



Historical perspective

Motion of nanoprobes in complex liquids within the framework of the length-scale dependent viscosity model



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ABSTRACT

This paper deals with the recent phenomenological model of the motion of nanoscopic objects (colloidal particles, proteins, nanoparticles, molecules) in complex liquids. We analysed motion in polymer, micellar, colloidal and protein solutions and the cytoplasm of living cells using the length-scale dependent viscosity model. Viscosity monotonically approaches macroscopic viscosity as the size of the object increases and thus gives a single, coherent picture of motion at the nano and macro scale. The model includes interparticle interactions (solvent-solute), temperature and the internal structure of a complex liquid. The depletion layer ubiquitously occurring in complex liquids is also incorporated into the model. We also discuss the biological aspects of crowding in terms of the length-scale dependent viscosity model.

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1. Introduction

Complex soft matter systems are ubiquitous in nature. Their hierarchical structure spans over several orders of magnitude of length-scale starting from nanometres up to tens of micrometres. The most distinctive example of a multi-length-scale hierarchical system is the cytoplasm of a living eukaryotic cell. In cytoplasm large supramolecular polymers such as actin filaments, reaching the micrometre length-

scale, are immersed in a colloidal solution of far smaller proteins with sizes in the range of nanometres. Understanding the rules governing the motion of nano-probes in complex liquids is key to the correct description of out-of-equilibria processes taking part in cell metabolism [1] or in protein crystallization [2]. A description of the motion of nano-probes in both natural (the interior of living cells) and synthetic (polymers, colloids) complex systems, however, eludes out of the framework of simple diffusive motion described by the Stokes–Sutherland–Einstein (SSE) equation [3,4]: $D = kT / \zeta_m$ with ζ_m being the hydrodynamic drag defined by the Stokes relation $\zeta_m = 6\pi\eta_m r_p$. In this equation η denotes the viscosity of the solution and the index “m” relates to its macroscopic value. r_p is the hydrodynamic radius of the particle undergoing diffusive motion. The SSE equation is valid in simple liquids where the probe particles are: i) much bigger than the solvent

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particles, and *ii*) highly diluted. Difficulties in the use of the SSE equation arise when the hydrodynamic radius of the probe particle r_p becomes comparable to, or smaller than the hydrodynamic radius of the solvent/co-solvent particles R_h . In complex liquids R_h is often in the range of tens of nanometres. For nano-probes, whose $r_p \leq R_h$ the diffusion coefficient often satisfies the inequality $D \gg kT/\zeta_m$. On this basis one would suggest that the SSE equation is not valid in a complex liquid.

A variety of models have been proposed to explain the deviation from the SSE equation for nanoscopic particles undergoing diffusion in complex liquids. The models include those based on the obstruction effect [5–8], on hydrodynamic theories [9–16], on the free volume theory [17–23], and on anomalous diffusion [24,25]. The motion of bigger probes (r_p in the range from fractions to several micrometres), is usually described in terms of microrheology [26,27]. All the above models are widely used and have been reviewed [24–28], and will not be discussed in too much detail in this paper.

The main focus of this review is the recently proposed model of length-scale dependent viscosity [29,30], that describes the motion of nano-probes in complex liquids. A strong advantage of this model is that it can be applied to many types of complex liquids including polymer [29–33], micellar [30,34], or colloidal solutions [2], or the cytoplasm of mammalian [30,35] or bacterial [35–38] cells.

The article is organized as follows: in Section 2 we discuss the length-scale dependent viscosity model. In Section 3, we describe how the length-scale dependent viscosity model depends on the internal structure of a complex liquid. Next (in Section 4) we discuss the influence of temperature on the motion in complex liquids. We also discuss the influence of interparticle interactions on motion in the complex liquids. The influence of the depletion interactions on motion of a probe particle and its relation to the anomalous diffusion model is described in Section 5. In Section 6 we discuss the biological aspects of crowding in terms of the model. Our conclusions are given in Section 7.

2. The model

The SSE equation is classified as a fluctuation–dissipation (FD) relation [39,40]. According to the fluctuation–dissipation theorem the diffusion coefficient D is inversely proportional to the friction ζ experienced by a particle during motion [3,4]. One would expect transport coefficients such as diffusion coefficient D , electrophoretic mobility μ , and sedimentation coefficient s connected in complex liquids according to the following relation:

$$\frac{D_0}{D} = \frac{\mu_0}{\mu} = \frac{s_0}{s} = \frac{\zeta}{\zeta_0} = \frac{\eta_m}{\eta_0}, \quad (1)$$

