Exact solutions of the Boeder differential equation for macromolecular orientations in a flowing liquid

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Abstract

The Boeder differential equation is solved in this work over a wide range of \( \alpha \), yielding the probability density functions (PDF), that describe the average orientations of rod-like macromolecules in a flowing liquid. The quantity \( \alpha \) is the ratio of the hydrodynamic shear rate to the rotational diffusion coefficient. It characterises the coupling of the motion of the macromolecules in the hydrodynamic flow to their thermal diffusion. Previous analytical work is limited to approximate solutions for small values of \( \alpha \). Special analytical as well as numerical methods are developed in the present work in order to calculate accurately the PDF for a range of \( \alpha \) covering several orders of magnitude, \( 10^{-6} \leq \alpha \leq 10^8 \). The mathematical nature of the differential equation is revealed as a singular perturbation problem when \( \alpha \) becomes large. Scaling results are obtained over the differential equation for \( \alpha \geq 10^3 \). Monte Carlo Brownian simulations are also constructed and shown to agree with the numerical solutions of the differential equation in the bulk of the flowing liquid, for an extensive range of \( \alpha \). This confirms the robustness of the developed analytical and numerical methods.

Keywords: Polymers, Monte-Carlo, Rotational Diffusion.
I. INTRODUCTION

The most widely used experimental technique for the observation of rotational diffusion of macromolecules in hydrodynamic flow is that corresponding to birefringence [1,2]. The authors in [2], for example, have observed the existence of a depletion layer in dilute xanthan solutions subjected to simple shear flow, using the technique of evanescent induced fluorescence. The motion and average orientations of macromolecules at dilute concentrations in a flowing liquid are determined by two conflicting forces, the first is a hydrodynamic force stemming from shear flow, and the other thermal, originating from Brownian rotational diffusion.

Boeder [3] is the first to have studied this problem in the bulk of a flowing liquid from the theoretical point of view. He suggested, without the use of the Langevin formalism or the Fokker-Planck equation [4,5], an ordinary differential equation, which governs a probability distribution function $P(\theta)$ describing the average orientations of the macromolecules:

$$P'' + (\alpha \sin^2(\theta) P)' = 0$$  \hspace{1cm} (1)

This differential equation is derived for the motion of macromolecular rod-like particles, of negligible cross-sectional area, in the plane of the flow, without any boundary conditions. The angle $\theta$ describes the orientations of the macromolecules with respect to a reference direction. The quantity $\alpha$ is the ratio

$$\alpha = \frac{\dot{\gamma}}{D_{Br}}$$  \hspace{1cm} (2)

where $\dot{\gamma}$ is the shear rate in the hydrodynamic flow, and $D_{Br}$ is a diffusion coefficient governing the Brownian rotational motion of the rod. The differing nature of the macromolecules and macromolecular polymers in their solutions leads to differing values of $D_{Br}$, whereas the hydrodynamic flow of the solution is characterised by given values of $\dot{\gamma}$. As has been pointed out [3], a solution in closed form for this ordinary differential equation cannot be obtained. Boeder gave a series solution valid only for small values of $\alpha$. Although some
improvements have been made, on one hand to remove restrictions on the cross-sectional areas of the macromolecules, and on the other to be able to consider rotational diffusion in three dimensions [6,7], the available solutions are still limited to small values of $\alpha$. To the best of the authors’ knowledge there does not exist in the literature a general approach to solve the Boeder differential equation for arbitrarily large values of $\alpha$, or for a wide range of its values. It is the purpose of this work to provide such an approach, using different analytical and numerical methods. Another interest is to compare the analytical approach with Brownian simulations of the PDF, under the same conditions in the bulk of a flowing liquid. This comparison is useful because it can confirm the robustness of the analytical methods. It also provides a necessary limiting bulk condition for similar simulations near solid surfaces where one is often led to making reasonable but unverifiable assumptions concerning the touching collision of the macromolecule with the solid surface, [4,5,8]. Although simulations have been developed in the past, as for polymers in plane bulk Poiseuille flow [8], and for the dispersion of rod-like particles in a bulk shear flow [9], there is an absence of a detailed comparison between the simulations and the analytical results in the bulk, precisely because exact solutions of this differential equation have not been available. In Section 2, we present an accurate analysis of the Boeder differential equation to obtain the probability distribution function (PDF), for a wide range of $\alpha$. In Section 3, four numerical methods are proposed for the general solution of the differential equation in different intervals of $\alpha$, and numerical results are presented to illustrate this. Scaling results are also presented in this section for large values of $\alpha$. In Section 4, Monte Carlo Brownian simulations are presented for the PDF, and compared with the results of Section 3. The conclusions are given in Section 5. 2.

