J. Fluid Mech. (1989), vol. 204, pp. 97–119
Printed in Great Britain

On the foundations of generalized Taylor dispersion theory

By I. FRANKEL† AND H. BRENNER‡
† Faculty of Aerospace Engineering, Technion, Haifa 32000, Israel
‡ Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

(Received 12 September 1988)

Generalized Taylor dispersion theory extends the basic long-time, asymptotic scheme of Taylor and Aris greatly beyond the class of rectilinear duct and channel flow dispersion problems originally addressed by them. This feature has rendered it indispensable for studying flow and dispersion phenomena in porous media, chromatographic separation processes, heat transfer in cellular media, sedimentation of non-spherical Brownian particles, and transport of flexible clusters of interacting Brownian particles, to mention just a few examples of the broad class of non-unidirectional transport phenomena encompassed by this scheme. Moreover, generalized Taylor dispersion theory enjoys the attractive feature of conferring a unified paradigmatic structure upon the analysis of such apparently disparate physical problems. For each of the problems thus treated it provides an asymptotic, macroscale description of the original microscale transport process, being based upon a convective–diffusive 'model' problem characterized by a set of constant (position- and time-independent) phenomenological coefficients.

The present contribution formally substantiates the scheme. This is accomplished by demonstrating that the coarse-grained (macroscale) transport 'model' equation leads to a solution which accords asymptotically with the leading-order behaviour of the comparable solution of the exact (microscale) convective–diffusive problem underlying the transport process. It is also shown, contrary to current belief, that no *systematic* improvement in the asymptotic order of approximation is possible through the incorporation of higher-order gradient terms into the model constitutive equation for the coarse-grained flux. Moreover, the inherent difference between the present rigorous asymptotic scheme and the dispersion models resulting from Gill–Subramanian moment-gradient expansions is illuminated, thereby conclusively resolving a long-standing puzzle in longitudinal dispersion theory.

1. Introduction

Generalized Taylor dispersion theory provides a robust scheme for the study of dispersion phenomena arising from solute-velocity (and other phenomenological-coefficient) inhomogeneities in convective–diffusive transport processes. A fundamental feature of this generalized theory is that it is not confined to unidirectional duct or channel flows. This contrasts with the original Taylor (1953, 1954)–Aris (1956) theory, as well as its subsequent extensions and varied applications by others (e.g. Gill & Sankarasubramanian 1970, 1971; Sankarasubramanian & Gill 1973; Doshi, Daiya & Gill 1978; Chatwin 1970, 1972; Chatwin & Sullivan 1982; Smith 1981*a*, *b*, 1985, 1987*a*, *b*; DeGance & Johns 1978*a*, *b*, 1985, to name a few), each one of which continued to be addressed to this limited class of rectilinear duct and channel flows.

Since its original paradigmatic presentation (Brenner 1980*a*, 1982*a*), additional physical elements have been incorporated into generalized Taylor dispersion theory, followed by successful application to a wide variety of transport problems. These include, *inter alia*: (i) sedimentation of non-spherical particles (Brenner 1979, 1981); (ii) dispersion accompanying solute flow through porous media (unconsolidated: Brenner 1980*b*; consolidated: Adler & Brenner 1984); (iii) surface transport (Dill & Brenner 1982*a*; Brenner & Adler 1982); (iv) direct 'coupling' effects (Brenner 1982*b*), which later enabled study of the transport of flexible bodies and chains of interacting Brownian particles without having recourse to *ad hoc* preaveraging schemes (Brenner, Nadim & Haber 1987; Nadim & Brenner 1989); (v) time-periodic non-unidirectional flows (Dill & Brenner 1982*b*, 1983*a*); (vi) cellular flows characterized by a vortical microscale flow with no net macroscale flow (Nadim, Cox & Brenner 1986*a*; Dungan & Brenner 1988); (vii) chemically reactive (Shapiro & Brenner 1986, 1987*a*, 1988) and aerosol filtration (Shapiro & Brenner 1989) systems, involving non-conserved Brownian tracers; (viii) effects of finite-size particles applied to chromatographic separation (Brenner & Gaydos 1977,† Gajdos & Brenner 1978,† Mavrovouniotis & Brenner 1988); (ix) turbulent flow fields (Shapiro, Oron & Gutfinger 1989); and (x) dispersion of 'momentum tracers' in relation to the rheology of suspensions (Mauri & Brenner 1989).

Thus, while owing its basic conceptual notions to the now classical Taylor–Aris rectilinear-flow dispersion problems, the scope of generalized Taylor dispersion theory greatly transcends that of the classical Taylor–Aris theory (and includes the latter as a special case). An attractive feature of the general scheme is that it confers a unified, indeed paradigmatic, structure upon the analysis of an apparently widely disparate class of physical problems. The starting point of generalized Taylor dispersion theory is the exact convective–diffusive description of the motion of a Brownian tracer particle through an abstract multidimensional phase space $\boldsymbol{Q}_\infty \oplus \boldsymbol{q}_o$, which consists respectively of a 'local' (usually bounded) subspace $\boldsymbol{q}_o$, composed of a set of coordinates $\boldsymbol{q} \in \boldsymbol{q}_o$, and a 'global' unbounded subspace $\boldsymbol{Q}_\infty$, composed of a set of one-, two- or three-dimensional physical-space coordinates $\boldsymbol{Q} \in \boldsymbol{Q}_\infty$. This so-called 'microscale' description is obtained through the formulation of the appropriate convective–diffusive initial- and boundary-value *physical* problem for the conditional probability density function $P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{q}')$ of finding the Brownian tracer at the location $(\boldsymbol{Q}, \boldsymbol{q})$ at time $t > 0$, provided that it was introduced at the position $(\boldsymbol{0}, \boldsymbol{q}')$ at time $t = 0$.

