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Generalized Taylor dispersion phenomena in unbounded homogeneous shear flows

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Generalized Taylor dispersion theory is extended so as to enable the analysis of the transport in unbounded homogeneous shear flows of Brownian particles possessing internal degrees of freedom (e.g. rigid non-spherical particles possessing orientational degrees of freedom, flexible particles possessing conformational degrees of freedom, etc.). Taylor dispersion phenomena originate from the coupling between the dependence of the translational velocity of such particles in physical space upon the internal variables and the stochastic sampling of the internal space resulting from the internal diffusion process.

Employing a codeformational reference frame (i.e. one deforming with the sheared fluid) and assuming that the eigenvalues of the (constant) velocity gradient are purely imaginary, we establish the existence of a coarse-grained, purely physical-space description of the more detailed physical-internal space (*microscale*) transport process. This *macroscale* description takes the form of a convective–diffusive 'model' problem occurring exclusively in physical space, one whose formulation and solution are independent of the internal ('local'-space) degrees of freedom.

An Einstein-type diffusion relation is obtained for the long-time limit of the temporal rate of change of the mean-square particle displacement in physical space. Despite the nonlinear (in time) asymptotic behaviour of this displacement, its Oldroyd time derivative (which is the appropriate one in the codeformational view adopted) tends to a constant, time-independent limit which is independent of the initial internal coordinates of the Brownian particle at zero time.

The dyadic dispersion-like coefficient representing this asymptotic limit is, in general, not a positive-definite quantity. This apparently paradoxical behaviour arises due to the failure of the growth in particle spread to be monotonic with time as a consequence of the coupling between the Taylor dispersion mechanism and the shear field. As such, a redefinition of the solute's dispersivity dyadic (appearing as a phenomenological coefficient in the coarse-grained model constitutive equation) is proposed. This definition provides additional insight into its physical (Lagrangian) significance as well as rendering this dyadic coefficient positive-definite, thus ensuring that solutions of the convective–diffusive model problem are well behaved. No restrictions are imposed upon the magnitude of the rotary Péclet number, which represents the relative intensities of the respective shear and diffusive effects upon which the solute dispersivity and mean particle sedimentation velocity both depend.

The results of the general theory are illustrated by the (relatively) elementary problem of the sedimentation in a homogeneous unbounded shear field of a size-fluctuating porous Brownian sphere (which body serves to model the behaviour of a macromolecular coil). It is demonstrated that the well-known case of the

translational diffusion in a homogeneous shear flow of a rigid, non-fluctuating sphere (for which the Taylor mechanism is absent) is a particular case thereof.

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1. Introduction

Consider the temporal evolution of a dilute 'cloud' of colloidal, monodisperse, internally homogeneous, non-neutrally buoyant, triaxial ellipsoidal particles sedimenting in an unbounded spatially homogeneous shear flow. In addition to being passively convected by the shear field, the particles exhibit translational 'slip' relative to the suspending fluid owing to the action of external forces (typically gravity), as well as undergoing both translational and rotational diffusion.

Rather than studying the entire multiparticle system comprising the cloud, it suffices in the dilute limit to focus on but a single 'tracer' particle. The state of this particle in space is completely specified by $\boldsymbol{R} \equiv (x, y, z)$, the instantaneous position vector in three-dimensional physical space of its 'locator point' (any fixed material point of the particle; e.g. its centre) relative to an arbitrary space-fixed origin O, and by its instantaneous orientation represented by the triplet $(\theta, \phi, \psi) \equiv \boldsymbol{\phi}$, say, corresponding to an appropriate set of Eulerian angles relating a triad of particle-fixed Cartesian axes to a comparable triad of space-fixed Cartesian axes (Goldstein 1950).

Owing to the stochastic (i.e. Brownian or turbulent) elements affecting its motion, the trajectory of the ellipsoidal particle can be given only a statistical rather than deterministic description. This is expressed in terms of the conditional probability density $P(\boldsymbol{R}, \boldsymbol{\phi}, t \,|\, \boldsymbol{R}', \boldsymbol{\phi}')$ of finding the particle at the six-dimensional phase-space point $(\boldsymbol{R}, \boldsymbol{\phi}) \equiv (x, y, z; \theta, \phi, \psi)$ at time $t > 0$, given that it was initially introduced into the fluid at $t = 0$ at $(\boldsymbol{R}', \boldsymbol{\phi}')$. This probability satisfies the continuity equation

$$\frac{\partial P}{\partial t} + \nabla_R \cdot \boldsymbol{J} + \nabla_\phi \cdot \boldsymbol{j} = 0, \tag{1.1}$$

together with appropriate constitutive equations (Brenner & Condiff 1974) for the respective translational and rotational flux density vectors appearing therein:

$$\boldsymbol{J} = [\boldsymbol{V}(\boldsymbol{R}') + (\boldsymbol{R} - \boldsymbol{R}') \cdot \boldsymbol{G} + \boldsymbol{F} \cdot \boldsymbol{M}(\boldsymbol{\phi})] P - \boldsymbol{D}(\boldsymbol{\phi}) \cdot \nabla_R P \tag{1.2}$$

and

$$\boldsymbol{j} = [\omega_f - \boldsymbol{B}(\boldsymbol{\phi}) : \boldsymbol{S}] P - \boldsymbol{d}(\boldsymbol{\phi}) \cdot \nabla_\phi P. \tag{1.3}$$

In the above, $\nabla_R \equiv \partial / \partial \boldsymbol{R}$ and $\nabla_\phi \equiv \partial / \partial \boldsymbol{\phi}$ (with $\delta \boldsymbol{\phi}$ the infinitesimal rotation pseudovector (Goldstein 1950; Landau & Lifshitz 1960)) are, respectively, the physical- and orientation-space (cf. Brenner & Condiff 1972) gradient operators. In addition, $\boldsymbol{M}$, $\boldsymbol{D}$, $\boldsymbol{d}$ and $\boldsymbol{B}$ are intrinsic, material particle tensors (which are constant in a frame rotating with the particle). The translational mobility dyadic $\boldsymbol{M}$ and pseudotriadic $\boldsymbol{B}$ were respectively calculated for an ellipsoid by Overbeek (1876) and Jeffery (1922). The corresponding ellipsoidal translation and rotary diffusion dyadics, $\boldsymbol{D}$ and $\boldsymbol{d}$, are also available (Perrin 1934, 1936; the rotational mobility from which $\boldsymbol{d}$ is obtained was calculated by Edwardes 1892), having been obtained by application of the appropriate Stokes–Einstein relations (Gans 1928; cf. also Brenner 1967). Thus, from the point of view of a space-fixed observer, each of these material tensors is a known function of the instantaneous particle orientation $\boldsymbol{\phi}$, as suggested by the argument affixed to them in the constitutive equations (1.2)–(1.3). The vector $\boldsymbol{F}$ is the external force acting on the ellipsoid. It is assumed independent of $\boldsymbol{R}$ (but may, more generally, be a specified function of $\boldsymbol{\phi}$). The vector $\boldsymbol{V}(\boldsymbol{R}') + (\boldsymbol{R} - \boldsymbol{R}') \cdot \boldsymbol{G}$

represents the undisturbed fluid velocity at $\boldsymbol{R}$ in terms of its value $\boldsymbol{V}(\boldsymbol{R}')$ at $\boldsymbol{R}'$ and the constant (position- and time-independent) undisturbed velocity gradient dyadic $\boldsymbol{G}$. The pseudovector $\boldsymbol{\omega}_f$ is the angular velocity of the undisturbed fluid (appropriately related to the antisymmetric portion of $\boldsymbol{G}$) and $\boldsymbol{S}$ is the rate-of-strain dyadic, representing the symmetric portion of $\boldsymbol{G}$. The specified, homogeneous shear flow parameters $\boldsymbol{\omega}_f$, $\boldsymbol{S}$ and $\boldsymbol{G}$ appearing in the constitutive equations (1.2)–(1.3) are, of course, constant tensors only in the space-fixed reference frame. This contrasts with the material tensors appearing in these constitutive equations, which are constant only in the particle-fixed reference frame, but appear as functions of orientation $\boldsymbol{\phi}$ when expressed in the space-fixed frame.

To (1.1)–(1.3) we adjoin the boundary conditions

$$|\boldsymbol{R}-\boldsymbol{R}'|^m(P,\boldsymbol{J},\boldsymbol{j}) = (0,\boldsymbol{0},\boldsymbol{0}) \quad \text{as} \quad |\boldsymbol{R}-\boldsymbol{R}'| \to \infty \quad (m = 0,1,2,\ldots), \tag{1.4}$$

thus assuring that P decays exponentially rapidly at infinity (ultimately assuring convergence of all physical-space moments of P). Furthermore, we require that P be continuous and single-valued in $\boldsymbol{\phi}$, in addition to satisfying the initial condition

$$P = \begin{cases} \delta(\boldsymbol{R}-\boldsymbol{R}')\,\delta(\boldsymbol{\phi}-\boldsymbol{\phi}') & \text{for} \quad t = 0 \qquad (1.5a) \\ 0 & \text{for} \quad t < 0, \qquad (1.5b) \end{cases}$$

with δ the Dirac delta function. The appearance of the unit coefficient implicitly multiplying the right-hand side of (1.5a) automatically assures that the probability

$$\int_{\boldsymbol{R}_\infty}\int_{\boldsymbol{\phi}_o} P\,\mathrm{d}\boldsymbol{\phi}\,\mathrm{d}\boldsymbol{R}$$

of the ellipsoid possessing *some* position and *some* orientation in space is unity for all times $t > 0$ following its introduction into the system. Here, the integration domains,

$$\boldsymbol{R}_\infty \equiv \{-\infty < x < \infty,\ -\infty < y < \infty,\ -\infty < z < \infty\} \tag{1.6}$$

and

$$\boldsymbol{\phi}_o \equiv \{0 \leqslant \theta \leqslant \pi,\ 0 \leqslant \phi < 2\pi,\ 0 \leqslant \psi < 2\pi\}, \tag{1.7}$$

respectively, constitute all of the physical and orientation subspaces, whereas $\mathrm{d}\boldsymbol{R} \equiv \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ and $\mathrm{d}\boldsymbol{\phi} \equiv \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\psi$ denote 'volume' elements therein.

The foregoing problem uniquely determines the conditional probability density $P(>0)$ in the six-dimensional phase space $(\boldsymbol{R},\boldsymbol{\phi})$. Its solution is, however, daunting. (Indeed, the detailed formulation (1.1)–(1.5) of this six-dimensional, unsteady-state, initial- and boundary-value problem would have appeared even more forbidding had the various orientation-space operations and phenomenological coefficients, together with contractions between tensors expressed relative to particle-fixed and space-fixed reference frames (e.g. $\boldsymbol{B}$ and $\boldsymbol{S}$, respectively) appearing in (1.2)–(1.3), been expressed explicitly in terms of Eulerian angles.)

Existing literature addresses (and solves) specialized forms of the above problem. Thus, the diffusion of spherical Brownian particles in general homogeneous shear flows has been extensively studied (Elrick 1962; Frankel & Acrivos 1968; San Miguel & Sancho 1979; Foister & van de Ven 1980; Dufty 1984; Hess & Rainwater 1984, to cite just a few contributions); so too has the sedimentation of non-spherical Brownian particles in quiescent, non-sheared fluids been studied (Gallily & Cohen 1976; Goren 1979; Brenner 1979, 1981; Dill & Brenner 1983; Frankel 1991, etc.). Cerda & van de Ven (1983) examined the translational motion of a neutrally buoyant Brownian spheroid in simple shear flow. Assuming large rotary Péclet numbers, they *decoupled* their translational and rotary motions (in a manner which does not appear to us to be entirely consistent). In any event, no rigorous treatment of the full dispersion problem posed above is known to us, and only the *full* problem manifests Taylor dispersion phenomena.

Rather than seeking the exhaustively detailed, unsteady state, six-dimensional (purely numerical) solution $P(\boldsymbol{R}, \boldsymbol{\phi}, t \mid \boldsymbol{R}', \boldsymbol{\phi}')$ of the problem posed, and even then only for the one particular choice of initial orientation $\boldsymbol{\phi}'$, physical interest in the temporal behaviour of the ellipsoid often focuses only on an asymptotic description of its motion provided by the long-time limit of the orientation-averaged density, namely

$$\bar{P} \overset{\text{def.}}{=} \int_{\boldsymbol{\phi}_0} P \,\mathrm{d}\boldsymbol{\phi}, \tag{1.8}$$

which represents the conditional probability for finding the particle at the physical-space position $\boldsymbol{R}$ at time t irrespective of the particle's instantaneous orientation at that time. In particular, we seek to formulate the appropriate initial- and boundary-value problem governing (the leading-order asymptotic behaviour of) $\bar{P}(\boldsymbol{R}, t \mid \boldsymbol{R}', \boldsymbol{\phi}') \sim \bar{P}(\boldsymbol{R}, t \mid \boldsymbol{R}')$ in the long-time limit, which intuition suggests should represent the solution of the following physical-space, convective–diffusive–sedimentation, initial- and boundary-value problem (cf. (1.1)–(1.5)):

$$\frac{\partial \bar{P}}{\partial t} + \boldsymbol{\nabla}_R \cdot \bar{\boldsymbol{J}} = 0, \tag{1.9a}$$

$$\bar{\boldsymbol{J}} \overset{\text{def.}}{=} [\boldsymbol{V}(\boldsymbol{R}') + (\boldsymbol{R} - \boldsymbol{R}') \cdot \boldsymbol{G} + \bar{\boldsymbol{U}}^*] \bar{P} - \bar{\boldsymbol{D}}^* \cdot \boldsymbol{\nabla}_R \bar{P}, \tag{1.9b}$$

$$|\boldsymbol{R} - \boldsymbol{R}'|^m (\bar{P}, \bar{\boldsymbol{J}}) \rightarrow (0, \boldsymbol{0}) \quad \text{as} \quad |\boldsymbol{R} - \boldsymbol{R}'| \rightarrow \infty \quad (m = 0, 1, 2, \ldots) \tag{1.9c}$$

and

$$\bar{P} = \begin{cases} \delta(\boldsymbol{R} - \boldsymbol{R}') & \text{for} \quad t = 0 \\ 0 & \text{for} \quad t < 0, \end{cases} \tag{1.9d}$$

with $\bar{\boldsymbol{U}}^*$ the *mean* sedimentation velocity vector of the ellipsoid (relative to the fluid) and $\bar{\boldsymbol{D}}^*$ its dispersivity dyadic, each constant relative to space-fixed axes, and supposed to be determined entirely by the specified orientation-specific phenomenological data ($\boldsymbol{F}, \boldsymbol{M}, \boldsymbol{D}, \boldsymbol{B}$ together with the prescribed velocity gradient $\boldsymbol{G}$, and, hence, $\boldsymbol{\omega}_f$ and $\boldsymbol{S}$) appearing in the six-dimensional microscale transport problem posed by (1.1)–(1.5). The phenomenological coefficients $\bar{\boldsymbol{U}}^*$ and $\bar{\boldsymbol{D}}^*$ appearing in the 'model problem' (1.9) provide a macroscale description (free of any explicit dependence upon the ellipsoid's orientational degrees of freedom) of the overall transport process in physical space.

The possibility of constructing such a purely physical-space description is based upon recognizing inherent differences existing between the respective translational and rotational degrees of freedom of the particle or, more precisely, the disparity existing in timescales for relaxation of the respective transport processes in the physical and orientational subspaces. The rotary motion (cf. (1.3)) depends only upon the velocity gradient, which in a homogeneous shear field is, by definition, constant throughout physical space. Consequently, the ellipsoid's rotary motion is entirely independent of its instantaneous physical-space position. This independence, in conjunction with the existence of rotary diffusion, enables the particle to attain a stationary orientational equilibrium (after it has sampled all orientations (1.7) sufficiently many times), which state is independent of the ellipsoid's initial orientation $\boldsymbol{\phi}'$. Obviously, no comparable equilibrium can be achieved in the physical-space domain (1.6) owing to its unboundedness.

Despite the foregoing qualitative argument, it is not *a priori* obvious that the macrotransport description embodied in (1.9) (or indeed *any* purely physical-space description of the mean transport) is possible for unbounded shear flows, and – if it is – then how is one to calculate the macroscale phenomenological coefficients $\bar{\boldsymbol{U}}^*$ and $\bar{\boldsymbol{D}}^*$ appearing therein from the given microscale orientation-specific phenomenological data and prescribed shear parameters appearing in equations (1.2)–(1.3).

Such issues have been previously addressed by generalized Taylor dispersion theory† in a variety of physical contexts. In fact, the formulation (1.1)–(1.5) conforms to the structure of the generic microscale transport problem underlying the latter theory (cf. Frankel & Brenner 1989, their (2.1)–(2.6)) when one identifies the following equivalence relations:

$$\boldsymbol{R} \rightarrow \boldsymbol{Q} \quad \text{and} \quad \boldsymbol{\phi} \rightarrow \boldsymbol{q}, \tag{1.10}$$

i.e. the three-dimensional physical-space position vector corresponds to the 'global' coordinate $\boldsymbol{Q}$ and the triplet of Eulerian angles to the 'local' coordinate $\boldsymbol{q}$.

The questions posed above cannot, however, be resolved by existing generalized Taylor dispersion theory since a fundamental feature of the paradigm underlying that theory is the basic hypothesis that all the phenomenological coefficients appearing in the exact microscale formulation of the problem governing the conditional probability density $P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{Q}', \boldsymbol{q}')$ are independent of the global coordinate $\boldsymbol{Q}$ – being at most (prescribed) functions of the local coordinate $\boldsymbol{q}$ (and, perhaps, periodic functions of the time too; cf. Shapiro & Brenner 1990). This requirement is obviously not satisfied in the present problem (owing to the occurrence of the shear term in (1.2)).

As will appear, application of the Taylor dispersion multiple-timescale scheme to the above example, as well as to other Taylor dispersion problems in *unbounded* shear flows, necessitates a major extension of the original theory (cf. Frankel & Brenner 1989), requiring reconsideration of some of its basic tenets. This extension constitutes the goal of the present contribution. (The lengthy explicit numerical results for the problem of the transport of Brownian ellipsoidal particles in homogeneous shear, which furnished the motivation for this extension, will be reported separately in a forthcoming contribution.)

