

Three-dimensional Monte Carlo simulations of the dynamics of macromolecular particles in solutions flowing in mesopores

Research Article

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Abstract: Numerical simulations are developed to calculate the dynamic equilibrium probability distribution functions (PDF) for macromolecular rod-like particles suspended in a fluid under hydrodynamic flow inside mesopores. The simulations take into account the effects of Brownian and hydrodynamic forces acting on the particles, as well as diffusive collisions of the particles with the solid surface boundaries. An algorithm is developed for this purpose based on Jeffery's equations for the dynamics of ellipsoidal objects in bulk fluids, and on a mechanism of restitution for the diffusive collisions. The results are presented with a focus on the depletion layer next to two types of solid boundaries, ideally flat and rough. They demonstrate the significance of numerical simulations in 3D compared to previous results based on a 2D approach. In particular, we are able to obtain a complete topography for the PDFs segmented as a hierarchy in the depletion layer.

Keywords: Biophysics • Colloidal suspensions • Numerical simulations.

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1. Introduction

The dynamics and motion of macromolecular particles suspended in fluids flowing in mesopore systems and their diffusive collisions and possible adsorption at solid surfaces are subjects of fundamental interest for physical and biological studies. Several biological and engineering applications involve the flow of a suspension of particles in a fluid. Many researchers have addressed different aspects of the dynamics of particles suspended in a flowing solution [1-5]. This theme also has promising new applications in the context of mesopore nanotechnology.

The analysis of macromolecular motion in a fluid flowing inside mesopores is necessary to understand a variety of complex phenomena, such as the motion of red blood cells and viruses and the motion of suspended nanoparticles in pipe flow, in polymer processing and in composite manufacturing [6].

The dynamic properties under non-equilibrium conditions of suspensions of such macromolecular particles in fluid flow inside mesopores depends on the nanodynamics of diffusive collisions at the solid boundaries. However, a detailed understanding of the nanomechanical nature of the diffusive collisions of macromolecular particles at the solid boundaries of mesopores is still needed. This study concerns the modelling of diffusive collisions of rod-like macromolecular particles in the neighbourhood of the solid surface boundaries of mesopores at the nanoscale. To fix the range of physical dimensions in this work, the mesopore systems are considered to have widths of approximately 10^1 to 10^3 nm. The simulations are, however, quite general.

Our study is focused on the determination of the probability distributions of the positions and the orientations of macromolecular rod-like particles in 3D in the mesopore system under the influence of both

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Brownian and hydrodynamic motion. In particular, we are interested in the study of the equilibrium dynamics under these conditions, and the extent to which the diffusion collisions on the surface boundaries may be important to the equilibrium dynamics.

The orientations of macromolecules at low concentrations in the bulk of a flowing fluid have been studied early by Boeder, who introduced a differential equation (BDE) in a 2D frame [7], taking into account the dynamic effects due to the Brownian and hydrodynamic forces acting on the particles. The BDE governs the variations of the probability distribution function (PDF), $P(\theta)$, of the macromolecules as a function of their orientations θ in the bulk with respect to the direction of the shear flow. Derived in two dimensions for rod-like particles of negligible cross-sectional area, the BDE depends on $\alpha = \dot{\gamma}/D_{\text{rot}}$, the Peclet number, where $\dot{\gamma}$ is the shear rate of flow and D_{rot} is the rotational diffusion coefficient of the macromolecules. The analytical solution of the BDE equation in the bulk has been obtained successfully for a wide range of α [8], where special analytical as well as numerical methods were developed in order to calculate accurately the PDF distributions for arbitrary values of α .

The BDE equation, however, is not sufficient to study the dynamics of macromolecules in the neighbourhood of solid surface boundaries. In the depletion layer, the macromolecules undergo random diffusive collisions at the solid boundary, the detailed nature of which is complex, varying with the topography of the solid boundaries and with the nature of the macromolecular species. The analytical approach is hence severely limited at solid boundaries and does not provide an appropriate treatment for the diffusive collisions. A mechanical restitution model for diffusive collisions on boundaries, due to Brownian and hydrodynamic effects, has hence been developed for this purpose [8-9]. This restitution mechanism is integrated into an appropriate algorithm to evaluate the contributions of diffusive collisions to the PDFs under conditions of global dynamic equilibrium. The ensuing Monte Carlo development has

produced a variety of numerical simulation methods to calculate the PDF distributions for the positions and angular orientations of macromolecular rigid rod-like particles in suspension in a flowing fluid in the depletion layer next to ideally flat solid surfaces. However, these results have been limited to a two dimensional Cartesian model, and despite their utility fail to indicate the extent to which the third degree of freedom modifies the results in real space.

