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Polymer stretch in dilute fixed beds of fibres or spheres

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A theory is developed to describe the conformation change of polymers in flow through dilute, random fixed beds of spheres or fibres. The method of averaged equations is used to analyse the effect of the stochastic velocity fluctuations on polymer conformation via an approach similar to that used in our previous analysis of particle orientation in flow through these beds (Shaqfeh & Koch 1988*a*, *b*). The polymers are treated as passive tracers, i.e. the polymeric stress in the fluid is neglected in calculating the stochastic flow field. Simple dumbbell models (either linear or FENE) are used to model the polymer conformation change. In all cases we find that the long-range interactions provide the largest contribution (in the limit of vanishingly small bed volume fraction) to an evolution equation for the probability density of conformation. These interactions create a conformation-dependent diffusivity in such an equation. Solutions for the second moment of the distribution demonstrate that there is a critical pore-size Deborah number beyond which the radius of gyration of a linear dumbbell will grow indefinitely and that of the FENE dumbbell will grow to a large fraction of its maximum extensibility. This behaviour is shown to be related to the development of 'algebraic tails' in the distribution function. The physical reasons for this critical condition are examined and its dependence on bed structure is analysed. These results are shown to be equivalent to those which we derive by the consideration of a polymer in a class of anisotropic Gaussian flow fields. Thus, our results are explicitly related to recent work regarding polymer stretch in model turbulent flows. Finally, the effect of close interactions and their modification of our previous results is discussed.

1. Introduction

In their experimental work, James & MacClaren (1975) demonstrated that the addition of a small concentration of flexible polymer to a Newtonian solvent could cause a significant increase in the pressure drop necessary to pump the fluid through a fixed bed of glass spheres at a constant flow rate. This was shown to occur even for flows without inertia and was associated with significant conformation change and stretch of the polymer. The latter was inferred through pressure drop measurements made at various points along the column of fixed spheres and by evidence of polymer degradation during flow. Significant polymer stretch was argued to increase the stress within the solution and thus increase the friction factor for a given flow rate. No direct correlation between polymer conformation change in fixed beds and increased particle drag was determined because no direct measurement of the polymer stretch was accomplished. Later research (Durst, Haas & Kaczmar 1981 and Kaser & Keller 1980) verified and extended these experimental results.

In subsequent work, a number of researchers have attempted to explain the postulated 'coil-stretch' transition in fixed beds by employing models based on simple deterministic flows. In fact, strong flow criteria available for a number of linear steady flows were applied more or less directly to the complicated flow field experienced by a polymer molecule as it traversed a disordered fixed network (Olbricht, Rallison & Leal 1982; Prud'homme & Hoagland 1983). A number of other studies have employed the periodic constricted tube or channel as a model for the flow in a fixed bed of spheres (Dieber & Schowalter 1979; Zick & Homsy 1984; Phan-Thien & Khan 1987; Pilitsis & Beris 1989; James *et al.* 1990). Still others have used unsteady linear flows in certain periodic combination to model the sampling of the complicated flow in a fixed bed (Nollert & Olbricht 1985). In all of this work, researchers have chosen to concentrate on deterministic models and to neglect the stochastic element of flow through disordered fixed beds. Although stochastic flow models have been used extensively in trying to understand the dispersion of a passive tracer in fixed beds (Saffman 1959; Koch & Brady 1985) these same models have not been applied to the study of polymer conformation in the flow. However, there have been important attempts to consider the conformation of polymers in stochastic flows which model fully developed, turbulent flows, most notably by Lumley (1972) and Jhon, Sekhon & Armstrong (1987).

In the present discourse, we build upon the recent work by Shaqfeh & Koch (1988*a*, *b*) who demonstrated that the orientation of small axisymmetric 'tracer' particles flowing through random, dilute fixed beds of spheres or fibres could be described rigorously via the method of averaged equations. Although our analysis was restricted to dilute fixed beds ($\phi_f \ll 1$ where ϕ_f is the solids volume fraction of the fixed bed) and to dilute suspensions of tracer particles, we demonstrated that the resulting stochastic flow field caused the particle orientations to evolve to a non-random steady state. Moreover, we showed that the axisymmetric particles tend to orient with their 'thin side' in the direction of the flow even when the Darcy pore size of the bed was much larger than the size of the suspended axisymmetric particles. Thus, there existed no 'steric selection' of particle orientations and any particle alignment was induced solely by the hydrodynamic interactions in the bed. The degree of this particle alignment was predicted and shown to be a strong function of tracer particle aspect ratio. For the details the reader is referred to the specific publications. Recently these results have been verified using light scattering measurements (see Frattini *et al.* 1991).

This theory is now applied to describe the conformation and stretch of model polymer molecules in the flow through random, dilute fixed beds of spheres or fibres. The suspension of polymers considered is very dilute such that the polymers can be treated as passive tracers in the bed, i.e. the polymeric stresses are neglected in calculating the flow field within the bed. The polymer molecules are modelled as simple dumbbells whose conformation can be completely specified by their end-to-end vector, $\boldsymbol{r}$. In §2, an evolution equation for the probability density function of the end-to-end vector, $\langle\Omega\rangle(\boldsymbol{r})$, during the flow through a random, isotropic fixed bed of fibres is derived. The theory is first developed for linear or Hookean dumbbells. The evolution equation is an averaged equation with the average taken over the statistics of the bed. It is argued that the leading-order effect for small volume fraction is due to far-field hydrodynamic interactions in the bed, and it is demonstrated that these create a hydrodynamically induced conformation-dependent diffusivity in the averaged evolution equation. This diffusivity tensor is quadratic in the end-to-end vector, and the fourth-order proportionality tensor is calculated explicitly as a

certain velocity gradient correlation function. Although, it is difficult to derive analytic expressions for the normalized probability density function, we derive and solve simple equations for the moments of the distribution as functions of time. It is demonstrated that the radius of gyration depends on the volume fraction of the bed solids, ϕ_f, and the *pore-size Deborah number*, $De = U\lambda/\kappa^{\frac{1}{2}}$, where U is the magnitude of the average velocity, $\kappa^{\frac{1}{2}}$ is the Darcy pore size or Brinkman screening length, and λ is a characteristic polymer relaxation time. Below a certain critical Deborah number (which depends on the solids volume fraction, ϕ_f) it is demonstrated that the dumbbell reaches a steady conformation which shows marked stretch, particularly in the flow direction. Above the critical Deborah number, we demonstrate that a Hookean dumbbell appears to grow exponentially for all time, achieving no finite steady state. Thus our theory predicts that beyond a certain flow rate, there exists a large change in the r.m.s. value of the end-to-end vector of the polymer and therefore in any quantities which scale with this measure of conformation. We continue to explore this basic result in the remainder of the paper. In §2, we demonstrate that the critical condition is related to 'algebraic tails' in the probability density function, and thus, that the critical Deborah number depends on the moment that is being examined. Finally, we remove the aphysical singularity in the steady-state stretch by considering the effects of finite extensibility via the Warner dumbbell model. Beyond the critical condition calculated for the Hookean spring, we find that the finitely extensible nonlinear elastic (FENE) dumbbell stretches to a large fraction of its maximum extensibility.

In §3, our results are examined in the light of previous work and via a different approach. It is demonstrated that, in the dilute limit, the stochastic flow field created by the long-range hydrodynamic interactions in a random fixed bed is equivalent to a stochastic flow with certain anisotropic Gaussian statistics. The average over the positions and configurations of the fixed bed particles can then be replaced by an average over the statistics of the Gaussian flow field. It follows that both long-time tracer dispersion and polymer configuration in fixed beds depends only on the covariance of the disturbance flow in the dilute approximation. We rederive our results for polymer conformation by considering the polymer in a Gaussian field which it samples through its motion with the mean velocity – a good approximation for weak fluctuations. The derivation employs previous results based on diagrammatic or renormalized perturbation methods. It is thus demonstrated that our approximate expressions are equivalent to Kraichnan's direct interaction approximation (Kraichnan 1959, 1970; Roberts 1961) when applied to this problem. Finally, this section delineates the similarities and differences between our work and the conformation transition predicted by Jhon *et al.* (1987) and Lumley (1972) in their consideration of polymers in isotropic Gaussian flows with no mean velocity as models of fully, developed turbulence. We define a new strong flow criterion for our class of anisotropic Gaussian flow fields which are sampled with a non-zero mean flow.

We demonstrate in §4 that our results apply to any dilute random fixed bed structure, because any such bed gives rise to a Gaussian flow field. This approach is then applied to the flow of polymers through fixed beds of spheres. In contrast to our calculations for flow through isotropic fibre beds, we demonstrate that in the limit of infinite dilution (where polymers are interacting with only single spheres) there is no critical condition or critical value of the Deborah number. In order to determine the critical conditions, one must consider the interactions of a polymer with at least two spheres, and thus the critical Deborah number is predicted at the next order in a

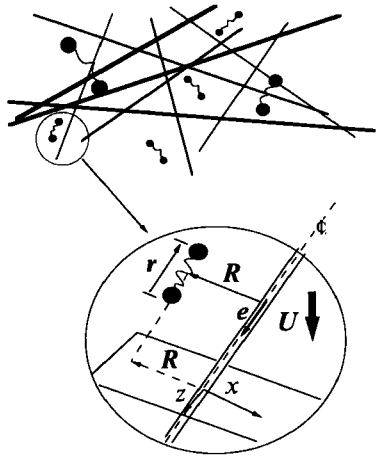

FIGURE 1. Polymer molecules modelled as dumbbells flowing through a dilute, isotropic fixed fibre bed at mean velocity U. The nomenclature used throughout §2 is shown.

concentration expansion. The physical reasons for this are examined in the light of the fore–aft symmetry of the disturbance flow created by a single fixed sphere. In particular, it is shown that when this symmetry is broken by the presence of a second fixed sphere, the covariance of the equivalent Gaussian field also changes form. It is this change that causes the ultimate critical stretch of a Hookean spring. Thus, it becomes clear which interactions in dilute, random fixed beds cause large or 'super-critical deformation' and this is quantified with a specific statistical measure.

In the final section, we examine the effects of close interactions between FENE dumbbells and fibres in flow through a fixed-fibre bed. We show that even though the average effect of these interactions is of higher order in volume fraction than the effects due to long-range interactions, they may be important. This is primarily due to the highly stretched 'strands' which exist following the rear stagnation point in flow past cylinders. This effect has been reported elsewhere (see Harlen 1990; Harlen, Rallison & Chilcott 1990; Chilcott & Rallison 1988). Scaling arguments are developed to determine when these close range interactions are important in dilute beds. These arguments include a consideration of a cascade of short-range interactions as a means of increasing polymer conformation change – a mechanism that has recently been noted in numerical results for flow in periodic fibre arrays by Chmielewski, Petty & Jayaraman (1990).

We conclude by looking forward to an experimental investigation of our results.

2. Polymer stretch in isotropic fibre beds: long-range hydrodynamic interactions

2.1. *Linear dumbbell*

We shall begin by considering the conformation of linear dumbbells in a Newtonian solvent as they flow under Stokes flow conditions through an isotropic, random bed of fibres. The dumbbells are defined by two Brownian beads connected by a Hookean spring, cf. figure 1. It is well known that the Hookean dumbbell is a useful approximate model for the deformation of the more exact descriptions of flexible macromolecules as many bead chains, when subject to small deformation (see Larson 1988). We shall also use the model in the present instance to crudely describe larger

deformations, although nonlinear dumbbell models will be introduced below. We shall assume that the polymer solution is sufficiently dilute that we can safely neglect polymer–polymer interactions. Within these assumptions we can define $P(\boldsymbol{x}, \boldsymbol{r})$ as the probability density for finding a dumbbell with centre-of-mass at position $\boldsymbol{x}$ and configured such that the beads are at positions $\boldsymbol{x}+\frac{1}{2}\boldsymbol{r}$ and $\boldsymbol{x}-\frac{1}{2}\boldsymbol{r}$. The probability density satisfies a conservation equation of the form

$$\frac{\partial P}{\partial t} - D\nabla^2 P + \nabla\cdot[\boldsymbol{u}(\boldsymbol{x})P] - 2D\nabla_r^2 P + \nabla_r\cdot[\dot{\boldsymbol{r}}P] = 0, \tag{1}$$

where $\boldsymbol{u}$ is the centre-of-mass velocity of a dumbbell at a point in the bed, $\dot{\boldsymbol{r}}$ is the relative velocity of the beads, and ∇ and ∇_r are the del operators with respect to the centre-of-mass and the relative bead coordinates respectively. In addition, D is the centre-of-mass diffusivity of the dumbbell, and we shall neglect hydrodynamic interactions between the beads. Thus, D is given by the scalar Stokes–Einstein relation, namely:

$$D = kT/\zeta_{\mathrm{D}},$$

where, ζ_{D} is the drag coefficient on the dumbbell which, in the light of the assumptions, does not depend on $\boldsymbol{r}$. It follows that the correct relative diffusivity describing the inter-bead separation, $\boldsymbol{r}$, is $2D$ as shown in (1). Also, we shall begin by assuming that the spring is Hookean and that the flow always scales on lengths which are much larger than the size of the dumbbell itself. Under these conditions we obtain the following relation for $\dot{\boldsymbol{r}}$:

$$\dot{\boldsymbol{r}} = \boldsymbol{r}\cdot\nabla\boldsymbol{u}(\boldsymbol{x}) - \tfrac{1}{2}\xi\boldsymbol{r}, \tag{2}$$

where ξ^{-1} is the ratio of the drag on a single bead to the restoring force of the linear spring, or, in other words, is the characteristic time for the spring to relax upon being stretched (see Larson 1988).

In the absence of flow, the steady solution of (1) demonstrates that the equilibrium radius of gyration, $R_{\mathrm{g}} = (\overline{\boldsymbol{r}\cdot\boldsymbol{r}})^{\frac{1}{2}}$ (where the overbar refers to an average over the configurational distribution function $\Omega(\boldsymbol{r})$), is such that

$$R_{\mathrm{g}}^2 = 12D/\xi. \tag{3}$$

With flow, however, P becomes a function of the entire configuration of the fixed particles because both the centre-of-mass velocity and the velocity gradient depend on all the hydrodynamic interactions within the fixed bed. This can be simplified if we restrict ourselves to dilute beds where the interactions of the dumbbells with single fixed fibres (through an averaged or Darcy medium) give the largest contribution to the evolution of the dumbbell conformation. For dilute beds, we can then use the method of averaged equations (see Hinch 1977; Koch & Brady 1986; Shaqfeh & Koch 1988*a*, *b*) to average (1) and then truncate based on diluteness. In addition, if we assume that the polymer solution is sufficiently dilute, then the flow field experienced by a given polymer will not be significantly different than that which occurs in the Newtonian flow through the bed. The following development is very similar to that presented by Shaqfeh & Koch (1988*a*) in their consideration of orientation of particles in the Newtonian flow through fixed beds, and thus we shall only outline the important steps.

First, we shall make all positions $\boldsymbol{x}$ dimensionless with $\kappa^{\frac{1}{2}}$ which we recall is the Darcy pore size or screening length in the fixed medium. The permeability, κ is known for the Newtonian flow in isotropic, dilute fibre beds both through theoretical

calculation and through many careful experiments (see Spielman & Goren 1968; Howells 1974; Koch & Brady 1986; Jackson & James 1986). It is given approximately by the relation

$$\kappa^{\frac{1}{2}} \approx \left[\frac{3a^2 \ln (1/\phi_f)}{20\phi_f}\right]^{\frac{1}{2}},$$

where a is the radius of the fibres in the bed.

Next, we make all velocities dimensionless with U, the magnitude of the average velocity through the bed. This also gives a characteristic timescale $\kappa^{\frac{1}{2}}/U$ which is the average time that a polymer molecule spends interacting with a given fibre in the bed. Finally, we shall make all relative bead positions dimensionless with R_g. With these non-dimensionalizations (1) becomes

$$\frac{\partial P}{\partial t} - \frac{1}{Pe}\nabla^2 P + \boldsymbol{u}(\boldsymbol{x})\cdot\nabla P - \frac{1}{6De}\nabla_r^2 P + \nabla_r\cdot[\dot{\boldsymbol{r}}P] = 0, \tag{4a}$$

and

$$\dot{\boldsymbol{r}} = \boldsymbol{r}\cdot\nabla\boldsymbol{u} - \frac{\boldsymbol{r}}{2De}, \tag{4b}$$

where the Péclet number, Pe, and the Deborah number, De, are defined

$$Pe \equiv U\kappa^{\frac{1}{2}}/D; \quad De \equiv U/(\xi\kappa^{\frac{1}{2}}). \tag{5}$$

Note that in writing (4a) we have neglected any disturbance velocities created by the small dumbbells and thus their centre-of-mass velocities become incompressible.

In (4) and (5), the Péclet number is the ratio of the time that it would take a polymer to diffuse across a screening length to the time it takes to be convected through the same distance. Since the translational diffusivities of macromolecules are small, the Péclet number will generally be very large. We will take the Péclet number to be sufficiently large that the centre-of-mass diffusion (i.e. the second term in (4a)) can be neglected.