In the following derivation we found it preferable to use standard, albeit abstract, general Taylor dispersion theory notation, not only because of its conciseness, but also as a means of emphasizing that the subsequent theory developed has implications and applications well beyond the specific ellipsoid example discussed thus far. This fact will be illustrated by applying the general theory to be developed to the (relatively) elementary problem of transport in a shear flow of a sedimenting, size-fluctuating porous sphere (which geometry is a commonly accepted model for a macromolecular polymer coil; Wiegel 1980).

A brief review of the subsequent developments now follows. In §2 we formulate the generic microscale problem of generalized Taylor dispersion in unbounded homogeneous shear flows. This is followed by a transformation to a codeformational frame of reference (Bird, Armstrong & Hassager 1987), which transformation restores the structure of the 'classical' non-sheared problem (cf. Frankel & Brenner 1989). Section 3 makes use of the method of statistical moments to obtain an asymptotic

† Schemes other than Taylor dispersion moment methods that have also been used to effect the requisite coarse graining of microscale equations are homogenization (Bensoussan, Lions & Papanicolau 1978) and invariant manifold schemes (cf. Muncaster 1983).

expansion of the local-space-averaged conditional probability density for circumstances wherein the eigenvalues of the velocity gradient $\boldsymbol{G}$ are either zero or purely imaginary. Explicit forms of this expansion are then obtained for the corresponding subclass of plane two-dimensional homogeneous shear flows. Results of the preceding sections are utilized in §4 to substantiate the existence of a 'purely global' macroscale description based upon a convective–diffusive model problem. Further insight into the physical significance of the dispersivity dyadic is gained in §5 by having recourse to a Lagrangian description in the original domain. Section 6 addresses cases of zero 'slip velocity', for which circumstances the Taylor dispersion mechanism is absent (e.g. a *rigid* Brownian sphere in an unbounded homogeneous shear flow), as particular cases of the general theory developed here. Some of the results of the general theory are illustrated in §7 by considering the dispersion accompanying the sedimentation in a shear field of a size-fluctuating porous Brownian sphere. Finally, §8 summarizes the main results of the present analysis and outlines some desirable future applications and theoretical extensions thereof.

2. Formulation of the problem

Following standard (Frankel & Brenner 1989) notation, the conditional probability density $P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{Q}',\boldsymbol{q}')$ governing the solute tracer transport process satisfies the conservation equation (cf. (1.1) for the case of an ellipsoid)

$$\frac{\partial P}{\partial t}+\boldsymbol{\nabla}_Q\cdot\boldsymbol{J}+\boldsymbol{\nabla}_q\cdot\boldsymbol{j}=0, \tag{2.1}$$

in which the constitutive equations for the respective global- and local-space flux density vectors appearing therein are (cf. (1.2) and (1.3) for the case of an ellipsoid)

$$\boldsymbol{J}=[\boldsymbol{U}(\boldsymbol{q})+\boldsymbol{V}(\boldsymbol{Q}')+(\boldsymbol{Q}-\boldsymbol{Q}')\cdot\boldsymbol{G}]P-\boldsymbol{D}(\boldsymbol{q})\cdot\boldsymbol{\nabla}_Q P \tag{2.2}$$

and

$$\boldsymbol{j}=\boldsymbol{u}(\boldsymbol{q})P-\boldsymbol{d}(\boldsymbol{q})\cdot\boldsymbol{\nabla}_q P. \tag{2.3}$$

The respective solute velocity vectors $\boldsymbol{U}(\boldsymbol{q})$, $\boldsymbol{u}(\boldsymbol{q})$ and molecular diffusivity dyadics $\boldsymbol{D}(\boldsymbol{q})$, $\boldsymbol{d}(\boldsymbol{q})$ are henceforth assumed to be (known) functions of $\boldsymbol{q}$ alone; $\boldsymbol{V}(\boldsymbol{Q}')$ denotes the undisturbed fluid (i.e. solvent) velocity vector at $\boldsymbol{Q}'$, whereas $\boldsymbol{G}$ is the (constant, position- and time-independent) undisturbed fluid velocity-gradient dyadic. In (2.2) the combination of terms, $\boldsymbol{V}(\boldsymbol{Q}')+(\boldsymbol{Q}-\boldsymbol{Q}')\cdot\boldsymbol{G}$ (with $\boldsymbol{Q}$ the three-dimensional position vector relative to an arbitrary, space-fixed origin) corresponds to an unbounded ($\boldsymbol{Q}\in\boldsymbol{Q}_\infty$) homogeneous shear flow. This dependence of the global convective velocity, $\boldsymbol{U}(\boldsymbol{q})+\boldsymbol{V}(\boldsymbol{Q}')+(\boldsymbol{Q}-\boldsymbol{Q}')\cdot\boldsymbol{G}$, upon the global coordinate $\boldsymbol{Q}$ marks the point of departure of the present problem from the classical case, since the latter is underlain by the assumption that *all* the phenomenological functions, including the velocity field, depend upon $\boldsymbol{q}$ *alone* (Brenner 1980, 1982).

The foregoing equations are supplemented by the following respective global- and local-space boundary conditions (cf. (1.4) for the ellipsoid)†

$$|\boldsymbol{Q}-\boldsymbol{Q}'|^m(P,\boldsymbol{J},\boldsymbol{j})\rightarrow(0,\boldsymbol{0},\boldsymbol{0}) \quad \text{as} \quad |\boldsymbol{Q}-\boldsymbol{Q}'|\rightarrow\infty \quad \text{for all} \quad m\geqslant 0, \tag{2.4}$$

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j}=0 \quad \text{on} \quad \partial\boldsymbol{q}_o, \tag{2.5}$$

† Since the orientation space is closed upon itself, no counterpart of (2.5) appears explicitly in the ellipsoid problem outlined in (1.1)–(1.7). Rather, the latter problem merely requires that the probability and flux density fields $(P,\boldsymbol{J},\boldsymbol{j})$ be single-valued and continuous in the orientational variables, $\boldsymbol{\phi}(\equiv\boldsymbol{q})$.

together with the initial condition (cf. (1.5) for the ellipsoid problem)

$$P = \begin{cases} \delta(\boldsymbol{Q}-\boldsymbol{Q}')\,\delta(\boldsymbol{q}-\boldsymbol{q}') & \text{for} \quad t = 0 \\ 0 & \text{for} \quad t < 0. \end{cases} \tag{2.6}$$

In (2.5), $\hat{\boldsymbol{n}}$ is a unit normal to $\partial \boldsymbol{q}_o$, the boundary of the local subspace.

Thus, making use of the equivalence relations (1.10), the convective–diffusive problem for the transport of a Brownian ellipsoid, (1.1)–(1.5) and the above problem are readily seen to possess the same structure, as has already been explicitly indicated in connection with (2.1)–(2.6).

The preceding problem formulation is somewhat simplified upon applying the transformation $\boldsymbol{Q} \rightarrow \boldsymbol{Q}^{(1)}$ of the independent global variable, embodying the new choice $\boldsymbol{Q}^{(1)}$ of global coordinate:

$$P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{Q}',\boldsymbol{q}') \overset{\text{def.}}{=} P^{(1)}(\boldsymbol{Q}^{(1)},\boldsymbol{q},t\,|\,\boldsymbol{Q}',\boldsymbol{q}')\,\mathrm{e}^{-(\boldsymbol{I}:\boldsymbol{G})t}, \tag{2.7}$$

$$\boldsymbol{Q}^{(1)} \overset{\text{def.}}{=} (\boldsymbol{Q}-\boldsymbol{Q}')\cdot\mathrm{e}^{-\boldsymbol{G}t} - [\boldsymbol{V}(\boldsymbol{Q}')+\bar{\boldsymbol{U}}]\cdot\int_0^t \mathrm{e}^{-\boldsymbol{G}t_1}\,\mathrm{d}t_1, \tag{2.8}$$

with $\bar{\boldsymbol{U}}$ a constant vector, ultimately defined in (3.15). (Equation (2.8) is, in fact, the integral of the kinematic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{Q}-\boldsymbol{Q}') = (\boldsymbol{Q}-\boldsymbol{Q}')\cdot\boldsymbol{G}+\bar{\boldsymbol{U}}^{(1)}$$

governing the motion of a particle whose initial global-space position is

$$\boldsymbol{Q}-\boldsymbol{Q}' = \boldsymbol{Q}^{(1)}, \quad \text{say, at} \quad t = 0,$$

and which drifts with a constant 'slip velocity' $\bar{\boldsymbol{U}}^{(1)}$ relative to the carrier fluid, which itself undergoes a homogeneous shear characterized by the velocity gradient $\boldsymbol{G}$. Thus, (2.7) and (2.8) constitute a transformation to a codeformational coordinate system (cf. Bird *et al.* 1987, as well as §5 of the present paper). When $\boldsymbol{G} = \boldsymbol{0}$, (2.8) degenerates to the form

$$\boldsymbol{Q}^{(1)} = \boldsymbol{Q}-\boldsymbol{Q}'-\bar{\boldsymbol{U}}^{(1)}t,$$

which represents a Galilean transformation to a frame of reference moving with the constant velocity $\bar{\boldsymbol{U}}^{(1)}$.)

The resulting initial- and boundary-value problem posed for the conditional probability density $P^{(1)}$ obeys the following system of equations:

$$\frac{\partial P^{(1)}}{\partial t} + \nabla_{Q^{(1)}}\cdot\boldsymbol{J}^{(1)} + \nabla_q\cdot\boldsymbol{j} = 0, \tag{2.9a}$$

$$\boldsymbol{J}^{(1)} = \Delta\boldsymbol{U}(\boldsymbol{q})\cdot\mathrm{e}^{-\boldsymbol{G}t}P^{(1)} - \mathrm{e}^{-\boldsymbol{G}^\dagger t}\cdot\boldsymbol{D}(\boldsymbol{q})\cdot\mathrm{e}^{-\boldsymbol{G}t}\cdot\nabla_{Q^{(1)}}P^{(1)}, \tag{2.9b}$$

$$\boldsymbol{j} = \boldsymbol{u}(\boldsymbol{q})\,P^{(1)} - \boldsymbol{d}(\boldsymbol{q})\cdot\nabla_q P^{(1)}, \tag{2.9c}$$

$$|\boldsymbol{Q}^{(1)}|^m(P^{(1)},\boldsymbol{J}^{(1)},\boldsymbol{j}) \rightarrow (0,\boldsymbol{0},\boldsymbol{0}) \quad \text{as} \quad |\boldsymbol{Q}^{(1)}| \rightarrow \infty \quad (m = 1,2,3,\ldots), \tag{2.9d}$$

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j} = 0 \quad \text{on} \quad \partial\boldsymbol{q}_o \tag{2.9e}$$

and

$$P^{(1)}(\boldsymbol{Q}^{(1)},\boldsymbol{q},t\,|\,\boldsymbol{Q}',\boldsymbol{q}') = \begin{cases} \delta(\boldsymbol{Q}^{(1)})\,\delta(\boldsymbol{q}-\boldsymbol{q}') & (t = 0) \\ 0 & (t < 0), \end{cases} \tag{2.9f}$$

where, in (2.9*b*), † denotes a transposition operator. Appearing in (2.9*b*) is the solute-velocity disparity,

$$\Delta \boldsymbol{U}(\boldsymbol{q}) \overset{\text{def.}}{=} \boldsymbol{U}(\boldsymbol{q}) - \bar{\boldsymbol{U}}, \tag{2.10}$$

where the constant vector $\bar{\boldsymbol{U}}$ is explicitly chosen later to be equal to the long-time-average global 'slip velocity' of the tracer (cf. (3.15)).

Since the problem satisfied by $P^{(1)}$ in the transformed domain includes no explicit or implicit dependence upon $\boldsymbol{Q}'$, the functional dependence of $P^{(1)}$ is, in fact, such that

$$P^{(1)} \equiv P^{(1)}(\boldsymbol{Q}^{(1)}, \boldsymbol{q}, t \mid \boldsymbol{q}'), \tag{2.11}$$

rather than what appears on the right-hand side of (2.7). The transformation has thus removed the global-coordinate dependence of the global-space phenomenological coefficients, albeit at the expense of now rendering the latter time-dependent. Apart from this new feature, the resulting problem is now identical with the comparable formulation of that for the 'classical' case (Frankel & Brenner 1989), occurring for $\boldsymbol{G} = \boldsymbol{0}$. In what follows the upper indices will be consistently omitted from both $P^{(1)}$ and $\boldsymbol{Q}^{(1)}$ in the interest of notational simplicity. Where confusion with the original variables P and $\boldsymbol{Q}$ may result, we will render the distinction explicit.

In the following we seek an asymptotic, long-time description of the local-space-domain-averaged probability density,

$$\bar{P}(\boldsymbol{Q}, t \mid \boldsymbol{q}') = \int_{q_0} P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}, \tag{2.12}$$

as $t \rightarrow \infty$. This description will be obtained from respective asymptotic expansions of the statistical moments of P, without requiring explicit, *a priori* knowledge of P itself.

3. Long-time asymptotic expansion of $\bar{P}$

We seek an asymptotic approximation of $\bar{P}(\boldsymbol{Q}, t \mid \boldsymbol{q}')$ in the long-time limit,

$$\|\boldsymbol{d}\|\, t \gg 1, \tag{3.1}$$

wherein $\|\boldsymbol{d}\|$ denotes an appropriate norm of the dyadic $\boldsymbol{d}$. The Fourier transform $\tilde{\bar{P}}$ of $\bar{P}$ is defined as

$$\tilde{\bar{P}}(\omega, t \mid \boldsymbol{q}') = \int_{Q_\infty} \bar{P}(\boldsymbol{Q}, t \mid \boldsymbol{q}') \exp(\mathrm{i}\omega \cdot \boldsymbol{Q})\, \mathrm{d}\boldsymbol{Q} \equiv \sum_{m=0}^{\infty} \frac{1}{m!} (\mathrm{i}\omega)^m (\cdot)^m \boldsymbol{M}_m(t \mid \boldsymbol{q}'), \tag{3.2}$$

which possesses the indicated series expansion, with

$$\boldsymbol{M}_m(t \mid \boldsymbol{q}') = \int_{Q_\infty} \int_{q_0} \boldsymbol{Q}^m P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}\, \mathrm{d}\boldsymbol{Q} \quad (m = 0, 1, 2, \ldots) \tag{3.3}$$

the total polyadic statistical moments of P; the multiple dot-product operator $(\cdot)^m$ denotes m successive contractions. Alternatively, the total moments are expressible as

$$\boldsymbol{M}_m(t \mid \boldsymbol{q}') = \int_{q_0} \boldsymbol{P}_m\, \mathrm{d}\boldsymbol{q} \quad (m = 0, 1, 2, \ldots), \tag{3.4}$$

with
$$\boldsymbol{P}_m(\boldsymbol{q},t\,|\,\boldsymbol{q}') = \int_{\boldsymbol{Q}_\infty} \boldsymbol{Q}^m P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{Q} \quad (m = 0,1,2,\ldots) \tag{3.5}$$

the local polyadic moments. The initial- and boundary-value problems respectively satisfied by each of the $\boldsymbol{P}_m$ may be derived via appropriate integrations over the global-space domain $\boldsymbol{Q}_\infty$ in conjunction with use of the global-space boundary conditions (2.4). This yields the following sequence of equations:

$$\frac{\partial \boldsymbol{P}_m}{\partial t} + \nabla_q \cdot \boldsymbol{j}_m = m[\![\Delta \boldsymbol{U}(\boldsymbol{q})\cdot \mathrm{e}^{-\boldsymbol{G}t}\boldsymbol{P}_{m-1}]\!]^{\mathrm{s}} + m(m-1)[\![\mathrm{e}^{-\boldsymbol{G}^\dagger t}\cdot \boldsymbol{D}(\boldsymbol{q})\cdot \mathrm{e}^{-\boldsymbol{G}t}\boldsymbol{P}_{m-2}]\!]^{\mathrm{s}}, \tag{3.6a}$$

$$\boldsymbol{j}_m = \boldsymbol{u}(\boldsymbol{q})\,\boldsymbol{P}_m - \boldsymbol{d}(\boldsymbol{q})\cdot\nabla_q \boldsymbol{P}_m, \tag{3.6b}$$

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j}_m = \boldsymbol{0} \quad \text{on} \quad \partial \boldsymbol{q}_o \tag{3.6c}$$

and
$$\boldsymbol{P}_m = \begin{cases} \delta_{m0}\,\delta(\boldsymbol{q}-\boldsymbol{q}') & (t=0) \\ 0 & (t<0), \end{cases} \tag{3.6d}$$

where, in (3.6a), $[\![\,]\!]^{\mathrm{s}}$ denotes the symmetrization operator (cf. Frankel & Brenner 1989). In fact, the foregoing recursive system is identical with that pertaining to the case $\boldsymbol{G} = \boldsymbol{0}$ (Frankel & Brenner 1989) upon simply replacing $\Delta \boldsymbol{U}$ and $\boldsymbol{D}$ there, respectively by $\Delta\boldsymbol{U}\cdot\exp(-\boldsymbol{G}t)$ and $\exp(-\boldsymbol{G}^\dagger t)\cdot\boldsymbol{D}\cdot\exp(-\boldsymbol{G}t)$.