II. ACCURATE ANALYSIS OF THE BOEDER EQUATION

In this section, a procedure for the accurate numerical analysis of the Boeder ordinary differential equation and its associated probability distribution function, $P(\theta)$, is given for a
wide range of \( \alpha \). Turbulence effects are known to take place for values of \( \alpha \geq 10^4 \). Although the Boeder differential equation ceases to apply in a strict physical sense beyond this limit, the present mathematical analysis is not limited by this, and numerical solutions may be calculated in our approach for values of \( \alpha \geq 10^6 \). \( P(\theta) \) is the solution of a second-order ordinary differential equation, Eq. (1). Since the Boeder PDF is periodic with a period equal to \( \pi \), as the macromolecular rods are indistinguishable when oriented at \( \theta \) or \( \theta + \pi \), the periodic boundary conditions

\[
P(0) = P(\pi) \quad \text{and} \quad P'(0) = P'(%28\pi\%29)
\]

(3)

apply. In addition, the PDF has to be normalised over the interval:

\[
\int_0^\pi P(\theta)d\theta = 1
\]

(4)

The determination of the Boeder PDF is consequently a constrained boundary value problem. Eq. (1), however, is not the only possible form for the Boeder equation, actually two other versions of the equation exist. The first takes the form of:

\[
P' + \alpha sin^2(\theta)P = C
\]

(5)

provided the initial value \( P(0) \) and the constant \( C \) are known. The second may be presented as:

\[
du/d\theta = v, \quad \text{(6)}
\]

\[
dv/d\theta = -\alpha sin(\theta)[sin(\theta)v + 2cos(\theta)u]
\]

(7)

where \( u(\theta) = P(\theta), v(\theta) = P'(\theta) \).

Several technical procedures may be used to determine \( P(\theta) \), depending on the different possible formulations of the problem, as an initial value problem or as a boundary value problem. In all cases two quantities, the constant \( C \) in Eq. (5), equal to \( P'(0) \) or \( v(0) \), and
the initial value \( P(0) \) or \( u(0) \), have to be evaluated from \( \alpha \) for any of its given values. We have developed two methods, described below, to determine \( C \) and \( P(0) \). Firstly, a direct method based on the solution of Eq. (5), and secondly a minimisation method based on a multidimensional secant or Broyden method. The direct method to evaluate \( C \) and \( P(0) \) is as follows. The formal solution of Eq. (5) may be given generally as

\[
P(\theta) = C \exp[\alpha \sin(2\theta)/2 - \theta]/2] \int_{-\infty}^{\theta} \exp[-\alpha(\sin(2x)/2 - x)/2] dx
\]  

(8)

The lower limit \(-\infty\) is surprising since the problem is defined over the angular interval \([0, \pi]\). It is probably true to say, however, that the assumption to limit the space of stochastic events to this interval has retarded the analytical approach until now. We can analytically show that the lower limit \(-\infty\) is the only possibility compatible with the boundary conditions given by Eq. (3). Physically this implies that the stochastic space is cumulative over an infinite number of events and hence angles. Performing a change of variables, the solution may then be written as

\[
P(\theta) = (2C/\alpha) \exp[\alpha \sin(2\theta)/4] \int_{0}^{\infty} \exp(-x) \exp[\alpha \sin(4x/\alpha - 2\theta)/4] dx
\]  

(9)

The form in Eq. (9) is more stable numerically than the previous one of Eq. (8), since the numerically troublesome \( \exp(\theta) \) and \( \exp(-\theta) \) terms are avoided. Nevertheless when \( \alpha \) increases the \( \exp[\alpha \sin(\theta)/4] \) term will cause problems despite the bounded values of the sine function, forcing us to turn to other methods based on extrapolation techniques. The constant \( C \) is next determined from the normalisation condition of the Boeder PDF, as in Eq. (4), yielding

\[
C = \alpha / \left[ 2 \int_{-\pi/2}^{\pi/2} d\theta \int_{0}^{\infty} dx \exp(-x) \exp[(\alpha/2) \sin(2x/\alpha) \cos(2\theta - 2x/\alpha)] \right]
\]  

(10)

whereas \( P(0) \) is given by

\[
P(0) = (2C/\alpha) \int_{0}^{\infty} \exp(-x) \exp[\alpha \sin(4x/\alpha)/4] dx
\]  

(11)
The PDF depends on a which we want to vary over several orders of magnitude. The difficulty in solving the differential equation stems from the fact that its nature may be modified when \( \alpha \) increases, turning the problem into a singular perturbation one in \( \alpha^{-1} \).