The Deborah number is the ratio of a polymer relaxation time, $(\xi)^{-1}$, to the time it takes for a polymer to flow through a Brinkman screening length. (Alternatively, it is the product of $(\xi)^{-1}$ with a characteristic shear rate $U/\kappa^{\frac{1}{2}}$ in the pores of the bed.) In the subsequent analysis we shall emphasize the case in which the polymer's relaxation during its interaction with a given fibre is small and thus $De \gg 1$. It will be seen that this is the only case in which significant polymer stretch created by long-range interactions occurs.

Our main task is to derive an averaged equation for the non-equilibrium conformational distribution function, $\Omega(\boldsymbol{r})$, averaged over the configuration statistics (i.e. positions and orientations) of the fibres in the bed. The function Ω is defined (in dimensionless variables) through the relation

$$\Omega(\boldsymbol{r}) = \frac{\kappa^{\frac{3}{2}}}{V}\int P(\boldsymbol{x},\boldsymbol{r})\,\mathrm{d}\boldsymbol{x},$$

with the normalization condition

$$\int \mathrm{d}\boldsymbol{r}\,\Omega(\boldsymbol{r}) = 1,$$

where we have made $P(\boldsymbol{x},\boldsymbol{r})$ dimensionless with n_p/R_g^3 (n_p is the number density of polymers in solution) and Ω with $1/R_g^3$. We shall use two types of averages over bed

particle configuration: (i) an unconditional ensemble average, denoted by $\langle\cdot\rangle$, over all the positions and orientations of the fixed fibres in the bed, and (ii) a conditional average, denoted by $\langle\cdot\rangle_1$, in which the average is taken over the sub-ensemble with a single fibre held fixed at a given orientation.

The derivation of the equations for the unconditionally and conditionally averaged conformational probabilities are directly analogous to those for the averaged orientational probabilities given by Shaqfeh & Koch (1988*a*, *b*). The analogy follows since the relative position of the beads, their relative velocity and the Deborah number are analogous to the orientation of the tracer particles, their rotation rate and the rotary Péclet number in our previous analysis. The relative position of the beads responds to the fluctuating local velocity gradient experienced by the dumbbell as it flows through the bed in a manner analogous to the way in which tracer particles change orientation as they rotate in the fluctuating field. The relative velocity induced by the spring force between the two beads has no similar analogy, but this is easily averaged because it does not depend on the fixed-bed geometry. We assume that all flow fields are governed by the Stokes equations and therefore both inertial effects and elastic stresses can be neglected in their calculation.

An outline of the derivation is as follows. First, we unconditionally average (4) and then break the nonlinear averages based on diluteness, keeping only the leading-order terms for small ϕ_f. We thus obtain (cf. (62) of Shaqfeh & Koch 1988*a*)

$$\frac{\partial\langle\Omega\rangle}{\partial t}-\frac{1}{6De}\nabla_r^2\langle\Omega\rangle-\frac{1}{2De}\nabla_r\cdot(\boldsymbol{r}\langle\Omega\rangle)+\frac{\phi_f\kappa}{\pi a^2}\int d\boldsymbol{e}\,g(\boldsymbol{e})\int d\boldsymbol{R}\,\nabla_r\cdot\langle\dot{\boldsymbol{r}}'\rangle_1\langle P'\rangle_1=0, \quad (6)$$

where $\langle\dot{\boldsymbol{r}}'\rangle_1=\boldsymbol{r}\cdot\nabla\langle\boldsymbol{u}'\rangle_1$ and $\langle P'\rangle_1=\langle P\rangle_1-\langle\Omega\rangle$. In addition, $\langle\boldsymbol{u}'\rangle_1\equiv\langle\boldsymbol{u}\rangle_1-\langle\boldsymbol{u}\rangle$ is the conditionally averaged velocity disturbance created by a single fibre in the fibrous bed. In deriving (6) we have used the facts that: (i) quantities averaged with a single fibre held fixed are only functions of the vector $\boldsymbol{R}$ which lies in the plane perpendicular to the local orientation vector, $\boldsymbol{e}$, of the fibre; (ii) the dimensional probability of a fibre passing through any given point in the random bed is $(\phi_f/a^2\pi)g(\boldsymbol{e})$ where $g(\boldsymbol{e})$ is the probability density of orientation; and (iii) $\langle\dot{\boldsymbol{r}}\rangle=0$ since the dimensionless, bed-averaged velocity is a constant, namely

$$\langle\boldsymbol{u}\rangle\equiv\boldsymbol{U}/U=\boldsymbol{i}_z.$$

To complete the evolution equation (6) we need to derive the expression for $\langle P'\rangle_1$. This is accomplished by averaging (4) conditionally. After some manipulations we obtain the coupled equations for the averaged probability distributions in a fixed bed of fibres (cf. (46) and (47) in Shaqfeh & Koch 1988*b*):

$$\frac{\partial\langle\Omega\rangle}{\partial t}-\frac{1}{6De}\nabla_r^2\langle\Omega\rangle-\frac{1}{2De}\nabla_r\cdot(\boldsymbol{r}\langle\Omega\rangle)+\frac{\phi_f\kappa\epsilon}{\pi a^2}\int d\boldsymbol{e}\,g(\boldsymbol{e})\int d\boldsymbol{R}\,\nabla_r\cdot\langle\dot{\boldsymbol{r}}'\rangle_1\langle P'\rangle_1=0, \quad (7a)$$

$$\frac{\partial\langle P'\rangle}{\partial t}+[\boldsymbol{i}_z\cdot(\boldsymbol{I}-\boldsymbol{ee})]\cdot\nabla_R\langle P'\rangle_1+\epsilon\langle\boldsymbol{u}'\rangle_1\cdot(\boldsymbol{I}-\boldsymbol{ee})\cdot\nabla_R\langle P'\rangle_1$$

$$+\epsilon\nabla_r\cdot\langle\dot{\boldsymbol{r}}'\rangle_1\langle P'\rangle_1-\frac{1}{6De}\nabla_r^2\langle P'\rangle_1-\frac{1}{2De}\nabla_r\cdot[\boldsymbol{r}\langle P'\rangle_1]=-\epsilon\nabla_r\cdot[\langle\dot{\boldsymbol{r}}'\rangle_1\langle\Omega\rangle], \quad (7b)$$

where $\epsilon=1/\ln(\kappa^{\frac{1}{2}}/a)\ll 1$. In arriving at (7*a*, *b*) we have used the fact that in a bed of fixed fibres

$$|\langle\boldsymbol{u}'\rangle_1|\sim O(\epsilon)$$

(Koch & Brady 1986; Shaqfeh & Koch 1988*b*), and we have rescaled both $\langle \boldsymbol{u}' \rangle_1$ and $\langle \dot{\boldsymbol{r}}' \rangle_1$ with ϵ such that they will remain $O(1)$ throughout the analysis.

The detailed derivation of (7*a*, *b*) involves a number of important steps and consequences, which are discussed in our previous publications (see Shaqfeh & Koch 1988*a*, *b*). Probably the most important is the realization that since $\langle \dot{\boldsymbol{r}} \rangle = 0$, any polymer stretch or any change in the conformation density function, $\langle \Omega \rangle$, from its equilibrium value must arise solely as a result of the velocity fluctuations in the bed.

In the limit of small ϵ and large Deborah number, the function $\langle P' \rangle_1$ can be determined to a first approximation as

$$\langle P' \rangle_1 \sim -\frac{\epsilon}{|\boldsymbol{i}_z \cdot (\boldsymbol{I} - \boldsymbol{ee})|} \int_{-\infty}^{Z} \mathrm{d}Z' \, \boldsymbol{\nabla}_r \cdot [\langle \dot{\boldsymbol{r}}' \rangle_1 (X, Z') \langle \Omega \rangle] + O(\epsilon^2, \epsilon/De),$$

where Z is defined as the coordinate in the $\boldsymbol{R}$-plane which runs along the direction $\boldsymbol{i}_z \cdot (\boldsymbol{I} - \boldsymbol{ee})$, and X is a second orthogonal coordinate in the same plane. Substituting this result back into (7*a*) and noting that $\boldsymbol{\nabla}_r \cdot \langle \dot{\boldsymbol{r}}' \rangle_1 = 0$, we obtain the final evolution equation

$$\frac{\partial \langle \Omega \rangle}{\partial t} - \frac{1}{6De} \nabla_r^2 \langle \Omega \rangle - \frac{1}{2De} \frac{\partial}{\partial r_m} (r_m \langle \Omega \rangle) - \frac{\phi_f \kappa \epsilon^2}{\pi a^2} A_{jkmn} r_k r_n \frac{\partial^2}{\partial r_j \partial r_m} \langle \Omega \rangle = 0, \tag{8}$$

where A_{jkmn} is defined

$$A_{jkmn} = \int \mathrm{d}\boldsymbol{e} \frac{g(\boldsymbol{e})}{|\boldsymbol{i}_z \cdot (\boldsymbol{I} - \boldsymbol{ee})|} \int \mathrm{d}\boldsymbol{R} \frac{\partial \langle u_j' \rangle_1}{\partial R_k} \int_{-\infty}^{Z} \mathrm{d}Z' \frac{\partial \langle u_m' \rangle_1}{\partial R_n}. \tag{9}$$

We note for future reference, that in the results above and throughout the remaining discussion, we shall use Einstein or indicial notation where repeated indices imply summation. From (8) it is clear that the leading-order effect of the hydrodynamic interactions in the fixed bed is to create a conformation-dependent diffusion, characterized by the correlation function, A_{jkmn}. This function is the average over the plane containing the vector $\boldsymbol{R}$ of the conditionally averaged velocity gradient correlated with all previous velocity gradients along an approximately straight polymer flow path. It has been determined for an isotropic bed in our previous publication (see Shaqfeh & Koch 1988*b*), namely

$$\begin{aligned} A_{jkmn} = \beta_1 [(\delta_{kn} - \delta_{k3}\delta_{n3})(\delta_{j3}\delta_{m3})] - \beta_2 [\delta_{jk}\delta_{mn} + \delta_{jn}\delta_{km} - 3\delta_{jm}\delta_{kn} - \delta_{j3}\delta_{k3}\delta_{mn} \\ - \delta_{k3}\delta_{m3}\delta_{jn} - \delta_{j3}\delta_{n3}\delta_{km} - \delta_{m3}\delta_{n3}\delta_{jk} + 2\delta_{j3}\delta_{m3}\delta_{kn} + 3\delta_{k3}\delta_{n3}\delta_{jm}]. \end{aligned} \tag{10}$$

In (10), $\boldsymbol{i}_3 = \boldsymbol{i}_z$ and β_1 and β_2 are positive functions of the volume fraction ϕ_f that approach constants in the dilute limit. The constant values have been determined in our previous publication (cf. Shaqfeh & Koch 1988*b*), namely

$$\beta_1 = \frac{\pi}{1024} [11(f_\parallel^2 + f_\perp^2) + 10 f_\parallel f_\perp], \quad \beta_2 = \frac{\pi}{1024} [(f_\parallel - f_\perp)^2], \tag{11a, b}$$

where $f_\parallel$ and $f_\perp$ are the dimensionless force per unit length for flow parallel and perpendicular to the fibre's orientation. In the dilute limit, $f_\parallel \sim 2\pi$ and $f_\perp \sim 4\pi$. We recall, as discussed by Shaqfeh & Koch (1988*b*), that the second term in (10), which is proportional to β_2, arises from the fact that the disturbance velocity is not fore–aft symmetric about the direction of the mean flow for fibres of arbitrary orientation. This follows since $f_\parallel$ and $f_\perp$ are not equal. If they were, then $\beta_2 = 0$, and only the first term in (10) would remain.

To simplify the form of (8) and the subsequent analysis, we shall rescale the time with the characteristic relaxation time of the polymer. Therefore, defining $\tau = t/De$ and $\mathbb{D} = 2De\,\phi_f \kappa\epsilon^2/(\pi a^2)$ (where $\mathbb{D}$ can be interpreted physically as the Deborah number based on the shear rate characteristic of the velocity fluctuations in the bed) we obtain a modified form of (8):

$$\frac{\partial\langle\Omega\rangle}{\partial t} - \tfrac{1}{2}\nabla_r\cdot(\boldsymbol{r}\langle\Omega\rangle) - \nabla_r\cdot\boldsymbol{d}^{\mathrm{h}}\cdot\nabla_r\langle\Omega\rangle = 0 \tag{12a}$$

and

$$d^{\mathrm{h}}_{jm} = \tfrac{1}{2}[\tfrac{1}{3}\delta_{jm} + \mathbb{D}A_{jkmn}\,r_k\,r_n]. \tag{12b}$$

Although we shall return to some of the characteristics of the solution for the distribution function, $\langle\Omega\rangle$, which satisfies (12*a*), here we shall concentrate on the moments of the distribution. In particular, we shall examine the second moment in detail. Although this choice may appear to be somewhat arbitrary, a number of important physical quantities can be calculated from the second moment (including the radius of gyration, the birefringence, and the mean entropic stress in the suspension) and, moreover, we shall show that the important qualitative features of the functionality of other moments with the Deborah number are demonstrated by that of the second moment.

Thus, multiplying (12) by $\boldsymbol{rr}$ and integrating over all conformational space, we obtain after a number of manipulations

$$\frac{\mathrm{d}\overline{r_j r_k}}{\mathrm{d}\tau} + \overline{r_j r_k} - \tfrac{1}{3}\delta_{jk} - \mathbb{D}\,A_{jmkn}\,\overline{r_m r_n} = 0, \tag{13}$$

where the overbar refers to an average over the distribution function $\langle\Omega\rangle$,

$$\overline{\boldsymbol{rr}} = \int \mathrm{d}\boldsymbol{r}\langle\Omega\rangle\,\boldsymbol{rr}.$$

Note that to obtain a closed equation for the second moment defined by (13) we did not have to introduce approximations for higher moments or truncate an infinite series of coupled moment equations arbitrarily. This is a consequence of the quadratic form of the diffusivity $\boldsymbol{d}^{\mathrm{h}}$ (see Lundgren 1981).

Because of the symmetry of the physical system, we need only determine the magnitudes of the projections of the dumbbell in the plane perpendicular to the average flow and in the flow direction itself, to completely specify $\overline{r_i r_j}$. Thus

$$\overline{r_i r_j} = \overline{r_3^2}\,\delta_{i3}\,\delta_{j3} + \overline{\rho^2}[\delta_{ij} - \delta_{i3}\,\delta_{j3}] \tag{14a}$$

and

$$\overline{r^2} = \overline{r_3^2} + 2\overline{\rho^2}. \tag{14b}$$

Therefore, if we substitute our expression for A_{jkmn} into (13), then after some manipulations we can obtain the following three differential equations for $\overline{r^2}$, $\overline{r_3^2}$ and $\overline{\rho^2}$:

$$\frac{\mathrm{d}\overline{r^2}}{\mathrm{d}\tau} + \overline{r^2} - 1 - 2\mathbb{D}\,(5\beta_2 + \beta_1)\,\overline{\rho^2} = 0, \tag{15a}$$

$$\frac{\mathrm{d}\overline{r_3^2}}{\mathrm{d}\tau} + \overline{r_3^2} - \tfrac{1}{3} - 2\mathbb{D}\,(\beta_1 + \beta_2)\,\overline{\rho^2} = 0, \tag{15b}$$

$$\frac{\mathrm{d}\overline{\rho^2}}{\mathrm{d}\tau} + \overline{\rho^2} - \tfrac{1}{3} - 4\mathbb{D}\beta_2\,\overline{\rho^2} = 0. \tag{15c}$$

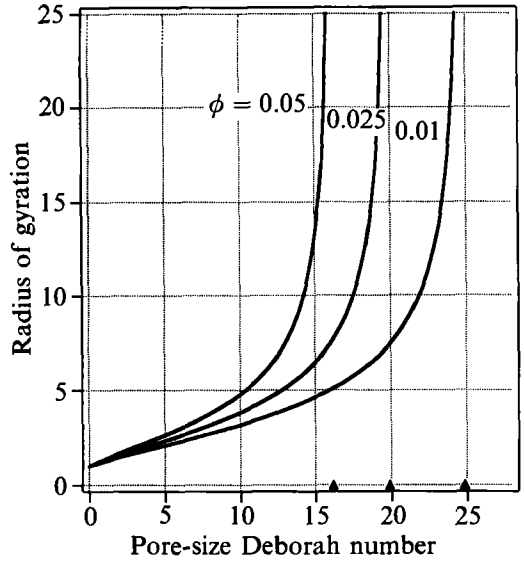

FIGURE 2. The dimensionless radius of gyration for flow through an isotropic fibrous bed *vs.* *De*, for bed volume fractions of 0.01, 0.025, and 0.05. The model for the polymer is a Hookean dumbbell and the critical conditions are indicated at the bottom as solid triangles.

