to simultaneously resolve D_R and D_T. To investigate opaque nanofluids reliably, a DLS setup was established where sufficiently low laser powers are applied and the scattered light is analyzed in reflection direction. By ensuring a heterodyne detection scheme where much stronger reference light is superimposed to the scattered light, the uncertainties of the measured diffusivities could be reduced. As model system, water-based nanofluids containing stabilized gold nanorods with a volume fraction of 10^{-5} were investigated from 271 to 323 K. To account for variations in the particle concentration and in the viscosity of the liquid phase ranging between 0.5 and 9.0 mPa·s, volume fractions of the gold nanorods from 10^{-5} down to 3.7×10^{-6} and water-glycerol mixtures with glycerol volume fractions up to 0.67 were studied at 303 K.

In agreement with theory [2], the measured correlation functions of the polarized component of the scattered light intensity contain two superimposed exponentials which appear on different time scales. The slower mode is associated with the isotropic component of the scattered light, i.e. with the translational diffusivity. The faster mode is connected to the combined translational and rotational motion of the gold nanorods. On average, the orientation-averaged D_T and D_R values measured by DLS at 303 K are $(8.9 \pm 0.7)\times10^{-12}$ m^2·s^{-1} and $(7.9 \pm 3.4)\times10^{3}$ s^{-1}. Compared to these values, the D_T and D_R data predicted by the stick hydrodynamic theory [3] based on results for length and aspect ratio of the gold nanorods analyzed from scanning electron micrographs agree with the experimental data. For D_T and D_R, temperature-dependent behaviors described by a modified Andrade-equation and decreasing trends with decreasing particle volume fractions below 4×10^{-6} were found. For all measurements performed at a particle volume fraction of 10^{-5} in connection with the water-based systems as a function of temperature and the water-glycerol-based systems at 303 K, generalized relations between the ratio of the diffusivities to temperature and the dynamic viscosity of the liquid phase were observed. Here, a weaker viscosity-dependent trend is given for D_R than for D_T.

References

[1] K. N. Shukla, T. M. Koller, M. H. Rausch, A. P. Fröba: *Effective thermal conductivity of nanofluids – a new model taking into consideration Brownian motion*. Int. J. Heat Mass Transfer **99**, 532–540 (2016).

[2] A. Levin, E. Shmytkova, B. Khletsov: *Multipolarization dynamic light scattering of nonspherical nanoparticles in solution*. J. Phys. Chem. C **121**, 3070–3077 (2017).

[3] J. M. Tsay, S. Doose; S. Weiss: *Rotational and translational diffusion of peptide-coated CdSe/CdS/ZnS nanorods studied by fluorescence correlation spectroscopy*. J. Am. Chem. Soc. **128**, 1639–1647 (2006).