Mobility of interacting inorganic nanoparticles

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Abstract. The mobility of the 110 nm-Fe₂O₃ particles in a viscous sucrose solution depends on the concentration of the nanoparticles. When the average particle–particle nearest neighbor distance $\langle r \rangle$ is less than 250 nm, the particle interaction slows down their mobility. When $\langle r \rangle$ is more than 170 nm, the small mobility of nanoparticles does not depend on their concentration. The critical distance is approximately equal to $2R_h = 260$ nm, where R_h is the hydrodynamic radius, determined by the dynamic light scattering (DLS) method.

Key words: dynamic light scattering • hematite nanoparticles • mobility • Mössbauer spectroscopy • viscosity

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Introduction

The speed of life processes at the cellular level exceeds by a few orders of magnitude in its value expected from the theoretical calculation, where classically evaluated efficiency of the diffusional transport of the macromolecules in cytoplasm is applied. This problem has been partly, at least formally, solved in the last decade by introducing the concept of the ‘local’ or ‘microscopic’ viscosity η , which now becomes the function of the radius of the migrating particles [1]. In fact, we have already shown that submicrometer Fe₂O₃ particles in an apparently solid matrix of gelatin exhibit robust Brownian motion [2–4]. Thus, the microscopic viscosity depends on the ratio of the sizes of migrating particles and the surrounding objects. In particular, if the diffusing particles are smaller than the structural frameworks, for example, amides vs. organelles in cells or Fe₂O₃ particles vs. collagen chains, for the bound diffusion estimation the local viscosity of the medium should be applied rather than the macroscopic viscosity of the system. In the opposite case, we deal with the classical case, described by the Navier–Stokes equations.

In this work we attempt to elucidate the intermediate case, which is the interaction of the diffusing nanoparticles with objects of the same size, that is, with themselves suspended in a viscous sucrose solution.

Experiment

We used Fe_2O_3 particles of size approximately $d = 110$ nm (red pigment Bayfrenx 120), where d is the diameter, suspended in a 60 wt% solution of sucrose to water. The viscosity of sucrose at different concentrations and temperatures is well known [5]. In particular, the viscosity of a 60% solution of sucrose at 20°C is very close to the viscosity of mammal cytoplasm (~ 50 mPa·s) [6]. The studied specimens were prepared by grinding Fe_2O_3 powder with the sucrose solution in an agate mortar and subsequently washing in the ultrasonic cleaner for 20 min at an elevated temperature (40°C). After this procedure, still some sedimentation of the Fe_2O_3 was observed but the remaining solution was stable for many days, at least at room temperature. For the Mössbauer study, the liquid was filled in a tight plastic container. The actual Fe_2O_3 concentration was determined from the total area of the spectrum, compared with the spectrum of a known powder absorber thickness, prepared in a dry form. The selected spectra are shown in Fig. 1 (left), and the distribution of the ‘isomer shift’ is identical to the distribution of the nanoparticle velocities [3] in Fig. 1 (right).

The hydrodynamic radius of Fe_2O_3 nanoparticles, R_h , was determined by an independent experiment, using the dynamic light scattering (DLS) method. This parameter refers to how a particle diffuses within a fluid; thus, the radius obtained by this technique is the radius of a sphere that has the same translational diffusion coefficient as the particle. This coefficient depends on the total size of the particle, and thus on any additional sphere attached to the particle. DLS analyzes the speed at which the particles diffuse, and the speed is measured by the detection of the rate at which the intensity of the scattered light fluctuates. At the end, the

Fig. 1. Selected Mössbauer spectra of different Fe_2O_3 nanoparticle weighted concentrations s (left) and velocity distribution of the nanoparticles at corresponding weighted concentrations, s (right).

Fig. 2. DLS distribution profiles of the hydrodynamic diameters of Fe_2O_3 nanoparticles. The solid line shows an average value.

detected intensity of fluctuations is correlated with itself at particular points of time.

A Malvern Nano ZS light-scattering apparatus (Malvern Instruments Ltd.) was used for measurements, which were performed at 20°C . The samples of solutions were illuminated by a 633-nm laser, and the intensity of light scattered at an angle of 173° was measured by an avalanche photodiode. The final value of the nanoparticle size distribution, $R_h = 120(10)$ nm, was calculated by the standard algorithms implemented in the software. Typical spectra obtained during DLS measurements are presented in Fig. 2.