In most applications one is not explicitly interested in the detailed stochastic tracer trajectory embodied in the exact microscale solution $P(\boldsymbol{Q}, \boldsymbol{q}, t \mid \boldsymbol{q}')$, but rather only in the coarser-grained, so-called 'macroscale' description furnished by the local-space average $\bar{P}(\boldsymbol{Q}, t \mid \boldsymbol{q}')$ of the latter (see (2.9)). Generalized Taylor dispersion theory seeks a long-time asymptotic approximation to $\bar{P}$, obtained by matching its moments (cf. (3.3)) as $t \to \infty$ to the comparable moments of a 'model' probability density $P^*(\boldsymbol{Q}, t)$, which in turn is assumed to satisfy a purely global, macroscale, convection–diffusion 'model' problem in $\boldsymbol{Q}$-space with constant phenomenological coefficients (cf. §4). This matching determines the phenomenological invariants which serve to characterize the overall transport process at the macroscale.

† Chronologically, these two papers actually *preceded* development of the generalized theory by several years. However, they already embodied several of the novel ideas ultimately incorporated into the general theory (Brenner 1980*a*, 1982*a*).

The main goals of the present study are twofold:

(i) *Substantiation of the asymptotic scheme.* Our first goal is to provide generalized Taylor dispersion theory with a rigorous basis. Such substantiation (comparable to that given by Aris 1956 for the original unidirectional tube-flow problem) has heretofore been lacking. Explicitly, as will be demonstrated, the usual formulation of the model problem allows matching of only the dominant asymptotic terms of the *even*-order moments; in particular, matching of the *odd* statistical moments is impossible, as too is matching of the higher-order terms appearing in the even moments. It thus appears desirable to investigate the asymptotic relation between the respective 'exact' ($\bar{P}$) and the 'model' ($P^{\bullet}$) macroscale probability densities. Specifically, an explicit long-time asymptotic expansion for $\bar{P}$ is required. Such an expansion has been previously obtained for the classical Taylor–Aris case by Chatwin (1970), who studied the approach to normality for unidirectional pipe flow by anticipating an asymptotic expansion in inverse powers of $t^{\frac{1}{2}}$, in conjunction with an appropriate longitudinal similarity transformation. While his approach could be extended to non-unidirectional flows, it would not serve our purpose of substantiating generalized Taylor dispersion theory, since his scheme is inherently different from the method-of-moments scheme underlying the present theory.

(ii) *Improvement of the scheme via moment-gradient expansions?* In the course of examining the foundations of Taylor dispersion theory – either classical or generalized – there naturally arises the question of the feasibility of improving the accuracy of the 'purely global' model through the incorporation of higher-order gradient terms in the model constitutive equation for the flux density vector. The results of our analysis ultimately enable conclusive resolution of this long-standing matter. Previous studies of the latter issue were based upon *ad hoc* moment-gradient expansions (Gill & Sankarasubramanian 1970, 1971), aimed at obtaining asymptotic results of earlier temporal validity than those of Taylor and Aris. These original studies, confined exclusively to rectilinear duct flows, were recently extended by Nadim, Pagitsas & Brenner (1986*b*) to the abstract $\boldsymbol{Q}_{\infty} \oplus \boldsymbol{q}_0$ multidimensional phase-space flows of generalized Taylor dispersion theory. The second principal goal of our analysis is thus to clarify the explicit relationship existing between the present asymptotic scheme and these moment-gradient expansions. This, in turn, will ultimately lead to resolution of a long-standing puzzle in longitudinal-dispersion theory.

For subsequent reference, §2 reformulates the exact generic microscale transport equations governing $P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')$. This is followed in §3 by derivation of the asymptotic expansion for $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ as $t\rightarrow\infty$. Section 4 examines the significance of the 'purely global' macroscale model, in particular the feasibility of its improvement. In §5, the explicit relationship existing between generalized Taylor dispersion theory and dispersion models resulting from moment-gradient expansions is clarified. These issues are explicitly illustrated within the context of Taylor's original (1953, 1954) tube-flow problem; yet the general conclusions emanating therefrom impact equally upon the non-unidirectional dispersion analysis embodied in generalized Taylor dispersion theory.

2. Problem formulation

Employing standard generalized Taylor dispersion-theory notation (Brenner 1982*a*), the conditional probability density function $P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')$ satisfies the convective–diffusive continuity equation

$$\frac{\partial P}{\partial t}+\nabla_Q\cdot\boldsymbol{J}+\nabla_q\cdot\boldsymbol{j}=0, \tag{2.1}$$

along with the respective global and local constitutive equations

$$\boldsymbol{J}=\Delta\boldsymbol{U}(\boldsymbol{q})\,P-\boldsymbol{D}(\boldsymbol{q})\cdot\nabla_Q P \tag{2.2}$$

and

$$\boldsymbol{j}=\boldsymbol{u}(\boldsymbol{q})\,P-\boldsymbol{d}(\boldsymbol{q})\cdot\nabla_q P \tag{2.3}$$

for the comparable global and local flux-density vectors $(\boldsymbol{J},\boldsymbol{j})$, wherein the phenomenological coefficients, namely the velocities $(\Delta\boldsymbol{U},\boldsymbol{u})$ and diffusivities $(\boldsymbol{D},\boldsymbol{d})$ are all assumed to be known functions of $\boldsymbol{q}$, independent of $\boldsymbol{Q}$ (and t). Supplementing these equations we impose the global-space boundary conditions

$$|\boldsymbol{Q}|^m(P,\boldsymbol{J},\boldsymbol{j})=(0,\boldsymbol{0},\boldsymbol{0})\quad \text{as}\,|\boldsymbol{Q}|\to\infty\quad (m=0,\,1,\,2,\ldots), \tag{2.4a, b, c}$$

assuring that P decays faster than any finite power of $|\boldsymbol{Q}|$, together with the local-space zero-normal-flux boundary condition

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

with $\hat{\boldsymbol{n}}$ a unit normal on $\partial\boldsymbol{q}_o$, the boundary of $\boldsymbol{q}_o$; this expresses the impenetrability of the local-space boundary to solute transport. To these we adjoin the initial condition

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

(with δ the Dirac delta function), formally expressing the fact that the tracer was introduced into the system at time $t=0$ at the phase-space location $(\boldsymbol{Q},\boldsymbol{q})\equiv(\boldsymbol{0},\boldsymbol{q}')$. In (2.2),

$$\Delta\boldsymbol{U}(\boldsymbol{q})\overset{\text{def}}{=}\boldsymbol{U}(\boldsymbol{q})-\bar{\boldsymbol{U}}, \tag{2.7}$$

in which $\bar{\boldsymbol{U}}$ denotes the constant velocity vector of our reference frame, which is left unspecified for the time being.