III. NUMERICAL SOLUTIONS AND SCALING OF THE BOEDER EQUATION

In order to cope with the wide range over which \( \alpha \) may vary, we classify the various methods for solving the problem according to the value of \( \alpha \). Essentially, there are at least four methods to evaluate the PDF.

Method a. For \( \alpha \) in the range : \([10^{-3}, 10^2]\). Direct calculation from the analytic solution of the first-order differential equation.

Method b. For \( \alpha \) in the range : \([10^{-3}, 10^2]\). If \( C \) and \( P(0) \) are known, a simple 1D Runge-Kutta method is used to solve the first-order differential equation.

Method c. For \( \alpha \) in the range : \([10^{-6}, 10^2]\). Find \( C \) and \( P(0) \) by a minimisation method based on a multidimensional secant or Broyden method, and do a 2D Runge-Kutta method to solve the system of two first-order differential equations, Eqs. (6) and (7). The condition \( \min|P(0) - P(\pi)| \) comes from periodicity, and that of \( \min|\int_0^\pi P(\theta) - 1| \) is from the normalisation of the PDF.

Method d. For \( \alpha \) in the range : \([10^2, 10^8]\) and above. Calculate \( C \) and \( P(0) \) by an extrapolation method and solve Eq. (5), or Eqs. (6) and (7), with singular perturbation integration methods. To illustrate the different numerical methods used in our approach to solve the Boeder differential equation, and to calculate the PDF, some numerical results are presented, for a wide range of values of \( \alpha \). In Figs. 1-4, the continuous curves depict these PDF functions, for relatively high values of \( \alpha = 100, 1000, 2000, \) and 5000, respectively. The
PDF results are normalised with respect to unity. The PDF for other values of \( \alpha \) have been numerically calculated in a wide range, though they are not given here. The scaling results are presented next for large values of \( \alpha \). Eq. (10) can be bounded by replacing the cosine term in the exponential integrand by 1, and reducing the double integration appearing in the \( C \) denominator into a simpler one, namely:

\[
D_C = \pi \int_0^\infty e^{(-x)}e^{(\pm(\alpha/2)\sin(2x/\alpha))]dx}
\] (12)

The sine term in Eq. (12) may be expanded for large values of \( \alpha \) to yield \( D_C \sim \alpha^{2/3} \) for the upper bound case (+ sign case), and \( D_C \sim \alpha^0 \) for the lower bound case (- sign case). Since \( C = \alpha/2D_C \) ; we obtain the limits on the behaviour of \( C \), namely \( C \sim \alpha^{1/3} \) for the upper bound. case (+ sign case), and \( C \sim \alpha^1 \) for the lower bound case (- sign case).

Consider that \( C \sim \alpha^{2/3} \) is an intermediate case in the space of stochastic events, when \( \alpha \) is large. It is then possible to show that:

\[
P(0) \sim \alpha^{1/3} \\
\theta_{\text{max}} \sim \alpha^{-1/3} \\
P(\theta_{\text{max}}) \sim \alpha^{1/3}
\] (13)

The proof is as follows. Expanding the argument of the exponential integrand in Eq. (11), yields

\[
P(0) = (2C/\alpha)\int_0^\infty e^{(-8x^3/3\alpha^2)]dx}
\] (14)

The integral in Eq. (14) behaves as \( \sim \alpha^{2/3} \), hence the result expressed in first part of Eq. (13). In order to prove the result of second part of Eq. (13), consider Eq. (5) at \( \theta = \theta_{\text{max}}, \) which may be written in this case as

\[
\alpha \sin^2(\theta_{\text{max}})P(\theta_{\text{max}}) = C
\] (15)
For large values of $\alpha$, the abscissa $\theta_{\text{max}}$ of the maximum of the Boeder PDF is relatively small, and Eq. (15) may be approximated to yield

$$\alpha \theta_{\text{max}}^2 P(\theta_{\text{max}}) = C$$  \hspace{1cm} (16)