Results and discussion

The broadening of the resonant absorption lines, defined as the standard deviation of distribution of the central position of the sextets, is just the distribution of the average velocity of the nanoparticle, in the life time, τ , of the ^{57}Fe in a 14.4 keV excited state, $\tau = 141$ ns. From the Einstein theory of the Brownian motion, this distribution should have a Gaussian form with the standard deviation σ_v parameter, determined by the radius of the particle, R ; viscosity of the liquid, η ; and temperature, T .

$$(1) \quad R = \frac{kT}{3\pi\eta\sigma_v^2}$$

From the visual inspection of Fig. 1, it appears obvious that the velocity distribution depends on the nanoparticle weight concentration, s . This parameter may be correlated with the number of nanoparticles in a unit volume, which is regular concentration, ρ , by the following relationship: $\rho [\mu\text{m}^{-3}] = 353.2 \times s$. This calculation does not include the volume of the particles, because we deal with $s < 0.1$, and the volume of the nanoparticles in the colloid is in the range of a few percent, only.

Next, we intend to describe the particle–particle interactions, rather in terms of their nearest neighbor distances, than their concentration. This problem was solved by Hertz in 1909 [7], but here we present a simple derivation.

The average number of neighbors, λ , in the volume dV at the distance r from the nearest neighbor is:

$$(2) \quad \lambda = \rho dV = 4\pi\rho r^2 dr$$

The probability that in this volume is only one particle is given by the Poisson distribution:

$$(3) \quad p(k, \lambda) = \frac{\lambda^k e^{-\lambda}}{k!}$$

$$(4) \quad p(k=1, \lambda, r) = 4\pi r^2 \rho e^{-4\pi r^2 \rho dr} dr \approx 4\pi\rho r^2 dr$$

Due to the requirement that this particle be the nearest neighbor, this probability must be multiplied by the probability that at a distance less than r , there is no particle:

$$(5) \quad p(k=0, \lambda, r < r_{k=1}) = e^{-\frac{4}{3}\pi\rho r^3}$$

Finally, the probability of finding the nearest neighbor at distance r is:

$$(6) \quad p(r) = P(0, \lambda)p(1, \lambda) = 4\pi r^2 \rho e^{-\frac{4}{3}\pi\rho r^3}$$

The most probable nearest neighbor distance, r_p , is:

$$(7) \quad r_p = \frac{1}{\sqrt[3]{2\pi\rho}}$$

The average nearest neighbor distance, $\langle r \rangle$, is:

$$(8) \quad \langle r \rangle = \int_0^\infty 4\pi r^3 \rho e^{-\frac{4}{3}\pi\rho r^3} dr$$

This integral is expressed by the Euler function $\Gamma(1/3)$, and finally, one obtains $\langle r \rangle = 1.022 r_p$.

For example, for $\rho = 1 \mu\text{m}^{-3}$ (one particle per $1 \mu\text{m}^3$) $r_p = 0.54 \mu\text{m} \approx \langle r \rangle$.

The value of σ_v as a function of r_p is shown in Fig. 3. For a low concentration, $s < 0.08$, and $r_p > 200 \text{ nm}$, σ_v stabilizes at $\sim 0.8 \text{ mm/s}$. By inserting this value in Eq. (1) one obtains the value of the ‘effective’ radius of the mobile particles, $R = 105 \text{ nm}$, nearly twice more than the radius of Fe_2O_3 nanoparticles. This value should be compared with the hydrodynamic radius, $R_h = 121(10) \text{ nm}$, obtained from the DLS measurements. This region is assigned to the classical Brownian motion range, where the chaotic movement of particles is not correlated – the particles ‘do not see each other’.

The standard deviation of the velocity distribution experienced by hematite nanoparticles as the function of the most probable nearest neighbor distance is displayed in Fig. 3. In very concentrated suspensions, $s > 0.1$, the nanoparticles are still moveable, but their mobility is rather small, $\sigma_v \sim 0.1 \text{ mm/s}$, independent of s . We postulate that in this region of concentration, sucrose solution acts as a ‘grease’, which reduces the solid state friction, the friction that freezes the mobility of nanoparticles in powder pellets.

The most intriguing case is that of $170 \text{ nm} < r_p < 200 \text{ nm}$. If the interparticle distances are comparable with $2R_h$, the particles interact decreasing their mobility. Phenomenologically, it may be described as the increase of the local viscosity.

Fig. 3. The standard deviation of the velocity distribution experiences by hematite nanoparticles σ_v expressed as the function of the most probable nearest neighbor distance r_p .

Thus, the problem of local vs. macroscopic viscosity may be formulated as follows. If the diffusing particles are much bigger than the medium-forming objects, the macroscopic viscosity is a good parameter for the description of the particle mobility. If the diffusing particles are much smaller than the objects forming the soft network of the medium, the local (or microscopic) viscosity should be applied. In the intermediate case, if particles diffuse in the medium containing particles of comparable sizes, the viscosity becomes dependent on the concentration of the particles. The critical concentration for transition from macroscopic to microscopic viscosity corresponds to the interparticle distance equal to $2R_h$. The value of R_h is determined by the molecular interactions between solvent and particles.

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