If we assume that the polymer is initially in an equilibrium conformation then the solutions of (15*a–c*) are

$$\overline{r^2} = \tfrac{1}{3}[1+2e^{-s\tau}] + \frac{2[\mathbb{D}(\beta_2+\beta_1)+1]}{3s}(1-e^{-s\tau}), \tag{16a}$$

$$\overline{r_3^2} = \tfrac{1}{3} + \frac{2\mathbb{D}(\beta_2+\beta_1)}{3s}(1-e^{-s\tau}), \quad \overline{\rho^2} = \frac{1}{3}\left[e^{-s\tau} + \frac{1}{s}(1-e^{-s\tau})\right], \tag{16b, c}$$

where $s = 1-4\mathbb{D}\beta_2$. It is clear from (16) that the parameter space of the Deborah number can be separated into two regions. If $s > 0$ then the solutions for the moments of the dumbbell reach a steady solution in the long-time limit, and this steady solution can be summarized by the following equations:

$$\overline{r^2} = \tfrac{1}{3} + \frac{2[\mathbb{D}(\beta_2+\beta_1)+1]}{3s}, \quad \overline{r_3^2} = \tfrac{1}{3} + \frac{2\mathbb{D}(\beta_2+\beta_1)}{3s}, \quad \overline{\rho^2} = \frac{1}{3s}. \tag{17a–c}$$

Note that from (17), it is also clear that the effect of the flow is to increase the size of all the moments over their equilibrium values.

However, if $s \leqslant 0$ there are no steady solutions to (15). Instead, the solutions defined by (16*a–c*) grow in time without bound. This can be examined if we first note that for $s = 0$,

$$4\mathbb{D}\beta_2 = 1 \quad \text{or} \quad De_{\text{crit}} = \frac{\pi a^2}{8\phi_f \kappa \epsilon^2 \beta_2}. \tag{18a, b}$$

Substituting the known results $\beta_2, \kappa^{\frac{1}{2}}$ and ϵ for dilute fibrous beds (Shaqfeh & Koch 1988*a*, *b*) (cf. (3), (7*b*), and (11*b*)) into (18*b*), we obtain

$$De_{\text{crit}} = 5.40\ldots \ln(1/\phi_f). \tag{19}$$

The results for $\overline{r^2}$ *vs.* *De* for $\phi_f = 0.01$, 0.025, and 0.05 are plotted in figure 2 and those for $\overline{r_3^2}$ and $\overline{\rho^2}$ *vs.* *De* are portrayed in figure 3. An examination of these figures leads

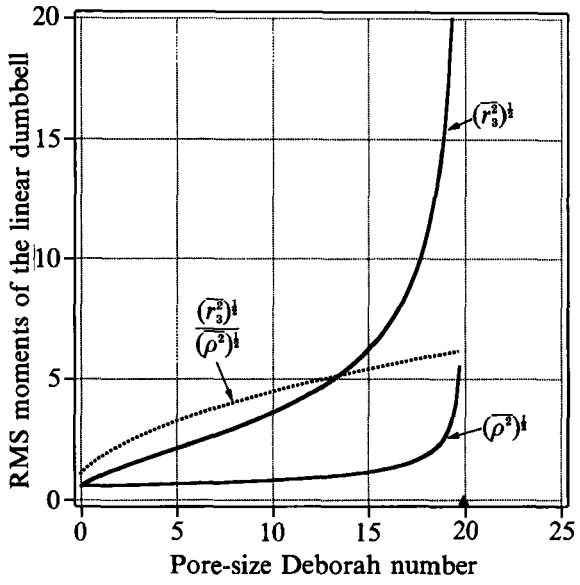

FIGURE 3. The steady, root-mean-squared moments of the linear dumbbell *vs.* *De*, for flow in an isotropic fibre bed. Both the moments perpendicular and parallel to the mean flow are shown. There are no steady solutions for either component past the critical condition $De_{\text{crit}} = 19.9$ shown at the bottom as a solid triangle. The bed volume fraction is 0.025.

immediately to three important conclusions. First, for all $0 \leqslant De < 5.4 \ldots \ln(1/\phi_f)$ the steady stretch in the direction of flow is significantly larger than that in the plane perpendicular to flow. As one approaches the critical condition, $(De)_{\text{crit}} = 5.40 \ln(1/\phi_f)$, the ratio $\overline{r_3^2}/\overline{\rho^2} \to 6.131\ldots$. It follows that the surfaces of constant probability density, $\langle \Omega \rangle$ = constant, are bodies of revolution with their principal axis lying along the flow direction and their aspect ratio increasing with increasing *De* to approximately 6 near the critical condition.

Secondly, we note that at the critical point, $[De]_{\text{crit}} = 5.4 \ln(1/\phi_f)$, the steady predictions for both $\overline{r_3^2}$ and $\overline{\rho^2}$ become unbound. For $s < 0$, from (16*a–c*) we find that both moments grow exponentially in time without bound. Furthermore, we note that at $s = 0$, the growth in time is again unbound, but algebraic, as one can demonstrate by taking the limit of the results in (16*a–c*) as $s \to 0$. The behaviour in a fibrous bed of volume fraction $\phi_f = 0.025$ is depicted in figure 4, where we have plotted $(\overline{r^2})^{\frac{1}{2}}$ *vs.* τ for various subcritical and supercritical values of the Deborah number.

Thirdly, if $\beta_2 = 0$, or, in other words, if the disturbance velocity created by the bed particles were always fore–aft symmetric about the mean flow direction, then there would be no finite critical Deborah number (cf. (18*b*)). This is important in an analysis of other fixed-bed structures, which we consider in §§3 and 4.

In discussing these results, one should keep in mind, that there are definite limitations of the Hookean dumbbell as a model for describing the deformation of a polymer molecule in flow. In the simplest example, the conformation change and stretch exhibited by a polymer molecule is clearly limited by its maximum end-to-end length. No such limitation exists in the Hookean spring model. Furthermore, entropic considerations demonstrate that a polymer which is stretched by a large amount relative to its equilibrium radius of gyration, will recoil via a force that is nonlinear in its end-to-end distance (Tanner 1985; Larson 1988). Moreover, recent

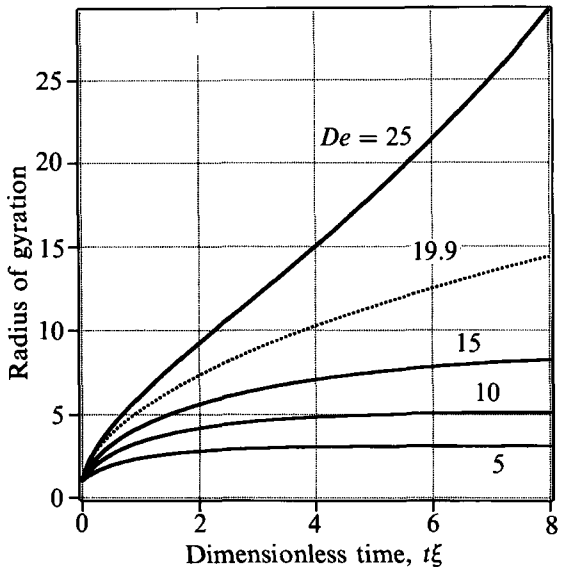

FIGURE 4. The radius of gyration of a linear dumbbell *vs.* time for flow through an isotropic fibrous bed at subcritical and supercritical values of the pore-size Deborah number ($De_{crit} = 19.9$). The bed volume fraction is 0.025.

studies demonstrate that, in certain extensional flows, the polymer will adopt a certain folded conformation in the presence of strong extension (Larson 1990). This conformation tends to unravel very slowly by comparison to the time necessary to attain the folded state. In §2.3 we shall consider a certain finitely extensible dumbbell model (FENE), i.e. the Warner dumbbell (Tanner 1985; Larson 1988), and examine its conformation change in flow through isotropic fibre beds.

There is another physical mechanism by which the singularity in the stretch of a Hookean dumbbell can be removed in these beds. We have consistently neglected the polymeric stresses in calculating the velocities within the bed based on the assumed diluteness of the polymer solution. However, for any small but finite concentration, if the polymer stretch becomes large enough, this approximation will become invalid since the elastic stresses will scale like $n_p[\overline{r^2}]^{\frac{3}{2}}$. One may then ask the question whether the change in the velocity field induced by these polymeric or elastic stresses will actually mitigate the large extension incurred by a linear dumbbell? Thus, it is imagined that at large values of the Deborah number the dumbbells approach a finite but large radius of gyration because of the differences between the disturbance velocity fluctuations created in an elastic fluid versus those in a Newtonian liquid. Rallison & Hinch (1988) have shown that for steady strong flows, such as purely extensional flow, the 'coil-stretch' transition is not prevented by these large elastic stresses. However, in initial studies we have shown (Koch & Shaqfeh 1990) that the first effects of the polymeric stresses are to mildly reduce the stretch incurred by a polymer in a fixed bed of fibres. Only further research can resolve this question. In the present discussion, we will continue to assume that the polymer concentrations remain sufficiently small such that the polymer stresses can always be neglected. One might keep in mind that for any finite concentration this approximation is not a good one for sufficiently large polymer deformation.

Regardless of the questions discussed above, the results in (17)–(19) demonstrate that beyond a certain critical Deborah number, large polymer conformation change and stretch can be expected in the flow through an isotropic fixed fibre bed. This

effect occurs in the presence of a mean flow which, by itself, would create no stretch in the polymer whatsoever. The effect is therefore fluctuation-induced and created by hydrodynamic conformational diffusion. We shall investigate this phenomenon in more detail in the following section where the meaning of the critical condition is examined in terms of the distribution function, $\langle \Omega \rangle$.

2.2. *Algebraic decay of the distribution function,* $\langle \Omega \rangle$

Although the critical Deborah number was defined in the previous section in terms of the second moment and its characteristics, we can relate this critical phenomenon to more general characteristics of the distribution function, $\langle \Omega \rangle$. To do this, we return to (12) which becomes (in the coordinates ρ and $r_3 \equiv z$)

$$\frac{\partial \langle \Omega \rangle}{\partial \tau} - \frac{1}{2\rho}\frac{\partial}{\partial \rho}\rho^2 \langle \Omega \rangle - \frac{1}{2}\frac{\partial}{\partial z} z \langle \Omega \rangle - \frac{1}{6}\frac{1}{\rho}\frac{\partial}{\partial \rho}\rho \frac{\partial}{\partial \rho}\langle \Omega \rangle - \frac{1}{6}\frac{\partial^2}{\partial z^2}\langle \Omega \rangle$$

$$-\tfrac{1}{2}\mathbb{D}(\beta_1+\beta_2)\rho^2 \frac{\partial^2}{\partial z^2}\langle \Omega \rangle + \mathbb{D}\beta_2 \rho^2 \frac{\partial^2}{\partial \rho^2}\langle \Omega \rangle - \tfrac{3}{2}\mathbb{D}\beta_2 \rho \frac{\partial}{\partial \rho}\rho \frac{\partial}{\partial \rho}\langle \Omega \rangle = 0, \quad (20)$$

along with the normalization condition

$$2\pi \int_{-\infty}^{\infty}\int_{0}^{\infty} \langle \Omega \rangle (\rho, z)\, \rho \, \mathrm{d}\rho \, \mathrm{d}z = 1. \quad (21)$$

Although it is difficult to make progress analytically with the system defined by (20) and (21), it is easier to work with the reduced distribution, $\omega(\rho)$, which is defined:

$$\omega(\rho) = 2\pi \int_{-\infty}^{\infty} \Omega(\rho, z)\, \mathrm{d}z, \quad (22)$$

where

$$\int_{0}^{\infty} \omega(\rho)\, \rho \, \mathrm{d}\rho = 1.$$

Integrating (20) over the range $-\infty \leqslant z \leqslant \infty$ and assuming that Ω decays sufficiently rapidly that the integral in (22) exists, we obtain at steady state

$$\frac{1}{2\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\rho^2 \omega + \frac{1}{6\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\rho \frac{\mathrm{d}}{\mathrm{d}\rho}\omega - \mathbb{D}\,\beta_2 \rho^2 \frac{\mathrm{d}^2}{\mathrm{d}\rho^2}\omega + \tfrac{3}{2}\mathbb{D}\,\beta_2 \rho \frac{\mathrm{d}}{\mathrm{d}\rho}\rho \frac{\mathrm{d}}{\mathrm{d}\rho}\omega = 0. \quad (23)$$

For $\rho \gg 1$, (23) becomes

$$\tfrac{1}{2}\mathbb{D}\,\beta_2 \rho^2 \omega'' + \tfrac{1}{2}[\rho + 3\mathbb{D}\,\beta_2 \rho]\omega' + \omega = 0, \quad (24)$$

where the primes in (24) indicate differentiation with respect to ρ. Equation (24) is equidimensional and mathematically represents the balance of the spring restoring force and the hydrodynamic diffusion. The important point is that the hydrodynamic diffusion dominates over the Brownian diffusion when the polymer is in a highly stretched conformation.

The solution of (24) is of the form

$$\omega \approx \rho^{-\alpha} \quad (25)$$

and substituting (25) into (24) gives a quadratic equation with two possible solutions for α,

$$\alpha = 2, \frac{1}{\mathbb{D}\,\beta_2}. \quad (26)$$

If $\alpha = 2$ then $\overline{\rho^2}$ does not exist even in the absence of flow. It follows that

$$\alpha = 1/(\mathbb{D}\,\beta_2)$$

and steady solutions for ω decay for $\rho \gg 1$ like $\omega \approx \rho^{-1/\mathbb{D}\beta_2}$. In order for $\overline{\rho^2}$ to exist then, from (25) and (26), the integral

$$I = \int_0^\infty \rho^{3-1/\mathbb{D}\beta_2}\,\mathrm{d}\rho \tag{27}$$

must exist, which once again gives the restriction $4\beta_2\,\mathbb{D} < 1$. This is identical to (18*a*). Therefore, it is clear that the critical condition is directly related to algebraic tails in the distribution function ω (and in Ω as shown below). These algebraic tails indicate that there exist enough polymers in a highly stretched conformation in order to render impossible any attempt at calculating the steady second moment of the distribution function.

The fact that these algebraic tails create essentially 'infinite' (long-time) moments in the present analysis is, to a certain degree, a product of the aphysical character of the Hookean dumbbell in describing highly stretched polymers. For any polymer model which includes finite extensibility, all moments of the distribution function exist for all values of $\mathbb{D}$ as a direct consequence of the finite domain of Ω. In that instance, we would expect that, for values of $\mathbb{D}$ beyond the condition (18*a*), enough polymers will be highly extended such that $[\overline{\rho^2}]^{\frac{1}{2}}$ (and $[\overline{r^2}]^{\frac{1}{2}}$) will be significant fractions of the maximum extension length of the polymer. This will be verified in the next section.

The qualitative features of the transition described in §§2.1 and 2.2, bear strong similarities to that described by Lumley (1972) and Jhon *et al.* (1987) in their considerations of polymer stretch in model turbulent flows. The transitions which these researchers reported were also fluctuation-induced, but the transitions were time-dependent and occurred in the absence of any mean flow. In addition, for simple Hookean spring models, they were a consequence of the algebraic tails in the probability density function. Although much of the physical details of the problem considered herein and that analysed by Lumley (1972) and Jhon *et al.* (1987) are quite different, we shall investigate in §3 whether there are any common physical principles governing these transitions.

Finally, although (25) and (26) merely demonstrate that an algebraic tail exists in the distribution $\omega(\rho)$, this result can be extended to the distribution Ω. If we notice that when Ω is written in the spherical coordinates r and θ (defined

$$\rho = r\sin\theta, \quad z = r\cos\theta),$$

then for $r \gg 1$, (20) becomes equidimensional in the coordinate r. If we retain only the equidimensional terms in (20) then, at steady state, we have

$$\rho\frac{\partial\Omega}{\partial\rho} + z\frac{\partial\Omega}{\partial z} + 3\Omega + \mathbb{D}(\beta_1+\beta_2)\rho^2\frac{\partial^2\Omega}{\partial z^2} + \mathbb{D}\,\beta_2\rho^2\frac{\partial^2\Omega}{\partial\rho^2} + 3\mathbb{D}\,\beta_2\rho\frac{\partial\Omega}{\partial\rho} = 0. \tag{28}$$

The similarity solution of (28) is of the form

$$\Omega = \rho^\gamma f(z/\rho) = r^\gamma \sin^\gamma\theta f(\cot\theta). \tag{29}$$

If we return to the definition of $\omega(\rho)$, (22), then for $\rho \gg 1$

$$K\rho^{-1/\mathbb{D}\beta_2} = \rho^{\gamma+1}\int_{-\infty}^{\infty} f(\cot\theta)\,\mathrm{d}(\cot\theta), \tag{30}$$

where K is a constant. It follows that

$$\gamma = -\frac{1}{\mathbb{D}\beta_2} - 1. \tag{31}$$

Equation (31) along with (29) is consistent with the critical condition (18) when evaluating $\overline{r^2}$.

2.3. *Finite extensibility*

In the previous sections, we demonstrated that a polymer molecule, modelled as a Hookean spring, will undergo a large conformation change or stretch beyond a certain critical pore-size Deborah number in flow through an isotropic bed of fibres. For conformational changes which are large compared to the equilibrium radius of gyration, we expect from both theoretical and experimental work (Tanner 1985; Larson 1988) that the restoring force will be nonlinear. To be specific, instead of

$$f_i = -\tfrac{1}{2}\xi r_i \tag{32a}$$

where $\boldsymbol{f}$ is the spring force, we expect

$$f_i = -\tfrac{1}{2}\xi h(r/r_0)\, r_i, \tag{32b}$$

where $h \to \infty$ as $r/r_0 \to 1$, and r_0 is the maximum radius of extension for the polymer. We further expect (if the polymer is of large molecule weight), that $R_g/r_0 \ll 1$ where R_g is the equilibrium radius of gyration. In addition, to be consistent with the Hookean spring model for small conformational changes, we require $h \to 1$ for $r/r_0 \ll 1$.