Since $\theta_{\text{max}}$ is small, we can expand $P(\theta_{\text{max}})$ around $\theta = 0$; such that

$$P(\theta_{\text{max}}) \cong P(0) + \theta_{\text{max}}^2 P''(\theta_{\text{max}})/2 + ...$$  \hspace{1cm} (17)

$P(\theta_{\text{max}}) \cong P(0)$ is hence accurate to second-order in $\theta_{\text{max}}$. This may be seen graphically, for example, in Figs. 2 and 3 for values of $\alpha = 1000$ and 2000, and also for higher values. The result expressed in last part of Eq. (13) follows accordingly. Another direct consequence follows from Eq. (17) since it is now possible to write that

$$\theta_{\text{max}} P(0) \sim \theta_{\text{max}} P(\theta_{\text{max}}) \sim \text{constant}$$  \hspace{1cm} (18)

which has a simple geometric interpretation. From the normalisation of the Boeder PDF in Eq. (4) and when $\alpha$ is large, the area under the curve of the PDF is roughly the product $\theta_{\text{max}} P(\theta_{\text{max}})$, the distribution function being sharply peaked around $\theta_{\text{max}}$, leading to a PDF approximately triangular in shape with a height $P(\theta_{\text{max}})$ and a base of $2\theta_{\text{max}}$. See, Figs. 2 and 3 to illustrate. The exponents controlling the asymptotic behaviour in Eqs. (13) are all consistent with respect to each other, and have been checked numerically up to quite large values of $\alpha \leq 10^8$. Note finally that the scaling results are valid in this high range of $\alpha$ values, but are inadequate in the range of $\sim 1 \leq \alpha \leq \sim 500$.

**IV. SIMULATIONS AND COMPARISON WITH THE BOEDER EQUATION**

In this section, Brownian simulations are presented to obtain the PDF, and a comparison is made with the results of Section 3. The simulation is characterised by the presence of both Brownian and hydrodynamic forces acting on the macromolecule in the dilute solution.
The hydrodynamic forces tend to act on the rod-like particles turning them in the shear flow with an average angular speed $w$, given, [3], for any orientation $\theta$, by

$$w = \dot{\gamma} \sin^2(\theta)$$

(19)

where $\dot{\gamma}$ is the constant shear rate of the linear flow. To simulate the effects of hydrodynamic forces in an interval $\Delta t(n + 1; n)$; between successive simulation events, we compute $\Delta \theta_{\text{hyd}}(n + 1; n)$, that is the hydrodynamic rotation about the centre of mass of the rod-like particles, using the following algorithm:

$$\Delta \theta_{\text{hyd}}(n + 1; n) = \theta(t_{n+1}) - \theta(t_n) - \dot{\gamma} \sin^2(\theta) \Delta t(n + 1; n)$$

(20)

$\Delta \theta_{\text{hyd}}(n + 1; n)$ is always positive, following the direction of the hydrodynamic flow. In contrast the Brownian forces in the bulk create a diffusive rotational motion of the macromolecules over the orientations $\theta$. The Brownian variable $\Delta \theta_{B_r}(n + 1; n)$ may be given from a random Gaussian distribution. It turns out, however, that it is more convenient to work with a simplified Monte Carlo random variable

$$\Delta \theta_{B_r}(n + 1; n) = \pm \Delta \theta_{B_r}$$

(21)

where $\Delta \theta_{B_r}$ is a fixed value for a group of simulation runs, for a given $\alpha$. An appropriate random number generator is used in the algorithm to select random events, avoiding cumulative errors. The fixed value $\Delta \theta_{B_r}$ must satisfy the Brownian condition corresponding to a simulation interval $\Delta t(n + 1; n) \gg 1/\delta_{r,\alpha}$ where $\delta_{r,\alpha} = k_B T / [D_{B_r} I_{cm}]$ and $I_{cm}$ is the moment of inertia of the rod-like particles about their centre of mass. Using this procedure $\Delta t(n + 1; n)$ may be given as a virtual variable

$$\Delta \theta_{B_r}^2(n + 1; n) = 2D_{B_r} \Delta t(n + 1; n)$$

(22)

where $D_{B_r}$ is the coefficient of rotational diffusion, [10]. $\Delta t(n + 1; n)$ may be eliminated now from the algorithm. This procedure avoids ambiguities that may arise owing to
the arbitrary choice of simulation time intervals, [5], and Eq. (20) is used to rewrite the hydrodynamic algorithm component as

\[ \Delta \theta_{hyd}(n + 1; n) = \alpha \sin^2(\theta)[\Delta \theta_{Br}^2/2] \quad (23) \]