where D , μ , and s , ζ , η_m relate to values measured in a complex liquid. The values of D_0 , μ_0 , s_0 , and ζ_0 correspond to the values measured in pure solvent (assuming infinite dilution of the probe particles). η_0 denotes the solvent viscosity. In 1952, however, Schachman and Harrington [41] observed that small and large probes sedimenting in DNA solutions exhibited sedimentation coefficients significantly different from those expected by the use of Eq. (1). This result was the first experimental evidence that the relation (1) is violated in complex liquids. Later experiments confirmed Schachman's and Harrington's observation in other complex systems. Laurent et al. [42] studied the sedimentation of bovine serum albumin in solutions of hyaluronic acid while Chrambach and Rodbard [43,44] used capillary electrophoresis to investigate the motion of various proteins and dyes in polyacrylamide gel. In both examples the mobility of nano-probes depended exponentially on the concentration of crowding agents constituting the complex liquid and on the probe size. Odijk [45] summarized the experimental papers concerning diffusion [46–49], sedimentation [7,41,50] and electrophoresis [43,44,51,52] in polymer systems.

In the above mentioned examples a clear dependence of the relative transport coefficients on the size of the probe particles was observed. A

theoretical description of the length-scale dependent motion of nanoscopic objects in polymer solutions was recently proposed by Cai et al. [53]. They proposed three different regimes for particle diffusion in polymer solutions. Transitions between these regimes are not continuous. The regimes depend on the relation between the diameter of the probe particle d and characteristic length-scales in the polymer network. The first length-scale ξ is the distance between a monomer of one chain and the nearest monomer of another chain. ξ is defined as: $\xi = R_g(c/c^*)^{-\beta}$ where c and c^* is the polymer concentration and the polymer overlap concentration, respectively, R_g is the radius of gyration and $\beta = \nu/(3\nu - 1)$, $\nu = 0.588$ for an athermal polymer and $\nu = 0.5$ for a polymer under θ -conditions. The second length-scale L is the distance between entangle points of polymer chains. Both ξ and L depend on the concentration of the polymers. In the first regime where $d < \xi$ the diffusion of the probe particle is still not affected by the polymer mesh. When $\xi < d < L$, in short time scales, the motion of the probe particle is not affected by the presence of polymers. The long-time self-diffusion coefficient is affected by the presence of polymer chains. The probe in motion experiences an effective viscosity that scales with the square of the d/ξ ratio. In the regime where $d > L$ the motion of the probe particle is affected by relaxation of the polymer chains and the probe experiences the macroscopic viscosity of the solution. Cai's approach follows the suggestion of H. Benoît, contained in a book by P.G. de Gennes [15], that a probe with diameter exceeding ξ should experience an effective viscosity that is very similar to the macroscopic viscosity of the polymer solution. From the experiments of Langevin and Rondelez [50], however, we know that this is not the case.

The recent experimental observations of Kohli and co-workers for diffusion in solutions of linear polymers [54] confirm this unusual length-scale dependence. The authors used fluorescence correlation spectroscopy to monitor the diffusion coefficient of gold nanoparticles. They observed that deviations from the SSE equation increase with a decreasing r_p/R_g ratio; where R_g denotes the radius of gyration of the polymer. Before Kohli's work, Holyst et al. [29] had also observed length-scale dependence of the transport properties of complex liquids. Holyst et al. [29] performed fluorescence correlation spectroscopy measurements to monitor the diffusion of fluorescent dyes and fluorescently labelled proteins in poly(ethylene) glycol solutions. They also used capillary electrophoresis to monitor the electrophoretic mobility of the same proteins in polymer matrices as well as in micellar matrices [55] composed of rigid elongated micelles of non-ionic surfactant C₁₂E₆ [56]. Szymanski et al. [55] used the protein charge ladder method [57], where a set of lysozyme regioisomers differing in charge but not in size were dragged through a solution under an external electric field. In both works [29,55] the authors interpreted their data in terms of the effective viscosity, η_{eff} , experienced by the probe in motion; cf. Fig. 1. They showed that although neither $D_0/D \neq \eta_m/\eta_0$ nor $\mu_0/\mu \neq \eta_m/\eta_0$ there was equality between the relative diffusion coefficient and the relative electrophoretic mobility:

$$\frac{\eta_{\text{eff}}}{\eta_0} = \frac{D_0}{D} = \frac{\mu_0}{\mu}. \quad (2)$$

Holyst et al. [29] followed Langevin and Rondelez's [50] observations and proposed an approximate model that describes the effective viscosity experienced by a probe undergoing motion in a complex liquid. They defined a function f such that:

$$\frac{D_0}{D} = f = \frac{\eta_{\text{eff}}}{\eta_0} \quad (3)$$

where

$$\ln(f) \propto \begin{cases} (2r_p/\xi)^a & \text{for } r_p \ll R_g, \\ (R_g/\xi)^a & \text{for } r_p \gg R_g, \end{cases} \quad (4)$$

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