Substituting the model equation (32b) into (2) and proceeding with the manipulations leading to (12), we arrive at

$$\frac{\partial \boldsymbol{\Omega}}{\partial \tau} - \tfrac{1}{2}\boldsymbol{\nabla}_r \cdot h\left(\frac{r^2}{R_0^2}\right)\boldsymbol{r}\boldsymbol{\Omega} - \boldsymbol{\nabla}_r \cdot \boldsymbol{d}^{\mathrm{h}} \cdot \boldsymbol{\nabla}_r \boldsymbol{\Omega} = 0, \tag{33a}$$

where

$$d^{\mathrm{h}}_{jm} = \tfrac{1}{2}[\tfrac{1}{3}\delta_{jm} + \mathbb{D}\, A_{jkmn} r_k r_n], \qquad R_0^2 = \xi r_0^2/(12D), \tag{33b, c}$$

and where one must remember that all lengths have been made dimensionless with

$$[12D/\xi]^{\frac{1}{2}}$$

which is *not* the equilibrium radius of gyration, R_g, because of the influence of the nonlinear spring force. However, the difference between R_g and $[12D/\xi]^{\frac{1}{2}}$ is not a large one if $R_0^2 \gg 1$.

Because the solution of (33) is, again, difficult to obtain analytically, we wish to average (33) and thereby determine information about the moments of $\boldsymbol{\Omega}$. Unfortunately, averaging (33) introduces nonlinear averages (because of h) which cannot be exactly closed. We therefore employ the preaveraging approximation which gives

$$\frac{\partial \langle \boldsymbol{\Omega} \rangle}{\partial \tau} - \tfrac{1}{2}\boldsymbol{\nabla}_r \cdot h(\overline{r^2}/R_0^2)\, \boldsymbol{r} \langle \boldsymbol{\Omega} \rangle - \boldsymbol{\nabla}_r \cdot \boldsymbol{d}^{\mathrm{h}} \cdot \boldsymbol{\nabla}_r \langle \boldsymbol{\Omega} \rangle = 0, \tag{34}$$

where we have set $h(r^2/R_0^2)$ equal to $h(\overline{r^2}/R_0^2)$ as a first approximation. Such a formulation has been shown to give qualitatively correct results for polymer conformation changes in situations where one encounters large polymer deformation (Tanner 1985). We can now multiply (34) by $r_i r_j$ and average over the distribution function to obtain the analog of (13), namely

$$\frac{\mathrm{d}\overline{r_i r_j}}{\mathrm{d}\tau} + h\left(\frac{\overline{r^2}}{R_0^2}\right)\overline{r_i r_j} - \tfrac{1}{3}\delta_{ij} - \mathbb{D}\, A_{ijmn}\, \overline{r_m r_n} = 0. \tag{35}$$

We choose for $h(\overline{r^2}/R_0^2)$ the Warner spring function

$$h(\overline{r^2}/R_0^2) = \frac{1}{1-\overline{r^2}/R_0^2}. \tag{36}$$

The restoring force given by (32*b*) along with (36) is a good approximation to the exact statistical mechanical restoring force for a freely jointed chain in the limit as the number of joints approaches infinity (Larson 1988; Tanner 1985; Bird *et al.* 1987).

Substituting the model equation (36) into (35), we obtain a nonlinear equation for $\overline{r_i r_j}$. At steady state and in the absence of flow, this yields

$$\frac{\overline{r^2}}{1-\overline{r^2}/R_0^2} = 1 \quad \text{or} \quad \overline{r^2} = \frac{R_0^2}{R_0^2+1}. \tag{37a, b}$$

Therefore, within the context of this model, the equilibrium radius of gyration is given by the expression

$$R_g^2 = \frac{R_0^2}{1+R_0^2}\frac{12D}{\xi},$$

or $R_g^2 \approx 12D/\xi$ for $R_0^2 \gg 1$ with errors which are $O(1/R_0^2)$.

The general nonlinear, time-dependent equations for $\overline{r^2}, \overline{\rho^2}$ and $\overline{r_3^2}$ are, from (35),

$$\frac{\mathrm{d}\overline{r^2}}{\mathrm{d}\tau} + h\overline{r^2} - 1 - 2\mathbb{D}(5\beta_2+\beta_1)\overline{\rho^2} = 0, \tag{38a}$$

$$\frac{\mathrm{d}\overline{r_3^2}}{\mathrm{d}\tau} + h\overline{r_3^2} - \tfrac{1}{3} - 2\mathbb{D}(\beta_1+\beta_2)\overline{\rho^2} = 0, \tag{38b}$$

$$\frac{\mathrm{d}\overline{\rho^2}}{\mathrm{d}\tau} + h\overline{\rho^2} - \tfrac{1}{3} - 4\mathbb{D}\beta_2\overline{\rho^2} = 0, \tag{38c}$$

where $h = h[\overline{r^2}/R_0^2]$. In what follows we shall concentrate on the steady-state solution for $\overline{r^2}$. This can most easily be obtained by using (38*c*) (at steady state) to obtain an algebraic relationship between $\overline{\rho^2}$ and $\overline{r^2}$, then substituting directly into (38*a*) to obtain a quadratic equation for $\chi = \overline{r^2}$. The resulting quadratic is

$$\{(1-s)\gamma - \gamma^2\sigma\}\chi^2 + \{s+\gamma+2\gamma\sigma\}\chi - \sigma - 1 = 0, \tag{39}$$

where, $\sigma = \frac{2}{3}(\beta_1-\beta_2)\mathbb{D}$, and $\gamma = 1/R_0^2$. Only one of the two solutions to (39) has physical meaning, since the second gives negative values for $\overline{r^2}$ even in the limit as $\mathbb{D} \to 0$. The final solution is therefore

$$\chi = \frac{-[s+\gamma(1+2\sigma)] + \{[s+\gamma(1+2\sigma)]^2 + 4\gamma(1-s-\gamma\sigma)(\sigma+1)\}^{\frac{1}{2}}}{2\gamma[1-s-\gamma\sigma]}. \tag{40}$$

In figure 5, we plot $(1+R_0^2)\chi/R_0^2 \equiv \overline{r^2}/R_g^2$ *vs. De* for fibre volume fractions $\phi_f = 0.01$, 0.025, and 0.05. For $s \equiv 1-4\beta_2\mathbb{D}$ greater than zero the qualitative behaviour is very similar to that pictured in figure 2. As the Deborah number increases, the dimensionless radius of gyration increases and, near the critical point $s = 0$, begins to undergo a large change. However, for $s \leqslant 0$ this large stretching transition is bound by the finite extensibility of the dumbbell. For very large Deborah number,

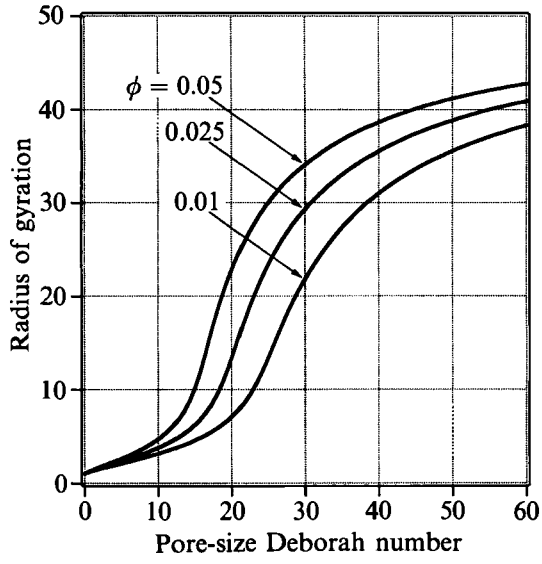

FIGURE 5. The radius of gyration of a FENE (Warner) dumbbell *vs.* *De* in flow through an isotropic fibre bed. The dimensionless maximum radius $R_0 = 50$ and the bed volume fractions are 0.01, 0.025, 0.05 as shown.

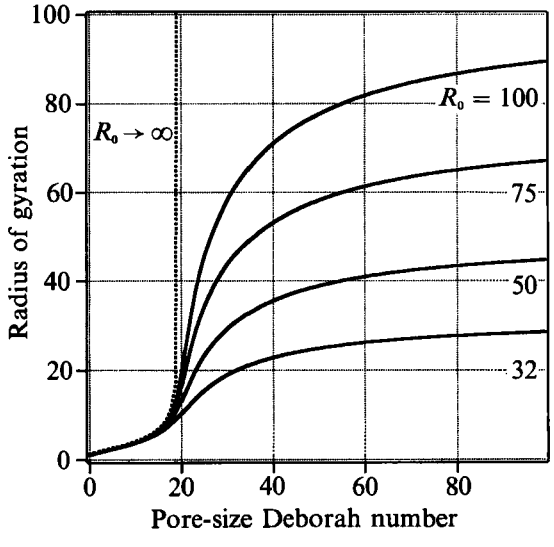

FIGURE 6. The steady radius of gyration of a Warner dumbbell for flow through an isotropic fibre bed *vs.* *De* at various values of the dimensionless maximum radius, R_0. The critical Deborah number for the Hookean dumbbell is 19.9 at a bed volume fraction of 0.025.

it can be shown from (40) that $\chi \to R_0^2$, if $R_0^2 \gg 1$ – that is to say the dumbbell approaches its maximum extensibility. The behaviour of the FENE dumbbell is shown even more clearly in figure 6, where we plot $(1+R_0^2)\chi/R_0^2$ *vs.* *De* at fixed volume fraction for $R_0 = 32, 50, 75, 100, \infty$.

The qualitative differences between our results using the FENE model versus the Hookean spring were perhaps easy to predict *a priori*. However, most interesting about our findings is their striking comparison to the predicted coil-stretch transition of FENE dumbbells in strong purely extensional flows. In figure 7 we have plotted

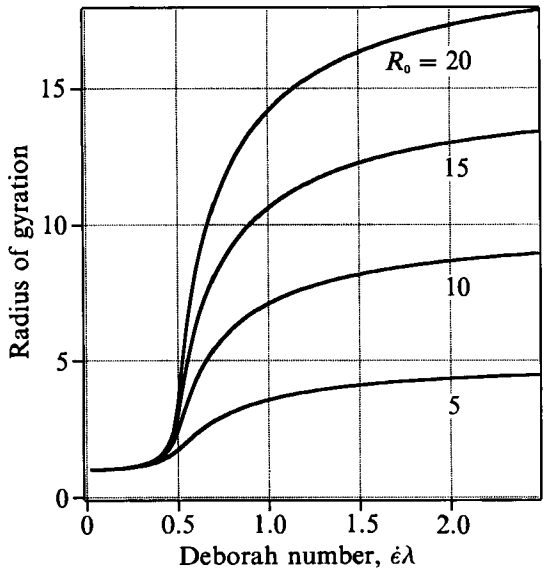

FIGURE 7. The dimensionless radius of gyration of a Warner dumbbell in a planar extensional flow *vs.* *De* at various values of the maximum extensibility, R_0. The *De* is defined as $\dot{\epsilon}\lambda$ where $\dot{\epsilon}$ is the strain rate. The well-known critical condition for a linear dumbbell is $De = \frac{1}{2}$.

the steady radius of gyration $\overline{r^2}$ versus the Deborah number (defined as $\dot{\epsilon}\lambda$ where $\dot{\epsilon}$ is the rate of strain) for a Warner dumbbell in a planar extensional flow. These results are well-known and can be found in any number of texts concerning polymer rheology (see for example Bird *et al.* 1987). For such a dumbbell model in an extensional flow the tensor $\overline{r_m r_n}$ satisfies the equation

$$-De[\overline{r_m r_i}E_{in}+\overline{r_n r_i}E_{im}]+h[\overline{r^2}/R_0^2]\overline{r_m r_n} = \tfrac{1}{3}\delta_{mn},$$

where E_{ij} is the dimensionless rate-of-strain tensor, and where we have again used the preaveraging approximation. It is easy to show from these equations that the 'strong flow criterion' for planar straining flow is $De = \dot{\epsilon}\lambda \geqslant \frac{1}{2}$. Beyond these strain rates, the polymer stretches to a large fraction of its maximum length. Comparing figures 6 and 7 we see that in terms of the qualitative behaviour of the radius of gyration, these two transitions are very similar. These results suggest that any measuring technique (such as flow birefringence) sensitive to the steady second moment of the distribution function should see much the same behaviour in the two flows. (The strong flow criterion for the fluctuation-induced transition in the fixed-fibre bed will be discussed in the next section.)

3. Polymer conformation in equivalent Gaussian fields

In the previous section, we demonstrated that when a polymer moves through the stochastic flow field in a dilute, isotropic fibre bed it can become highly stretched simply through its sampling of the long-range, hydrodynamic fluctuations. In this development we have treated the diffusive process of polymer conformation change via the method of averaged equations that we have used elsewhere in our study of particle orientation in fixed beds (Shaqfeh & Koch 1988*a*, *b*). However, recently, Koch & Shaqfeh (1992), have used diagrammatic methods to treat the problem of time-dependent tracer dispersion in Gaussian random velocity fields and applied these results to mechanical dispersion in flow through fixed beds. In the present

application, we seek to relate our results described in the previous section to an equivalent problem where a polymer molecule's conformation changes in a certain Gaussian flow field. We can then use techniques to develop well-known approximations (e.g. the direct interaction approximation (Kraichnan 1959; Roberts 1961)) for describing the evolution of polymer conformation in this equivalent flow.

In the Appendix we demonstrate explicitly that, in the dilute limit, the stochastic flow field in a fixed bed of fibres or spheres induced via the long-range hydrodynamic interactions can be replaced, in so far as tracer dispersion, pair dispersion, or polymer conformation change is concerned, with a certain anisotropic Gaussian flow field. Mathematically, this means that, to leading order for dilute beds, (4*a*, *b*) can be replaced by

$$\frac{\partial P}{\partial t} - D\nabla^2 P + [U\boldsymbol{i}_z + \boldsymbol{w}(\boldsymbol{x})]\cdot\nabla P - 2D\nabla_r^2 P + \nabla_r\cdot[\dot{\boldsymbol{r}}P] = 0, \tag{41a}$$

and

$$\dot{\boldsymbol{r}} = \boldsymbol{r}\cdot\nabla\boldsymbol{w} - \tfrac{1}{2}\xi\boldsymbol{r}, \tag{41b}$$

where $\boldsymbol{w}(\boldsymbol{x})$ is an anisotropic Gaussian velocity field. Thus, the probability density function defining $\boldsymbol{w}$ can be completely specified by the covariance of $\boldsymbol{w}$, which is defined

$$\mathcal{A}(\boldsymbol{x}, \boldsymbol{x}') \equiv \langle \boldsymbol{w}(\boldsymbol{x})\, \boldsymbol{w}(\boldsymbol{x}')\rangle, \tag{42a}$$

where the angle brackets now refer to an average over the Gaussian statistics of the field. The equivalence of (41*a*, *b*) and the original problem defined by (1) and (2) follows from the fat that, in the dilute limit, the long-range hydrodynamic fluctuations created by the bed particles are considered to be independent. However, a given polymer molecule interacts simultaneously with a large number of bed particles since the interaction length (i.e. the Brinkman screening length) is large compared to the characteristic length scale of the particles. In dilute beds of spheres, a given polymer interacts with an $O(n\kappa^{\frac{3}{2}})$ number of bed particles, or equivalently an $O(1/\phi^{\frac{1}{2}})$ number of particles (Koch & Brady 1985; Shaqfeh & Koch 1988*a*, *b*). In dilute beds of fibres a given polymer interacts with an $O[\phi_f \kappa/\pi a^2)]$ or, equivalently, an $O[\ln(1/\phi_f)]$ number of fibres. Clearly, in the limit as $\phi_f \to 0$ a given molecule interacts with a large number of random, independent fluctuations and thus, as a direct consequence of the central limit theorem (Van Kampen 1981), we can replace these fluctuations with a Gaussian-distributed field. The details of this procedure are provided in the Appendix.