2. Model Algorithm

In this communication, we generalise the algorithm to numerical simulations in three-dimensional Cartesian space, with a view to calculate the PDFs of rod-like macromolecular particles in the vicinity of solid surface boundaries. Furthermore, the boundaries are treated as rough since they are known to be disordered at the nano-scale.

In particular, the mechanical restitution model is generalized to three dimensions, and combined with a fuller implementation of the Jeffery-Bretherton equations which govern the motion of ellipsoidal particles in an unbounded linear flow field [10-11]. It is also assumed that the fluid is Newtonian in the bulk and that the particles are non-sedimenting. Jeffery's equations for the angular velocity of an ellipsoid in a laminar simple shear flow are:

$$\dot{\theta} = \dot{\gamma} \frac{1}{4} \left(\frac{r_e^2 - 1}{r_e^2 + 1} \right) \sin 2\varphi \sin 2\theta \quad (1)$$

$$\dot{\varphi} = -\dot{\gamma} \left(\frac{1}{r_e^2 + 1} \right) (r_e^2 \sin^2 \varphi + \cos^2 \varphi) \quad (2)$$

In these equations, $\dot{\gamma}$ is the shear rate; $r_e = L/d$ (L and d are respectively the length and diameter of the macromolecule) is the aspect ratio of the ellipsoidal particles, φ is defined as the angle of the particle with respect to the flow direction, θ as the vorticity axis, where $\theta = \pi/2$ corresponds to the alignment of the rod like particles normal to the flow direction. It can be

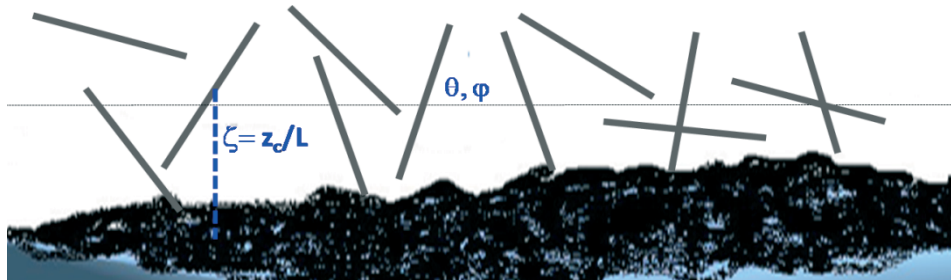


Figure1. Schematic representaion of the rigid-like macromolecular particles in the depelction layer next to the solid surface boundary of one of the two plates which confine the hydrodynamic flow of the fluid

seen that the angular velocity $\dot{\varphi}$ is maximum when the ellipsoid is perpendicular to the flow direction ($\theta = \pi/2$) and minimum when it is along the flow direction ($\varphi = 0$).

We apply Jeffery's equations of the ellipsoidal particles to the motion of rigid rod-like cylindrical forms by extending the length of the macromolecular particles (major axis) versus the diameter (minor axis) so that the aspect ratio r_e increases greatly ($r_e \gg 1$). It is this version which is used in the present model to calculate the PDFs for macromolecular rigid rod-like particles in the neighbourhood of rough solid surface boundaries. Jeffery's differential equations become:

$$\dot{\theta} = \dot{\gamma} \frac{1}{4} \left(\frac{r_e^2 - 1}{r_e^2 + 1} \right) \sin 2\varphi \sin 2\theta \cong \dot{\gamma} \frac{1}{4} \sin 2\varphi \sin 2\theta \quad (3)$$

$$\dot{\varphi} = -\dot{\gamma} \left(\frac{1}{r_e^2 + 1} \right) (r_e^2 \sin^2 \varphi + \cos^2 \varphi) \cong -\dot{\gamma} \sin^2 \varphi \quad (4)$$

Since the detailed nature of the collisions between a macromolecular particle and a given solid surface is quite complex and varies with the topography of the surface and the macromolecular species [12-13], we develop an appropriate simulation algorithm at the solid boundary, regardless of the surface type, based on two coefficients of mechanical restitution [8-9,14-15] for both Brownian and hydrodynamics events. This is done to describe the mechanical restitution of the macromolecules from the solid surface, following a diffusive impact for the Brownian and hydrodynamic events, covering a complete range of possible situations. The merit of this approach is that it applies to a wide range of solid surface boundaries and macromolecular species.