An important advantage of the formulation in the transformed domain is that the zero-order scalar term P_0, representing the solution of (3.6) for $m = 0$, can serve as the appropriate Green's function (cf. Shapiro & Brenner 1987 for the comparable $\boldsymbol{G} = \boldsymbol{0}$ case),

$$\boldsymbol{P}_m(\boldsymbol{q},t\,|\,\boldsymbol{q}') = \int_0^t \int_{q_o} P_0(\boldsymbol{q},t-t_1\,|\,\boldsymbol{q}_1)\{m[\![\Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_1}\boldsymbol{P}_{m-1}(\boldsymbol{q}_1,t_1\,|\,\boldsymbol{q}')]\!]^{\mathrm{s}}$$
$$+\,m(m-1)[\![\mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot\boldsymbol{D}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_1}\boldsymbol{P}_{m-2}(\boldsymbol{q}_1,t_1\,|\,\boldsymbol{q}')]\!]^{\mathrm{s}}\}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1, \tag{3.7}$$

for the higher-order polyadic terms. Thus, each $\boldsymbol{P}_m$ $(m = 1,2,3,\ldots)$ can, in principle, be determined recursively by quadrature of the above once P_0 is known. Following this, each total moment may then be obtained by straightforward integration of (3.4).

By virtue of the vanishing of the right-hand side of (3.6a) for $m = 0$, the system of equations governing P_0 shows no explicit dependence upon $\boldsymbol{G}$; as such, it possesses a structure identical to the corresponding zero-shear case, $\boldsymbol{G} = \boldsymbol{0}$. We shall, therefore, make use of the decomposition (Brenner 1982)

$$P_0(\boldsymbol{q},t\,|\,\boldsymbol{q}') = P_0^\infty(\boldsymbol{q}) + p(\boldsymbol{q},t\,|\,\boldsymbol{q}'), \tag{3.8}$$

for which $P_0^\infty(\boldsymbol{q})$ represents the stationary, local-space distribution, achieved for $t \to \infty$. This time-independent distribution satisfies the system of equations (Brenner 1982)

$$\nabla_q\cdot\boldsymbol{j}_0^\infty = 0, \tag{3.9a}$$

$$\boldsymbol{j}_0^\infty = \boldsymbol{u}P_0^\infty - \boldsymbol{d}\cdot\nabla_q P_0^\infty, \tag{3.9b}$$

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j}_0^\infty = 0 \quad \text{on} \quad \partial\boldsymbol{q}_0 \tag{3.9c}$$

and
$$\int_{q_o} P_0^\infty\,\mathrm{d}\boldsymbol{q} = 1. \tag{3.9d}$$

(The latter derives from the normalization condition

$$\int_{Q_\infty}\int_{q_o} P\,\mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{Q} = 1, \tag{3.10}$$

whose validity can readily be verified for the field P which solves the system of equations (2.9).) The non-stationary contribution $p(\boldsymbol{q},t\,|\,\boldsymbol{q}')$ to the density (3.8) vanishes exponentially rapidly for the sufficiently long times described by the inequality (3.1).

Let ν_i $(i = 1,2,3)$ denote the eigenvalues of $\boldsymbol{G}$. Subsequent analysis is confined to circumstances for which

$$\mathrm{Re}\{\nu_i\} = 0 \quad (i = 1,2,3), \tag{3.11}$$

where Re{} denotes the real part of the argument in braces. The kinematical significance of this restriction is that it eliminates the possibility that the deterministic convection of the material tracer particle in the homogeneous shear field may lead to an exponentially rapid divergence of its global-space position vector. Since $\boldsymbol{G}$ is real, its three eigenvalues are either all real or else one is real, the other two being complex conjugates. If we further impose the condition (3.11), then $\exp(\boldsymbol{G}t)$ can only assume one of the following two forms (cf. Gantmacher 1960):

(*a*) $\nu_{1,2} = \pm\mathrm{i}\omega$, $\nu_3 = 0$:

$$\mathrm{e}^{\boldsymbol{G}t} = \boldsymbol{I} + \omega^{-1}\sin\omega t\,\boldsymbol{G} + \omega^{-2}(1-\cos\omega t)\,\boldsymbol{G}\cdot\boldsymbol{G}; \tag{3.12}$$

or (*b*) $\nu_i = 0$ $(i = 1,2,3)$:

$$\mathrm{e}^{\boldsymbol{G}t} = \boldsymbol{I} + \boldsymbol{G}t + \tfrac{1}{2}\boldsymbol{G}\cdot\boldsymbol{G}t^2. \tag{3.13}$$

Substitution of (3.12) into (2.8), with the last term on the right-hand side deleted, shows that in the case of purely imaginary eigenvalues, the global-space position vector is time periodic and the concomitant streamlines closed. If, on the other hand, all the eigenvalues vanish as in (3.13), the position vector then grows algebraically with t, corresponding to either a constant acceleration or constant velocity (the latter if $\boldsymbol{G}\cdot\boldsymbol{G} = \boldsymbol{0}$, in which case the streamlines are straight lines). Only when (3.11) is not satisfied, i.e. there exists a value of ν_i such that $\mathrm{Re}\{\nu_i\} \neq 0$ can the position vector (as well as the velocity and acceleration of the material tracer) diverge exponentially rapidly. No restrictions are imposed upon the magnitude of the Péclet number,

$$Pe = \frac{\|\boldsymbol{G}\|}{\|\boldsymbol{d}\|}, \tag{3.14}$$

wherein $\|\boldsymbol{G}\|$ represents an appropriate norm of the dyadic $\boldsymbol{G}$.

Finally, the resulting expressions are simplified by the following choice of the vector $\bar{\boldsymbol{U}}$ appearing in the definition (2.10) of $\Delta\boldsymbol{U}(\boldsymbol{q})$:

$$\bar{\boldsymbol{U}} = \int_{q_o} P_0^\infty(\boldsymbol{q})\,\boldsymbol{U}(\boldsymbol{q})\,\mathrm{d}\boldsymbol{q}. \tag{3.15}$$

Thus, $\bar{\boldsymbol{U}}$ represents the long-time-average global 'slip velocity' of the tracer.

Substitution into (3.7) of (3.8) and (3.15) in conjunction with the condition (3.11), followed by a tedious asymptotic calculation, yields long-time expansions of the local moments $\boldsymbol{P}_m$ as well as of the total moments $\boldsymbol{M}_m$ (cf. the Appendix).

Anticipating that the leading-order asymptotic behaviour of P is Gaussian leads us to utilize the cumulant expansion

$$\tilde{\tilde{P}}(\omega, t \mid \boldsymbol{q}') = \exp\left[\sum_{n=1}^{\infty} \frac{(\mathrm{i}\omega)^n}{n!}(\cdot)^n \boldsymbol{C}_n(t \mid \boldsymbol{q}')\right] \tag{3.16}$$

rather than the moment expansion (3.2). Upon making use of the expressions for the cumulants in terms of the total moments (Abramowitz & Stegun 1968) and the asymptotic expansions of the latter [(A 11) and (A 12)], one obtains†

$$\boldsymbol{C}_1 \sim \boldsymbol{A}(\boldsymbol{q}') + \exp, \tag{3.17a}$$

$$\boldsymbol{C}_2 \sim 2[\mathscr{D}(t) + \boldsymbol{A}_2(\boldsymbol{q}') - \tfrac{1}{2}\boldsymbol{A}^2(\boldsymbol{q}')] + \exp, \tag{3.17b}$$

$$\boldsymbol{C}_3 \sim 3![\mathscr{D}_3(t) + [\![\boldsymbol{A}_3(\boldsymbol{q}') - \boldsymbol{A}_2(\boldsymbol{q}')\,\boldsymbol{A}(\boldsymbol{q}') + \tfrac{1}{3}\boldsymbol{A}^3(\boldsymbol{q}')]\!]^{\mathrm{s}}] + \exp, \tag{3.17c}$$

$$\boldsymbol{C}_4 \sim 4![\mathscr{D}_4(t) + [\![\boldsymbol{A}_4(\boldsymbol{q}') - \tfrac{1}{2}\boldsymbol{A}_2^2(\boldsymbol{q}') - \boldsymbol{A}_3(\boldsymbol{q}')\,\boldsymbol{A}(\boldsymbol{q}') + \boldsymbol{A}_2(\boldsymbol{q}')\,\boldsymbol{A}^2(\boldsymbol{q}') - \tfrac{1}{4}\boldsymbol{A}^4(\boldsymbol{q}')]\!]^{\mathrm{s}}] + \exp, \tag{3.17d}$$

where the $\boldsymbol{q}'$-independent n-adics $\mathscr{D}_n(t)$ are defined as

$$\mathscr{D}_n(t) \overset{\text{def.}}{=} \int_0^t \boldsymbol{D}_n^*(\cdot)^n(\mathrm{e}^{-\boldsymbol{G}t_1})^n\,\mathrm{d}t_1 \quad (n = 2, 3, 4, \ldots). \tag{3.18}$$

(We have suppressed the subscript in (3.17 b) for the special case where $n = 2$ in order to achieve consistency with prior notation (Frankel & Brenner 1989).) The various m-adic coefficients $\boldsymbol{D}_m^*$ appearing above, as well as the $\boldsymbol{q}'$-dependent n-adic fields $\boldsymbol{A}_n(\boldsymbol{q}')$, are respectively defined in the Appendix. In (3.18) it was found useful to introduce the notation $\boldsymbol{A}_n(\cdot)^n(\boldsymbol{B})^n$ to denote the polyadic whose Cartesian tensor components are

$$[\boldsymbol{A}_n(\cdot)^n(\boldsymbol{B})^n]_{ijk\ldots} = A_{pqr\ldots}B_{pi}B_{qj}B_{rk}\ldots. \tag{3.19}$$

It is interesting to note that not only do the resulting expansions degenerate to ones already known (Frankel & Brenner 1989) from the zero-shear, $\boldsymbol{G} = \boldsymbol{0}$ case, but that they can also be recovered easily from these classical zero-shear expressions by simply invoking the following 'equivalence' relations:

$$P_0^{\infty}(\boldsymbol{q})\,\boldsymbol{B}_n(\boldsymbol{q}) \rightarrow P_0^{\infty}(\boldsymbol{q})\,\boldsymbol{B}_n(\boldsymbol{q})(\cdot)^n(\mathrm{e}^{-\boldsymbol{G}t})^n \quad (n = 1, 2, 3, \ldots), \tag{3.20a}$$

$$\boldsymbol{D}_n^{\cdot} \rightarrow \boldsymbol{D}_n^{\cdot}(\cdot)^n(\mathrm{e}^{-\boldsymbol{G}t})^n, \tag{3.20b}$$

$$\boldsymbol{D}_n^{\cdot}\,t \rightarrow \mathscr{D}_n(t) \quad (n = 2, 3, \ldots), \tag{3.20c}$$

in which the $\boldsymbol{B}_n$ are defined in the Appendix.

Substitute into (3.16) the asymptotic expressions (3.17) for the $\boldsymbol{C}_n$ while applying the transformation

$$\tilde{\tilde{P}}(\omega, t \mid \boldsymbol{q}') \equiv \underline{\tilde{\tilde{P}}}(\varpi, t \mid \boldsymbol{q}'), \tag{3.21a}$$

in which

$$\varpi \overset{\text{def.}}{=} \omega\cdot\mathscr{D}^{\frac{1}{2}} \quad (\text{or } \omega = \varpi\cdot\mathscr{D}^{-\frac{1}{2}}), \tag{3.21b}$$

and wherein $\mathscr{D}^{\frac{1}{2}}$ is defined in terms of $\mathscr{D}$ by the expression

$$\mathscr{D}^{\frac{1}{2}}\cdot(\mathscr{D}^{\frac{1}{2}})^{\dagger} = \mathscr{D}. \tag{3.22}$$

(Since $\boldsymbol{M}_2$ is positive definite by definition, so too must be $\mathscr{D}$, at least in the long-time

† The above expressions seem to suggest that, in general,

$$\boldsymbol{C}_n \simeq n!\,\mathscr{D}_n(t) + \bar{\boldsymbol{A}}_n(\boldsymbol{q}') + \exp,$$

where the n-adic, $\bar{\boldsymbol{A}}_n(\boldsymbol{q}')$, depends upon the local-space initial position $\boldsymbol{q}'$, but is time-independent.

limit; in turn, this assures that the dyadic $\mathscr{D}^{\frac{1}{2}}$ defined above is real.) This yields the following expansion of (3.16):

$$\tilde{\underline{\bar{P}}}(\bar{\boldsymbol{\omega}},t\,|\,\boldsymbol{q}') \sim \exp\{\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\mathscr{D}^{-\frac{1}{2}}\cdot \boldsymbol{A}(\boldsymbol{q}')+(\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\mathscr{D}^{-\frac{1}{2}})^2(\cdot)^2\bar{A}_2(\boldsymbol{q}') + (\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\mathscr{D}^{-\frac{1}{2}})^3(\cdot)^3[\mathscr{D}_3+\bar{A}_3(\boldsymbol{q}')]+(\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\mathscr{D}^{-\frac{1}{2}})^4(\cdot)^4[\mathscr{D}_4+\bar{A}_4(\boldsymbol{q}')]+\ldots\}\exp(-\bar{\boldsymbol{\omega}}\cdot\bar{\boldsymbol{\omega}}). \quad (3.23)$$

The original function $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ is recovered from $\tilde{\bar{P}}(\boldsymbol{\omega},t\,|\,\boldsymbol{q}')$ via the inverse transform (cf. (3.2)), which for an n-dimensional global space is

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') = \frac{1}{(2\pi)^n}\int_{\boldsymbol{\omega}_\infty}\tilde{\bar{P}}(\boldsymbol{\omega},t\,|\,\boldsymbol{q}')\exp(-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{\omega}.$$

Into the above, introduce (3.21b) together with the additional definition

$$\bar{\boldsymbol{Q}} = \mathscr{D}^{-\frac{1}{2}}\cdot\boldsymbol{Q} \quad (\text{or } \boldsymbol{Q} = \mathscr{D}^{\frac{1}{2}}\cdot\bar{\boldsymbol{Q}}), \quad (3.24)$$

to obtain

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') = \left(\frac{1}{(2\pi)^n|\mathscr{D}|^{\frac{1}{2}}}\int_{\bar{\boldsymbol{\omega}}_\infty}\tilde{\underline{\bar{P}}}(\bar{\boldsymbol{\omega}},t\,|\,\boldsymbol{q}')\exp(-\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\bar{\boldsymbol{Q}})\,\mathrm{d}\bar{\boldsymbol{\omega}}\right) \equiv \frac{\underline{\bar{P}}(\bar{\boldsymbol{Q}},t\,|\,\boldsymbol{q}')}{|\mathscr{D}|^{\frac{1}{2}}}, \quad (3.25)$$

wherein $\underline{\bar{P}}(\bar{\boldsymbol{Q}},t\,|\,\boldsymbol{q}')$ is the inverse Fourier transform of $\tilde{\underline{\bar{P}}}(\bar{\boldsymbol{\omega}},t\,|\,\boldsymbol{q}')$ and $|\mathscr{D}| \overset{\text{def.}}{=} \det\mathscr{D}$. Use of the identity

$$\frac{1}{(2\pi)^n}\int_{\bar{\boldsymbol{\omega}}_\infty}\exp(-\bar{\boldsymbol{\omega}}\cdot\bar{\boldsymbol{\omega}})\exp(-\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\bar{\boldsymbol{Q}})\,\mathrm{d}\bar{\boldsymbol{\omega}} = \frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\bar{\boldsymbol{Q}})}{(4\pi)^{n/2}} \quad (3.26)$$

together with (3.25) thereby demonstrates that the leading-order asymptotic behaviour of $\bar{P}$ is

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') \equiv \frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\bar{\boldsymbol{Q}})}{(4\pi)^{n/2}|\mathscr{D}|^{\frac{1}{2}}} \equiv \frac{\exp(-\frac{1}{4}\boldsymbol{Q}\cdot\mathscr{D}^{-1}\cdot\boldsymbol{Q})}{(4\pi)^{n/2}|\mathscr{D}|^{\frac{1}{2}}}, \quad (3.27)$$

provided that all terms in the first exponent of (3.23) can be shown to be of $o(1)$ as $t\rightarrow\infty$. This, in turn, enables the approximation of $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ in the long-time limit by the solution $P^{\bullet}(\boldsymbol{Q},t)$, say of the 'purely global', $\boldsymbol{q}'$-independent, model problem, discussed in the next section.

In the following we focus on plane (two-dimensional) shear flows, which facilitates calculation of the long-time expressions for $\mathscr{D}_n$ and $\mathscr{D}^{-\frac{1}{2}}$. This permits us to explicitly address the 'convergence' issues raised above.

3.1. *Plane (two-dimensional) shear flows*

For this class of flows we have that

$$\boldsymbol{G} = G\hat{\boldsymbol{G}}, \quad \hat{\boldsymbol{G}} = \begin{pmatrix} 0 & \alpha & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (3.28)$$

All possible cases are spanned by the range of parametric values $-1 \leqslant \alpha \leqslant 1$; ($\alpha = -1$ corresponds to 'pure rotation', $\alpha = 0$ to 'simple shear', and $\alpha = 1$ to elongational 'hyperbolic' flow (cf. Kao, Cox & Mason 1977)). The dyadic $\boldsymbol{G}$ given above possesses the eigenvalues

$$\nu_i = 0, \quad \pm\alpha^{\frac{1}{2}}G \quad (i = 1,2,3), \quad (3.29)$$

where the criterion (3.11) necessitates satisfaction of the inequality $\alpha \leqslant 0$. Explicit calculation of the asymptotic long-time expressions for $\mathscr{D}_n$, though fairly straightforward, is quite tedious. The following exposition is therefore limited to outlining the essential results of the calculation, omitting details.