The covariance $\mathcal{A}(\boldsymbol{x}, \boldsymbol{x}')$ has a precise meaning in terms of the conditionally averaged disturbance velocity $\langle \boldsymbol{u}'\rangle_1$ (cf. (7) and following) created by particles in the fixed bed. For example, for random fibre beds (see the Appendix)

$$\mathcal{A} \equiv \frac{\phi_f}{\pi a^2}\int d\boldsymbol{e}\, g(\boldsymbol{e}) \int d\boldsymbol{R}\, \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{e}, \boldsymbol{R})\, \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{e}, \boldsymbol{R}), \tag{42b}$$

where $\boldsymbol{R}, \boldsymbol{e}$, and $g(\boldsymbol{e})$ are defined in the discussion following (6). It follows that the covariance for the equivalent Gaussian field in a fixed bed is of a special form. In particular, since the beds are assumed homogeneous, translational invariance requires that transform of the covariance, defined as

$$\hat{\mathcal{A}}(\boldsymbol{k}, \boldsymbol{k}') \equiv \int d\boldsymbol{x}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \int d\boldsymbol{x}'\, e^{-i\boldsymbol{k}'\cdot\boldsymbol{x}'}\, \mathcal{A}(\boldsymbol{x}, \boldsymbol{x}'), \tag{43}$$

satisfies the following relations:

$$\begin{aligned}\hat{\mathcal{A}}(\boldsymbol{k}, \boldsymbol{k}') &= \widehat{\langle \boldsymbol{w}(\boldsymbol{x})\, \boldsymbol{w}(\boldsymbol{x}')\rangle} = (2\pi)^3\delta(\boldsymbol{k}+\boldsymbol{k}')\, \langle \hat{\boldsymbol{w}}(\boldsymbol{k})\, \hat{\boldsymbol{w}}(-\boldsymbol{k})\rangle \\ &= (2\pi)^3\delta(\boldsymbol{k}+\boldsymbol{k}')\, \langle \widehat{\boldsymbol{w}(\boldsymbol{x})\, \boldsymbol{w}(\boldsymbol{0})}\rangle.\end{aligned} \tag{44}$$

In addition, we note that $\langle \hat{\boldsymbol{w}}(\boldsymbol{k})\,\hat{\boldsymbol{w}}(-\boldsymbol{k})\rangle$ can only depend on the vectors $\tilde{\boldsymbol{U}} \equiv \boldsymbol{U}/|\boldsymbol{U}| = \boldsymbol{i}_z$ and $\tilde{\boldsymbol{k}} \equiv \boldsymbol{k}/|\boldsymbol{k}|$, and, moreover, since the disturbance fields created by the fixed bed particles are solenoidal,

$$\boldsymbol{k}\cdot\langle \hat{\boldsymbol{w}}(\boldsymbol{k})\,\hat{\boldsymbol{w}}(-\boldsymbol{k})\rangle = \langle \hat{\boldsymbol{w}}(\boldsymbol{k})\,\hat{\boldsymbol{w}}(-\boldsymbol{k})\rangle\cdot\boldsymbol{k} = 0. \tag{45}$$

It follows that for any homogeneous, dilute fixed bed $\hat{\boldsymbol{A}}$ must be of the general form

$$\hat{A}_{ij} = (2\pi)^3\,\delta(\boldsymbol{k}+\boldsymbol{k}')\,[K_1\,\tilde{U}_l\,\tilde{U}_m(\delta_{il}-\tilde{k}_i\,\tilde{k}_l)\,(\delta_{jm}-\tilde{k}_j\,\tilde{k}_m)+K_2(\delta_{ij}-\tilde{k}_i\,\tilde{k}_j)]. \tag{46}$$

In (46), K_1 and K_2 are scalar functions of k and $\tilde{\boldsymbol{U}}\cdot\boldsymbol{k} = k_z$. These functions can be determined for any given fixed bed structure via the methods discussed in detail in the Appendix. Furthermore, the first term on the right-hand side of (46) can be characterized as the 'anisotropic' part of the covariance and the second term the 'isotropic' part, since the latter is of the form that the covariance would take if the stochastic field were isotropic and incompressible. Only the second term was included in the covariance in previous research regarding the effect of stochastic fields on polymer conformation (see Lumley 1972 and Jhon *et al.* 1987). The first term is introduced solely because of anisotropy associated with the fact that the fluctuations (i.e. the disturbance velocities in the bed) are created by the presence of a mean flow $\boldsymbol{U}$.

We are interested in the average behaviour of a polymer molecule as it samples the stochastic Gaussian field. To develop an approximation for that behaviour, we first make (41*a*, *b*) dimensionless to obtain equations analogous to (4*a*, *b*), namely

$$\frac{\partial P}{\partial t}-[Pe]^{-1}\nabla^2 P+\frac{\partial P}{\partial z}-[6De]^{-1}\nabla_r^2 P+\nabla_r\cdot[\dot{\boldsymbol{r}}P] = -\boldsymbol{w}\cdot\nabla P, \tag{47a}$$

$$\dot{\boldsymbol{r}} = \boldsymbol{r}\cdot\nabla\boldsymbol{w}-\tfrac{1}{2}\boldsymbol{r}\,De, \tag{47b}$$

where Pe and De are as defined in (5). Note that the characteristic length $\kappa^{\frac{1}{2}}$ now is the correlation length of the velocity fluctuations $\boldsymbol{w}$ in the equivalent Gaussian field. This follows directly from (42*b*). We now consider the Green function, $G(\boldsymbol{x},\boldsymbol{r},t)$, of the stochastic differential equations (47), where we add to the right-hand side the source term $S(\boldsymbol{r},\boldsymbol{x},t) = \delta(\boldsymbol{x})\,\delta(\boldsymbol{r})\,\delta(t)$. Therefore, G satisfies

$$\frac{\partial G}{\partial t}-[Pe]^{-1}\nabla^2 G+\frac{\partial G}{\partial z}-[6De]^{-1}\nabla_r^2 G-[2De]^{-1}\nabla_r\cdot\boldsymbol{r}G$$

$$= -\nabla_r\cdot[(\boldsymbol{r}\cdot\nabla\boldsymbol{w})\,G]-\boldsymbol{w}\cdot\nabla G+\delta(\boldsymbol{x})\,\delta(\boldsymbol{r})\,\delta(t). \tag{48}$$

We seek appropriate solutions for $\langle G\rangle$.

To motivate our solution method, we briefly summarize the analysis of a simpler stochastic differential equation considered in our previous publication (see Koch & Shaqfeh 1992). We consider the Green function, $G(\boldsymbol{x},t)$ which satisfies the equation

$$\left\{\frac{\partial}{\partial t}+\frac{\partial}{\partial z}\right\}G = \delta(\boldsymbol{x})\,\delta(t)-\boldsymbol{w}\cdot\nabla G. \tag{49}$$

Equation (49) describes the spreading of a passive tracer in a stochastic flow field where the dimensionless mean velocity is $\boldsymbol{i}_z$ and $\boldsymbol{w}$ is the perturbing stochastic field (see Roberts 1961; Koch & Shaqfeh 1992). In our previous work, we developed useful approximate solutions to (49) for $\langle G\rangle$ by first Fourier transforming in space and time to yield

$$\hat{G}(\boldsymbol{k},\omega) = \hat{G}_0(\boldsymbol{k},\omega)+\hat{G}_0\,T(\boldsymbol{k})\,\hat{G}(\boldsymbol{k},\omega). \tag{50}$$

In (50), $\boldsymbol{k}$ and ω are respectively the wavevector and frequency in the transform domain and $\hat{G}_0$ is defined

$$\hat{G}_0 = \frac{1}{\mathrm{i}(\omega + k_z)}. \tag{51}$$

In addition, $T(\boldsymbol{k})$ is an operator defined such that

$$T(\boldsymbol{k})\,\hat{G}(\boldsymbol{k},\omega) = -\mathrm{i}\int_{\boldsymbol{k}'} \boldsymbol{k}\cdot\tilde{\boldsymbol{w}}(\boldsymbol{k}-\boldsymbol{k}')\,\hat{G}(\boldsymbol{k}'), \tag{52}$$

where

$$\int_{\boldsymbol{k}'} \equiv \frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}'.$$

As has been shown previously, one can average (50) and apply renormalized perturbation theory (see Kraichnan 1959; Roberts 1961; Koch & Shaqfeh 1992) to derive the direct interaction approximation (DIA) for $\langle\hat{G}\rangle$, namely

$$\langle\hat{G}\rangle = \frac{1}{\mathrm{i}(\omega + k_z) + \boldsymbol{k}\boldsymbol{k}:\boldsymbol{D}(\boldsymbol{k})}, \tag{53}$$

where $\boldsymbol{D}(\boldsymbol{k})$ is a non-local diffusivity tensor defined

$$\boldsymbol{D} = \int_{\boldsymbol{k}'} \langle\hat{\boldsymbol{w}}(\boldsymbol{k}-\boldsymbol{k}')\,\hat{\boldsymbol{w}}(\boldsymbol{k}'-\boldsymbol{k})\rangle\,\langle\hat{G}\rangle\,(\boldsymbol{k}',\omega). \tag{54}$$

This approximation is particularly good for 'weak' fluctuations, i.e.

$$|\langle\hat{\boldsymbol{w}}(\boldsymbol{k})\,\hat{\boldsymbol{w}}(-\boldsymbol{k})\rangle| \ll 1,$$

and time long compared to that necessary for the mean flow to traverse the correlation length of the fluctuations. In this dual limit, the DIA gives the correct long-time behaviour for $\langle\hat{G}\rangle$. Note that we are interested in situations where the fluctuations are weak, since the conditionally averaged disturbance velocities are small relative to the mean flow at distances of $O(\kappa^{\frac{1}{2}})$ from the bed particles (cf. (7) and (42*a*)).

If we denote by $\langle\hat{G}\rangle_\infty$ the Green function for long time, then for weak fluctuations we have (as demonstrated elsewhere, see Roberts 1961; Koch & Brady 1985; Koch & Shaqfeh 1992)

$$\langle\hat{G}\rangle_\infty \to \frac{1}{\mathrm{i}(\omega + k_z) + \boldsymbol{k}\boldsymbol{k}:\boldsymbol{D}^\infty}, \tag{55a}$$

where

$$\boldsymbol{D}^\infty = \lim_{|\boldsymbol{k}|\to 0,\,\omega\to 0}\left[\int_{\boldsymbol{k}'} \langle\hat{\boldsymbol{w}}(\boldsymbol{k}-\boldsymbol{k}')\,\hat{\boldsymbol{w}}(\boldsymbol{k}'-\boldsymbol{k})\,\langle\hat{G}\rangle\,(\boldsymbol{k}',w)\right] \tag{55b}$$

$$\approx \frac{1}{2}\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{\xi}\,\langle\hat{\boldsymbol{w}}(\boldsymbol{\xi})\,\hat{\boldsymbol{w}}(-\boldsymbol{\xi})\rangle, \tag{55c}$$

where $\boldsymbol{D}^\infty$ is the long-time, constant diffusivity created by the fluctuating velocity field and $\boldsymbol{\xi}$ is the wavenumber in the two-dimensional plane perpendicular to $\tilde{\boldsymbol{U}}$, i.e. $\xi_i = (\delta_{ij} - \tilde{U}_i\tilde{U}_j)\,k_j$. The result (55*c*) is equivalent to that derived by Koch & Brady (1985) (for mechanical dispersion at large Péclet number) and briefly discussed by Koch & Shaqfeh (1992).

We can now apply the same techniques to the solution of (48). Defining the transform of $G(\boldsymbol{x},\boldsymbol{r},t)$ through the expression

$$\hat{G}(\boldsymbol{k},\boldsymbol{\alpha},\omega) = \int \mathrm{d}\boldsymbol{x}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}\int \mathrm{d}\boldsymbol{r}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{\alpha}\cdot\boldsymbol{r}}\int \mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}\,G(\boldsymbol{x},\boldsymbol{r},t), \tag{56}$$

we can transform (48) to yield the expression

$$\mathrm{i}(\omega+k_z)\,\hat{G}+(Pe)^{-1}k^2\hat{G}+(6De)^{-1}\alpha^2\hat{G}+(2De)^{-1}\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}_{\alpha}\hat{G}=T^{\alpha}(\boldsymbol{k},\boldsymbol{\alpha})\,\hat{G}+T(\boldsymbol{k})\,\hat{G}+1, \tag{57a}$$

where

$$T^{\alpha}(\boldsymbol{k},\boldsymbol{\alpha})\,\hat{G}=\mathrm{i}\alpha_j\frac{\partial}{\partial\alpha_l}\int_{k'}(k_l-k_l')\,\hat{w}_j(\boldsymbol{k}-\boldsymbol{k}')\,\hat{G}. \tag{57b}$$

Note that (57a, b) are now stochastic integro-differential equations since

$$\boldsymbol{\nabla}_r\cdot\boldsymbol{r}G=-\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}_{\alpha}\hat{G}.$$

However, this does not prevent us from applying renormalized perturbation theory to calculate the DIA. Since the fluctuations are 'weak' in the sense described previously and because we are most interested in conformational diffusion rather than centre-of-mass diffusion, we shall neglect the fluctuations in the centre-of-mass position, i.e. the T-operator in (57a) throughout the remaining development. This small centre-of-mass diffusion will create negligibly small changes in the configurational diffusion as we shall indicate below. Neglecting the centre-of-mass fluctuations, it follows directly that the DIA for $\hat{G}$ becomes the solution of the following equation in wavenumber space:

$$\mathrm{i}(\omega+k_z)\langle\hat{G}\rangle+[Pe]^{-1}k^2\langle\hat{G}\rangle+[6De]^{-1}\alpha^2\langle\hat{G}\rangle+[2De]^{-1}\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}_{\alpha}\langle\hat{G}\rangle=\alpha_i\alpha_j d_{ij}\langle\hat{G}\rangle+1, \tag{58}$$

where d_{ij} is the configurational diffusion operator, defined

$$d_{ij}\langle\hat{G}\rangle=-\int_{k'}(k_l-k_l')\langle\hat{w}_i(\boldsymbol{k}-\boldsymbol{k}')\,\hat{w}_j(\boldsymbol{k}'-\boldsymbol{k})\rangle\,(k_m'-k_m)\frac{\partial}{\partial\alpha_l}\left[\langle\hat{G}\rangle\frac{\partial\langle\hat{G}\rangle}{\partial\alpha_m}\right]. \tag{59}$$

Equation (59) represents the non-local configurational diffusion created by the fluctuations. For large values of the Deborah number and weak fluctuations, changes in the polymer configuration during the sampling of any given fluctuation can be neglected. This is equivalent to simplifying the first factor of $\langle\hat{G}\rangle$ in (59), and we therefore approximate $d_{ij}\langle\hat{G}\rangle$ as

$$d_{ij}\langle\hat{G}\rangle\approx-\int_{k'}(k_l-k_l')\langle\hat{w}_i(\boldsymbol{k}-\boldsymbol{k}')\,\hat{w}_j(\boldsymbol{k}'-\boldsymbol{k})\rangle\frac{(k_m'-k_m)}{\mathrm{i}(\omega+k_z')+Pe^{-1}k'^2}\frac{\partial^2\langle\hat{G}\rangle}{\partial\alpha_l\,\partial\alpha_m}. \tag{60}$$

Note that if we were to retain the centre-of-mass diffusion created by the hydrodynamic fluctuations then in the denominator of the integrand in (60) we would include the non-local diffusion terms found in (53) and (54). These would create small corrections in the remaining development because the diffusivity is proportional to the small covariance tensor. Finally, for very large values of the Péclet number, $Pe\gg1$, and in the long-time limit, where the polymer's centre-of-mass has spread over great distances relative to the correlation length of the fluctuations, we have

$$\lim_{|k|\to0,\,\omega\to0}d_{ij}\langle\hat{G}\rangle\equiv\frac{1}{2}\frac{1}{(2\pi)^2}\int\mathrm{d}\boldsymbol{\xi}\,\xi_l\langle\hat{w}_i(\boldsymbol{\xi})\,\hat{w}_j(-\boldsymbol{\xi})\rangle\,\xi_m\frac{\partial^2\langle\hat{G}\rangle}{\partial\alpha_l\,\partial\alpha_m}. \tag{61}$$

Substituting this result back into (58) and inverting the transform, we find that the averaged equation defining $\langle G\rangle$ in the long-time limit is

$$\frac{\partial\langle G\rangle}{\partial t}+\frac{\partial\langle G\rangle}{\partial z}-[Pe]^{-1}\boldsymbol{\nabla}^2\langle G\rangle-[2De]^{-1}\partial\boldsymbol{\nabla}_r\cdot\boldsymbol{r}\langle G\rangle-\frac{1}{De}\frac{\partial}{\partial r_j}d_{jk}^{\mathrm{h}}\frac{\partial\langle G\rangle}{\partial r_k}=\delta(\boldsymbol{x})\,\delta(\boldsymbol{r})\,\delta(t) \tag{62a}$$

where
$$d^{\mathrm{h}}_{jm} = \tfrac{1}{2}[\tfrac{1}{3}\delta_{jm} + r_k r_n B_{jkmn}], \tag{62b}$$

$$B_{jkmn} \equiv \frac{De}{4\pi^2}\int \mathrm{d}\boldsymbol{\xi}\, \xi_k \langle \hat{w}_j(\boldsymbol{\xi})\, \hat{w}_m(-\boldsymbol{\xi})\rangle\, \xi_n. \tag{62c}$$

Equations (62*b*, *c*) serve as the definition of the full conformational diffusivity which includes conformational diffusion created by long-range hydrodynamic interactions in any dilute fixed bed. Clearly the form of the integral

$$\int \mathrm{d}\boldsymbol{\xi}\, \xi_k \langle \hat{w}_j(\boldsymbol{\xi})\, \hat{w}_m(-\boldsymbol{\xi})\rangle\, \xi_n$$

is crucial in determining any critical conditions which occur due to flow in the bed. With the aid of (46), it is now possible to derive such conditions for a general covariance and, therefore, a general fixed bed structure.