Equations (2.1)–(2.6) serve to determine P uniquely. It is readily verified that this unique solution satisfies the normalization condition

$$\int_{Q_\infty}\int_{q_o}P\,\mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{Q}=1 \tag{2.8}$$

for all $t>0$, where $\mathrm{d}\boldsymbol{q}$ and $\mathrm{d}\boldsymbol{Q}$ are, respectively, the local- and global-sub-space 'volume' elements. According to (2.8) the total probability of finding the tracer somewhere within the phase space is equal to unity for all times ($t>0$) following its introduction into the system.†

† A more detailed account of the foregoing generic formulation can be found in Brenner (1980*a*, 1982*a*).

Of special interest in the subsequent analysis is the local-space-averaged conditional probability density

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') \stackrel{\text{def}}{=} \int_{q_0} P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}, \tag{2.9}$$

whose long-time asymptotic expansion will be obtained in §3 without requiring detailed *a priori* knowledge of the integrand P.

Observe for future reference that the probability density $\Pi(\boldsymbol{Q},\boldsymbol{q},t)$, which satisfies (2.1)–(2.5), and with (2.6) replaced by the general initial condition

$$\Pi(\boldsymbol{Q},\boldsymbol{q},t) = \begin{cases} f(\boldsymbol{Q},\boldsymbol{q}) & \text{for } t=0, \\ 0 & \text{for } t<0, \end{cases} \tag{2.10}$$

can be calculated from knowledge of the Green function P via the superposition theorem (cf. Brenner 1980*a*)

$$\Pi(\boldsymbol{Q},\boldsymbol{q},t) = \int_{Q_\infty}\int_{q_0} P(\boldsymbol{Q}-\boldsymbol{Q}',\boldsymbol{q},t\,|\,\boldsymbol{q}')f(\boldsymbol{Q}',\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}'\,\mathrm{d}\boldsymbol{Q}'. \tag{2.11}$$

Similarly, the coarse-grained density

$$\bar{\Pi}(\boldsymbol{Q},t) \stackrel{\text{def}}{=} \int_{q_0} \Pi(\boldsymbol{Q},\boldsymbol{q},t)\,\mathrm{d}\boldsymbol{q} \tag{2.12}$$

can be expressed as

$$\bar{\Pi}(\boldsymbol{Q},t) = \int_{Q_\infty}\int_{q_0} \bar{P}(\boldsymbol{Q}-\boldsymbol{Q}',t\,|\,\boldsymbol{q}')f(\boldsymbol{Q}',\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}'\,\mathrm{d}\boldsymbol{Q}'. \tag{2.13}$$

3. Asymptotic long-time expansion of $\bar{P}$

The Fourier transform, $\tilde{\bar{P}}$, of $\bar{P}$ may be expressed as

$$\tilde{\bar{P}}(\boldsymbol{\omega},t\,|\,\boldsymbol{q}') = \int_{Q_\infty} \bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')\exp(\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{Q} \equiv \sum_{m=0}^{\infty}\frac{1}{m!}(\mathrm{i}\boldsymbol{\omega})^m(\cdot)^m\boldsymbol{M}_m(t\,|\,\boldsymbol{q}') \tag{3.1}$$

through power series expansion of the exponential factor followed by termwise integration. In the above,

$$\boldsymbol{M}_m \stackrel{\text{def}}{=} \int_{Q_\infty}\int_{q_0} \boldsymbol{Q}^m P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{Q} \quad (m=0,\,1,\,2,\ldots) \tag{3.2}$$

are the 'total' statistical polyadic moments of order m, and $(\cdot)^m$ denotes m successive scalar multiplications. In Cartesian tensor terminology, $\boldsymbol{\omega}^m = \omega_{i_1}\omega_{i_2}\ldots\omega_{i_m}$ and $\boldsymbol{M}_m = M_{j_1 j_2\ldots j_m}$ are each of rank m, and are completely symmetric in all their indices. Moreover, the 'operator' $(\cdot)^m$ denotes m successive contractions on the tensor indices using the 'nesting convention' of Chapman & Cowling (1961); however, as all the operands throughout this paper will prove to be completely symmetric in all their tensor indices, this convention will prove irrelevant.

Equation (3.2) may be interpreted as resulting from the sequential pair of successive integrations

$$\boldsymbol{M}_m = \int_{q_0} \boldsymbol{P}_m(\boldsymbol{q},t\,|\,\boldsymbol{q}')\,\mathrm{d}\boldsymbol{q}, \tag{3.3}$$

wherein

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

are the 'local' statistical polyadic moments of order m. The latter satisfy the following sequence of $\boldsymbol{q}$-space initial- and boundary-value problems, obtained (Brenner 1982a) via integrations over $\boldsymbol{Q}_\infty$ of (2.1)–(2.6):

$$\frac{\partial \boldsymbol{P}_m}{\partial t} + \nabla_q \cdot \boldsymbol{j}_m = [m\Delta \boldsymbol{U}\boldsymbol{P}_{m-1} + m(m-1)\,\boldsymbol{D}\boldsymbol{P}_{m-2}]^s, \tag{3.5}$$

in which

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

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j}_m = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o, \tag{3.7}$$

and

$$\boldsymbol{P}_m = \begin{cases} \delta_{m0}\,\delta(\boldsymbol{q}-\boldsymbol{q}') & \text{for } t = 0, \quad (3.8a) \\ \boldsymbol{0} & \text{for } t < 0. \quad (3.8b) \end{cases}$$

Here, δ_{ij} denotes the Kronecker delta, whereas $[\;]^s$ denotes a symmetrization operator such that for any Cartesian tensor of rank m,

$$[\boldsymbol{A}]^s_{i_1 i_2 \ldots i_m} = \frac{1}{m!}(A_{i_1 i_2 i_3 \ldots i_m} + A_{i_2 i_1 i_3 \ldots i_m} + \ldots), \tag{3.9}$$

in which the summation extends over all $m!$ permutations of the indices. In (3.6), the polyadic $\boldsymbol{j}_m$ of rank $m+1$ represents the momental flux density of $\boldsymbol{P}_m$.