For $\alpha \leqslant 0$ it can be verified that

$$\mathscr{D}_n = t\boldsymbol{\delta}_n(\tau), \tag{3.30}$$

wherein the $\boldsymbol{\delta}_n(\tau)$ ($n = 2, 3, 4, \ldots$) are, respectively, n-adics whose scalar components consist of products of the scalar components of $\boldsymbol{D}_n^*$ with powers (up to and including the nth) of $\tau = Gt$. Making use of the explicit expressions for $\boldsymbol{\delta}_n$ (which are omitted here†) one obtains

$$\mathscr{D}^{-\frac{1}{2}} = t^{-\frac{1}{2}}\boldsymbol{\delta}^{-\frac{1}{2}}, \tag{3.31a}$$

wherein all the scalar components of $\boldsymbol{\delta}^{-\frac{1}{2}}$ are $O(1)$ for $t \rightarrow \infty$. Furthermore,

$$(\boldsymbol{\delta}^{-\frac{1}{2}})^n(\cdot)^n\boldsymbol{\delta}_n \sim O(1) \quad (n = 3, 4, \ldots), \tag{3.31b}$$

whence
$$(\mathscr{D}^{-\frac{1}{2}})^n(\cdot)^n\bar{\boldsymbol{A}}_n(\boldsymbol{q}') \sim O(t^{-n/2}) \quad (n = 1, 2, \ldots) \tag{3.31c}$$

and
$$(\mathscr{D}^{-\frac{1}{2}})^n(\cdot)^n\mathscr{D}_n \sim O(t^{-n/2+1}) \quad (n = 3, 4, \ldots). \tag{3.31d}$$

Substitute the preceding into (3.23) to obtain

$$\begin{aligned}\tilde{\underline{\bar{P}}} \sim \exp(-\bar{\boldsymbol{\omega}}\cdot\bar{\boldsymbol{\omega}})\exp\{&[\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\boldsymbol{\delta}^{-\frac{1}{2}}\cdot\boldsymbol{A}(\boldsymbol{q}') + (\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\boldsymbol{\delta}^{-\frac{1}{2}})^3(\cdot)^3\boldsymbol{\delta}_3]\,t^{-\frac{1}{2}} \\ &+ [(\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\boldsymbol{\delta}^{-\frac{1}{2}})^2(\cdot)^2\bar{\boldsymbol{A}}_2(\boldsymbol{q}') + (\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\boldsymbol{\delta}^{-\frac{1}{2}})^4(\cdot)^4\boldsymbol{\delta}_4]\,t^{-1} + O(t^{-\frac{3}{2}})\}.\end{aligned} \tag{3.32}$$

Perform a power series expansion of the second exponential term on the right, and use (3.25) and (3.26) jointly with the identity

$$\frac{1}{(2\pi)^n}\int_{\omega_\infty}(-\mathrm{i}\boldsymbol{\omega})^n\tilde{f}(\boldsymbol{\omega})\exp(-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{\omega} = \boldsymbol{\nabla}_Q^n f(\boldsymbol{Q})$$

together with the associativity of the product

$$(\mathrm{i}\bar{\boldsymbol{\omega}}\cdot\boldsymbol{\delta}^{-\frac{1}{2}})^n(\cdot)^n\boldsymbol{A}_n = (\mathrm{i}\bar{\boldsymbol{\omega}})^n(\cdot)^n[(\boldsymbol{\delta}^{-\frac{1}{2}})^n(\cdot)^n\boldsymbol{A}_n],$$

valid for every n-adic $\boldsymbol{A}_n$ (the latter being a direct result of the definition (3.19)). This leads to the asymptotic expansion

$$\begin{aligned}\bar{P} \sim \{1 - t^{-\frac{1}{2}}&[\boldsymbol{A}(\boldsymbol{q}')\cdot\boldsymbol{\delta}^{-\frac{1}{2}}\cdot\boldsymbol{\nabla}_Q + \boldsymbol{\delta}_3(\cdot)^3(\boldsymbol{\delta}^{-\frac{1}{2}})^3(\cdot)^3\boldsymbol{\nabla}_Q^3 \\ &+ t^{-1}[\boldsymbol{A}_2(\boldsymbol{q}')(\cdot)^2(\boldsymbol{\delta}^{-\frac{1}{2}})^2(\cdot)^2\boldsymbol{\nabla}_Q^2 + [\![\boldsymbol{\delta}_4 + \boldsymbol{\delta}_3\boldsymbol{A}(\boldsymbol{q}')]\!]^s(\cdot)^4(\boldsymbol{\delta}^{-\frac{1}{2}})^4(\cdot)^4\boldsymbol{\nabla}_Q^4 \\ &+ \tfrac{1}{2}[\![\boldsymbol{\delta}_3^2]\!]^s(\cdot)^6(\boldsymbol{\delta}^{-\frac{1}{2}})^6(\cdot)^6\boldsymbol{\nabla}_Q^6] + O(t^{-\frac{3}{2}})\}\,\frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\bar{\boldsymbol{Q}})}{(4\pi t)^{n/2}|\boldsymbol{\delta}|^{\frac{1}{2}}}.\end{aligned} \tag{3.33}$$

(Here, n denotes the same dimensionality as in (3.27).) Thereby, it is established for all planar shear flows corresponding to $\alpha \leqslant 0$ that the leading asymptotic behaviour of $\bar{P}$ consists of a $\boldsymbol{q}'$-independent Gaussian, the latter being characterized by the dyadic $\mathscr{D}$ (or, equivalently, by $\boldsymbol{\delta}$).

It is remarkable that the resulting expansion possesses a structure similar to that for the corresponding zero-shear case, $\boldsymbol{G} = \boldsymbol{0}$ (Frankel & Brenner 1989). Indeed, one needs only replace the various $\boldsymbol{D}_n^*$ appearing in the $\boldsymbol{G} = \boldsymbol{0}$ case by $\boldsymbol{\delta}_n$ in order to recover (3.33).

† Details may be obtained upon request directly from the authors or the Journal of Fluid Mechanics Editorial Office.

4. The 'purely global' model

Generalized Taylor dispersion theory seeks to approximate $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ in the long-time limit by a $\boldsymbol{q}$-independent field, $P^{\bullet}(\boldsymbol{Q},t)$, say, satisfying an appropriate convective–diffusive, initial- and boundary-value 'model' problem that is formulated in the global subspace exclusively.

In the light of the preceding discussion pertaining to the relation between the present shear flow case and the classical $\boldsymbol{G} = \boldsymbol{0}$ no-shear case, the proper formulation of the present model problem (whose validity will, in fact, be confirmed *a posteriori*) would appear to be as follows:

$$\frac{\partial P^{\bullet}}{\partial t} + \boldsymbol{\nabla}_Q \cdot \boldsymbol{J}^{\bullet} = 0, \tag{4.1a}$$

$$\boldsymbol{J}^{\bullet} = -\mathrm{e}^{-\boldsymbol{G}^{\dagger}t} \cdot \boldsymbol{D}^{\bullet} \cdot \mathrm{e}^{-\boldsymbol{G}t} \cdot \boldsymbol{\nabla}_Q P^{\bullet}, \tag{4.1b}$$

$$|\boldsymbol{Q}|^m (P^{\bullet}, \boldsymbol{J}^{\bullet}) \rightarrow (0, \boldsymbol{0}) \quad \text{as} \quad |\boldsymbol{Q}| \rightarrow \infty \quad (m = 0, 1, 2, \ldots) \tag{4.1c}$$

and

$$P^{\bullet} = \begin{cases} \delta(\boldsymbol{Q}) & (t = 0) \\ 0 & (t < 0). \end{cases} \tag{4.1d}$$

Relative to the classical zero-shear case, the only modification appearing in the above is that the phenomenological coefficient $\boldsymbol{D}^{\bullet}$ is here replaced by

$$\exp(-\boldsymbol{G}^{\dagger}t) \cdot \boldsymbol{D}^{\bullet} \cdot \exp(-\boldsymbol{G}t)$$

in the constitutive equation (4.1*b*) for the dispersive flux.

It is readily shown that the 'model' moments, defined as

$$\boldsymbol{M}^{\bullet}_m(t) = \int_{Q_\infty} \boldsymbol{Q}^m P^{\bullet}(\boldsymbol{Q},t)\,\mathrm{d}\boldsymbol{Q} \quad (m = 0, 1, 2, \ldots), \tag{4.2a}$$

are given exactly (i.e. for all times $t > 0$) by the expressions

$$\boldsymbol{M}^{\bullet}_{2k} = \frac{(2k)!}{k!} [\![(\mathscr{D}^{\bullet})^k]\!]^{\mathrm{s}}, \quad \boldsymbol{M}^{\bullet}_{2k+1} = \boldsymbol{0} \quad (k = 0, 1, 2, \ldots). \tag{4.2b, c}$$

Here, similarly to $\mathscr{D}(t)$, $\mathscr{D}^{\bullet}$ denotes the dyadic

$$\mathscr{D}^{\bullet} = \int_0^t \mathrm{e}^{-\boldsymbol{G}^{\dagger}t_1} \cdot \boldsymbol{D}^{\bullet} \cdot \mathrm{e}^{-\boldsymbol{G}t_1}\,\mathrm{d}t_1. \tag{4.3}$$

From the above it is straightforward to show that the model equation cumulants are given by the expressions

$$\boldsymbol{C}^{\bullet}_m = \begin{cases} 2\mathscr{D}^{\bullet} & (m = 2) \\ \boldsymbol{0} & (m = 1, 3, 4, \ldots), \end{cases}$$

whence

$$P^{\bullet} = \frac{\exp(-\tfrac{1}{4}\boldsymbol{Q} \cdot \mathscr{D}^{\bullet -1} \cdot \boldsymbol{Q})}{(4\pi)^{n/2} |\mathscr{D}^{\bullet}|^{\frac{1}{2}}}. \tag{4.4}$$

A central issue is how to select $\boldsymbol{D}^{\bullet}$ in (4.1*b*) such that $P^{\bullet}$ displays the same asymptotic behaviour (3.27) as does $\bar{P}$. An obvious choice is

$$\mathscr{D}^{\bullet} = \mathscr{D}. \tag{4.5}$$

In order that the latter equation be valid for all $t > 0$, one needs to select

$$\boldsymbol{D}^{\bullet} = \boldsymbol{D}^{*}. \tag{4.6}$$

As will become clear in the subsequent analysis, $\boldsymbol{D}^*$ is not necessarily positive definite – a fact which may, in turn, lead to the dyadic $\mathscr{D}^{\bullet}$ also failing to be positive definite (at short times). Bearing in mind that $P^{\bullet}$, given by (4.4), is required to approximate only the leading long-time asymptotic behaviour (3.29) of $\bar{P}$, it suffices to impose the requirements

$$|\mathscr{D}| \sim |\mathscr{D}^{\bullet}|\,[1+o(1)] \tag{4.7a}$$

and

$$\mathscr{D}^{\frac{1}{2}}\cdot\mathscr{D}^{\bullet-1}\cdot(\mathscr{D}^{\frac{1}{2}})^{\dagger} = \boldsymbol{I}+\boldsymbol{\epsilon}, \tag{4.7b}$$

where all components of the dyadic $\boldsymbol{\epsilon}$ are of $o(1)$. Equations (4.7) are less stringent than is (4.5) since they do not require strict equality of $\boldsymbol{D}^{\bullet}$ with $\boldsymbol{D}^*$. This, in turn, will subsequently enable the choice of a positive-definite $\boldsymbol{D}^{\bullet}$.

4.1. *The $\boldsymbol{B}(\boldsymbol{q})$-field and the coefficient $\boldsymbol{D}^*$*

The vector $\boldsymbol{B}(\boldsymbol{q})$-field is given by the asymptotic relation (A 4). It is preferable, however, to express $\boldsymbol{B}$ in an alternative form that does not require explicit knowledge of the transient portion $p(\boldsymbol{q},t\,|\,\boldsymbol{q}')$ of (3.8). Towards this end, substitute the asymptotic expression (A 2) into the problem defining $\boldsymbol{P}_1$, namely (3.6) with $m = 1$. Upon neglecting exponentially small terms and making use of the properties of P_0^{∞} (cf. (3.9)) we obtain

$$\nabla_q\cdot[\boldsymbol{u}P_0^{\infty}\boldsymbol{B}-\boldsymbol{d}\cdot\nabla_q(P_0^{\infty}\boldsymbol{B})]-P_0^{\infty}\boldsymbol{B}\cdot\boldsymbol{G} = P_0^{\infty}\,\Delta\boldsymbol{U} \tag{4.8a}$$

and

$$\hat{\boldsymbol{n}}\cdot[\boldsymbol{u}P_0^{\infty}\boldsymbol{B}-\boldsymbol{d}\cdot\nabla_q(P_0^{\infty}\boldsymbol{B})] = \boldsymbol{0} \quad \text{on} \quad \partial\boldsymbol{q}_o. \tag{4.8b}$$

These are supplemented by the normalization condition

$$\int_{q_o} P_0^{\infty}\,\boldsymbol{B}\,\mathrm{d}\boldsymbol{q} = \boldsymbol{0}, \tag{4.8c}$$

the latter resulting from (A 4) in conjunction with the normalization conditions (3.9d) and (3.10) respectively satisfied by P_0^{∞} and P. Equations (4.8) permit the $\boldsymbol{B}$-field to be uniquely determined from knowledge of $P_0^{\infty}(\boldsymbol{q})$ alone, rather than from (A 4).

Upon utilizing several vector identities in conjunction with the foregoing equations, it can be shown that

$$\int_{q_o} P_0^{\infty}[\![\boldsymbol{B}\Delta\boldsymbol{U}]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q} = \int_{q_o} P_0^{\infty}(\nabla_q\boldsymbol{B})^{\dagger}\cdot\boldsymbol{d}\cdot\nabla_q\boldsymbol{B}\,\mathrm{d}\boldsymbol{q} - \left[\!\!\left[\int_{q_o} P_0^{\infty}\,\boldsymbol{B}\boldsymbol{B}\,\mathrm{d}\boldsymbol{q}\cdot\boldsymbol{G}\right]\!\!\right]^{\mathrm{s}}$$

(cf. Brenner 1982 for the $\boldsymbol{G} = \boldsymbol{0}$ case). Substitution of the latter into (A 5) yields

$$\boldsymbol{D}^* = \bar{\boldsymbol{D}}^* - \left[\!\!\left[\int_{q_o} P_0^{\infty}\,\boldsymbol{B}\boldsymbol{B}\,\mathrm{d}\boldsymbol{q}\cdot\boldsymbol{G}\right]\!\!\right]^{\mathrm{s}}, \tag{4.9a}$$

where

$$\bar{\boldsymbol{D}}^* = \int_{q_o} P_0^{\infty}[\![\boldsymbol{D}+(\nabla_q\boldsymbol{B})^{\dagger}\cdot\boldsymbol{d}\cdot\nabla_q\boldsymbol{B}]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}. \tag{4.9b}$$

By virtue of the appearance of the last term on the right-hand side of (4.9a), $\boldsymbol{D}^*$ might fail to be positive definite. It is important to note in this context that $\boldsymbol{M}_2$ is positive definite by definition, which requires, in turn, only that $\mathscr{D}$ be positive definite in the long-time limit. (In shear flows, $\mathscr{D}$ replaces $\boldsymbol{D}^*t$; cf. (3.20c).) We now proceed to show that this requirement is indeed satisfied.

Substitution of (4.9) into (3.18) for $m = 2$, accompanied by integration by parts of the last term, leads to the expression

$$\mathscr{D} = \int_0^t \mathrm{e}^{-\boldsymbol{G}^\dagger t_1} \cdot \int_{q_o} P_0^\infty [\![\boldsymbol{D} + (\nabla_q \boldsymbol{B})^\dagger \cdot \boldsymbol{d} \cdot \nabla_q \boldsymbol{B}]\!]^s \,\mathrm{d}\boldsymbol{q} \cdot \mathrm{e}^{-\boldsymbol{G}t_1} \,\mathrm{d}t_1$$

$$+ \tfrac{1}{2} \mathrm{e}^{-\boldsymbol{G}^\dagger t} \cdot \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \mathrm{e}^{-\boldsymbol{G}t} - \frac{1}{2} \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q}. \qquad (4.10)$$

The first term on the right-hand side is clearly positive definite. In all of the cases for which condition (3.11) is satisfied, the sum of the other two terms is either non-negative or else becomes negligible relative to the first term in the long-time limit.

(i) $\nu_i = 0, \pm\omega$. In this case, when use is made of (3.12), one obtains

$$\mathscr{D} \sim [(\boldsymbol{I} - \omega^{-2} \boldsymbol{G}^\dagger \cdot \boldsymbol{G}^\dagger) \cdot \bar{\boldsymbol{D}}^* \cdot (\boldsymbol{I} - \omega^{-2} \boldsymbol{G} \cdot \boldsymbol{G}) + \tfrac{1}{2} \omega^{-2} \boldsymbol{G}^\dagger \cdot \bar{\boldsymbol{D}}^* \cdot \boldsymbol{G}$$

$$+ \tfrac{1}{2} \omega^{-4} \boldsymbol{G}^\dagger \cdot \boldsymbol{G}^\dagger \cdot \bar{\boldsymbol{D}}^* \cdot \boldsymbol{G} \cdot \boldsymbol{G}] t + O(1). \qquad (4.11)$$

As the contributions made by the last two terms of (4.10) are both bounded, i.e. of $O(1)$ for all t, $\mathscr{D}$ is evidently positive definite as $t \to \infty$ owing to the dominance of the leading term in this limit.

(ii) $\nu_i = 0$. For this case, when (3.13) is substituted, it is found that the sum of the last two terms appearing on the right-hand side of (4.10), namely

$$\tfrac{1}{8} \boldsymbol{G}^\dagger \cdot \boldsymbol{G}^\dagger \cdot \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \boldsymbol{G} \cdot \boldsymbol{G} t^4 - \frac{1}{2} \left[\!\!\left[\boldsymbol{G}^\dagger \cdot \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \boldsymbol{G} \cdot \boldsymbol{G} \right]\!\!\right]^s t^3$$

$$+ \frac{1}{2} \left\{ \left[\!\!\left[\int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \boldsymbol{G} \cdot \boldsymbol{G} \right]\!\!\right]^s + \boldsymbol{G}^\dagger \cdot \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \boldsymbol{G} \right\} t^2 - \left[\!\!\left[\int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \boldsymbol{G} \right]\!\!\right]^s t,$$

is clearly non-negative (for $t \to \infty$).