The mesopore is modelled as two infinite solid plates which confine the fluid flow along a Cartesian direction in the x-y plane parallel to the plates. The separation D between the plates along the z axis is considered mesoscopic in its dimensions but somewhat

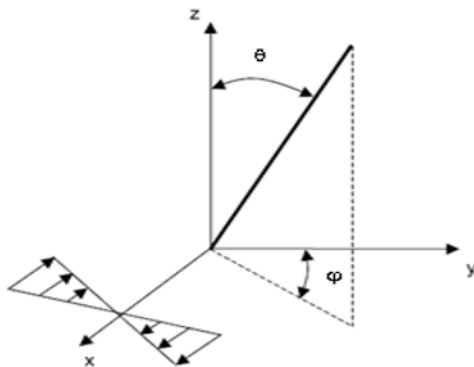


Figure 2. Coordinate system for a rod-like particle centered at the origin and subjected to a simple shear in the xy plane

greater than the length L of the macromolecular rigid rod-like particle, so that $D > L$ ($2L = D$), so that the particles do not collide with the upper and lower solid surface boundaries at the same time. In this case, the particles have the liberty to move dynamically in the flow in translational and rotational movements, in all directions in 3D space, under the combined influence of the Brownian and the hydrodynamic forces and of the diffusive collisions at the solid surface boundary. The behaviour of macromolecules in the confined mesopore channel with $D < L$ is completely different from previous models. In this novel situation, it is necessary to modify the simulation algorithm to account for the collisions on two boundary surfaces and to test the sequence of the collisions that take place and their consequences.

The simulations have quite a general character. To define a particular rigid rod-like particle, consider for example the case of the TMV (Tobacco Mosaic Virus) for which typically the length is $L = 100$ nm and the width is 4 nm, suspended in blood flowing inside a vein of a relatively wide width $d = 8L = 800$ nm. Consider the blood viscosity as $\eta = 3.8$ mPa s [16], which yields a rotational diffusion coefficient $D_{rot} = 3771.5$ s⁻¹ at human body temperatures for the TM virus in blood, using the expression given by Eimer and Pecora [17]. Assuming a linear shear flow for the blood in the vein, the Peclet number has values $\alpha = 1, 10$, and 100 for maximum blood speeds in the middle of the vein of 3.77×10^{-4} ms⁻¹, 3.77×10^{-3} ms⁻¹, and 3.77×10^{-2} ms⁻¹, respectively.

3. Results and Conclusions

The simulation results are presented for the depletion layer over the interval $0 \leq \zeta = z/L \leq 0.5$ next to the solid surface boundary. The simulations are performed for two types of solid surface boundaries, namely ideally flat and rough. Note that in the latter case, $\zeta = 0$ is the reference plane corresponding to the lowest material levels that a particle extremity can touch in diffusive collisions on a rough boundary. For the purpose of the simulations, we consider in particular a Gaussian rough surface.

Fig. 3 shows an example of our results for the normalized PDFs at Peclet number $\alpha = 10$, in 3D space near an ideally flat solid surface boundary, as a function of the accessible orientation angles θ and φ , in the region where the height of the particles' centres of mass with respect to the solid surface boundary is between 0.2 and 0.5 (i.e., $0.2 < \zeta < 0.5$). Fig. 4 shows simulation results for the same conditions as in Fig. 3, but for the case of a Gaussian rough solid surface boundary.