The scalar $P_0(\boldsymbol{q}, t \mid \boldsymbol{q}')$, which represents the solution of the above system of equations for $m = 0$, is the conditional probability density of finding the tracer at $\boldsymbol{q}$ at time t irrespective of its global-space location $\boldsymbol{Q}$, given its initial introduction at $t = 0$ at the local-space position $\boldsymbol{q}'$. It can be utilized as an appropriate Green function (Shapiro & Brenner 1987b), enabling $\boldsymbol{P}_m(\boldsymbol{q}, t \mid \boldsymbol{q}')$ to be explicitly expressed in the form

$$\boldsymbol{P}_m(\boldsymbol{q}, t \mid \boldsymbol{q}') = \int_0^t \int_{q_o} P_0(\boldsymbol{q}, t-t_1 \mid \boldsymbol{q}_1)[m\Delta \boldsymbol{U}(\boldsymbol{q}_1)\boldsymbol{P}_{m-1}(\boldsymbol{q}_1, t_1 \mid \boldsymbol{q}') + m(m-1)\,\boldsymbol{D}(\boldsymbol{q}_1)\boldsymbol{P}_{m-2}(\boldsymbol{q}_1, t_1 \mid \boldsymbol{q}')]^s\, \mathrm{d}\boldsymbol{q}_1\, \mathrm{d}t_1. \tag{3.10}$$

Hence, once P_0 is known, $\boldsymbol{P}_1, \boldsymbol{P}_2, \ldots$ can be determined recursively by quadrature of the latter. Long-time asymptotic expansions for $\boldsymbol{P}_m$ can be derived via the fundamental decomposition (Brenner 1982a)

$$P_0(\boldsymbol{q}, t \mid \boldsymbol{q}') = P_0^\infty(\boldsymbol{q}) + p(\boldsymbol{q}, t \mid \boldsymbol{q}'), \tag{3.11}$$

of P_0 into respective time-independent and time-dependent portions, to which separate contributions the following normalization relations respectively apply:

$$\int_{q_o} P_0^\infty(\boldsymbol{q})\, \mathrm{d}\boldsymbol{q} = 1, \quad \int_{q_o} p(\boldsymbol{q}, t \mid \boldsymbol{q}')\, \mathrm{d}\boldsymbol{q} = 0. \tag{3.12a, b}$$

Here, P_0^∞ is a stationary local equilibrium distribution function, whereas $p(\boldsymbol{q}, t \mid \boldsymbol{q}')$ is a function that becomes exponentially small as $t \to \infty$. The resulting expressions are considerably simplified by the choice

$$\bar{\boldsymbol{U}} \stackrel{\text{def}}{=} \int_{q_o} P_0^\infty(\boldsymbol{q})\, \boldsymbol{U}(\boldsymbol{q})\, \mathrm{d}\boldsymbol{q}, \tag{3.13}$$

i.e. by choosing a frame of reference that moves with the long-time, time-independent, average global velocity $\bar{U}$ of the Brownian tracer (cf. (2.7)).

A tedious calculation deriving from (3.10) and (3.11) (the results of which are summarized in Appendix A) yields a pair of asymptotic expansions for $\boldsymbol{P}_m$ as $t \to \infty$, according as m is even or odd. The following asymptotic expansions for the total moments (3.3) are readily obtained therefrom via integrations over $\boldsymbol{q}_o$ while making use of the normalization relations (3.12):

$$\begin{aligned}\boldsymbol{M}_{2k}(t\,|\,\boldsymbol{q}') \sim {} & \frac{(2k)!}{k!}[(\boldsymbol{D}^*t)^k]^s + \frac{(2k)!}{(k-1)!}[(\boldsymbol{D}^*t)^{k-1}\{\boldsymbol{A}_2^{(1)} + \boldsymbol{A}_2^{(2)}(\boldsymbol{q}')\}]^s \\ & + \frac{(2k)!}{(k-2)!}[(\boldsymbol{D}^*t)^{k-2}\{\boldsymbol{D}_4^* + \boldsymbol{D}_3^*\,\boldsymbol{A}(\boldsymbol{q}')\}t]^s \\ & + \frac{(2k)!}{2(k-3)!}[(\boldsymbol{D}_3^*t)^2(\boldsymbol{D}^*t)^{k-3}]^s + O(t^{k-2}) \end{aligned} \tag{3.14}$$

and

$$\boldsymbol{M}_{2k+1}(t\,|\,\boldsymbol{q}') \sim \frac{(2k+1)!}{k!}[(\boldsymbol{D}^*t)^k\boldsymbol{A}(\boldsymbol{q}')]^s + \frac{(2k+1)!}{(k-1)!}[(\boldsymbol{D}^*t)^{k-1}\boldsymbol{D}_3^*\,t]^s + O(t^{k-1}). \tag{3.15}$$

(Here and throughout, the polyadic or tensorial order of the boldface sans serif coefficients $\boldsymbol{A}_2$, $\boldsymbol{D}_3^*$, $\boldsymbol{D}_4^*$, etc. is as indicated by the subscript. We have not deemed it appropriate to be completely systematic in this regard, since consistency would have required abandoning the standard dispersion dyadic symbol $\boldsymbol{D}^*$ in favour of $\boldsymbol{D}_2^*$. As usual, boldface italic symbols without a subscript, e.g. $\boldsymbol{A}$, are understood to be vectors, with unity implicitly understood in the subscript position.)