3.1. *Critical conditions for general covariance*

Proceeding to derive these conditions, we note that (44) and (46) give the result

$$\langle \hat{w}_i(\boldsymbol{k})\, \hat{w}_j(-\boldsymbol{k})\rangle = [K_1(k, \tilde{\boldsymbol{U}}\cdot\boldsymbol{k})\, \tilde{U}_l \tilde{U}_m(\delta_{il} - \tilde{k}_i \tilde{k}_l)(\delta_{jm} - \tilde{k}_j \tilde{k}_m) + K_2(k, \tilde{\boldsymbol{U}}\cdot\boldsymbol{k})(\delta_{ij} - \tilde{k}_i \tilde{k}_j)], \tag{63}$$

where K_1 and K_2 have been made dimensionless. If we substitute (63) into (62*c*), then we obtain after some straightforward algebra

$$B_{jkmn} = \frac{De}{4\pi^2}\{\beta_3[(\delta_{kn} - \tilde{U}_k \tilde{U}_n)(\tilde{U}_j \tilde{U}_m)] - \beta_4[\delta_{jk}\delta_{mn} + \delta_{jn}\delta_{km} - 3\delta_{jm}\delta_{kn} - \tilde{U}_j \tilde{U}_k \delta_{mn}$$
$$- \tilde{U}_k \tilde{U}_m \delta_{jn} - \tilde{U}_j \tilde{U}_n \delta_{km} - \tilde{U}_m \tilde{U}_n \delta_{jk} + 2\tilde{U}_j \tilde{U}_m \delta_{kn} + 3\tilde{U}_k \tilde{U}_n \delta_{jm}]\}, \tag{64a}$$

where
$$\beta_3 = \pi \int_0^\infty \mathrm{d}\xi\, \xi^3 [K_1(\xi, 0) + \tfrac{3}{4} K_2(\xi, 0)], \quad \beta_4 = \frac{\pi}{4}\int_0^\infty \mathrm{d}\xi\, \xi^3 K_2(\xi, 0) \tag{64b, c}$$

and $\xi = |\boldsymbol{\xi}|$. Note that to within a multiplicative constant, B_{jkmn} is equal to A_{jkmn} defined in (10). In addition, if we integrate (62*a*) over the spatial variable $\boldsymbol{x}$ and use the fact that $\int \mathrm{d}\boldsymbol{x} \langle G\rangle = \langle \Omega\rangle$, then we again arrive at (12*a*) except where d^{h}_{jk} defined by (62*b*). It follows that there exists a critical value of De for a general covariance which is determined by the values of β_3 and β_4. To determine this condition we need only calculate the analogues of (15) and (16), using the result (62*b*) for the conformational diffusivity. The results are

$$\frac{\mathrm{d}\overline{r^2}}{\mathrm{d}\tau} + \overline{r^2} - 1 - \frac{De}{2\pi^2}(5\beta_4 + \beta_3)\overline{\rho^2} = 0, \tag{65a}$$

$$\frac{\mathrm{d}\overline{r_3^2}}{\mathrm{d}\tau} + \overline{r_3^2} - \tfrac{1}{3} - \frac{De}{2\pi^2}(\beta_3 + \beta_4)\overline{\rho^2} = 0, \tag{65b}$$

$$\frac{\mathrm{d}\overline{\rho^2}}{\mathrm{d}\tau} + \overline{\rho^2} - \tfrac{1}{3} - \frac{De\,\beta_4}{\pi^2}\overline{\rho^2} = 0; \tag{65c}$$

$$\overline{r^2} = \tfrac{1}{3}[1 + 2\mathrm{e}^{-s\tau}] + \frac{[De(\beta_4 + \beta_3)/2\pi^2 + 2]}{3s}(1 - \mathrm{e}^{-s\tau}), \tag{66a}$$

$$\overline{r_3^2} = \tfrac{1}{3} + \frac{De(\beta_4 + \beta_3)}{6\pi^2 s}(1 - \mathrm{e}^{-s\tau}), \tag{66b}$$

$$\overline{\rho^2} = \tfrac{1}{3}[\mathrm{e}^{-s\tau} + (1/s)(1 - \mathrm{e}^{-s\tau})], \tag{66c}$$

where now $s \equiv 1-(De\,\beta_4)/\pi^2$. These are identical to (15) and (16) except where

$$\frac{De\,\beta_3}{4\pi^2} = \mathbb{D}\,\beta_1, \quad \frac{De\,\beta_4}{4\pi^2} = \mathbb{D}\,\beta_2. \tag{67a, b}$$

We note, as an aside, that if one calculates the covariance in an isotropic bed of fibres and then calculates the values of β_3 and β_4, the equalities (67a) are identically satisfied. However, we omit the proof here.

From (65) and (66), it follows that the critical condition for a general covariance is

$$De_{\text{crit}} \equiv \frac{\pi^2}{\beta_4} = \frac{4\pi}{\int_0^\infty \mathrm{d}\xi\,\xi^3 K_2(\xi, 0)}. \tag{68}$$

It is most important to note that De_{crit} only depends on K_2 and therefore only on the isotropic part of the covariance. The anisotropic part does not cause a critical stretch to occur. In addition, we note from (67b) that the isotropic part of the covariance, at least for isotropic fibre beds, is created entirely from the lack of fore–aft symmetry of the disturbance velocity fields in the bed. Thus, if β_2 were zero, then it follows that K_2 would also vanish. We shall further examine the inter-relationship of the isotropic part of the covariance and the fore–aft symmetry of the disturbance velocity in the next section where we discuss flow through dilute beds of spheres.

Finally, the results of this section demonstrate the link between the large configuration change in fixed beds and that already reported by Jhon *et al.* (1987) and Lumley (1972) for turbulent flows. Namely, that in both instances it is the isotropic fluctuations which cause a critically large polymer configuration change. In the case of fixed beds, the long-range, disordered disturbance velocities create a velocity covariance with both anisotropic and isotropic parts. In turbulent flows, it is often assumed that the covariance is isotropic. In the case examined by Lumley (1972) and Jhon *et al.* (1987) the transition is time-dependent because they assume that there is no mean flow and thus the polymers sample the fluctuations in time rather than as they move through space. Nevertheless, although the means by which the polymer samples the fluctuations differ, the result is the same – the isotropic fluctuating field will create large conformation change at a certain value of the Deborah number.

4. Polymer stretch in fixed beds of spheres: long-range interactions

In this section, we briefly discuss the application of our theory to flow of polymers through dilute beds of spheres. We shall analyse the flow using the general scheme developed in the previous section. Alternatively, we could employ the results from Shaqfeh & Koch (1988a, b) and develop a kinetic theory which accounts for polymer/sphere interactions just as we did for fibre beds in §2. These two methods are completely equivalent and yield identical results.

For dilute beds of spheres, the dimensionless covariance of the equivalent Gaussian field is

$$\boldsymbol{\Delta} = n\kappa^{\frac{3}{2}} \int \mathrm{d}\boldsymbol{R}\,\langle \boldsymbol{u}' \rangle_1(\boldsymbol{x}-\boldsymbol{R}\,|\,\boldsymbol{R})\,\langle \boldsymbol{u}' \rangle_1(\boldsymbol{x}'-\boldsymbol{R}\,|\,\boldsymbol{R}), \tag{69}$$

where $\langle \boldsymbol{u}' \rangle_1$ is the conditionally averaged disturbance velocity (in the far field) for a sphere centred at $\boldsymbol{R}$ and $\boldsymbol{\Delta}$ is made dimensionless with U^2. We have assumed that the

spheres are randomly positioned in space and therefore that the probability density function for finding a sphere at $\boldsymbol{R}$ is n – the number density of spheres. Transforming (69) gives

$$\hat{\boldsymbol{A}} = n\kappa^{\frac{3}{2}} 2\pi^3 \delta(\boldsymbol{k}+\boldsymbol{k}') \langle \hat{\boldsymbol{u}}' \rangle_1(\boldsymbol{k}) \langle \hat{\boldsymbol{u}}' \rangle_1(-\boldsymbol{k}). \tag{70}$$

For dilute beds of spheres, it is well known that far from the sphere the conditionally averaged velocity disturbance is (see Hinch 1977; Koch & Brady 1985)

$$\langle \hat{u}_i' \rangle_1 = \frac{6\pi a \tilde{U}_j(\delta_{ij} - \tilde{k}_i \tilde{k}_j)}{\kappa^{\frac{1}{2}}(k^2+1)}, \tag{71}$$

where $\boldsymbol{k}$ is the dimensionless wavenumber. Substituting this result into the definition of $\hat{\boldsymbol{A}}$, we obtain

$$\hat{A}_{ij} = (2\pi)^3 \delta(\boldsymbol{k}+\boldsymbol{k}') \left[\frac{9\sqrt{2\pi}\phi_f^{\frac{1}{2}}}{(k^2+1)^2} \tilde{U}_l \tilde{U}_m (\delta_{il} - \tilde{k}_i \tilde{k}_l)(\delta_{jm} - \tilde{k}_j k_m) \right], \tag{72}$$

where we have used the fact that for a dilute bed of spheres, $a/\kappa^{\frac{1}{2}} \approx (\frac{9}{2}\phi)^{\frac{1}{2}}$ (Howells 1974) and where a is the sphere radius. Comparing (72) to the general expression (46), we find

$$K_1 = \frac{9\sqrt{2\pi}\phi_f^{\frac{1}{2}}}{(k^2+1)^2}, \quad K_2 = 0. \tag{73}$$

Thus, there is no critical conformation change due to long-range hydrodynamic interactions in the dilute limit. Again, this is because the disturbance velocity is fore–aft symmetric about the mean flow, giving only the anisotropic term in the covariance (cf. (72)). The equations for the moments can be determined in this case by calculating β_3 from (64*b*)

$$\beta_3 \approx 9\sqrt{2}\pi^2 \phi_f^{\frac{1}{2}} \int_0^{\kappa^{\frac{1}{2}}/a} \mathrm{d}\xi \frac{\xi^3}{(\xi^2+1)^2} \approx 9\sqrt{2}\pi^2 \phi_f^{\frac{1}{2}} \ln(\kappa^{\frac{1}{2}}/a). \tag{74}$$

Note that the integral in (64*b*) is actually conditionally convergent and therefore yields a logarithmically large contribution coming from wavenumbers large compared to $1/a$ (interactions on lengths between a and $\kappa^{\frac{1}{2}}$). This has been discussed in detail in our previous publication concerning particle orientation in fixed beds (see Shaqfeh & Koch 1988*a*).

Substituting (74) along with $\beta_4 = 0$ into (66*a–c*), we find

$$\overline{r^2} = \tfrac{1}{3}(1+2\mathrm{e}^{-\tau}) + (\mathbb{D}+\tfrac{2}{3})(1-\mathrm{e}^{-\tau}), \quad \overline{r_3^2} = \tfrac{1}{3} + \mathbb{D}(1-\mathrm{e}^{-\tau}), \quad \overline{\rho^2} = \tfrac{1}{3}, \tag{75a–c}$$

where

$$\mathbb{D} = \frac{De\,\beta_3}{6\pi^2} = \frac{3\sqrt{2}}{2}\phi_f^{\frac{1}{2}} De \ln(\kappa^{\frac{1}{2}}/a). \tag{75d}$$

For all values of the Deborah number there is a finite steady-state solution given by

$$\overline{r^2} \to \mathbb{D}+1; \quad \overline{r_3^2} \to \tfrac{1}{3}+\mathbb{D}; \quad \overline{\rho^2} = \tfrac{1}{3}. \tag{76}$$

We note that for these fluctuations, which are symmetric about the mean flow, $\overline{\rho^2}$ does not change from its equilibrium value for all time. However, the stretch in the flow direction defined by $\overline{r_3^2}$ increases linearly with the Deborah number, resulting in a linear increase in $\overline{r^2}$.

Thus, to obtain a 'critical stretch' for a polymer in flow through a dilute bed of spheres, one must break the symmetry of the disturbance velocity field created by

the spheres. A simple way of accomplishing this is to introduce a second sphere during the hydrodynamic interaction between a polymer and a given sphere. The presence of a second sphere (through its disturbance velocity) perturbs the direction of the force on a given sphere away from the mean flow direction. As we show below, these interactions then produce an isotropic component to the covariance and a critical condition. This demonstrates that the presence of multi-particle, long-range interactions sharply increases the probability of large polymer conformation change in these beds.

To demonstrate this effect, we return to (69) for the dimensional covariance. We note that the first effect of two-sphere interactions is for a second sphere to induce a point force at the centre of the first sphere due to the disturbance flow of the second. Again the largest effect of these two-sphere interactions comes from the long-range effect (i.e. lengths of $O(\kappa^{\frac{1}{2}})$) where the spheres appear as point forces. Mathematically, using $\hat{\boldsymbol{u}}$ to denote the disturbance velocity created by a single sphere centred at the origin we have

$$\hat{\boldsymbol{u}} = \hat{\boldsymbol{u}}^{(0)}(\boldsymbol{k}) + \hat{\boldsymbol{u}}^{(1)}(\boldsymbol{k};\boldsymbol{\zeta}) + \ldots, \tag{77a}$$

$$\hat{u}_i^{(0)} \equiv \langle \hat{\boldsymbol{u}} \rangle_1 = \frac{6\pi a\, \tilde{U}_j(\delta_{ij} - \tilde{k}_i \tilde{k}_j)}{\kappa^{\frac{1}{2}}(k^2+1)}, \tag{77b}$$

$$\hat{u}_i^{(1)} = \frac{6\pi a u_j^{(0)}(\boldsymbol{\zeta})\,(\delta_{ij} - \tilde{k}_i \tilde{k}_j)}{\kappa^{\frac{1}{2}}(k^2+1)}, \tag{77c}$$

where the second term on the right-hand side of (77a) is the leading-order effect of the second sphere on the disturbance created by the first sphere (i.e. the first reflection interaction). In (77a, c) $\boldsymbol{\zeta}$ is the interparticle separation between the point forces. Note that (77a) is a power series in $a/\kappa^{\frac{1}{2}}$ and that higher-order terms include multiple reflections plus multiparticle interactions.

If we now use the result (77a) as the velocity fluctuation or disturbance created by a single sphere, then the covariance of the equivalent Gaussian field becomes

$$\hat{\Delta}_{ij} = (2\pi)^3 \delta(\boldsymbol{k}+\boldsymbol{k}') \left[n\kappa^{\frac{3}{2}} \hat{u}_i^{(0)} \hat{u}_j^{(0)} + n^2 \kappa^3 \int \mathrm{d}\boldsymbol{\zeta}\, \hat{u}_i^{(1)} \hat{u}_j^{(1)} \right]. \tag{78}$$

The first term on the right-hand side of (78) corresponds to that already considered in (72). The second term provides a correction to the anisotropic part of the covariance as well as a new isotropic part. All corrections to the covariance created by the second term in (78) are $O(\phi_f)$ and are, therefore, a factor of $\phi_f^{\frac{1}{2}}$ smaller than the leading-order term in (72). This arises because of the weakness of the reflected velocities at distances of $O(\kappa^{\frac{1}{2}})$. Straightforward working yields the following result for the corrected covariance:

$$\hat{\Delta}_{ij} = (2\pi)^3 \delta(\boldsymbol{k}+\boldsymbol{k}') \left[\left(\frac{9\sqrt{2\pi}\phi_f^{\frac{1}{2}}}{(k^2+1)^2} + O(\phi_f) \right) \tilde{U}_l \tilde{U}_m (\delta_{il} - \tilde{k}_i \tilde{k}_l)(\delta_{jm} - \tilde{k}_j \tilde{k}_m) + \frac{27\pi\phi_f}{20(k^2+1)^2} (\delta_{ij} - \tilde{k}_i \tilde{k}_j) \right], \tag{79}$$

where we have not included the $O(\phi_f)$ correction to the anisotropic part because it is of small consequence to the solution for the moments. On the other hand, the isotropic term now gives the correction to (73) as

$$K_2 = \frac{27\pi\phi_f}{20(k^2+1)^2} \tag{80}$$

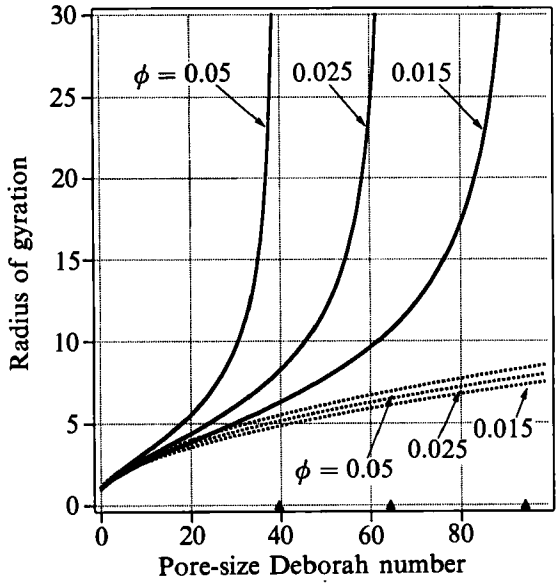

FIGURE 8. The radius of gyration of a Hookean dumbbell for flow through a dilute, fixed bed of spheres *vs.* *De*. The calculations are shown both with (——) and without (· · · · ·) two-sphere hydrodynamic interactions included. The critical conditions which arise from the two-sphere interactions are shown at the bottom as solid triangles.

and from (64*c*), β_4 becomes

$$\beta_4 = \frac{27\pi^2\phi_f}{80}\int_0^{\kappa^{\frac{1}{2}}/a} d\xi \frac{\xi^3}{(\xi^2+1)^2} \approx \frac{27\pi^2\phi_f \ln(\kappa^{\frac{1}{2}}/a)}{80}. \tag{81}$$

Substituting (81) into (68), we find

$$De_{\text{crit}} = \frac{80}{27\phi_f \ln(\kappa^{\frac{1}{2}}/a)} \approx \frac{5.9259\ldots}{\phi_f \ln(1/\phi_f)}. \tag{82}$$

Thus, including two-sphere interactions creates a critical value of the Deborah number beyond which the finite size of the polymer molecule must limit the conformation change. The steady values of $\overline{r^2}$ *vs.* *De* with and without two-sphere interactions are plotted in figure 8 for the linear dumbbell model. The qualitative difference between the behaviour of the dumbbell in the two different cases is clearly evident. Neglecting two-sphere interactions results in a monotone increase in $\overline{r^2}$ with the Deborah number, but steady values are always obtainable and the rate of increase is modest with $\overline{r^2} \approx 8$ at a value of *De* as large as 100. However, if we include two-sphere interactions then at a finite (but fairly large) value of the Deborah number, the radius of gyration approaches infinity and there are no steady solutions beyond that point. Although this critical value is large for these dilute calculations it decreases sharply with increasing volume fraction. Indeed, in practice, one expects that for large volume fractions other higher-order multiparticle interactions (e.g. three-sphere interactions) will increase the isotropic part of the covariance and thereby decrease the critical Deborah number even further. Finally, we note that the results are affected by two-sphere interactions well before the critical condition, resulting in a significant increase in the radius of gyration over that created by the flow past single spheres.