4.2. *Selection of the coefficient* $\boldsymbol{D}^{\bullet}$

Rewrite (4.10) in the form

$$\mathscr{D} = \bar{\mathscr{D}} + \tfrac{1}{2} \mathrm{e}^{-\boldsymbol{G}^\dagger t} \cdot \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q} \cdot \mathrm{e}^{-\boldsymbol{G}t} - \frac{1}{2} \int_{q_o} P_0^\infty \boldsymbol{BB} \,\mathrm{d}\boldsymbol{q},$$

wherein

$$\bar{\mathscr{D}} = \int_0^t \mathrm{e}^{-\boldsymbol{G}^\dagger t_1} \cdot \bar{\boldsymbol{D}}^* \cdot \mathrm{e}^{-\boldsymbol{G}t_1} \,\mathrm{d}t_1 \qquad (4.12)$$

depends only upon the positive-definite portion $\bar{\boldsymbol{D}}^*$ of $\boldsymbol{D}^*$. The foregoing discussion suggests that $\bar{\mathscr{D}}$ constitutes the asymptotically dominant portijon of $\mathscr{D}$ as $t \to \infty$, whence the pair of requirements (4.7) may be satisfied by selecting

$$\mathscr{D}^{\bullet} = \bar{\mathscr{D}}. \qquad (4.13)$$

A straightforward, albeit tedious calculation (whose details are omitted here) verifies this fact for the two-dimensional shear flows discussed in §3. One may thus select the phenomenological coefficient $\boldsymbol{D}^{\bullet}$ appearing in the model equation (4.1*b*) as

$$\boldsymbol{D}^{\bullet} = \bar{\boldsymbol{D}}^*, \qquad (4.14)$$

with $\bar{\boldsymbol{D}}^*$ given by (4.9*b*). In contrast with the choice (4.6), the choice (4.14) not only assures the long-time matching of $\bar{P}$ with $P^{\bullet}$, but also guarantees that the solution of the model problem (4.1) is well behaved at all times owing, *inter alia*, to the model phenomenological coefficient $\boldsymbol{D}^{\bullet}$ now being positive definite.

5. Lagrangian view in the original domain

Further insight into the physical significance of the foregoing results is obtained by considering the total statistical moments in the original domain (cf. (3.4)–(3.5)),

$$\boldsymbol{M}_m(t \mid \boldsymbol{Q}', \boldsymbol{q}') = \int_{q_0} \boldsymbol{P}_m \, \mathrm{d}\boldsymbol{q} \quad (m = 0, 1, 2, \ldots), \tag{5.1a}$$

$$\boldsymbol{P}_m(\boldsymbol{q}, t \mid \boldsymbol{Q}', \boldsymbol{q}') = \int_{Q_\infty} (\boldsymbol{Q} - \boldsymbol{Q}')^m P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{Q}', \boldsymbol{q}') \, \mathrm{d}\boldsymbol{Q} \quad (m = 0, 1, 2, \ldots), \tag{5.1b}$$

as well as their asymptotic behaviour for $t \to \infty$. The latter is recovered from the corresponding behaviour of the moments $\boldsymbol{M}_m^{(1)}$ and $\boldsymbol{P}_m^{(1)}$ in the transformed domain by making use of (2.8) to express $\boldsymbol{Q} - \boldsymbol{Q}'$ in terms of $\boldsymbol{Q}^{(1)}$. For future reference we list here the lowest-order pertinent identities thereby obtained:

$$P_0(\boldsymbol{q}, t \mid \boldsymbol{Q}', \boldsymbol{q}') = P_0^{(1)}(\boldsymbol{q}, t \mid \boldsymbol{q}'), \tag{5.2a}$$

$$\boldsymbol{P}_1(\boldsymbol{q}, t \mid \boldsymbol{Q}', \boldsymbol{q}') = \boldsymbol{P}_1^{(1)}(\boldsymbol{q}, t \mid \boldsymbol{q}') \cdot \mathrm{e}^{\boldsymbol{G}t} + P_0^{(1)}(\boldsymbol{q}, t \mid \boldsymbol{q}') [\boldsymbol{V}(\boldsymbol{Q}') + \bar{\boldsymbol{U}}] \cdot \int_0^t \mathrm{e}^{\boldsymbol{G}t_1} \, \mathrm{d}t_1, \tag{5.2b}$$

$$\boldsymbol{M}_1(t \mid \boldsymbol{Q}', \boldsymbol{q}') = \boldsymbol{M}_1^{(1)}(t \mid \boldsymbol{q}') \cdot \mathrm{e}^{\boldsymbol{G}t} + [\boldsymbol{V}(\boldsymbol{Q}') + \bar{\boldsymbol{U}}] \cdot \int_0^t \mathrm{e}^{\boldsymbol{G}t_1} \, \mathrm{d}t_1, \tag{5.2c}$$

$$\boldsymbol{M}_2 - \boldsymbol{M}_1 \boldsymbol{M}_1 = \mathrm{e}^{\boldsymbol{G}^\dagger t} \cdot (\boldsymbol{M}_2^{(1)} - \boldsymbol{M}_1^{(1)} \boldsymbol{M}_1^{(1)}) \cdot \mathrm{e}^{\boldsymbol{G}t}, \tag{5.2d}$$

the latter being the second central moment.†

5.1. *The vector $\bar{\boldsymbol{U}}$*

Form the time derivative of (5.2*c*) to obtain

$$\frac{\delta \boldsymbol{M}_1}{\delta t} \cdot \mathrm{e}^{-\boldsymbol{G}t} = \frac{\mathrm{d}\boldsymbol{M}_1^{(1)}}{\mathrm{d}t} + [\boldsymbol{V}(\boldsymbol{Q}') + \bar{\boldsymbol{U}}] \cdot \mathrm{e}^{-\boldsymbol{G}t},$$

wherein

$$\frac{\delta \boldsymbol{M}_1}{\delta t} = \frac{\mathrm{d}\boldsymbol{M}_1}{\mathrm{d}t} - \boldsymbol{M}_1 \cdot \boldsymbol{G}$$

is the Oldroyd derivative (Bird *et al.* 1987) of $\boldsymbol{M}_1$ in $\boldsymbol{Q}_\infty$ space (cf. the remarks following (2.8)). Upon utilizing the asymptotic expression (A 12) for $\boldsymbol{M}_1^{(1)}$ in conjunction with the condition (3.11), one obtains

$$\frac{\delta \boldsymbol{M}_1}{\delta t} \sim \boldsymbol{V}(\boldsymbol{Q}') + \bar{\boldsymbol{U}} \quad \text{as} \quad t \to \infty; \tag{5.3}$$

equivalently, upon rearrangement,

$$\bar{\boldsymbol{U}} \sim \frac{\mathrm{d}\boldsymbol{M}_1}{\mathrm{d}t} - [\boldsymbol{V}(\boldsymbol{Q}') + \boldsymbol{M}_1 \cdot \boldsymbol{G}].$$

The first term appearing on the right-hand side of the latter equation is the absolute average velocity of the tracer in the global subspace; the sum in square brackets represents the fluid velocity at the average global position ($\overline{\boldsymbol{Q} - \boldsymbol{Q}'} = \boldsymbol{M}_1$).

† Unlike the average global position vector given by (5.2*c*), the spread $\boldsymbol{M}_2 - \boldsymbol{M}_1 \boldsymbol{M}_1$ about this position is independent of $\boldsymbol{Q}'$ since this spread is affected only by the gradient of the fluid velocity, but not by the absolute velocity vector itself.

Thus, $\bar{U}$ is the local-space-averaged 'slip velocity' of the tracer relative to the fluid. In the present problem this constitutes the only meaningful average velocity possessing (observer-independent) invariant physical significance.

5.2. *The $B(q)$-field*

The quantity defined as

$$P_q(Q,t\,|\,q,Q',q') = \frac{P(Q,q,t\,|\,Q',q')}{P_0(q,t\,|\,Q',q')} \tag{5.4}$$

represents the conditional probability density of finding the tracer at the global-space position Q at time t given that its local-space position at the same time is q (cf. Reichl 1980). The moment

$$P_{1_q}(t\,|\,q,Q',q') \overset{\text{def.}}{=} \int_{Q_\infty} QP_q(Q,t\,|\,q,Q',q')\,\mathrm{d}Q \equiv \frac{P_1(q,t\,|\,Q',q')}{P_0(q,t\,|\,Q',q')} \tag{5.5}$$

thus represents the average global location of the particle given that its local position is q. As $t \to \infty$, one thereby obtains (upon making use of the asymptotic expansions of $P_1^{(1)}$ and $M_1^{(1)}$, namely (A 2) and (A 12) for $k = 0$, respectively, in conjunction with (5.2a) and (5.2b))

$$P_{1_q} - M_1 \sim B(q) + \exp; \tag{5.6}$$

that is, the deviation of P_{1_q} from the 'total' global average position M_1 becomes independent of both q' and t in the long-time limit. If instead of a single Brownian tracer we consider a 'cloud' of solute particles and divide it into subpopulations of the particles according to their respective instantaneous local-space positions, (5.6) may then be interpreted as meaning that the global-space position vector of the centroid of such a subset of particles relative to the centroid of the whole cloud becomes stationary, in which state it is functionally dependent only upon q.

5.3. *Comparison between D^* and $\bar{D}^*$*

Upon forming the time derivative of the expression (5.2d) one obtains

$$\mathrm{e}^{-G^\dagger t}\cdot\frac{\delta}{\delta t}(M_2 - M_1 M_1)\cdot \mathrm{e}^{-Gt} = \frac{\mathrm{d}}{\mathrm{d}t}(M_2^{(1)} - M_1^{(1)} M_1^{(1)}),$$

in which
$$\frac{\delta}{\delta t}(M_2 - M_1 M_1) = \frac{\mathrm{d}}{\mathrm{d}t}(M_2 - M_1 M_1) - 2[\![(M_2 - M_1 M_1)\cdot G]\!]^{\mathrm{s}} \tag{5.7}$$

is the Oldroyd derivative (cf. Bird *et al.* 1987) of the dyadic $M_2 - M_1 M_1$. (The last term on the right-hand side of (5.7) represents the contribution to the time rate of change arising from passive convection of the tracer by the shear field; the Oldroyd derivative eliminates this contribution from the total rate of change.)

From (A 11), (A 12) and (3.11) it follows that as $t \to \infty$

$$\frac{1}{2}\frac{\delta}{\delta t}(M_2 - M_1 M_1) \sim D^* + \exp. \tag{5.8}$$

Thus, $2D^*$ is the asymptotic temporal rate of change of $M_2 - M_1 M_1$ (in the 'Oldroyd' sense). It is remarkable that while the asymptotic time-dependence of the central moment is nonlinear, the latter result shows that by employing a codeformational frame of reference an Einstein-like relation is obtained between $\boldsymbol{D}^*$ and the asymptotic rate of spread. This interpretation of (5.8) constitutes the generalization of the comparable asymptotic relation (Frankel & Brenner 1989)

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1) \sim \boldsymbol{D}^*+\exp, \tag{5.9}$$

which holds as $t\rightarrow\infty$ in the absence of shear. (Similarly, (5.3) is the present generalization of the long-time, zero-shear relation (Brenner 1980) $(\mathrm{d}\boldsymbol{M}_1/\mathrm{d}t) \sim \boldsymbol{U}^*+\exp$.)

Focusing again on the population of solute particles characterized by the local-space coordinate $\boldsymbol{q}$, we define the dyadic

$$\begin{aligned}\boldsymbol{P}_{2_q}-\boldsymbol{P}_{1_q}\boldsymbol{P}_{1_q} &= \int_{Q_\infty}(\boldsymbol{Q}-\boldsymbol{P}_{1_q})^2 P_q(\boldsymbol{Q},t\,|\,\boldsymbol{q},\boldsymbol{Q}',\boldsymbol{q}')\,\mathrm{d}\boldsymbol{Q}\\ &\equiv \frac{\boldsymbol{P}_2}{P_0}-\frac{\boldsymbol{P}_1\boldsymbol{P}_1}{P_0^2},\end{aligned} \tag{5.10}$$

which describes the spread about the mean global-space position of the $\boldsymbol{q}$-specific population. Summation of these over q_o (i.e. over all such populations, $\boldsymbol{q}\in q_o$) yields

$$(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)_{\Sigma q} \overset{\text{def.}}{=} \int_{q_o} P_0(\boldsymbol{P}_{2_q}-\boldsymbol{P}_{1_q}\boldsymbol{P}_{1_q})\,\mathrm{d}\boldsymbol{q} \equiv \boldsymbol{M}_2-\int_{q_o}\frac{\boldsymbol{P}_1\boldsymbol{P}_1}{P_0}\,\mathrm{d}\boldsymbol{q}.$$

Use of (A 2) for $k=0$, together with (5.2*a*) and (5.2*b*) in the last term of the above, shows that for $t\rightarrow\infty$,

$$(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)-(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)_{\Sigma q} \sim \int_{q_o} P_0^\infty \boldsymbol{B}\boldsymbol{B}\,\mathrm{d}\boldsymbol{q}+\exp. \tag{5.11}$$

Thus, the two different measures of the spread, represented by the left-hand terms of (5.11), differ in the long-time limit by the constant, $\boldsymbol{q}'$-independent, positive-definite dyadic appearing on the right-hand side of (5.11). Alternatively, use of (5.6) in (5.11) shows that

$$\int_{q_o} P_0^\infty \boldsymbol{B}\boldsymbol{B}\,\mathrm{d}\boldsymbol{q} \sim \int_{q_o} P_0^\infty(\boldsymbol{P}_{1_q}-\boldsymbol{M}_1)^2\,\mathrm{d}\boldsymbol{q}+\exp,$$

involving the spread between the centroids of the various $\boldsymbol{q}$-specific populations about the centroid of the 'cloud' as a whole.

Form the Oldroyd time derivative of (5.11) while making use of (4.9) and (5.8) to obtain

$$\frac{1}{2}\frac{\delta}{\delta t}(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)_{\Sigma q} \sim \bar{\boldsymbol{D}}^*+\exp,$$

which should be compared with (5.8).

In the absence of shear (Frankel & Brenner 1989) the constant dyadic represented by the right-hand side of (5.11), by which the two measures of spread differ, does not affect the asymptotic time rates of change; hence, $\boldsymbol{D}^*=\bar{\boldsymbol{D}}^*$ for $\boldsymbol{G}=\boldsymbol{0}$.

The foregoing discussion indicates that while the dyadic $\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1$ is, by definition, a positive-definite quantity, it may not grow monotonically with time. A similar phenomenon occurs during oscillatory unidirectional flow (cf. Smith 1985, his

(5.1) *et seq.*], where the fact that $\boldsymbol{D}^*$ is not positive definite indicates that the cloud of solute particles may, during certain time intervals, actually undergo longitudinal *contraction* rather than expansion (i.e. 'spread'). In the present context, contraction of the cloud in certain directions during particular time intervals may result from the coupling between the non-uniform, global-space fluid velocity exhibited by the shear field and the Taylor dispersion mechanism. Following Yasuda (1982), Smith (1985; cf. his (5.2) and (5.3)) also suggests that the difficulties attending a dispersion coefficient (corresponding to our $\boldsymbol{D}^*$) capable of adopting negative values may be overcome by use of an alternative dispersivity definition, yielding a positive-definite coefficient comparable with our $\bar{\boldsymbol{D}}^*$.

In conclusion we now give a heuristic description of the physical mechanisms of spread respectively embodied in $\boldsymbol{D}^*$ and $\bar{\boldsymbol{D}}^*$. This provides a qualitative explanation as to why the latter is necessarily positive definite whereas the former may not be.

The spread of an aggregate of particles about its mean global position is

$$\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1=\sum_i \bar{\boldsymbol{Q}}_i\bar{\boldsymbol{Q}}_i,$$

where $\bar{\boldsymbol{Q}}_i$ is measured from the centre of mass of the aggregate to the ith particle, the summation extending over all particles comprising the cloud. We omit the contribution to this spread arising from the global-space molecular diffusivity $\boldsymbol{D}(\boldsymbol{q})$ and make use of the shear fluid velocity (cf. (2.2)) to express $\mathrm{d}\bar{\boldsymbol{Q}}_i/\mathrm{d}t$. In addition we use (5.6), (5.7) and (A 5) to obtain

$$\frac{1}{2}\frac{\delta}{\delta t}(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)=[\![\sum_i \bar{\boldsymbol{Q}}_i\,\boldsymbol{U}_i]\!]^{\mathrm{s}}=\int_{q_o} P_0^{\infty}[\![\boldsymbol{B}\Delta\boldsymbol{U}]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q},$$

with $\boldsymbol{U}_i$ the 'slip velocity' $\boldsymbol{U}(\boldsymbol{q})$ of the ith particle. Evidently, this rate of change depends upon the instantaneous configuration of the cloud within the global subspace, which configuration is determined *inter alia* by the convection arising from the non-uniform velocity field generated by the shear. Thus, application of $\delta/\delta t$ does not completely eliminate deterministic contributions from the above rate of spread.

A comparable interpretation is now suggested for

$$\int_{q_o} P_0^{\infty}(\boldsymbol{\nabla}_q\boldsymbol{B})^{\dagger}\cdot\boldsymbol{d}\cdot\boldsymbol{\nabla}_q\boldsymbol{B}\,\mathrm{d}\boldsymbol{q}$$

via an examination of the rate of change of $\boldsymbol{P}_{2_q}-\boldsymbol{P}_{1_q}\boldsymbol{P}_{1_q}$. Since all of the particles belonging to a specified subset $\boldsymbol{q}$ possess the same slip velocity $\boldsymbol{U}(\boldsymbol{q})$, no change comparable to that exhibited by the previous case occurs here. Omitting again the contribution of the global-space molecular diffusivity $\boldsymbol{D}$, the only source of variation in the spread stems from the fact that the population characterized by $\boldsymbol{q}$ does not consist at all times of the same individual particles. Owing to the action of the local-space molecular diffusion process (quantified by $\boldsymbol{d}$), particles continuously change their respective local-space positions. In the long-time limit there exists a local-space equilibrium distribution, with the particles excluded from the subset $\boldsymbol{q}$, being replaced by an equal number of particles from other subsets. The latter particles occupy different global-space positions than those excluded. Owing to the purely stochastic nature of the present process, this phenomenon may be expected to result in a monotonic growth of the total spread, $(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)_{\Sigma q}$.