Substitution of (3.14) and (3.15) into (3.1) gives, upon summation,

$$\begin{aligned}\tilde{\bar{P}}(\boldsymbol{\omega},t\,|\,\boldsymbol{q}') \sim {} & [1 + \mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{A}(\boldsymbol{q}') + (\mathrm{i}\boldsymbol{\omega})^3(\cdot)^3\boldsymbol{D}_3^*\,t - \boldsymbol{\omega}\cdot\{\boldsymbol{A}_2^{(1)} + \boldsymbol{A}_2^{(2)}(\boldsymbol{q}')\}\cdot\boldsymbol{\omega} \\ & + \boldsymbol{\omega}^4(\cdot)^4\{\boldsymbol{D}_4^* + [\boldsymbol{D}_3^*\,\boldsymbol{A}(\boldsymbol{q}')]^s\}t + \tfrac{1}{2}(\mathrm{i}\boldsymbol{\omega})^6(\cdot)^6[(\boldsymbol{D}_3^*t)^2]^s + \dots]\exp(-\boldsymbol{\omega}\cdot\boldsymbol{D}^*t\cdot\boldsymbol{\omega}).\end{aligned} \tag{3.16}$$

The first term on the right-hand side of this expansion derives from the respective first- (leading)-order terms of $\boldsymbol{M}_{2k}$ in (3.14); the next two terms are associated with the respective leading-order terms of $\boldsymbol{M}_{2k+1}$ in (3.15); the remaining terms correspond to the second-order $O(t^{k-1})$ terms in $\boldsymbol{M}_{2k}$. Subsequent higher-order terms, had they appeared explicitly, would have been contributed by the second-order terms in $\boldsymbol{M}_{2k+1}$, etc.

For an n-dimensional global subspace, $\bar{P}$ may be recovered from $\tilde{\bar{P}}$ via the inverse Fourier transform

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') = \frac{1}{(2\pi)^n}\int_{\boldsymbol{\omega}_\infty}\tilde{\bar{P}}(\boldsymbol{\omega},t\,|\,\boldsymbol{q}')\exp(-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{\omega}. \tag{3.17}$$

Upon making use of the integral formulae

$$\frac{1}{(2\pi)^n}\int_{\boldsymbol{\omega}_\infty}\exp(-\boldsymbol{\omega}\cdot\boldsymbol{D}^*t\cdot\boldsymbol{\omega})\exp(-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{\omega} = \frac{\exp\left(-\dfrac{1}{4t}\boldsymbol{Q}\cdot\boldsymbol{D}^{*-1}\cdot\boldsymbol{Q}\right)}{(4\pi t)^{\frac{1}{2}n}\,|\boldsymbol{D}^*|^{\frac{1}{2}}}, \tag{3.18}$$

where $|\boldsymbol{D}^*| \equiv \det\boldsymbol{D}^*$, and

$$\frac{1}{(2\pi)^n}\int_{\boldsymbol{\omega}_\infty}(-\mathrm{i}\boldsymbol{\omega})^n\tilde{f}(\boldsymbol{\omega})\exp(-\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{\omega} = \nabla_{\boldsymbol{Q}}^n f(\boldsymbol{Q}), \tag{3.19}$$

this inversion yields

$$\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}') \sim [1-\boldsymbol{A}(\boldsymbol{q}')\cdot\boldsymbol{\nabla}_Q-\boldsymbol{D}_3^*\,t(\cdot)^3\,\boldsymbol{\nabla}_Q^3+\{\boldsymbol{A}_2^{(1)}+\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')\}(\cdot)^2\,\boldsymbol{\nabla}_Q^2$$
$$+\{\boldsymbol{D}_4^*+[\boldsymbol{D}_3^*\,\boldsymbol{A}(\boldsymbol{q}')]^{\mathrm{s}}\}\,t(\cdot)^4\,\boldsymbol{\nabla}_Q^4+\tfrac{1}{2}[(\boldsymbol{D}_3^*\,t)^2]^{\mathrm{s}}(\cdot)^6\,\boldsymbol{\nabla}_Q^6+\dots]\frac{\exp\left(-\dfrac{1}{4t}\boldsymbol{Q}\cdot\boldsymbol{D}^{*-1}\cdot\boldsymbol{Q}\right)}{(4\pi t)^{\frac{1}{2}n}\,|\,\boldsymbol{D}^*|^{\frac{1}{2}}}. \tag{3.20}$$

The above derivation corresponds to the limit process

$$t\to\infty \quad (\boldsymbol{Q}\text{ fixed}). \tag{3.21}$$

Nevertheless, when one forms the explicit $\boldsymbol{Q}$-space derivatives $\boldsymbol{\nabla}_Q^k$, the resulting asymptotic expansion remains valid for the more general limit process

$$t\to\infty, \quad \boldsymbol{Q}=\bar{\boldsymbol{Q}}t^{\alpha} \quad (\bar{\boldsymbol{Q}}\text{ fixed}), \tag{3.22}$$

provided that $\alpha<\frac{2}{3}$. (For $\alpha\geqslant\frac{2}{3}$ the leading asymptotic behaviour is no longer Gaussian, and the derivation breaks down. In principle, an alternative asymptotic approximation could be sought that would be valid for $\alpha>\frac{2}{3}$. However, the following discussion proves this case to be practically insignificant.)

For $\alpha<\frac{1}{2}$ the exponential factor in (3.20) tends to unity as $t\to\infty$ for all finite $\bar{\boldsymbol{Q}}$, whereas for $\alpha>\frac{1}{2}$ it tends to zero exponentially rapidly for any finite $\bar{\boldsymbol{Q}}$. Consequently, the appropriate limit process is

$$\boldsymbol{Q}=\bar{\boldsymbol{Q}}t^{\frac{1}{2}}. \tag{3.23}$$

For this limit process, (3.20) yields

$$\bar{P}(\bar{\boldsymbol{Q}},t\,|\,\boldsymbol{q}') \sim \Big\{1-\frac{1}{t^{\frac{1}{2}}}[\boldsymbol{A}(\boldsymbol{q}')\cdot\boldsymbol{\nabla}_{\bar{Q}}+\boldsymbol{D}_3^*(\cdot)^3\,\boldsymbol{\nabla}_{\bar{Q}}^3]$$
$$+\frac{1}{t}[\{\boldsymbol{A}_2^{(1)}+\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')\}(\cdot)^2\,\boldsymbol{\nabla}_{\bar{Q}}^2+\{\boldsymbol{D}_4^*+[\boldsymbol{D}_3^*\,\boldsymbol{A}(\boldsymbol{q}')]^{\mathrm{s}}\}(\cdot)^4\,\boldsymbol{\nabla}_{\bar{Q}}^4$$
$$+\tfrac{1}{2}[(\boldsymbol{D}_3^*)^2]^{\mathrm{s}}(\cdot)^6\,\boldsymbol{\nabla}_{\bar{Q}}^6]+O(t^{-\frac{3}{2}})\Big\}\frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\boldsymbol{D}^{*-1}\cdot\bar{\boldsymbol{Q}})}{(4\pi t)^{\frac{1}{2}n}\,|\,\boldsymbol{D}^*|^{\frac{1}{2}}}, \tag{3.24}$$