The normalized PDFs in Figs. 3 and 4 are both symmetric about the angle $\theta = \pi/2$, which indicates

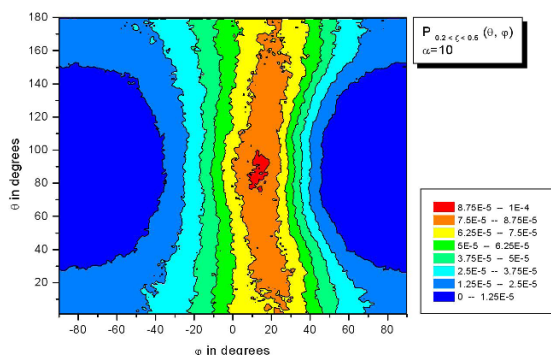


Figure 3. Simulation results for the normalized PDFs, $P_{0.2 < \zeta < 0.5}(\theta, \varphi)$, at Peclet number $\alpha = 10$, in the depletion layer near an ideally flat solid surface boundary.

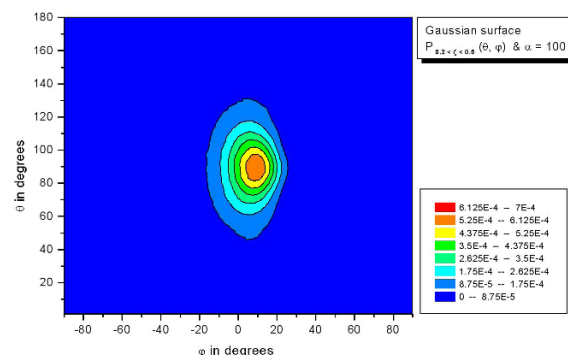


Figure 5. Simulation results for the normalized PDFs, $P_{0.2 < \zeta < 0.5}(\theta, \varphi)$, at relatively high Peclet number ($\alpha = 100$), in the depletion layer near a Gaussian rough solid surface boundary.

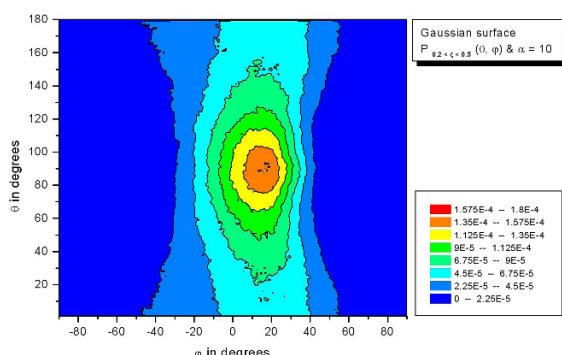


Figure 4. Simulation results as in Fig. 2, near a Gaussian rough solid surface boundary.

that the rod-like particles align themselves mostly in the plane of the shear flow. They also show a broad base distribution that indicates that the rod-like particles rotate in a family of closed orbits around the vorticity axis θ . The existence of such orbits comes from two random forces, the Brownian diffusion movement and the diffusive collisions of the extremities of the rods at the solid surface boundaries. The simulation results indicate that this base broadens out as the mobility region in the depletion layer is changed from $0 < \zeta < 0.2$ to $0.2 < \zeta < 0.5$, due to the wider range of angles accessible to the particles when they move away from the neighbourhood of the solid surface and towards the bulk. This is indeed a measure of the importance of the extra liberty afforded in 3D as compared to 2D [9] with regards to the dynamics and mobility of rod-like macromolecular particles confined in mesopores.

In Fig. 5 we present the simulation results for the normalized PDFs at the relatively high Peclet number $\alpha = 100$, in the depletion layer next to a Gaussian rough

solid surface boundary, in the region where $0.2 < \zeta < 0.5$. Comparison of these results with those in Fig. 4 shows how the high hydrodynamic flow reduces the set of closed orbits around the vorticity axis θ to a significantly narrower base.

4. Conclusion

In this communication, we present a Monte Carlo simulation model for the PDFs accessible to rod-like macromolecular particles under suspension in a flowing fluid inside mesopores. In conclusion our 3D results, presented in this paper, determine a comprehensive cartography of the phase space available for the PDF probability functions in 3D via the interactions of the macromolecular species with the solid boundaries of mesopores. This cartography is important for the development of a theoretical model which is being developed at present to study the adsorption and mobility of macromolecules inside mesopore systems.

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