Polymer 54 (2013) 1555–1566

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Three-dimensional simulations for the dynamics of dilute colloidal suspensions of ellipsoidal-like particles flowing in the bulk and near solid boundaries

Ali Atwi [a,b,*], Antoine Khater [a], Abbas Hijazi [b]

[a] Institut des Molécules et Matériaux du Mans (IMMM, UMR6283), Université du Maine, F-72085 Le Mans, France
[b] Département de Physique, Faculté des Sciences I, Université Libanaise, Hadath-Beirut, Lebanon

ARTICLE INFO

Article history:
Received 23 October 2012
Accepted 14 January 2013
Available online 1 February 2013

Keywords:
Colloidal suspension
Diffusive collision
Numerical simulation

ABSTRACT

Numerical simulations and algorithms are developed to analyze the dynamics of the ellipsoidal-like particles in a three-dimensional spatial frame. In particular we study in this case of an open channel pore for which we calculate the PDF distributions in the bulk and in the depletion layer next to a solid boundary. We develop a theoretical model based in this case on the equations of Jeffrey for the dynamics of solid particles in fluids and the molecular dynamics by mechanical restitution for the diffusive collisions of the particles at the solid boundaries. Simulations are carried out to calculate the *equilibrium* PDF distributions for ellipsoidal molecular particles in suspension in a fluid under hydrodynamic flow. The simulation results for the PDF distributions for the spatial positions and the orientations of ellipsoidal particles are calculated for the bulk liquid and in the depletion layers next to an atomically flat solid surface boundary. They are calculated over several orders of magnitude of the rotational Peclet number, and for variable aspect ratios characteristic of the ellipsoidal particles under study. They demonstrate the importance and significance of modeling in a three-dimensional spatial frame as compared to the simulation results based in the Boeder approach over a two-dimensional spatial frame. In particular we are able to produce a complete topography for the PDF distributions segmented as a hierarchy in the depletion layer, covering a complete range of orientations in 3D space. The simulations permit to calculate, for the colloidal suspension, the nematic order parameter over its tensorial representation, for a variety of forms of ellipsoidal particles selected to correspond to real polymer particles. Our results for the nematic order parameter which may be calculated locally inside the space of the depletion layer are innovating and represent a new input as regards these systems.

1. Introduction

Colloidal suspensions of particles in dilute liquid solutions flowing inside systems of mesopores, are of great importance in industrial processes, such as for example for coatings [1,2] and catalysis [3], and in biological processes, in protein diffusion in membranes [4] and in the circulation of red blood cells and platelets inside the human body [5,6].

There is a great amount of research work which has investigated the dynamics of colloidal particles suspended in a flowing solution at different scales [7–17]. This is motivated by the biological and engineering applications which involve the flow of a suspension of particles in the fluid [18–27].

Colloidal particles have general forms, including the ellipsoidal one, and show rich Brownian dynamics. The origin for current models for the study of the dynamics of colloidal non-spherical particles in a shear flow at low Reynolds numbers is historically the approach proposed some time ago by Jeffery [28]. This pioneering research work investigated the rotational behavior of a single ellipsoidal particle in a Newtonian fluid. Jeffery obtained a set of differential equations for the rotation of an ellipsoid, with analytic solutions depending on the initial conditions. This theoretical approach was confirmed experimentally [29], and has been studied and developed since by several groups and researchers, both theoretically and experimentally.

The overall rotation of the colloidal particles in the bulk liquid is referred to as a Jeffery orbit, which will be discussed in detail in Section 2. In particular Bretherton [30] showed that Jeffery's model

* Corresponding author. Département de Physique, Faculté des Sciences I, Université Libanaise, Hadath-Beirut, Lebanon. Tel.: +961 71 418 960.
E-mail address: atwiali-23@hotmail.com (A. Atwi).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.01.018

could be applied to any axis-symmetric particle, provided that an equivalent aspect ratio was introduced. The equivalent aspect ratio was used to estimate the period of rotation for non-interacting particles far away from solid surface boundaries and from other colloidal particles.

The study of the dynamics of spheroids has been carried out by a number of authors. In particular, the numerical simulation of the dynamics for spheroids moving near a solid surface boundary was carried out [31] using Jeffery's equations. The authors concluded that hydrodynamic forces and torque depend strongly on the spheroid orientation and its position relative to a wall boundary; they reported tumbling of spheroids that resulted in motion toward the wall, since the spheroids were turned around the point closest to the wall. Other simulations using Jeffery's equations [32] calculated the hydrodynamic forces on a fiber near a solid wall using a boundary integral equations model. They showed a lift force effect on the fiber due to the presence of the wall boundary. In addition, they found that the wall retards the fiber motion. Their study confirmed that periodic rotational motion was occurring in unbounded shear flow, and indicated that fibers close to the wall had longer periods between rotations.