which represents an asymptotic expansion proceeding in inverse powers of $t^{\frac{1}{2}}$. The $\boldsymbol{q}'$-independent Gaussian leading-order $O(1)$-term derives from the respective leading-order terms of the even moments. The next terms, of $O(t^{-\frac{1}{2}})$, are contributed by the respective leading-order terms of the odd moments. The $O(t^{-1})$ terms are associated exclusively with the second-order terms of $\boldsymbol{M}_{2k}$. Consequently, it may be anticipated that the next terms in (3.24) will be of $O(t^{-\frac{3}{2}})$, and will be contributed by the second-order terms in $\boldsymbol{M}_{2k+1}$, etc.

A similar analysis can be pursued to obtain the asymptotic expansion for $P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')$. Thus, analogous to (3.1), we have for the Fourier transform of P,

$$\tilde{P}(\boldsymbol{\omega},\boldsymbol{q},t\,|\,\boldsymbol{q}')=\int_{Q_\infty}P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}')\exp(\mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{Q})\,\mathrm{d}\boldsymbol{Q}=\sum_{m=0}^{\infty}\frac{1}{m!}(\mathrm{i}\boldsymbol{\omega})^m(\cdot)^m\,\boldsymbol{P}_m(\boldsymbol{q},t\,|\,\boldsymbol{q}'). \tag{3.25}$$

Introduce into the right-hand side of the latter the respective asymptotic expansions (A 1) and (A 2) for $\boldsymbol{P}_{2k}$ and $\boldsymbol{P}_{2k+1}$ given in Appendix A, and use the analogue of (3.17) in conjunction with (3.18) and (3.19) to obtain

$$P(\bar{\boldsymbol{Q}},\boldsymbol{q},t\,|\,\boldsymbol{q}')\sim P_0^{\infty}(\boldsymbol{q})\frac{\exp(-\frac{1}{4}\bar{\boldsymbol{Q}}\cdot\boldsymbol{D}^{*-1}\cdot\bar{\boldsymbol{Q}})}{(4\pi t)^{\frac{1}{2}n}\,|\,\boldsymbol{D}^*|^{\frac{1}{2}}}[1+O(t^{-\frac{1}{2}})], \tag{3.26}$$

after inversion. This corresponds collectively to an equilibrium or steady-state distribution $P_0^\infty(\boldsymbol{q})$ in the local space, together with a Gaussian distribution in the global space. Only the dominant, $O(1)$-term in brackets is independent of the initial local-space coordinate $\boldsymbol{q}'$. Similar remarks to those made following (3.24), pertaining to the respective sources of the various orders-of-magnitude of the neglected terms, apply here as well.

Subsequent discussion (cf. §5) makes use of a comparison between the predictions of the present scheme and results already existing in the longitudinal dispersion literature. Thus, while generalized Taylor dispersion theory is of much broader scope and has been successfully applied to a variety of other, non-unidirectional flow cases, we nevertheless find it useful to illustrate the explicit results of the foregoing derivation within the context of the classical Taylor–Aris problem, namely that of solute dispersion in circular Poiseuille flow.

Consider the dispersion process for a pointsize Brownian tracer particle moving within a circular cylindrical tube of radius a. The conditional probability density $P \equiv P(r, \vartheta, z, t \mid r', \vartheta')$, with (r, ϑ, z) cylindrical polar coordinates, is governed by the system of equations

$$\frac{\partial P}{\partial t}+\Delta U(r)\frac{\partial P}{\partial z}-D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial P}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2 P}{\partial \vartheta^2}+\frac{\partial^2 P}{\partial z^2}\right] = 0, \tag{3.27}$$

$$\frac{\partial P}{\partial r} = 0 \quad \text{at } r = a, \tag{3.28}$$

$$|z|^m\left(P, \frac{\partial P}{\partial z}\right) = (0,\ 0) \quad \text{as } |z| \to \infty \quad (m = 0,\ 1,\ 2, \ldots), \tag{3.29a, b}$$

$$P(r, \vartheta, z, t \mid r', \vartheta') = \begin{cases} r^{-1}\delta(r-r')\,\delta(\vartheta-\vartheta')\,\delta(z) & \text{for } t = 0, \quad (3.30a) \\ 0 & \text{for } t < 0, \quad (3.30b) \end{cases}$$

$$\Delta U(r) = 2\bar{U}\left(1-\frac{r^2}{a^2}\right)-\bar{V}. \tag{3.31}$$

Here, D and $\bar{U}$ are given constants, whereas the constant $\bar{V}$ is to be determined during the course of the solution scheme. In the notation of §2 the following equivalences are readily established (cf. Brenner 1980*a*):

$$\left.\begin{aligned} &\boldsymbol{Q} = \boldsymbol{e}_z z, \quad \boldsymbol{q} = \boldsymbol{e}_r r+\boldsymbol{e}_\vartheta \vartheta, \\ &\Delta U(\boldsymbol{q}) = \boldsymbol{e}_z \Delta U(r), \quad \boldsymbol{D}(\boldsymbol{q}) = \boldsymbol{e}_z \boldsymbol{e}_z D, \\ &\boldsymbol{u}(\boldsymbol{q}) = \boldsymbol{0}, \quad \boldsymbol{d}(\boldsymbol{q}) = (\boldsymbol{e}_r \boldsymbol{e}_r+\boldsymbol{e}_\vartheta \boldsymbol{e}_\vartheta) D \\ \text{and} \quad &\boldsymbol{J} = \boldsymbol{e}_z\left(\Delta UP-D\frac{\partial P}{\partial z}\right), \quad \boldsymbol{j} = -D\left(\boldsymbol{e}_r\frac{\partial P}{\partial r}+\boldsymbol{e}_\vartheta\frac{1}{r}\frac{\partial P}{\partial \vartheta}\right), \end{aligned}\right\} \tag{3.32}$$

where $(\boldsymbol{e}_r, \boldsymbol{e}_\vartheta, \boldsymbol{e}_z)$ are orthonormal unit vectors in the circular cylindrical coordinate system.