Typically \( \Delta \theta_{Br} \) is of the order of 0.005 radians, which engenders reasonable elementary hydrodynamic rotations in the interval \([0, \pi]\). This is adequate to construct viable statistics, [11], for the diffusion of macromolecules in solution. In Figs. 1-4, the simulation results for the PDF are also presented for values of \( \alpha = 100, 1000, 2000, \) and \( 5000 \), respectively, here as the black dots. For any given \( \alpha \), the simulation results are obtained as an average over several simulations, each based upon \( 10^8 \) hydrodynamic and stochastic events. The black dots are then mean values, and the error bars are the maximum uncertainty per mean value. The PDF simulations results are presented in comparison with the Boeder differential equation solutions of the PDF, given as the continuous curves in these figures. Both are normalised to unity. Other comparisons of this kind between the simulations and the analytical approach have been made for other \( \alpha \) values in a wide range, though not presented here.

V. CONCLUSIONS

The Boeder probability density function describing the average orientations of macromolecules in a flowing liquid is accurately determined over a wide range of \( \alpha = \frac{\dot{\gamma}}{D_{Br}} \), the ratio of the hydrodynamic shear rate to the rotational diffusion coefficient. The differing nature of macromolecules in their solutions leads to differing diffusion coefficients \( D_{Br} \), whereas the hydrodynamic flow of the solution may be characterised by differing values of \( \dot{\gamma} \). Special analytical as well as numerical methods are developed and presented in order to calculate accurately this probability distribution function for a wide range of \( 10^{-6} \leq \alpha \leq 10^6 \). Scaling results are also presented valid for \( \alpha \geq 10^3 \). The mathematical nature of the ordinary differential equation that the PDF should satisfy is revealed as a singular perturbation problem when \( \alpha \) becomes larger than about \( 10^3 \).
Brownian simulations are also presented and may be shown to agree with the numerical solutions of the Boeder differential equation in the bulk of the flowing liquid for arbitrary values of $\alpha$. This comparison confirms the solidity of the analytical solutions. It serves equally as a necessary limiting reference for this type of simulation near impenetrable solid surfaces where the simulations become a particularly useful tool, the Boeder problem being analytically intractable in this region.

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REFERENCES

Figure Captions

Fig. 1: The normalised probability distribution function, PDF, for the orientations of the macromolecular rod-like particles in a hydrodynamic flow, is presented for a high value of the shear to rotational diffusion ratio, $\alpha = \frac{\dot{\gamma}}{D_{br}}=100$. The numerical solution of the Boeder differential equation (continuous curve) is compared to the Monte Carlo simulation (black dots with error bars), for the same $\alpha$.

Fig. 2: The normalised PDF, for the orientations of the macromolecular rod-like particles in a hydrodynamic flow, is presented for a high value of the shear to rotational diffusion ratio, $\alpha = \frac{\dot{\gamma}}{D_{br}}=1000$. The numerical solution of the Boeder differential equation (continuous curve) is compared to the Monte Carlo simulation (black dots with error bars), for the same $\alpha$.

Fig. 3: The normalised PDF for the orientations of the macromolecular rod-like particles in a hydrodynamic flow, is presented for a high value of the shear to rotational diffusion ratio, $\alpha = \frac{\dot{\gamma}}{D_{br}}=2000$. The numerical solution of the Boeder differential equation (continuous curve) is compared to the Monte Carlo simulation (black dots with error bars), for the same $\alpha$.

Fig. 4: The normalised PDF for the orientations of the macromolecular rod-like particles in a hydrodynamic flow, is presented for a high value of the shear to rotational diffusion ratio, $\alpha = \frac{\dot{\gamma}}{D_{br}}=5000$. The numerical solution of the Boeder differential equation (continuous curve) is compared to the Monte Carlo simulation (black dots with error bars), for the same $\alpha$. 