In contrast the experimental study of the fiber motion in a planar Couette shear flow apparatus was investigated [9]. These authors introduced an effective shear rate to describe the wall boundary effect and showed a logarithmic decrease of this with increasing distance from the wall. Significantly, the results showed that a fiber centroid situated at a distance larger than its length from the wall verified Jeffery's model. The authors reported that higher aspect ratio fibers rotate faster in the region near the wall than those with lower aspect ratios. Recently new experiments [33] demonstrate the influence of shear close to a solid boundary for different planes parallel to the boundary for the fiber orientations with different fiber aspect ratios and concentrations. They show that as the aspect ratio increases the influence of the shear on the fiber orientations decreases for all the parallel planes. We show in this paper that our recent numerical simulation results confirm this experimentally measured behavior.

In the theoretical research work, cited above, the dynamic effects for colloidal particles due to their stochastic Brownian motion, and their diffusive collisions at the solid wall boundaries, are omitted. It is the purpose of the present work to treat these forces toward a comprehensive analysis of the dynamics of the colloidal particles, in a three-dimensional spatial frame (3D), in the bulk of the flowing fluid as well as near the surrounding solid surface boundaries. To that end we will develop in this paper appropriate algorithm integrating these random forces, in addition to the effect of the hydrodynamic forces at the heart of Jeffery's equations. Based on these algorithms we then carry out numerical simulations to analyze the dynamics of colloidal particles of general ellipsoidal forms, in dilute suspensions, in the bulk of the flowing liquid solution, and next to ideal atomically flat solid surface boundaries.

Our study is focused on the determination of the PDF distributions, under equilibrium dynamics, for the positions and the orientations of macromolecular ellipsoidal particles. In particular we seek to understand the extent to which the Brownian dynamics and the diffusive collisions at the solid surface boundaries may be important to such equilibrium dynamics.

It is well known that it is intractable to study by the only analytical means the dynamics of the molecular particles in dilute colloidal suspensions near solid surfaces, because of the random nature of the Brownian motion and the equally random nature of diffusive collisions. The only viable alternative is to do this by numerical simulations with appropriate algorithms.

In Section 2, we present a technical introduction to the problem and to liquid bulk macromolecular dynamics under Brownian and hydrodynamic motion. Section 3 presents the developed algorithm for diffusive collisions at the solid surface boundaries of open pore channels. Section 4 presents simulation results for the spatial and angular PDF distributions for colloidal suspensions, for a wide range of hydrodynamic conditions and for ellipsoidal particles with variable aspect ratios in bulk solution while Section 5 near the depletion layer. The calculation of the nematic order parameter S in 3D is presented in Section 6. Conclusions are presented in Section 7.

2. Colloidal particle model dynamics in 3D-spatial frames

Particles moving in a suspension tend to orient themselves in the direction of the shearing which can be quantified by fluid velocity gradients. As the macromolecular particle translates with the fluid, it is assumed that the velocity at that particle centroid is equal to the velocity of the fluid at this position. The macromolecular particle is affected by other particles or walls in close proximity. An ellipsoidal particle in simple shear flow spends most of its time aligned almost parallel to the streamlines but as the concentration of macromolecular particles in the suspension increase, the interaction of the particles with other particles and with the boundary solid surface leads to other induced ordinations. Particle–particle interaction has been the subject of study for many researchers [34–37].

Our present research work deals with dilute suspensions of colloidal particles and hence does not consider the interaction effects between the particles; we focus instead on the particle–solid surface boundary interactions.

The orientations of dilute concentrations of macromolecular particles in the bulk of a flowing fluid have been studied early by Boeder who introduced a differential equation (BDE) in a 2D-spatial frame [38], 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 functions (PDF), $P(\theta)$, of the particles as a function of their orientations θ in the bulk with respect to the direction of the shear flow. The BDE depends on the Peclet number $\alpha = \gamma'/D_{\text{rot}}$, where γ' is the shear rate of flow and D_{rot} is the rotational diffusion coefficient of the macromolecular particle about its center of mass. The rotational Peclet number α is the dimensionless ratio that characterizes the relative strengths of hydrodynamic and Brownian effects.

In this paper we generalize the algorithm used previously for the 2D-spatial frame [39–41], to establish an appropriate algorithm for a 3D-spatial frame. This is used to make numerical simulations for the 3D dimensional Cartesian space, in order to calculate the PDF distributions of ellipsoidal macromolecular particles in the bulk liquid solution and in the vicinity of solid surface boundaries.

In particular, the mechanical restitution model at the solid boundaries is generalized to three dimensions, and combined with a fuller implementation of the Jeffery's which govern the motion of ellipsoidal forms of the colloidal particle in an unbounded linear flow field. It is hence this complete version which is used in the present model to calculate the PDF distributions for macromolecular ellipsoidal particles in the neighborhood of solid surface boundaries.

We consider a simple shear flow acting on an ellipsoidal particle, such that

$$v_x = \dot{\gamma} y \text{ and } v_y = v_z = 0$$

$\dot{\gamma}$ is the hydrodynamic shear rate. The motion of a solid ellipsoid particle, suspended in a simple shear flow, was computed analytically [28], neglecting the inertia of the fluid and the particle. The ellipsoidal orientation is defined by three angles (θ, φ, ψ), which determine the Cartesian coordinates x, y, z. In contrast, a local