The various polyadic coefficients required in the asymptotic expansion (3.24) for $\bar{P}$ have been calculated; they are tabulated in Appendix B. Following substitution into (3.24) and non-dimensionalization of the independent varibles according to the definitions

$$x = \frac{r}{a}, \quad x' = \frac{r'}{a}, \quad z = (2D^* t)^{\frac{1}{2}}\zeta, \quad t = \frac{\bar{U}^2 a^4}{2D^* D^2}\tau, \tag{3.33}$$

one obtains

$$\bar{P}(\zeta,\tau\,|\,\chi') \sim \frac{D}{\bar{U}a^2\tau^{\frac{1}{2}}}\left\{Z^{(0)}(\zeta)-\frac{1}{8\tau^{\frac{1}{2}}}\left[(\chi'^4-2\chi'^2+\tfrac{2}{3})\,Z^{(1)}(\zeta)+\frac{K}{720}Z^{(3)}(\zeta)\right]\right.$$

$$+\frac{1}{64\tau}\left[(\tfrac{1}{4}\chi'^8-\tfrac{10}{9}\chi'^6+\tfrac{5}{3}\chi'^4-\chi'^2+\tfrac{1}{12})\,Z^{(2)}(\zeta)+\frac{K}{2885}(\chi'^4-2\chi'^2+\tfrac{101}{336})\,Z^{(4)}(\zeta)\right.$$

$$\left.\left.+\frac{K^2}{1036800}Z^{(6)}(\zeta)\right]+O(\tau^{-\frac{3}{2}})\right\}, \tag{3.34}$$

wherein (Abramowitz & Stegun 1968)

$$Z^{(n)}(\zeta) = \frac{1}{(2\pi)^{\frac{1}{2}}}\frac{d^n}{d\zeta^n}\exp\left(-\tfrac{1}{2}\zeta^2\right) \tag{3.35}$$

and

$$K = \frac{\bar{U}^2 a^2}{D^* D}. \tag{3.36}$$

Equation (3.34) constitutes the Green function required in (2.13). Thus, for those circumstances in which the initial distribution is uniform over the cross-section of the tube, and localized at $z = 0$, we substitute $(\pi a^2)^{-1}\delta(z)$ for the generic initial distribution $f(\boldsymbol{Q}',\boldsymbol{q}')$ appearing therein to obtain

$$\bar{\Pi}(\zeta,\tau) = 2\int_0^1 \chi'\bar{P}(\zeta,\tau\,|\,\chi')\,\mathrm{d}\chi' \sim \frac{D}{\bar{U}a^2\tau^{\frac{1}{2}}}\left\{Z^{(0)}(\zeta)-\frac{K}{5760\tau^{\frac{1}{2}}}Z^{(3)}(\zeta)\right.$$

$$\left.-\frac{1}{720\tau}\left[Z^{(2)}(\zeta)+\tfrac{41}{7168}KZ^{(4)}(\zeta)-\frac{K^2}{92080}Z^{(6)}(\zeta)\right]+O(\tau^{-\frac{3}{2}})\right\}. \tag{3.37}$$

In the limit $D/\bar{U}a \ll 1$ we obtain $K \sim 48$ (cf. (B 5) of Appendix B), whence the resulting expression agrees identically with equation (4.8) of Chatwin (1970). As mentioned in the Introduction, Chatwin's result was, however, obtained via a completely different scheme.

4. The 'purely global' model

Generalized Taylor dispersion theory suggests (cf. Brenner 1980a) that $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ can be approximated for $t\to\infty$ by the $\boldsymbol{q}'$-independent field $P^{\bullet}(\boldsymbol{Q},t)$, representing the solution of the following 'model problem':

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

wherein

$$\boldsymbol{J}^{\bullet} = -\boldsymbol{D}^{\bullet}\cdot\boldsymbol{\nabla}_Q P^{\bullet}, \tag{4.2}$$

and satisfying the boundary condition

$$|\boldsymbol{Q}|^m(P^{\bullet},\boldsymbol{J}^{\bullet}) = (0,\boldsymbol{0}) \quad \text{as } |\boldsymbol{Q}|\to\infty \quad (m = 0,\,1,\,2,\ldots) \tag{4.3}$$

and initial condition

$$P^{\bullet} = \begin{cases}\delta(\boldsymbol{Q}) & \text{for } t = 0, \quad (4.4a)\\ 0 & \text{for } t < 0. \quad (4.4b)\end{cases}$$

The initial- and boundary-value problem posed by these equations constitutes the 'purely global' counterpart of the problem posed by (2.1)–(2.6).

It is easy to show that the purely global moments $\boldsymbol{M}^{\bullet}_m(t)$, defined as

$$\boldsymbol{M}^{\bullet}_m = \int_{Q_\infty} \boldsymbol{Q}^m P^{\bullet}\, \mathrm{d}\boldsymbol{Q}, \tag{4.5}$$

are *exactly* given by the expressions

$$\boldsymbol{M}^{\bullet}_{2k} = \frac{(2k)!}{k!}[(\boldsymbol{D}^{\bullet} t)^k]^{\mathrm{s}}, \quad \boldsymbol{M}^{\bullet}_{2k+1} = \boldsymbol{0} \quad (k = 0, 1, 2, \ldots), \tag{4.6a, b}$$

according as m is even or odd. Thus, the choice

$$\boldsymbol{D}^{\bullet} = \boldsymbol{D}^{*} \tag{4.7}$$

of phenomenological coefficient in the constitutive equation (4.2) assures asymptotic matching of $\boldsymbol{M}^{\bullet}_{2k}$ with the leading term of $\boldsymbol{M}_{2k}$ in (3.14). Neither the higher-order terms of the even moments nor any of the odd moments (cf. (3.15)) can be matched by the purely global model; yet (3.24) *et seq.* demonstrate that this is irrelevant insofar as the dominant, leading-order behaviour of the coarse-grained density $\bar{P}$ is concerned.