An essential element underlying the latter mechanism is the existence of a non-zero local-space molecular diffusivity, $\boldsymbol{d}\neq\boldsymbol{0}$. If, on the other hand, $\boldsymbol{d}=\boldsymbol{0}$, the replacement process described above becomes simply the exchange of whole populations belonging to the various subsets $\boldsymbol{q}$. This, in turn, results in the exchange of corresponding values of $\boldsymbol{P}_{2_q}-\boldsymbol{P}_{1_q}\boldsymbol{P}_{1_q}$, without any net change in $(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1)_{\Sigma q}$.

6. The case of zero solute velocity disparity

As a limiting case, we consider in this section the particular situation for which

$$\Delta \boldsymbol{U}(\boldsymbol{q}) = \boldsymbol{0}, \tag{6.1}$$

such as occurs for rigid, neutrally buoyant, centrally symmetric particles, where the slip velocity vanishes ($\boldsymbol{U}=\boldsymbol{0}$), or for rigid spherical particles under a constant external force, where the slip velocity is constant ($\boldsymbol{U}=\bar{\boldsymbol{U}}$). Here, no Taylor dispersion mechanism exists, whence the spread of the tracer within the global subspace results only from microscale diffusion and the interaction of the latter with the shear velocity field. Upon substituting (6.1) into (3.7) we find that the odd moments vanish, i.e. $\boldsymbol{P}_{2k+1}=\boldsymbol{0}$ for all times. Furthermore, from their respective definitions, it readily follows that $P_0^\infty \boldsymbol{B}_{2k+1}(\boldsymbol{q})$, $\boldsymbol{A}_{2k+1}(\boldsymbol{q}')$ and $\boldsymbol{D}^*_{2k+1}$ also vanish identically. The requisite asymptotic expressions are obtainable from the foregoing results by simply deleting those terms which include these three quantities. In particular, we now have that

$$\boldsymbol{D}^* = \bar{\boldsymbol{D}}^* = \boldsymbol{D}^{\boldsymbol{\cdot}} = \int_{q_o} P_0^\infty(\boldsymbol{q})\,\boldsymbol{D}(\boldsymbol{q})\,\mathrm{d}\boldsymbol{q}. \tag{6.2}$$

From (3.33) the asymptotic expansion obtained for $\bar{P}$ is

$$\bar{P} \sim \{1+t^{-1}[\boldsymbol{A}_2(\boldsymbol{q}')(\cdot)^2(\boldsymbol{\delta}^{-\frac{1}{2}})^2(\cdot)^2\boldsymbol{\nabla}^2_{\bar{Q}}+\boldsymbol{\delta}_4(\cdot)^4(\boldsymbol{\delta}^{-\frac{1}{2}})^4(\cdot)^4\boldsymbol{\nabla}^4_{\bar{Q}}]+O(t^{-2})\}\frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\bar{\boldsymbol{Q}})}{(4\pi t)^{n/2}|\boldsymbol{\delta}|^{\frac{1}{2}}}.$$

The expansion of $\bar{P}$ now consists only of descending integral powers of t because the fractional powers appearing in the original expansion (3.33) were all associated exclusively with the odd moments. In particular, the correction to the leading-order Gaussian behaviour is now of $O(t^{-1})$ rather than $O(t^{-\frac{1}{2}})$.

6.1. *The case* $\boldsymbol{D}$ = *constant*

If, in addition to the vanishing of $\Delta\boldsymbol{U}$, $\boldsymbol{D}$ is independent of $\boldsymbol{q}$ (such as occurs for rigid spherical particles), one can directly integrate (2.9*a*) over $\boldsymbol{q}_o$ while making use of the boundary condition (2.9*e*), to obtain a system of equations which are identical to the model equations (4.1*a*) and (4.1*b*) when the selection $\boldsymbol{D}^{\boldsymbol{\cdot}}=\boldsymbol{D}$ is made. Furthermore, the solution of $\bar{P}$ is given by (4.4), which is now exactly valid for all $t>0$, rather than only in the long-time limit. It is also important to note that the latter result is valid for all $\boldsymbol{G}$, since no restrictions upon the eigenvalues ν_i were imposed in its derivation. Similarly, the Einstein-like asymptotic result (5.8) is now superseded by the *exact* relation

$$\frac{1}{2}\frac{\delta}{\delta t}(\boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1) = \boldsymbol{D}. \tag{6.3}$$

Upon making use of the transformation (2.8), $\bar{P}$ can be explicitly expressed in the original domain to furnish an invariant (and generalized) form of the solutions of Foister & van de Ven (1980) for the stochastic motion of a spherical Brownian particle or point-size tracer in a steady shear field. Substitution of their expressions for the central moment (which are nonlinear in t) readily verifies (6.3), which is another manifestation of the codeformational view.

It should be emphasized that it is only for spheres that the translational molecular diffusivity $\boldsymbol{D}$ is independent of the orientation $\boldsymbol{q}$ (say, the three Eulerian angles) of the body. The foregoing discussion demonstrates that non-spherical bodies diffusing in shear fields (Brenner & Condiff 1974) display a much more complex behaviour than do spheres, even in the zero-slip-velocity case (6.1).

7. An illustration: dispersion of a size-fluctuating porous sphere

As a simple illustration of the preceding general theory, we address the dispersion accompanying the sedimentation in a homogeneous shear field of a porous Brownian sphere undergoing thermal fluctuations in its radius (as well as in its position in physical space). Such a body serves as a simple model for a polymer macromolecule (Brinkman 1947; Debye & Bueche 1948; Wiegel 1980). 'Motion' of this sphere occurs in a four-dimensional phase space consisting of the position vector $\boldsymbol{R} = (x, y, z)$ of the sphere centre in physical space together with its instantaneous radius r_o, which varies with time owing to its Brownian fluctuations in the size-space $r_{o_1} < r_o < r_{o_2}$.

An exact microscale description of this motion is provided by the conditional probability density

$$P \equiv P(\boldsymbol{R}, r_o, t \mid \boldsymbol{R}', r'_o). \tag{7.1}$$

Thus, $4\pi P\, \mathrm{d}^3\boldsymbol{R} r_o^2\, \mathrm{d}r_o$ is the conditional probability of finding the sphere centre at time $t > 0$ within a small volume element $\mathrm{d}^3\boldsymbol{R}$ centred about the point $\boldsymbol{R}$ while simultaneously the sphere possesses a radius lying within the range between r_o and $r_o + \mathrm{d}r_o$, given that at $t = 0$ the sphere was introduced at the point $\boldsymbol{R}'$ and possessed a radius r'_o. P satisfies the continuity equation

$$\frac{\partial P}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{J} + \frac{1}{r_o^2} \frac{\partial}{\partial r_o} (r_o^2 j) = 0, \tag{7.2}$$

together with the following convective–diffusive constitutive equations for the respective flux densities:

$$\boldsymbol{J} = [M(r_o)\boldsymbol{F} + \boldsymbol{V}(\boldsymbol{R}') + (\boldsymbol{R} - \boldsymbol{R}') \cdot \boldsymbol{G}]P - D(r_o)\boldsymbol{\nabla} P \tag{7.3}$$

in physical space, with $\boldsymbol{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ the usual gradient operator, and

$$j = m(r_o) f P - d(r_o) \frac{\partial P}{\partial r_o} \tag{7.4}$$

the size-space flux density.

In the foregoing, $M(r_o)$ is the (scalar) translational mobility, which for a uniform porous sphere of radius r_o moving through a fluid of viscosity μ was first given by Debye & Bueche (1948) as

$$M(r_o) = \frac{1}{6\pi\mu r_o} \frac{1 + \frac{3}{2}K(1 - K^{\frac{1}{2}} \tanh K^{-\frac{1}{2}})}{1 - K^{\frac{1}{2}} \tanh K^{-\frac{1}{2}}}, \tag{7.5}$$

where $K = k/r_o^2$ is the dimensionless permeability of the porous material, with k the (dimensional) Darcy permeability coefficient. For the case of small solids concentration (appropriate to a polymer molecule), the dimensional permeability is (approximately) inversely proportional to ϕ, the volume fraction of solids within the porous sphere (Felderhof & Deutch 1975). In this case, K scales with r_o, being thus conveniently written as

$$K = \bar{K}\frac{r_o}{\bar{r}_o}, \tag{7.6}$$

where $\bar{K}$ = const. is the dimensionless permability, K, at a reference radius $r_o = \bar{r}_o$; $m(r_o)$ is the size-space mobility, whose inverse is the (hydrodynamic) resistance of the sphere to changes in its size. Frankel, Mancini & Brenner (1991) obtained the expression

$$m(r_o) = \frac{K}{\pi\mu r_o}[1-\phi(r_o)]. \tag{7.7a}$$

In the dilute case, where K is given by (7.6), one obtains

$$m(r_o) = \frac{\bar{K}}{\pi\mu\bar{r}_o}\left[1-\bar{\phi}\left(\frac{\bar{r}_o}{r_o}\right)^3\right], \tag{7.7b}$$

where $\phi = \bar{\phi}$ is the solids volume fraction for $r_o = \bar{r}_o$. The physical- and size-space diffusivities may be obtained from the respective pair of Stokes–Einstein relations

$$D(r_o) = kTM(r_o), \quad d(r_o) = kTm(r_o). \tag{7.8a, b}$$

$\boldsymbol{F}$ is the (constant) external force (e.g. gravitational or electrophoretic). The size-space force is assumed to be derivable from a non-dimensional potential $E(r_o)$:

$$f = -kT\frac{\mathrm{d}}{\mathrm{d}r_o}E(r_o). \tag{7.9}$$

The above are supplemented by respective physical- and size-space boundary conditions, namely

$$|\boldsymbol{R}-\boldsymbol{R}'|^m(P,\boldsymbol{J},j) \to (0,\boldsymbol{0},0) \quad \text{for} \quad |\boldsymbol{R}-\boldsymbol{R}'| \to \infty \quad (m = 0,1,2,\ldots) \tag{7.10}$$

and

$$j = 0 \quad \text{for} \quad r_o = r_{o_1}, r_{o_2}, \tag{7.11}$$

as well as by the initial condition

$$P = \begin{cases} (4\pi r_o^2)^{-1}\delta(\boldsymbol{R}-\boldsymbol{R}')\,\delta(r_o - r_o') & \text{for } t = 0 \\ 0 & \text{for } t < 0. \end{cases} \tag{7.12}$$

Equation (7.11) signifies that the sphere is confined to size fluctuations within the interval (r_{o_1}, r_{o_2}).

Equations (7.2)–(7.12) serve to uniquely determine $P \geqslant 0$, and a more detailed account of the foregoing formulation is to be found in Frankel *et al.* (1991). It is readily verified that this P satisfies the normalization condition

$$4\pi\int_{R_\infty}\int_{r_{o_1}}^{r_{o_2}} P(\boldsymbol{R}, r_o, t\,|\,\boldsymbol{R}', r_o')\, r_o^2\,\mathrm{d}r_o\,\mathrm{d}^3\boldsymbol{R} = 1 \tag{7.13}$$

for all times $t \geqslant 0$. In most cases one is interested not in the exact *microscale* density P, but rather in the coarser-scale description of the motion in physical space embodied in the *macroscale* density

$$\bar{P}(\boldsymbol{R}, t\,|\,\boldsymbol{R}', r_o') = 4\pi\int_{r_{o_1}}^{r_{o_2}} r_o^2 P(\boldsymbol{R}, r_o, t\,|\,\boldsymbol{R}', r_o')\,\mathrm{d}r_o, \tag{7.14}$$

representing the average of P over size space (which is not to be confounded with the ubiquitous pre-average (Brinkman 1947; Debye & Bueche 1948; Wiegel 1980; cf. also Nadim & Brenner 1989), where the fluctuating porous sphere is replaced by a rigid one of constant radius $\bar{r}_o$).

When one recognizes the 'equivalence relations'

$$\left.\begin{array}{l} \boldsymbol{Q} \to \boldsymbol{R}, \quad \boldsymbol{q} \to \hat{\boldsymbol{e}}_r r_o, \\ \boldsymbol{j} \to \hat{\boldsymbol{e}}_r j, \quad \boldsymbol{u} \to \hat{\boldsymbol{e}}_r u(r_o), \quad \boldsymbol{d} \to \hat{\boldsymbol{e}}_r \hat{\boldsymbol{e}}_r d(r_o), \\ \boldsymbol{U}(\boldsymbol{q}) \to M(r_o)\boldsymbol{F}, \quad \boldsymbol{D}(\boldsymbol{q}) \to D(r_o)\boldsymbol{I}, \quad \text{etc.}, \end{array}\right\} \tag{7.15}$$

(with $\hat{\boldsymbol{e}}_r$ a unit radial vector normal to the porous sphere surface), it is readily seen that the present physically posed problem, namely (7.2)–(7.4) and (7.10)–(7.12), possesses the same mathematical structure as the generic problem, (2.1)–(2.6). Here too we apply the transformation (2.7) and (2.8). In what follows, use will be made of the non-dimensional variables and parameters r, $\tilde{M}$ and $\tilde{m}$, defined respectively as

$$r = \frac{r_o}{\bar{r}_o}, \quad M(r_o) = \frac{\tilde{M}(r)}{\mu \bar{r}_o}, \quad m(r_o) = \frac{\tilde{m}(r)}{\mu \bar{r}_o}. \tag{7.16a, b, c}$$

The problem posed for $P_0^\infty(r_o)$, the long-time limit of the conditional probability density for finding the sphere to be of radius r_o (irrespective of its physical-space location), consists of (cf. (3.9) and (7.15)) the differential equation

$$\frac{1}{r_o^2}\frac{\mathrm{d}}{\mathrm{d}r_o}\left[kTm(r_o)\, r_o^2\, \mathrm{e}^{-E(r_o)}\frac{\mathrm{d}}{\mathrm{d}r_o}(P_0^\infty\, \mathrm{e}^{E(r_o)})\right] = 0, \tag{7.17a}$$

the no-flux boundary conditions†

$$kTm(r_o)\, \mathrm{e}^{-E(r_o)}\frac{\mathrm{d}}{\mathrm{d}r_o}(P_0^\infty\, \mathrm{e}^{E(r_o)}) = 0 \quad \text{for} \quad r_o = r_{o_1}, r_{o_2} \tag{7.17b}$$

and the normalization condition

$$4\pi \int_{r_{o_1}}^{r_{o_2}} r_o^2 P_0^\infty\, \mathrm{d}r_o = 1. \tag{7.17c}$$

While the generic problem (3.9) posed for P_0^∞ may be implicitly dependent upon $\boldsymbol{G}$ (through $\boldsymbol{u}(\boldsymbol{q})$, cf. (1.3)), (7.4) and (7.9) show in the present case that P_0^∞ is wholly unaffected by the existence of shear (cf. Frankel *et al.* 1991). One thus readily obtains

$$P_0^\infty = \frac{1}{4\pi \bar{r}_o^3\, W}\mathrm{e}^{-E(r)}, \tag{7.18a}$$

wherein

$$W = \int_{r_1}^{r_2} r^2\, \mathrm{e}^{-E(r)}\, \mathrm{d}r \tag{7.18b}$$

and

$$r_i = \frac{r_{o_i}}{\bar{r}_o} \quad (i = 1, 2). \tag{7.18c}$$

† In fact, it suffices to satisfy (7.17b) at *either* r_{o_1} or r_{o_2}, which automatically assures that the size-space flux $j_o^\infty = 0$ for *all* r_o in the range $r_{o_1} < r_o < r_{o_2}$.

From the latter result in conjunction with (3.15) and (7.15) one readily obtains

$$\bar{U} = \frac{F}{\mu \bar{r}_o}\tilde{\bar{M}}\hat{F}, \quad \tilde{\bar{M}} = \frac{1}{W}\int_{r_1}^{r_2} r^2 \tilde{M}(r)\,\mathrm{e}^{-E(r)}\,\mathrm{d}r, \tag{7.19a, b}$$

with $\hat{F} = F/F$ ($F = |F|$) a unit vector parallel to F. Owing to the spherical shape of the particle, it is not surprising that the average 'slip velocity' is parallel to the external force. Use the above in conjunction with the equivalence relations (7.15), and define the non-dimensional vector field $b(r)$ via the expression

$$P_0^\infty B = \frac{F}{kT\bar{r}_o} b(r), \tag{7.20}$$

to obtain from (4.8) the following boundary-value problem for the b-field:

$$-\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\tilde{m}(r)\,\mathrm{e}^{-E(r)}\frac{\mathrm{d}}{\mathrm{d}r}[b\,\mathrm{e}^{E(r)}]\right\} - \frac{\mu\bar{r}_o^3 G}{kT} b\cdot\hat{G} = \frac{\mathrm{e}^{-E(r)}}{4\pi W}[\tilde{M}(r) - \tilde{\bar{M}}]\hat{F}, \tag{7.21a}$$

$$\tilde{m}(r)\,\mathrm{e}^{-E(r)}\frac{\mathrm{d}}{\mathrm{d}r}[b\,\mathrm{e}^{E(r)}] = 0 \quad \text{at} \quad r = r_1, r_2 \tag{7.21b}$$

(it can readily be verified that one of these two conditions is redundant), and

$$\int_{r_1}^{r_2} r^2 b\,\mathrm{d}r = 0. \tag{7.21c}$$

We represent the solution of the above by making the Ansatz

$$b(r) = b_1(r)\hat{F} + b_2(r)\hat{F}\cdot\hat{G} + b_3(r)\hat{F}\cdot\hat{G}\cdot\hat{G}, \tag{7.22}$$

while employing the Cayley–Hamilton formula, which for planar shear flows (cf. (3.28)) as well as for shear fields satisfying (3.11) adopts the form

$$\hat{G}\cdot\hat{G}\cdot\hat{G} = \alpha\hat{G}. \tag{7.23}$$

Thereby, we obtain the following differential equations for the scalar $b_i(r)$-fields ($i = 1,2,3$):

$$-\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\tilde{m}\,\mathrm{e}^{-E}\frac{\mathrm{d}}{\mathrm{d}r}(b_1\mathrm{e}^E)\right\} = \frac{1}{4\pi W}[\tilde{M} - \tilde{\bar{M}}]\,\mathrm{e}^{-E}, \tag{7.24a}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\tilde{m}\,\mathrm{e}^{-E}\frac{\mathrm{d}}{\mathrm{d}r}(b_2\mathrm{e}^E)\right\} + \frac{\mu G\bar{r}_o^3}{kT} b_3\alpha = \frac{\mu G\bar{r}_o^3}{kT} b_1, \tag{7.24b}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\tilde{m}\,\mathrm{e}^{-E}\frac{\mathrm{d}}{\mathrm{d}r}(b_3\mathrm{e}^E)\right\} + \frac{\mu G\bar{r}_o^3}{kT} b_2 = 0, \tag{7.24c}$$

together with the boundary conditions

$$\tilde{m}(r)\,\mathrm{e}^{-E(r)}\frac{\mathrm{d}}{\mathrm{d}r}[b_1\mathrm{e}^{E(r)}] = 0 \quad \text{for} \quad r = r_1(r_2) \tag{7.25}$$

and normalization

$$\int_{r_1}^{r_2} r^2 b_i\,\mathrm{d}r = 0 \tag{7.26}$$

for each $i = 1, 2, 3$ in (7.25) and (7.26).