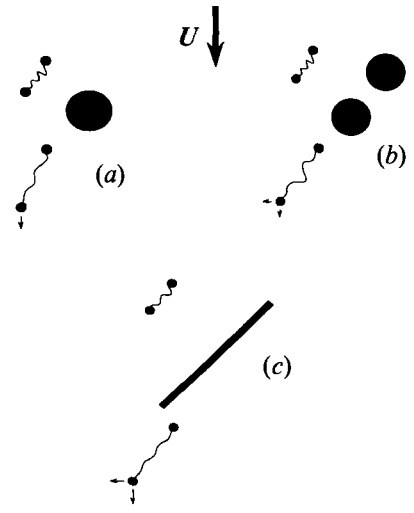

FIGURE 9. Pictorial representation of polymer flow past different fixed bed particles: (*a*) flow past a single sphere, (*b*) flow past a two-sphere pair, (*c*) flow past a fixed fibre.

In figure 9, we demonstrate pictorially the physical difference between the interaction of a polymer (dumbbell) and a single sphere versus an interaction with a two-sphere pair. If a dumbbell flows at a large distance past a single sphere and the restoring force is weak relative to the local shear force, it will deform such that the net change in the bead positions is a small displacement in the flow direction only. This is a consequence of the symmetry of the flow about the plane perpendicular to the mean velocity. The displacement simply results from the longer transit time of a bead which begins closer to the stationary sphere. However, if a dumbbell interacts under the same conditions with a two-sphere pair then, in general, it will suffer a displacement both in the directions perpendicular and parallel to the mean flow. In this case, the second sphere perturbs the symmetry of the disturbance flow created by the single sphere. If the relaxation time of the dumbbell is long enough such that it will not return to equilibrium before a subsequent particle interaction, then any residual displacement perpendicular to the mean flow will increase the displacement occurring in these later interactions. This follows since the difference in the transit times of the two beads increases as their relative displacement perpendicular to the mean flow increases. Thus, large polymer conformation change is greatly enhanced by any displacements perpendicular to the mean flow, but these can only occur in beds where the disturbance flows created by the bed particles are not fore–aft symmetric about the mean velocity. Of course, all these comments apply equally well to our results for fibre beds in §2. In that case, the velocity field created in flow past a single bed particle is not (in general) symmetric about the mean flow. Thus, two-particle interactions are not necessary for the calculation of a critical condition.

Although one must include multiparticle interactions to create a 'critical stretch' via the long-range interactions in some fixed beds, there is yet another mechanism where large conformation changes can occur through hydrodynamic interactions between a single bed particle and a polymer. As has been shown by Chilcott & Rallison (1988) and more recently by Harlen *et al.* (1990) and Harlen (1990), polymer molecules may undergo very large conformation changes in close interactions when they flow near the rear stagnation points of the fixed particles. Close interaction effects will be considered in the next section.

5. Close interactions

In the preceding sections we have examined the effects of long-range interactions on the conformation of a polymer flowing through a fixed bed. The point- or line-force approximation adopted for the velocity disturbance caused by the fixed bed particles is valid for interactions in which the minimum separation of the polymer from the fixed bed particles is $O(\kappa^{\frac{1}{2}})$. These long-range interactions are much more frequent than interactions in which a polymer comes within an $O(a)$ distance of a fixed bed particle. The justification for the neglect of such close interactions in the present analysis is analogous to that given in our previous study of particle orientation in a fixed bed (Shaqfeh & Koch 1988*a*, *b*), provided that the change in the polymer's end-to-end distance during an interaction is of the same order as its original end-to-end distance.

However, polymers that pass very close to the rear stagnation point of a fixed particle may become fully extended even if they are in the equilibrium state before the interaction (see Chilcott & Rallison 1988; Harlen 1990; Harlen *et al.* 1990). This type of interaction requires special attention. If a polymer with an initial end-to-end distance $r' = |\boldsymbol{r}'|$ passes close to a rear stagnation point of a fibre aligned perpendicular to the flow, then its final end-to-end distance $r = |\boldsymbol{r}|$ can be estimated by a scaling argument similar to that used by Harlen (1990) and Harlen *et al.* (1990). If we approximate the flow in the region behind the fibre as a planar extension with a maximum extension rate E, the position $X(t)$ of the polymer's centre-of-mass along the direction perpendicular to both the mean flow and the fibre's orientation is $X = X' \mathrm{e}^{-Et}$, where $\boldsymbol{X}'$ is the initial position. The polymer's end-to-end vector will move toward the mean flow direction (i.e. the axis of principle extension) and, if the Deborah number is sufficiently large such that the polymer relaxation can be neglected, then its length r is given by $r = r' \mathrm{e}^{Et}$. Using these relationships, the constraint that r cannot exceed its maximum extension r_0, and taking the initial position to be $X' = a$, we obtain

$$r = r'(a/X) \quad \text{for} \quad X > a(r'/r_0), \tag{83a}$$

$$r = r_0 \quad \text{for} \quad X < a(r'/r_0). \tag{83b}$$

The region of fully stretched polymer, $X \to a(r'/r_0)$ is referred to as a birefringent strand by Harlen *et al.* (1990).

If we consider a fixed bed initially filled with polymers in their equilibrium coiled configuration ($r' = R_g$) and start flow through the bed at a very large value of the Deborah number, then the initial growth rate of the mean-squared stretch due to close interactions will be

$$\frac{\mathrm{d}\langle r^2 \rangle}{\mathrm{d}t} \sim \frac{U\phi_f}{a^2} \int \mathrm{d}X\, r^2 \sim O\left(\frac{U\phi r_0 R_g}{a}\right). \tag{84}$$

The rate of growth of the mean-squared stretch due to long-range interactions, from (8) and (13), is $O(\phi_f^{\frac{1}{2}} U R_g^2/(a \ln^{\frac{3}{2}}(1/\phi_f)))$. These estimates indicate that close interactions will be important at least in the initial stages of polymer stretch, if the dimensionless maximum extensibility $R_0 \equiv r_0/R_g$ is sufficiently large, i.e.

$$R_0 > \phi_f^{-\frac{1}{2}} \ln^{-\frac{3}{2}}(1/\phi_f).$$

For reasonable estimates of R_0, this inequality is satisfied except for very small values of the volume fraction.

While close interactions may be effective in causing an initial growth of the second moment of the polymer conformation distribution, they become less important as polymer stretching progresses. The diffusivity that describes the effects of long-range interactions on the polymer conformation grows quadratically with increasing end-to-end distance, leading to an exponential growth of the second moment in time. However once a polymer is fully stretched by a close interaction, it cannot be stretched any further and so there is no subsequent enhancement of the growth rate.

This suggests a second way of assessing the relative importance of long-range and close interactions, which is to estimate the length of a fixed bed (in the limit of high Deborah number) that would be required to stretch all of the polymers close to their maximum extension if each mechanism were considered to act in isolation from the other. For long-range interactions, we can estimate this bed length from (16a) to be $O(a\phi_f^{-\frac{1}{2}} \ln^{\frac{3}{2}}(1/\phi_f) \ln R_0)$. For close interactions, if we assume that the effect occurs primarily due to full stretching of an initially relaxed polymer by a single fibre, we require a bed that is sufficiently long so that each polymer will pass through a strand behind at least one fibre as it passes through the bed. This corresponds to an $O(a\phi_f^{-1} R_0)$ bed length, which is much longer than that required for full stretch due to long-range interactions. If we allow for the possibility that a polymer may be extended successively by the extensional flow behind a number of different fibres (such as witnessed in periodic beds by Chmielewski *et al.* 1990), we are led to the conclusion that an $O(1)$ relative stretch r/r' due to many $O(\ln R_0)$ fibres is the dominant mechanism for producing fully stretched polymers by close interactions. However, this mechanism still requires an $O(a\phi_f^{-1} \ln R_0)$ bed length that is again larger than that required by long-range interactions alone. However, neither of these arguments describe the effect of both long and close interactions acting together, which might be significantly different than their effect separately.

A more detailed assessment of the effects of close interactions would require a solution of the coupled problem in which polymers are stretched by both types of interactions. The long-range hydrodynamic interactions have been described in terms of a conformational (or pair) diffusivity for the two beads in a dumbbell. In contrast, close interactions would not contribute diffusive terms to the evolution equation, because the relative change in the end-to-end distance $(r'-r)/r'$ during each interaction is not small. Instead the close interactions will contribute a non-local term to the evolution equation (8) of the form

$$\int d\boldsymbol{r}'[w(\boldsymbol{r},\boldsymbol{r}')\langle\Omega\rangle(\boldsymbol{r}') - w(\boldsymbol{r}',\boldsymbol{r})\langle\Omega\rangle(\boldsymbol{r})].$$

In the above, $w(\boldsymbol{r},\boldsymbol{r}')$ is the rate at which polymers originally within a differential volume $d\boldsymbol{r}'$ of $\boldsymbol{r}'$ are stretched to an end-to-end distance $\boldsymbol{r}$. This rate is proportional to $U\phi_f/a$ and is a strong function of $\boldsymbol{r}$ and $\boldsymbol{r}'$ as noted above.

Finally, we note that all scaling arguments made above are based on our results for long-range interactions in isotropic beds of fibres. Similar scaling arguments could easily be made for beds of spheres but we do not consider these here. In addition, from §2, we know that both the isotropic and the anisotropic parts of the covariance are of the same order in volume fraction for $\phi_f \ll 1$ in isotropic beds of fibres. This is not the case in beds of spheres or beds of fibres which are aligned in directions perpendicular to the mean flow. In these latter instances, the stretch induced by the long-range interactions is slightly weaker because the isotropic part of the covariance depends on multiparticle reflections as discussed in §4. The stretching due to close interactions is of similar magnitude for these beds and thus the relative importance

of close interactions may be greater. No stronger conclusions can be achieved without a detailed examination of the non-local equations.

6. Conclusion and summary

To conclude and summarize, §§2–5 represent a beginning to the theoretical description of how particle interactions affect polymer conformation in flow through fixed beds. We have shown in §§2–4 that long-range particle interactions in dilute beds can have surprising consequences for the conformation of simple dumbbells during flow. Even though the mean flow is constant in these beds, the manner in which the dumbbells sample the velocity gradient fluctuations in the bed is such that a significant fraction of the distribution can undergo a large conformation change. This occurs under conditions in which the relaxation time of the dumbbell is sufficiently long such that any displacement of the beads during an interaction has not completely relaxed before another interaction has occurred. In addition, this conformation change can be largest when the velocity fluctuations or disturbances are such that the beads can be displaced in directions both perpendicular and parallel to the mean flow. If this is the case, then (beyond a certain critical Deborah number) a Hookean dumbbell will not achieve a steady conformation in the bed. Moreover, a Warner dumbbell will stretch to a large fraction of its maximum extensibility. We have theoretically described all these phenomena for dilute beds of both spheres and fibres throughout the present discourse.

Although long-range interactions are very important in dilute fixed beds, close or short-range interactions can also be important under some circumstances. Scaling arguments are developed in §5 to estimate the effect that these close interactions might have on polymer stretch in disordered fixed beds.

Finally, we note that most of the theory developed herein has application beyond the analysis of polymer conformation in fixed beds. To our knowledge, §3 contains new results for polymer conformation in general stochastic fields including the direct interaction approximation for the conformational distribution function $\langle \Omega \rangle$. These results have direct application to pair diffusion in stochastic fields, because our model of a polymer molecule consists of independent beads connected by a spring. Finally, though perhaps clear intuitively, we have rigorously demonstrated the connection between the long-range hydrodynamic interactions in a dilute fixed bed and equivalent Gaussian velocity fields, specifically indicating the means of calculating the covariance of the equivalent field from the known form for the disturbance velocities created by the bed particles. Such a connection can now be used to link well-known results for dispersion in model fixed beds to other important results regarding dispersion in stochastic fields. In fact, we have begun to make just such a connection in another publication (see Koch & Shaqfeh 1992).

All of our results, while having very interesting theoretical consequences, must now be tested in the laboratory to determine whether they can describe at least the qualitative features of polymer conformation change in fixed beds. In this context, one should recall that there are a host of assumptions made as preliminaries to the theoretical development which, strictly speaking, are not true in most polymer flow systems of interest. However, these were important to make initial theoretical progress. Perhaps the most notable of these assumptions is that all velocity fields throughout our development could be calculated from the Stokes equations. Since we are more interested in large conformation change and stretch in polymer solutions, the resulting elastic stresses (which scale with the second moment of the distribution)

will be negligible in calculating any averaged flow fields only if the solutions are extremely dilute. Of course, the original work by James & McClaren (1975) involved measuring the change in particle drag as a function a flow rate and this was used as a means of inferring polymer conformation change. The drag force on a fixed bed particle would be nearly unchanged if the assumptions made in the present manuscript were strictly applied. Nevertheless, including the non-Newtonian nature of the flow fields self-consistently in any scheme to predict polymer conformation change in disordered beds is a very difficult task and one that should not be undertaken before the results presented in this manuscript are understood. We hope that our theory provides a 'qualitative guide' to the phenomena which occur under more general circumstances and we look forward to an experimental investigation of polymer conformation change in dilute, disordered fixed beds.

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Appendix. Equivalent Gaussian fields in fixed-bed theory

In this Appendix we demonstrate explicitly that the probability density functional (p.d.f.) describing the total velocity fluctuation created by the long-range hydrodynamic disturbances in a dilute fixed bed is of Gaussian form. This allows one to replace the explicit consideration of individual long-range hydrodynamic fluctuations with the equivalent stochastic field; a result we found to be particularly useful in our theoretical development in §3 and 4. To begin we define $\boldsymbol{u}'$ as the total velocity in the fixed bed of particles (spheres or fibres) minus the average velocity through the bed. Thus, it is the total velocity fluctuation. For dilute beds and including only the long-range hydrodynamic interactions (i.e. scaling all lengths on the screening length of the bed) we can approximate $\boldsymbol{u}'$ as

$$\boldsymbol{u}' \approx \sum_{i=1}^{N} \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \,|\, \boldsymbol{R}_i), \tag{A 1}$$

where $\langle \boldsymbol{u}' \rangle_1$ is the conditionally averaged velocity disturbance created by a bed particle (approximated as a point force for spheres and a line force for fibres) which includes the Brinkman screening created by the surrounding particles. In (A 1), $\boldsymbol{R}_i$ is the position of the centre of the ith particle (a position along the centreline of the ith fibre) and we assume that there are N bed particles. Equation (A 1) follows since at large lengths the particles intervening between a point in the bed and any given particle can be approximated as an averaged medium and any multiple reflections between particles at these distances create small corrections to the disturbance. We shall discuss these latter corrections at the end of this Appendix. We note, in this context, that (A 1) is part of an expansion which includes the additional effects of groups of 2, 3 and k particles, that has been discussed by Shaqfeh & Koch (1990). Finally, to completely specify the disturbance velocity created by a fibre in a fixed bed, one must also specify the orientation $\boldsymbol{e}_i$, which we will include in the following analysis whenever fibre beds are discussed.