The problem posed for b_1 may be uncoupled from the b_2 and b_3 problems, and is readily solved to obtain

$$b_1 = \frac{e^{-E(r)}}{4\pi W}[\beta_1(r)+\bar{b}_1], \tag{7.27a}$$

wherein
$$\beta_1 = -\int_{r_1}^{r} \frac{e^{E(\rho_1)}}{\rho_1^2\,\tilde{m}(\rho_1)}\,d\rho_1 \int_{r_1}^{\rho_1} \rho_2^2\, e^{-E(\rho_2)}[\tilde{M}(\rho_2)-\bar{\tilde{M}}]\,d\rho_2 \tag{7.27b}$$

and
$$\bar{b}_1 = -\frac{1}{W}\int_{r_1}^{r_2} r^2\, e^{-E(r)}\beta_1(r)\,dr. \tag{7.27c}$$

Thereby, b_1 is independent of $\boldsymbol{G}$. The solution of the system of equations (7.24)–(7.26) becomes particularly simple in the case of 'simple shear' ($\hat{\boldsymbol{G}}\cdot\hat{\boldsymbol{G}} = \mathbf{0}$, $\alpha = 0$), in which case (7.24*b*) and (7.24*c*) become uncoupled; b_2 is then readily obtained (similarly to b_1), whereas b_3 can be ignored since the last term on the right-hand side of (7.22) vanishes.

We next calculate the dispersivity dyadic

$$\boldsymbol{D}^* = \frac{kT}{\mu\bar{r}_0}\tilde{\boldsymbol{D}}^*, \tag{7.28}$$

where the non-dimensional $\tilde{\boldsymbol{D}}^*$ is decomposed into the sum

$$\tilde{\boldsymbol{D}}^* = \tilde{\boldsymbol{D}}^{\mathrm{M}} + \tilde{\boldsymbol{D}}^{\mathrm{C}}. \tag{7.29}$$

$\tilde{\boldsymbol{D}}^{\mathrm{M}}$ denotes the contribution which exists even in the absence of a 'Taylor' dispersion mechanism (that is, when either fluctuations in size or external forces are absent). It is equal to the long-time average of the physical-space diffusivity and, as such, is termed the 'molecular' dispersivity. It may be calculated from the first term on the right-hand side of (A 5) (appearing in the Appendix) in conjunction with (7.8*a*), (7.15), (7.16*b*) and (7.19*b*) to give

$$\tilde{\boldsymbol{D}}^{\mathrm{M}} = \bar{\tilde{M}}\boldsymbol{I}. \tag{7.30}$$

This 'molecular' contribution is unaffected by the shear, since P_0^∞ is shear-rate independent.

From the second term on the right-hand side of (A 5) jointly with (7.15), (7.20), (7.19*a*) and (7.21), one obtains the convective contribution

$$\tilde{\boldsymbol{D}}^{\mathrm{C}} = \left(\frac{F\bar{r}_0}{kT}\right)^2 \{\gamma_1 \hat{\boldsymbol{F}}\hat{\boldsymbol{F}} + \gamma_2[\![\hat{\boldsymbol{F}}\hat{\boldsymbol{F}}\cdot\hat{\boldsymbol{G}}]\!]^{\mathrm{s}} + \gamma_3[\![\hat{\boldsymbol{F}}\hat{\boldsymbol{F}}\cdot\hat{\boldsymbol{G}}\cdot\hat{\boldsymbol{G}}]\!]^{\mathrm{s}}\}, \tag{7.31a}$$

where
$$\gamma_i = 4\pi\int_{r_1}^{r_2} r^2 b_i(r)\,[\tilde{M}(r)-\bar{\tilde{M}}]\,dr \quad (i = 1,2,3). \tag{7.31b}$$

Upon making use of the expression (7.27) for b_1 in conjunction with the definition $\bar{\tilde{M}}$ it can be shown that

$$\gamma_1 = \frac{1}{W}\int_{r_1}^{r_2} dr\,\frac{e^{E(r)}}{r^2\tilde{m}(r)}\left\{\int_{r_1}^{r} d\rho_1\,\rho_1^2\, e^{-E(\rho_1)}[\tilde{M}(\rho_1)-\bar{\tilde{M}}]\right\}^2 \geqslant 0. \tag{7.32}$$

The first term on the right-hand side of (7.31*a*), which is shear-independent, is thus clearly non-negative. Owing to the appearance of the remaining two terms, this property is not necessarily true of $\tilde{\boldsymbol{D}}^{\mathrm{C}}$ itself. To confirm this conclusion, express $\hat{\boldsymbol{F}}$ in terms of its cartesian components $(\hat{F}_1, \hat{F}_2, \hat{F}_3)$, say, in our frame of reference, and use the expression (3.28) for $\boldsymbol{G}$ in plane two-dimensional homogeneous shear. The characteristic equation for the λ_i $(i = 1, 2, 3)$, namely the three eigenvalues of $\tilde{\boldsymbol{D}}^{\mathrm{C}}$, is then

$$
\begin{aligned}
|\tilde{\boldsymbol{D}}^{\mathrm{C}} - \lambda \boldsymbol{I}| = -\lambda\{\lambda^2 - [(\gamma_1 + \alpha\gamma_3)(\hat{F}_1^2 + \hat{F}_2^2) + \gamma_1 \hat{F}_3^2 + (1+\alpha)\gamma_2 \hat{F}_1 \hat{F}_2]\lambda \\
- [\gamma_2^2(\alpha \hat{F}_1^2 - \hat{F}_2^2)^2 + \alpha^2(\gamma_2 \hat{F}_1 + \gamma_3 \hat{F}_2)^2 \hat{F}_3^2 + (\alpha\gamma_3 \hat{F} + \gamma_2 \hat{F}_2)^2 \hat{F}_3^2]\} = 0. \quad (7.33)
\end{aligned}
$$

Unless both $\hat{F}_1, \hat{F}_2 = 0$, one of the eigenvalues necessarily satisfies the inequality $\lambda_i < 0$. Thus, whenever $\hat{\boldsymbol{F}} \cdot \hat{\boldsymbol{G}} \neq \boldsymbol{0}$, i.e. the external force is non-orthogonal to the fluid velocity gradient, $\tilde{\boldsymbol{D}}^{\mathrm{C}}$ will fail to be non-negative.

Finally, we consider the dyadic $\mathscr{D}$, which dominates the asymptotic behaviour of $\bar{P}$ as in (3.27).

(i) *The strongly rotational* $(\alpha < 0)$ *case*

Substitution of (3.12), (3.29) and (7.28)–(7.31) into (3.18) yields

$$
\mathscr{D} \equiv \bar{r}_o^2 \tilde{t} \begin{pmatrix} \frac{1}{2}[\tilde{\bar{M}}(1-\alpha^{-1}) + \left(\bar{r}_o F\right)^2 (\gamma_1 + \alpha\gamma_3)(\hat{F}_1^2 - \alpha^{-1}\hat{F}_2^2), & O(\tilde{t}^{-1}), & O(\tilde{t}^{-1}) \\ O(\tilde{t}^{-1}), & -\frac{1}{2}\alpha\left[\tilde{\bar{M}}(1-\alpha^{-1}) + (\gamma_1 + \alpha\gamma_3)\left(\frac{\bar{r}_o^2 F}{kT}\right)(\hat{F}_1^2 - \alpha^{-1}\hat{F}_2^2)\right] & O(\tilde{t}^{-1}) \\ O(\tilde{t}^{-1}), & O(\tilde{t}^{-1}), & \tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_3^2 \end{pmatrix}, \quad (7.34)
$$

where the dimensionless time $\tilde{t}$ is defined by the expression

$$
t = \frac{\bar{r}_o^3 \mu}{kT} \tilde{t} \quad \left(\text{or, equivalently, by } \tau = Gt \equiv \frac{\bar{r}_o^3 \mu G}{kT} \tilde{t}\right). \quad (7.35)
$$

Observe that the coefficient γ_2 of $[\![\hat{\boldsymbol{F}}\hat{\boldsymbol{F}} \cdot \hat{\boldsymbol{G}}]\!]^{s}$ in the expression (7.31*a*) for $\tilde{\boldsymbol{D}}^{\mathrm{C}}$ does not appear at the leading order of $\mathscr{D}$; as such, it will not influence the behaviour of $\bar{P}$. This seems plausible inasmuch as $\mathscr{D}$ should prove invariant to reversal of the flow direction (i.e. reversal of the sign of $\hat{\boldsymbol{G}}$). The coefficient γ_3 appears only in the combination $\gamma_1 + \alpha\gamma_3$, which can be shown to satisfy the inequality

$$
\gamma_1 + \alpha\gamma_3 \equiv \frac{1}{W}\int_{r_1}^{r_2} r^2 \tilde{m}(r)\, \mathrm{e}^{-E(r)} \left[\left(\frac{\mathrm{d}b_1}{\mathrm{d}r} - \alpha\frac{\mathrm{d}b_3}{\mathrm{d}r}\right)^2 - 2\alpha\left(\frac{\mathrm{d}b_2}{\mathrm{d}r}\right)^2\right] \mathrm{d}r \geqslant 0, \quad (7.36)
$$

thus assuring the positive definiteness of $\mathscr{D}$ as $t \to \infty$.

(ii) *Simple shear* $(\alpha = 0)$

Substitution of (3.13) and (7.28)–(7.31) into (3.18) yields

$$
\mathscr{D} \sim \bar{r}_o^2 \tilde{t} \begin{pmatrix} \frac{1}{3}\left[\tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2^2\right]\tau^2, & -\frac{1}{2}\left[\tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2^2\right]\tau, & -\frac{1}{2}\left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2 \hat{F}_3 \tau \\ -\frac{1}{2}\left[\tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2^2\right]\tau, & \tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2^2, & \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2 \hat{F}_3 \\ -\frac{1}{2}\left(\frac{\bar{r}_o F}{kT}\right)^2 \hat{F}_2 \hat{F}_3 \tau, & \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_2 \hat{F}_3, & \tilde{\bar{M}} + \left(\frac{\bar{r}_o F}{kT}\right)^2 \gamma_1 \hat{F}_3^2 \end{pmatrix} \quad (7.37)
$$

(assuming that $\tau \gg 1$).

Use of either of the above expressions for $\mathscr{D}$, together with the transformation (2.7) and (2.8) in conjunction with (3.27), yields the leading-order asymptotic expression for $\bar{P}$ in the original domain. Substitute $F_i = 0$ $(i = 1, 2, 3)$ and denote

$$D = \frac{kT}{\mu \bar{r}_o} \tilde{\bar{M}}. \tag{7.38}$$

Integration of $\bar{P}$ over z in the interval $(-\infty, \infty)$ then leads to expressions which agree with the leading-order behaviour of Foister & van de Ven's results (1980; cf. their equations (2.15)–(2.20)). It is evident that only in the complete absence of any Taylor effect can the fluctuating sphere be represented adequately, insofar as its mean convective and diffusive transport through the fluid is concerned, by some 'average' rigid sphere (e.g. of diffusivity given by (7.38)).

A related issue is whether or not the leading behaviour of $\bar{P}$ can be obtained by substituting the expression for $\boldsymbol{D}^*$ appropriate to a fluctuating sphere moving in a quiescent fluid into the known expressions (Foister & van de Ven 1980) for the dispersion of a *rigid* sphere in a shear field. Such a superposition neglects the effect of the shear field upon $\boldsymbol{D}^*$ and $\mathscr{D}$. In general, this coupling effect arises from the appearance of the shear term $P_0^\infty \boldsymbol{B} \cdot \boldsymbol{G}$ in the equation (4.8*a*) for the vector $\boldsymbol{B}$-field. (This coupling is then reflected both explicitly and implicitly (through γ_2 and γ_3) in the second and third terms on the right-hand side of (7.31*a*) expressing $\tilde{\boldsymbol{D}}^{\mathrm{C}}$, in particular by the latter not necessarily being non-negative (cf. (7.33) *et seq.*).) The leading behaviour of $\bar{P}$ is determined by the properties of $\mathscr{D}$. As noted above, in the strongly rotational ($\alpha < 0$) case, $\mathscr{D}$ (cf. (7.34)) depends upon γ_3, which is a shear-dependent coefficient of $\tilde{\boldsymbol{D}}^{\mathrm{C}}$. Obviously, the above-mentioned superposition fails under these circumstances. On the other hand, in the simple shear ($\alpha = 0$) case, the leading expression (7.37) for $\mathscr{D}$ depends only upon the shear-independent coefficient γ_1 (cf. (7.27) *et seq.* and (7.31*b*)). It is only in this latter case that the coupling between the shear flow and the size fluctuations does not affect the leading asymptotic behaviour of $\bar{P}$; hence, only in this case will superposition be valid.

Those readers interested in explicit physical examples, wherein the parameter magnitudes, $\bar{K}$, $\bar{\phi}$, $\bar{\rho}$, etc., are related to specific kinetic macromolecular data (e.g. molecular weight, effective bond length, etc.) are referred to a forthcoming paper by Frankel *et al.* (1991).

8. Concluding remarks

The present contribution extends the scope of generalized Taylor dispersion theory to problems of solute flow and dispersion in *unbounded* homogeneous shear flows for circumstances in which the Brownian solute particles possess internal (e.g. orientational, conformational, etc.) degrees of freedom. Generalized Taylor dispersion analyses of such transport processes have heretofore proven intractable using conventional paradigms (Brenner 1980, 1982) owing to the functional dependence of the global velocity field upon the global coordinate.

Employing an appropriate transformation of the global-space coordinates restores the classical structure of the initial- and boundary-value problem governing the conditional probability density function. Following that, subsequent analysis demonstrates that the pertinent asymptotic expansions of the statistical moments are then recoverable from familiar classical expressions (Frankel & Brenner 1989) via replacement of the global phenomenological coefficients, namely $\Delta \boldsymbol{U}$ and $\boldsymbol{D}$, by $\Delta \boldsymbol{U} \cdot \exp(-\boldsymbol{G}t)$ and $\exp(-\boldsymbol{G}^{\dagger}t) \cdot \boldsymbol{D} \cdot \exp(\boldsymbol{G}t)$, respectively. The asymptotic expansion for the local-space-averaged density $\bar{P}$ thereby obtained consists of a dominant Gaussian behaviour (which is independent of the local initial conformation $\boldsymbol{q}'$) plus higher-order correction terms proceeding in inverse powers of $t^{\frac{1}{2}}$. This result establishes the existence of a 'purely global' (i.e. macroscale) description appearing in the form of a convective–diffusive model of the mean solute transport process.

A central issue in the construction of the model problem is that of selecting the appropriate dyadic dispersivity coefficient $\boldsymbol{D}^{\bullet}$ appearing in the macroscale constitutive equation for the solute's dispersion flux vector. The traditional definition of $\boldsymbol{D}^{\bullet}$, which is based upon the long-time limit of the rate of change of the central moment $\boldsymbol{M}_2 - \boldsymbol{M}_1 \boldsymbol{M}_1$, fails because the asymptotic behaviour of the latter is, in general, nonlinear in t – as was first pointed out by Foister & van de Ven (1980) for rigid, neutrally buoyant, spherical particles. It is a remarkable feature of the codeformational view which, despite this nonlinear time dependence, restores an Einstein-like relation (cf. (5.8)) between the (stationary and invariant) coefficient $\boldsymbol{D}^*$ and the long-time limit of the Oldroyd rate of change of $\boldsymbol{M}_2 - \boldsymbol{M}_1 \boldsymbol{M}_1$. This latter limit, however, does not necessarily yield a positive-definite dispersivity. This occurs because, even in a codeformational frame, the central moment may not grow monotonically with time. Reconsideration of the several transport mechanisms involved in the dispersion process, i.e. passive convection by the shear flow, molecular diffusion, and the Taylor mechanism (as well as their mutual interactions) leads to a Lagrangian interpretation of the vector $\boldsymbol{B}$-field, as well as to a generalized dispersivity dyadic definition (comparable to that proposed by Smith 1985) which is positive definite – thus ensuring that solutions of the resulting model problem are well behaved.

The general theory is illustrated by the dispersion in unbounded homogeneous shear flow of a macromolecular coil, which is modelled as a size-fluctuating Brownian porous sphere. The results demonstrate the inadequacy of representing the macromolecule by some equivalent 'pre-averaged' rigid sphere.

As made clear in the Introduction, the general theory presented here provides a framework which enables a rigorous analysis of the dispersion of orientable particles (e.g. ellipsoids) in homogeneous, *unbounded* shear flows. The results of this study which explicitly illustrate the effect of shear rate on the macroscale dispersion of Brownian ellipsoidal particles in physical space are reported separately, in a forthcoming publication (Frankel & Brenner 1991).

Since the present theory is not confined to any specific range of Péclet numbers, the main limitation of its applicability originates from the assumption (3.11) regarding the eigenvalues of $\boldsymbol{G}$. This restriction rules out the possibility of an exponentially rapid divergence arising from passive convection in the shear field, thereby rendering it a 'slow' process relative to the diffusive sampling of the local (e.g. orientational, conformational, etc.) space. Any attempts at the eventual removal of this restriction involve questions of considerable interest regarding the formal, asymptotic existence of a 'purely global' macroscale convective–dispersive description of the solute transport process, and thus constitutes a natural possible extension of the present research.

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Appendix. Long-time asymptotic expansions

A tedious calculation deriving from (3.7) and (3.8) in conjunction with the condition (3.11) leads to the following pair of asymptotic expansions for the local moments $\boldsymbol{P}_m$.

Even orders ($m = 2k$; $k = 0, 1, 2, \ldots$):

$$\begin{aligned}
\boldsymbol{P}_{2k}(\boldsymbol{q}, t \mid \boldsymbol{q}') \sim (2k)!\, P_0^\infty(\boldsymbol{q}) \Bigg\{ & \frac{1}{k!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^k \right]\!\right]^s \\
& + \frac{1}{(k-1)!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^{k-1} \right. \right. \\
& \times [\boldsymbol{A}_2(\boldsymbol{q}') + \boldsymbol{A}(\boldsymbol{q}')\, \boldsymbol{B}(\boldsymbol{q}) \cdot \mathrm{e}^{-\boldsymbol{G}t} \\
& \left.\left. + \boldsymbol{B}_2(\boldsymbol{q})\, (\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t})^2] \right]\!\right]^s \\
& + \frac{1}{(k-2)!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^{k-2} \right. \right. \\
& \times \left\{ [\boldsymbol{B}(\boldsymbol{q}) \cdot \mathrm{e}^{-\boldsymbol{G}t} + \boldsymbol{A}(\boldsymbol{q}')] \int_0^t \boldsymbol{D}_3^*(\cdot)^3 (\mathrm{e}^{-\boldsymbol{G}t_2})^2 \,\mathrm{d}t_2 \right. \\
& \left.\left.\left. + \int_0^t \boldsymbol{D}_4^*(\cdot)^4 (\mathrm{e}^{-\boldsymbol{G}t_2})^4 \,\mathrm{d}t_2 \right\} \right]\!\right]^s + \frac{1}{2(k-3)!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^{k-3} \right.\right. \\
& \left.\left. \times \left[\int_0^t \boldsymbol{D}_3^*(\cdot)^3 (\mathrm{e}^{-\boldsymbol{G}t_2})^3 \,\mathrm{d}t_2 \right]^2 \right]\!\right]^s \Bigg\};
\end{aligned} \tag{A 1}$$

Odd orders ($m = 2k+1$; $k = 0, 1, 2, \ldots$):

$$\begin{aligned}
\boldsymbol{P}_{2k+1}(\boldsymbol{q}, t \mid \boldsymbol{q}') \sim (2k+1)!\, P_0^\infty(\boldsymbol{q}) \Bigg\{ & \frac{1}{k!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^k [\boldsymbol{A}(\boldsymbol{q}') + \boldsymbol{B}(\boldsymbol{q}) \cdot \mathrm{e}^{-\boldsymbol{G}t}] \right]\!\right]^s \\
& + \frac{1}{(k-1)!} \left[\!\left[\left[\int_0^t \boldsymbol{D}^*(\cdot)^2 (\mathrm{e}^{-\boldsymbol{G}t_1})^2 \,\mathrm{d}t_1 \right]^{k-1} \int_0^t \boldsymbol{D}_3^*(\cdot)^3 (\mathrm{e}^{-\boldsymbol{G}t_2})^3 \,\mathrm{d}t_2 \right]\!\right]^s \Bigg\}.
\end{aligned} \tag{A 2}$$

Whenever negative powers or factorials of negative numbers occur in the above, the corresponding terms should be replaced by exponentially small remainders.

The above expressions furnish the first two leading-order terms in the expansion of $\boldsymbol{P}_{2k}$, but only the dominant behaviour of $\boldsymbol{P}_{2k+1}$. These expressions can be verified in a straightforward manner by invoking inductive arguments, while making use of (3.7) together with the following definitions:

$$\boldsymbol{A}(\boldsymbol{q}') = \lim_{t \to \infty} \int_0^t \int_{q_0} p(\boldsymbol{q}_1, t_1 \mid \boldsymbol{q}')\, \Delta \boldsymbol{U}(\boldsymbol{q}_1) \cdot \mathrm{e}^{-\boldsymbol{G}t_1} \,\mathrm{d}\boldsymbol{q}_1 \,\mathrm{d}t_1, \tag{A 3}$$

$$\begin{aligned}
\int_0^t \int_{q_0} & p(\boldsymbol{q}, t - t_1 \mid \boldsymbol{q}_1) P_0^\infty(\boldsymbol{q}_1)\, \Delta\, \boldsymbol{U}(\mathrm{q}_1) \cdot \mathrm{e}^{-\boldsymbol{G}t_1} \,\mathrm{d}\boldsymbol{q}_1 \,\mathrm{d}t_1 \\
& \sim P_0^\infty(\boldsymbol{q})\, \boldsymbol{B}(\boldsymbol{q}) \cdot \mathrm{e}^{-\boldsymbol{G}t} + \exp \quad \text{as} \quad t \to \infty
\end{aligned} \tag{A 4}$$

(which asymptotic relation serving to define the $\boldsymbol{B}$-field is established at the conclusion of this Appendix),

$$\boldsymbol{D}^* = \int_{q_0} P_0^\infty(\boldsymbol{q})\,[\![\boldsymbol{D}(q) + \Delta \boldsymbol{U}(\boldsymbol{q})\,\boldsymbol{B}(\boldsymbol{q})]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}, \tag{A 5}$$

$$\int_0^t \int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q}, t-t_1\,|\,\boldsymbol{q}_1)\,\mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot[\![\boldsymbol{D}(\boldsymbol{q}_1) + \Delta \boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1)]\!]^{\mathrm{s}}\cdot\mathrm{e}^{-\boldsymbol{G}t_1}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1$$
$$\sim P_0^\infty(\boldsymbol{q})\,\mathrm{e}^{-\boldsymbol{G}^\dagger t}\cdot\boldsymbol{B}_2(\boldsymbol{q})\cdot\mathrm{e}^{-\boldsymbol{G}t} + \exp \quad \text{as} \quad t\to\infty \tag{A 6}$$

(cf. (A 16) *et seq.*),

$$\begin{aligned}\boldsymbol{A}_2(\boldsymbol{q}') = \lim_{t\to\infty}\Bigg\{ &\int_0^t \int_{q_0} \mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot\boldsymbol{D}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_1} p(\boldsymbol{q}_1, t_1\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t \\ &+ \int_0^t\int_0^{t_1}\int_{q_0}\int_{q_0} [\![\mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_2)\cdot\mathrm{e}^{-\boldsymbol{G}t_2}]\!]^{\mathrm{s}} \\ &\times p(\boldsymbol{q}_1, t_1-t_2\,|\,\boldsymbol{q}_2)\,p(\boldsymbol{q}_2, t_2\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}_2\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1 \\ &+ \int_0^t\int_0^{t_1}\int_{q_0}\int_{q_0} [\![\mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_2)\cdot\mathrm{e}^{-\boldsymbol{G}t_2}]\!]^{\mathrm{s}} \\ &\times P_0^\infty(\boldsymbol{q}_2)\,p(\boldsymbol{q}_1, t_1-t_2\,|\,\boldsymbol{q}_2)\,\mathrm{d}\boldsymbol{q}_2\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1 - \int_0^t\int_{q_0} P_0^\infty(\boldsymbol{q}_1) \\ &\times [\![\mathrm{e}^{-\boldsymbol{G}^\dagger t_1}\cdot\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_1}]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1\Bigg\},\end{aligned} \tag{A 7}$$

$$\boldsymbol{D}_3^* = \int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,[\![\boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1) + \Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1)]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1, \tag{A 8}$$

$$\begin{aligned}P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}_3(\boldsymbol{q})\,(\cdot)^3(\mathrm{e}^{-\boldsymbol{G}t})^3 \sim &\int_0^t\int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q}, t-t_1\,|\,\boldsymbol{q}_1) \\ &\times [\![\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1) + \boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1)]\!]^{\mathrm{s}}(\cdot)^3(\mathrm{e}^{-\boldsymbol{G}t_1})^3\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1 \\ &-\Bigg[\!\!\Bigg[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2 \int_0^{t_1} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q}, t-t_2\,|\,\boldsymbol{q}_1) \\ &\times \Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_2}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1\Bigg]\!\!\Bigg]^{\mathrm{s}} + \exp \quad \text{as} \quad t\to\infty\end{aligned} \tag{A 9}$$

(cf. (A 16) *et seq.*), and

$$\boldsymbol{D}_4^* = \int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,[\![\boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1) + \Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_3(\boldsymbol{q}_1)]\!]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1. \tag{A 10}$$

The total moments are now obtained via quadratures of (3.4) in conjunction with the normalization relations (3.9d) and (3.10), thereby obtaining

$$\begin{aligned}\boldsymbol{M}_{2k}(t\,|\,\boldsymbol{q}') \sim (2k)!\Bigg\{&\frac{1}{k!}\Bigg[\!\!\Bigg[\Bigg[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,\mathrm{d}t_1\Bigg]^k\Bigg]\!\!\Bigg]^{\mathrm{s}} \\ &+\frac{1}{(k-1)!}\Bigg[\!\!\Bigg[\Bigg[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,\mathrm{d}t_1\Bigg]^{k-1}\boldsymbol{A}_2(\boldsymbol{q}')\Bigg]\!\!\Bigg]^{\mathrm{s}} \\ &+\frac{1}{(k-2)!}\Bigg[\!\!\Bigg[\Bigg[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,dt_1\Bigg]^{k-2}\Bigg\{\Bigg[\int_0^t \boldsymbol{D}_3(\cdot)^3(\mathrm{e}^{-\boldsymbol{G}t_2})^3\,dt_2\Bigg]\boldsymbol{A}(\boldsymbol{q}')\end{aligned}$$

$$+\int_0^t \boldsymbol{D}_4^*(\cdot)^4(\mathrm{e}^{-\boldsymbol{G}t_2})^4\,\mathrm{d}t_2)\Big]\!\Big]^{\mathrm{s}}+\frac{1}{2(k-3)!}\Big[\!\Big[\Big[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,\mathrm{d}t_1\Big]^{k-3}$$

$$\times\Big[\int_0^t \boldsymbol{D}_3^*(\cdot)^3(\mathrm{e}^{-\boldsymbol{G}t_2})^3\,\mathrm{d}t_2\Big]^2\Big]\!\Big]^{\mathrm{s}}+\dots\Big\} \tag{A 11}$$

and

$$\boldsymbol{M}_{2k+1}\sim(2k+1)!\Big\{\frac{1}{k!}\Big[\!\Big[\Big[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,\mathrm{d}t_1\Big]^k \boldsymbol{A}(\boldsymbol{q}')\Big]\!\Big]^{\mathrm{s}}$$

$$+\frac{1}{(k-1)!}\Big[\!\Big[\Big[\int_0^t \boldsymbol{D}^*(\cdot)^2(\mathrm{e}^{-\boldsymbol{G}t_1})^2\,\mathrm{d}t_1\Big]^{k-1}\int_0^t \boldsymbol{D}_3^*(\cdot)^3(\mathrm{e}^{-\boldsymbol{G}t_2})^3\,\mathrm{d}t_2\Big]\!\Big]^{\mathrm{s}}+\dots\Big\}. \tag{A 12}$$

A.1. *Existence of the $\boldsymbol{B}_i(\boldsymbol{q})$-fields*

First-order field ($i = 1$)

Define

$$\boldsymbol{\mathscr{I}}(\boldsymbol{q},t)=\int_0^t\int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t-t_1\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot\mathrm{e}^{-\boldsymbol{G}t_1}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1, \tag{A 13}$$

and change the temporal integration variable such that $t_2 = t-t_1$. Time differentiation then yields

$$\frac{\mathrm{d}\boldsymbol{\mathscr{I}}}{\mathrm{d}t}+\boldsymbol{\mathscr{I}}\cdot\boldsymbol{G}=\int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\mathrm{d}\boldsymbol{q}_1\sim\exp\quad\text{as}\quad t\to\infty \tag{A 14}$$

since $p\sim\exp$ as $t\to\infty$.

We seek an asymptotic solution of this latter equation for $t\to\infty$. In general,

$$\boldsymbol{\mathscr{I}}=P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}(\boldsymbol{q})\cdot\mathrm{e}^{-\boldsymbol{G}t}+\bar{\boldsymbol{B}}(\boldsymbol{q},t), \tag{A 15}$$

where $\bar{B}$ denotes a particular solution of the inhomogeneous equation (A 14). Thus, $\bar{B}$ is of the form

$$\bar{\boldsymbol{B}}\sim\bar{\boldsymbol{B}}^{(0)}(\boldsymbol{q})+\exp,$$

in which the time-independent vector $\bar{\boldsymbol{B}}^{(0)}$ satisfies the orthogonality condition

$$\bar{\boldsymbol{B}}^{(0)}\cdot\boldsymbol{G}=\boldsymbol{0}.$$

(The vector field $\bar{\boldsymbol{B}}^{(0)}(\boldsymbol{q})$ may be non-zero provided that $\boldsymbol{G}$ is singular.) The latter orthogonality condition allows us to write

$$\bar{\boldsymbol{B}}^{(0)}(\boldsymbol{q})=\bar{\boldsymbol{B}}^{(0)}\cdot\mathrm{e}^{-\boldsymbol{G}t},$$

whence this term may be absorbed into the first term on the right-hand side of (A 15). Thereby, we have thus established the asymptotic relation (A 4).

Higher-order fields ($i = 2, 3, 4, \dots$)

The above result can be extended to general-order fields. In particular, the asymptotic identity

$$\boldsymbol{\mathscr{I}}_n(\boldsymbol{q},t)\overset{\text{def.}}{=}\int_0^t\int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t-t_1\,|\,\boldsymbol{q}_1)\boldsymbol{f}_n(\boldsymbol{q}_1)\,(\cdot)^n(\mathrm{e}^{-\boldsymbol{G}t_1})^n\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1$$

$$\sim P_0^\infty(\boldsymbol{q})\,\boldsymbol{F}_n(\boldsymbol{q})\,(\cdot)^n(\mathrm{e}^{-\boldsymbol{G}t})^n+\exp\quad\text{as}\quad t\to\infty \tag{A 16}$$

suffices to establish the existence of $\boldsymbol{B}_2(\boldsymbol{q})$, as in (A 6). At higher orders the definition of $\boldsymbol{B}_i(\boldsymbol{q})$ involves additional terms, the asymptotic estimate of which is exemplified in the following by the case $i = 3$.

Upon defining

$$\mathscr{I}(\boldsymbol{q},t,t_1) = \int_0^{t_1}\int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t-t_2\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot \mathrm{e}^{-\boldsymbol{G}t_2}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2, \qquad \text{(A 17)}$$

we wish to demonstrate that

$$\mathscr{I} = P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}^{(1)}(\boldsymbol{q},t-t_1)\cdot \mathrm{e}^{-\boldsymbol{G}t_1} + \bar{\boldsymbol{B}}^{(1)}(\boldsymbol{q},t),$$

wherein

$$\boldsymbol{B}^{(1)} = \begin{cases} \boldsymbol{B}(\boldsymbol{q}) & (t = t_1) \\ \exp & (t-t_1 \to \infty) \end{cases} \qquad \text{(A 18)}$$

and

$$\bar{\boldsymbol{B}}^{(1)} \sim \exp \quad \text{as} \quad t \to \infty.$$

To effect this demonstration, introduce the alternative integration variable $t_3 = t - t_2$ into (A 17) so as to obtain the relation

$$\mathscr{I} = \int_{t-t_1}^{t}\int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t_3\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot \mathrm{e}^{-\boldsymbol{G}(t-t_3)}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_3 = \mathscr{I}^{(1)}(\boldsymbol{q},t,t-t_1),$$

say. Time differentiation of the latter yields

$$\frac{\partial}{\partial t}\mathscr{I}^{(1)}\Big|_{\boldsymbol{q},\,t-t_1=\text{const.}} + \mathscr{I}^{(1)}\cdot\boldsymbol{G}$$

$$= \int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\mathrm{d}\boldsymbol{q}_1 \sim \exp(\boldsymbol{q},t) \quad \text{as} \quad t\to\infty. \qquad \text{(A 19)}$$

The general solution of the associated homogeneous equation is

$$\mathscr{I}_h^{(1)} = \mathscr{I}^{(2)}(\boldsymbol{q},t-t_1)\cdot \mathrm{e}^{-\boldsymbol{G}t} = P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}^{(1)}(\boldsymbol{q},t-t_1)\cdot \mathrm{e}^{-\boldsymbol{G}t_1},$$

whereas a particular solution of (A 19) is

$$\mathscr{I}_{\mathrm{p}}^{(1)} \sim \exp(\boldsymbol{q},t).$$

(The latter cannot depend upon $t-t_1$ inasmuch as the forcing term does not.)

Return to the original notation (cf. (A 17)) so as to obtain

$$\int_0^{t_1}\int_{q_0} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q},t-t_2\,|\,\boldsymbol{q}_1)\,\Delta\boldsymbol{U}(\boldsymbol{q}_1)\cdot \mathrm{e}^{-\boldsymbol{G}t_2}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2$$

$$\sim P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}^{(1)}(\boldsymbol{q},t-t_1)\cdot \mathrm{e}^{-\boldsymbol{G}t_1} + \exp(\boldsymbol{q},t).$$

For $t_1 = t$ the left-hand side of the above is equal to $P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}(\boldsymbol{q})\cdot\exp(-\boldsymbol{G}t)$ (cf. (A 14)). As $t\to\infty$ while keeping t_1 fixed, both the left-hand side and the second term on the right-hand side become exponentially small, whence (A 18) is established.

All of the foregoing results are independent of the assumption (3.11). As such, they retain their validity even when there exist eigenvalues such that $\mathrm{Re}\{\nu_i\} \neq 0$.

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