Denoting $\boldsymbol{u}_i' = \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \mid \boldsymbol{R}_i)$, we note that $\langle \boldsymbol{u}' \rangle = 0$ and therefore

$$\langle \boldsymbol{u}_i' \rangle = 0, \tag{A 2}$$

where the average $\langle \cdot \rangle$ is defined

$$\langle \cdot \rangle = \int \mathrm{d}\boldsymbol{R}_1 P(\boldsymbol{R}_1) \int \boldsymbol{R}_2 P(\boldsymbol{R}_2) \ldots \int \mathrm{d}\boldsymbol{R}_N P(\boldsymbol{R}_N) \tag{A 3}$$

for beds of spheres with $P(\boldsymbol{R}_i)$ being the probability density of finding the ith point force at position $\boldsymbol{R}_i$. The integrals are over the volume V of the system (assumed to be much larger than all microstructural dimensions) and for homogeneous random beds $P(\boldsymbol{R}_i) = 1/V$. For beds of fibres, the average is defined

$$\langle \cdot \rangle = \int \mathrm{d}\boldsymbol{R}_1 \int \mathrm{d}\boldsymbol{e}_1 P(\boldsymbol{R}_1) g(\boldsymbol{e}_1) \ldots \int \mathrm{d}\boldsymbol{R}_N \int \mathrm{d}\boldsymbol{e}_N P(\boldsymbol{R}_N) g(\boldsymbol{e}_N), \tag{A 4}$$

where the spatial integrals are over the plane perpendicular to the orientation vector $\boldsymbol{e}_i$ of the ith line force and the orientational integrals are over the unit sphere. $P(\boldsymbol{R}_i)$ is the probability density for the ith fibre to pass through the position $\boldsymbol{R}_i$ and $g(\boldsymbol{e}_i)$ is the probability density of orientation for the ith fibre. For homogeneous, random beds $P(\boldsymbol{R}_i) = \phi_f/(\pi a^2 N)$, where ϕ_f is the bed volume fraction and a is the fibre radius.

By definition of the probability density functional $P(\boldsymbol{u}_i')$ we have, for fixed beds of spheres, (see Van Kampen 1981)

$$P(\boldsymbol{u}_i') = \int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i) \, \delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \mid \boldsymbol{R}_i)). \tag{A 5}$$

For fibre beds, (A 5) would be of the same form but would include an average over $g(\boldsymbol{e}_i)$, namely

$$P(\boldsymbol{u}_i') = \int \mathrm{d}\boldsymbol{e}_i g(\boldsymbol{e}_i) \int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i) \, \delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \mid \boldsymbol{R}_i; \boldsymbol{e}_i)). \tag{A 6}$$

Our purpose is to derive an expression for the probability density functional $P(\boldsymbol{u}')$ using the results (A 1), (A 5), (A 6), and our knowledge of the characteristics of $\langle \boldsymbol{u}' \rangle_1$ in fixed beds of spheres or fibres.

We can formally write an expression for $P(\boldsymbol{u}')$ using a *functional integral* expression analogous to (A 6):

$$P(\boldsymbol{u}') = \prod_{i=1}^{N} \int \mathrm{D}\boldsymbol{u}_i' P(\boldsymbol{u}_i') \, \delta\left(\boldsymbol{u}' - \sum_{i=1}^{N} \boldsymbol{u}_i'\right), \tag{A 7}$$

where

$$\prod_{i=1}^{N} \int \mathrm{D}\boldsymbol{u}_i' \equiv \int \mathrm{D}\boldsymbol{u}_1' \int \mathrm{D}\boldsymbol{u}_2' \int \mathrm{D}\boldsymbol{u}_3' \ldots \int \mathrm{D}\boldsymbol{u}_N', \tag{A 8}$$

and where $\int \mathrm{D}\boldsymbol{u}_1'$ implies the functional integral over the velocity disturbance $\boldsymbol{u}_1'$. The functional integral is defined in the usual manner (see Jensen 1981) and implies dividing $\boldsymbol{x}$-space into a lattice and then integrating over the values of $\boldsymbol{u}_1'$ at each lattice point. Finally, we take the limit as the lattice spacing approaches zero. Note that the p.d.f. $P(\boldsymbol{u}')$ only has meaning through this kind of 'coarse graining' procedure and therefore it is not surprising that functional integrals naturally arise in the development. Combining (A 7) and (A 5) we have

$$P(\boldsymbol{u}') = \prod_{i=1}^{N} \int \mathrm{D}\boldsymbol{u}_i' \left\{ \int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i) \, \delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \mid \boldsymbol{R}_i)) \, \delta(\boldsymbol{u}' - \sum_i \boldsymbol{u}_i') \right\}. \tag{A 9}$$

For beds of fibres, the average within the brackets would include an orientational average exactly as included in (A 6).

To continue, we introduce the functional Fourier transform, which we will indicate by $\hat{}$ (just as we have indicated the usual Fourier transform in the text). So we define $\hat{P}(\boldsymbol{\eta})$ via the equation

$$\hat{P}(\boldsymbol{\eta}) = \int \mathrm{D}\boldsymbol{u}' \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{u}'(\boldsymbol{x})\right] P(\boldsymbol{u}') \tag{A 10}$$

and the inverse formula becomes

$$P(\boldsymbol{u}') = c\int D\boldsymbol{\eta} \exp\left[\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{u}'(\boldsymbol{x})\right]\hat{P}(\boldsymbol{\eta}), \tag{A 11}$$

where c is a constant defined $c = \prod_j 1/(2\pi)^3$ and the product is over all lattice points which comprise the discretized space. It follows that

$$\delta\left(\boldsymbol{u}' - \sum_{i=1}^{N} \boldsymbol{u}_i'\right) = c\int D\boldsymbol{\eta} \exp\left[\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\left(\boldsymbol{u}' - \sum_i \boldsymbol{u}_i'\right)\right]. \tag{A 12}$$

Substituting this result into (A 9) gives

$$P(\boldsymbol{u}') = c\int \mathrm{D}\boldsymbol{\eta} \exp\left[\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}\cdot\boldsymbol{u}'\right]\left[\prod_{i=1}^{N}\int \mathrm{D}\boldsymbol{u}_i'\left\{\int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i)\,\delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_i))\right.\right.$$
$$\left.\left.\times \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\sum_i \boldsymbol{u}_i'\right]\right\}\right], \tag{A 13a}$$

and the corresponding expression for fibre beds is

$$P(\boldsymbol{u}') = c\int \mathrm{D}\boldsymbol{\eta} \exp\left[\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}\cdot\boldsymbol{u}'\right]$$
$$\times\left[\prod_{i=1}^{N}\int \mathrm{D}\boldsymbol{u}_i'\left\{\int \mathrm{d}\boldsymbol{e}_i\, g(\boldsymbol{e}_i)\int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i)\,\delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_i;\boldsymbol{e}_i)) \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\sum_i \boldsymbol{u}_i'\right]\right\}\right]. \tag{A 13b}$$

Assuming that all of the fixed bed particles are identical and that their centre-of-mass and orientational statistics are described by the same density functions, we can write

$$\prod_{i=1}^{N}\int \mathrm{D}\boldsymbol{u}_i'\left\{\int \mathrm{d}\boldsymbol{R}_i P(\boldsymbol{R}_i)\,\delta(\boldsymbol{u}_i' - \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_i)) \exp\left[-\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\sum_i \boldsymbol{u}_i'\right]\right\}$$
$$= \left[\int \mathrm{D}\boldsymbol{u}_1'\left\{\int \mathrm{d}\boldsymbol{R}_1 P(\boldsymbol{R}_1)\,\delta(\boldsymbol{u}_1' - \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)) \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{u}_1'\right]\right\}\right]^N. \tag{A 14}$$

We can complete the functional integral in (A 14) over $\boldsymbol{u}_1'$ analytically and obtain

$$\left\{\int \mathrm{D}\boldsymbol{u}_1'\int \mathrm{d}\boldsymbol{R}_1 P(\boldsymbol{R}_1)\,\delta(\boldsymbol{u}_1' - \langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)) \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{u}_1'\right]\right\}^N$$
$$= \left\{\int \mathrm{d}\boldsymbol{R}_1 P(\boldsymbol{R}_1) \exp\left[-\mathrm{i}\int \mathrm{d}\boldsymbol{x}\, \boldsymbol{\eta}(\boldsymbol{x})\cdot\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)\right]\right\}^N. \tag{A 15}$$

Of course, (A 15) again holds strictly only for beds of spheres and the analogous expression for the right-hand side of (A 15) in the case of fibre beds is

$$\left\{\int \mathrm{d}\boldsymbol{e}_1\, g(\boldsymbol{e}_1) \int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1) \exp\left[-\int \mathrm{d}x\, \boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\right]\right\}^N.$$

To continue, we formally expand the exponential within the brackets on the right-hand side of (A 15), namely

$$\exp\left[-\mathrm{i}\int \mathrm{d}x\, \boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x)\right] = 1-\mathrm{i}\int \mathrm{d}x\, \boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x) - \frac{1}{2}\int \mathrm{d}x \int \mathrm{d}x'[\boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x)][\boldsymbol{\eta}(x')\cdot\langle \boldsymbol{u}'\rangle_1(x')]\ldots. \quad \text{(A 16)}$$

We can now perform the average in (A 15) (i.e. the integral over $\boldsymbol{R}_1$) by integrating this series term by term. Noting that

$$\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1) = 0$$

then the right-hand side of (A 15) becomes

$$\left\{\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1) \exp\left[-\mathrm{i}\int \mathrm{d}x\, \boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1)\right]\right\}^N$$

$$\approx\left[1-\frac{1}{2}\int \mathrm{d}x \int \mathrm{d}x'\, \boldsymbol{\eta}(x)\boldsymbol{\eta}(x'):\left(\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x'\,|\,\boldsymbol{R}_1)\right)+\ldots\right]^N. \quad \text{(A 17)}$$

For beds of fibres, a similar truncation yields the result

$$\left\{\int \mathrm{d}\boldsymbol{e}_1\, g(\boldsymbol{e}_1) \int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1) \exp\left[-\int \mathrm{d}x\, \boldsymbol{\eta}(x)\cdot\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\right]\right\}^N \approx \left[1-\frac{1}{2}\int \mathrm{d}x'\, \boldsymbol{\eta}(x)\boldsymbol{\eta}(x'):\right.$$

$$\left.\times\left(\int \mathrm{d}\boldsymbol{e}_1\, g(\boldsymbol{e}_1)\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\langle \boldsymbol{u}'\rangle_1(x'\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\right)+\ldots\right]^N. \quad \text{(A 18)}$$

The key step in the derivation is to realize that the truncated expansions shown in (A 17) and (A 18) give the exact asymptotic results in the limit as $N\to\infty$. This can be demonstrated through simple order-of-magnitude estimates. Considering first (A 17), we note that the long-range velocity disturbances $\langle \boldsymbol{u}'\rangle_1$ in beds of spheres extend over a volume $\kappa^{\frac{3}{2}}$ and are of magnitude $Ua/\kappa^{\frac{1}{2}}$ in that volume. Thus,

$$\left(\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x/\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x'\,|\,\boldsymbol{R}_1)\right) \sim O(U^2\phi_{\mathrm{f}}^{\frac{1}{2}}/N). \quad \text{(A 19)}$$

Higher-order terms in the expansion (A 16) are of smaller order both in powers of $1/N$ and $\phi_{\mathrm{f}}^{\frac{1}{2}}$ for $N\to\infty$ and $\phi_{\mathrm{f}}\ll 1$. For homogeneous beds of fibres, a similar scaling argument gives

$$\int \mathrm{d}x \int \mathrm{d}x'\, \boldsymbol{\eta}(x)\boldsymbol{\eta}(x'):\left(\int \mathrm{d}\boldsymbol{e}_1\, g(\boldsymbol{e}_1)\int \mathrm{d}\boldsymbol{R}_1\, P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(x\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\langle \boldsymbol{u}'\rangle_1(x'\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\right)$$

$$\sim O\{U^2/(N\ln(1/\phi_{\mathrm{f}}))\} \quad \text{(A 20)}$$

and again higher-order terms which represent higher-order velocity correlation functions are of smaller order in both $1/N$ and $1/\ln(1/\phi_{\mathrm{f}})$.

Thus, we have that, in the dual limit $N\to\infty$ and $\phi_t \ll 1$ (with the limits taken in that order),

$$\left[1-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\,\boldsymbol{\eta}(\boldsymbol{x}'):\left(\int d\boldsymbol{R}_1\,P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1)\right\}\right]^N$$

$$\to \exp\left[-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{\Delta}(\boldsymbol{x},\boldsymbol{x}')\cdot\boldsymbol{\eta}(\boldsymbol{x}')\right], \quad \text{(A 21)}$$

where

$$\boldsymbol{\Delta} = N\int d\boldsymbol{R}_1\,P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1)$$

$$= n\int d\boldsymbol{R}_1\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1). \quad \text{(A 22)}$$

Taking a similar limit for flow in fibre beds gives the result

$$\left[1-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\,\boldsymbol{\eta}(\boldsymbol{x}'):\right.$$

$$\left.\left(\int d\boldsymbol{e}_1\,g(\boldsymbol{e}_1)\int d\boldsymbol{R}_1\,P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\right)+\ldots\right]^N$$

$$\to \exp\left[-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{\Delta}(\boldsymbol{x},\boldsymbol{x}')\cdot\boldsymbol{\eta}(\boldsymbol{x}')\right], \quad \text{(A 23)}$$

where

$$\boldsymbol{\Delta} = N\iint d\boldsymbol{e}_1\,g(\boldsymbol{e}_1)\,d\boldsymbol{R}_1\,P(\boldsymbol{R}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1).$$

$$= \frac{\phi_t}{\pi a^2}\iint d\boldsymbol{e}_1\,g(\boldsymbol{e}_1)\,d\boldsymbol{R}_1\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1)\langle \boldsymbol{u}'\rangle_1(\boldsymbol{x}'\,|\,\boldsymbol{R}_1;\boldsymbol{e}_1). \quad \text{(A 24)}$$

Finally, substituting the results (A 21) or (A 23) back into (A 13) gives

$$P(\boldsymbol{u}') = c\int D\boldsymbol{\eta}\exp\left[i\int d\boldsymbol{x}\,\boldsymbol{\eta}\cdot\boldsymbol{u}'\right]\exp\left[-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{\Delta}(\boldsymbol{x},\boldsymbol{x}')\cdot\boldsymbol{\eta}(\boldsymbol{x}')\right]. \quad \text{(A 25)}$$

where $\boldsymbol{\Delta}$ is given by either (A 22) or (A 24) for beds of spheres or fibres respectively. Equation (A 25) is our final result, which states that the functional Fourier transform of the probability density functional is Gaussian, namely (cf. (A 11))

$$\hat{P}(\boldsymbol{\eta}) = \exp\left[-\frac{1}{2}\int d\boldsymbol{x}\int d\boldsymbol{x}'\,\boldsymbol{\eta}(\boldsymbol{x})\cdot\boldsymbol{\Delta}(\boldsymbol{x},\boldsymbol{x}')\cdot\boldsymbol{\eta}(\boldsymbol{x}')\right], \quad \text{(A 26)}$$

and therefore that the p.d.f. itself is Gaussian (Van Kampen 1981). In addition, (A 26) is particularly convenient since, in this form, it is clear that the covariance of the Gaussian p.d.f. is $\boldsymbol{\Delta}$ (see Van Kampen 1981). Note that the values of $\boldsymbol{\Delta}$ given by (A 22) and (A 24) for beds of spheres and fibres respectively are identically those given by (69) and (42*b*) in the text.

Finally, we discuss how corrections to the disturbance velocities created by multiparticle interactions affect the previous development. In §4 we used a corrected value of the covariance to describe the effect of two-sphere interactions on the configuration of a dumbbell in flow through a fixed bed. 'Two sphere' interactions in this context means those explicit hydrodynamic interactions beyond the average

screening in the bed. We can include these interactions by revising (A 1) to better approximate the velocity fluctuation in the bed. Thus, we write

$$\boldsymbol{u}' \approx \sum_{i=1}^{N} \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \,|\, \boldsymbol{R}_i) + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \langle \boldsymbol{u}'' \rangle_2(\boldsymbol{x} \,|\, \boldsymbol{R}_i, \boldsymbol{R}_j), \tag{A 27}$$

where $\langle \boldsymbol{u}'' \rangle_2(\boldsymbol{x} \,|\, \boldsymbol{R}_i, \boldsymbol{R}_j)$ is that part of the two-particle conditionally averaged velocity field which cannot be expressed as the sum of one-particle conditionally averaged fields, i.e.

$$\langle \boldsymbol{u}'' \rangle_2(\boldsymbol{x} \,|\, \boldsymbol{R}_i, \boldsymbol{R}_j) \equiv \langle \boldsymbol{u}' \rangle_2(\boldsymbol{x} \,|\, \boldsymbol{R}_i, \boldsymbol{R}_j) - \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \,|\, \boldsymbol{R}_i) - \langle \boldsymbol{u}' \rangle_1(\boldsymbol{x} \,|\, \boldsymbol{R}_j). \tag{A 28}$$

One can now redo our entire derivation (A 2)–(A 26) beginning with the result (A 27) and noting that the double summation is the sum over all two-particle pairs in the fixed bed. The final result is that the second term in (A 27) corrects the covariance (A 22) by a term which is $O(U^2 \phi_f)$ for beds of spheres. This result is found in (78) and (79) in the text. Note that for beds of fibres a similar correction for two-fibre interactions would contribute a term of $O(U^2/(\ln^2(1/\phi_f))$ to (A 24).

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