It is seemingly natural to seek to improve the formulation of the model problem so as to make the global model density $P^{\bullet}(\boldsymbol{Q},t)$ approximate the asymptotic behaviour of $\bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}')$ to higher orders (cf. §5). Towards this end one should attempt to remove the $\boldsymbol{q}'$ dependence from the higher-order terms in $\bar{P}$ appearing in (3.24), while simultaneously modifying the model constitutive equation (4.2) for $\boldsymbol{J}^{\bullet}$.

The former goal is apparently achieved by transforming the global variable from $\boldsymbol{Q}$ to a new coordinate $\boldsymbol{Q}^{(1)}(\boldsymbol{Q}\,|\,\boldsymbol{q}')$, defined as

$$\boldsymbol{Q}^{(1)} = \boldsymbol{Q} - \boldsymbol{A}(\boldsymbol{q}'), \tag{4.8}$$

with $\boldsymbol{A}$ as given in (A 3). This choice corresponds to a frame of reference whose origin coincides with the long-time-average global tracer location (as opposed to the former frame, which only travels with the average global velocity of the tracer).

The total moments in the new frame of reference are

$$\boldsymbol{M}^{(1)}_{2k} \sim \frac{(2k)!}{k!}[(\boldsymbol{D}^{*} t)^k]^{\mathrm{s}} + \frac{(2k)!}{(k-1)!}[(\boldsymbol{D}^{*} t)^{k-1}\{\boldsymbol{A}^{(1)}_2 + \boldsymbol{A}^{(2)}_2(\boldsymbol{q}') - \tfrac{1}{2}\boldsymbol{A}^2(\boldsymbol{q}')\}]^{\mathrm{s}}$$
$$+ \frac{(2k)!}{(k-2)!}[(\boldsymbol{D}^{*} t)^{k-2}\boldsymbol{D}^{*}_4\, t]^{\mathrm{s}} + \frac{(2k)!}{2(k-3)!}[(\boldsymbol{D}^{*} t)^{k-3}(\boldsymbol{D}^{*}_3\, t)^2]^{\mathrm{s}} + O(t^{k-2}) \tag{4.9}$$

and

$$\boldsymbol{M}^{(1)}_{2k+1} \sim \frac{(2k+1)!}{(k-1)!}[(\boldsymbol{D}^{*} t)^{k-1}\boldsymbol{D}^{*}_3\, t]^{\mathrm{s}} + O(t^{k-1}). \tag{4.10}$$

(In particular, $M^{(1)}_1 \sim \exp(t\,|\,\boldsymbol{q}')$. Since, by definition, the first-order total moment represents the average tracer location within the global subspace, this asymptotic behaviour is in accordance with the interpretation given above to the transformation (4.8).) Thus, $\boldsymbol{q}'$ is eliminated from the respective leading-order terms of $\boldsymbol{M}^{(1)}_{2k+1}$.

If the model constitutive equation (4.2) is now modified to the form

$$\boldsymbol{J}^{(1)\bullet} = -\boldsymbol{D}^{\bullet} \cdot \boldsymbol{\nabla}_{Q^{(1)}} P^{(1)\bullet} + \boldsymbol{D}^{\bullet}_3(\cdot)^2 \boldsymbol{\nabla}_{Q^{(1)}} \boldsymbol{\nabla}_{Q^{(1)}} P^{(1)\bullet}, \tag{4.11}$$

the following asymptotic expressions result:

$$\boldsymbol{M}_{2k}^{(1)\bullet} \sim \frac{(2k)!}{k!}[(\boldsymbol{D}^{\bullet}t)^{k}]^{s} + O(t^{k-1}) \tag{4.12}$$

and

$$\boldsymbol{M}_{2k+1}^{(1)\bullet} \sim \frac{(2k+1)!}{(k-1)!}[(\boldsymbol{D}^{\bullet}t)^{k-1}\boldsymbol{D}_3^{\bullet}t]^{s} + O(t^{k-1}). \tag{4.13}$$

These will be asymptotically matched to the corresponding terms in $\boldsymbol{M}_{2k}^{(1)}$ and $\boldsymbol{M}_{2k+1}^{(1)}$, respectively, provided that one chooses the phenomenological coefficients in the model constitutive equation (4.11) such that

$$\boldsymbol{D}^{\bullet} = \boldsymbol{D}^{*} \quad \text{and} \quad \boldsymbol{D}_3^{\bullet} = \boldsymbol{D}_3^{*}. \tag{4.14a, b}$$

It is impossible to remove the $\boldsymbol{q}'$ dependence from the respective second-order terms in $\boldsymbol{M}_{2k}$ and $\boldsymbol{M}_{2k+1}$. Thus, the addition of higher-order gradient terms to the model constitutive equation for $\boldsymbol{J}^{\bullet}$ results in additional terms in $P^{\bullet}$ of the same order as the ($\boldsymbol{q}'$-dependent) error terms in $\bar{P}$. Hence, the introduction of higher-order global gradient terms cannot lead to a consistent improvement of the approximation. Furthermore, even the apparent improvement associated with the above modifications (4.8) and (4.11) is of doubtful merit since a $\boldsymbol{q}'$ dependence of the model density $P^{\bullet}$ is implicit in the specific choice of reference frame. As such, the resulting model problem is not purely global in structure. The net effect of this is that each different (local-space) initial-value problem arising from the same overall conservation, constitutive and boundary-value formulation needs to be treated as a distinctly new problem in its own right. In such circumstances, where the asymptotic behaviour is dependent upon initial, local-space conditions, it is legitimate to question whether Taylor dispersion theory offers any real computational or conceptual advantages over the exact formulation of the original problem posed by (2.1)–(2.6).

In summary, although the simplest global model suggested by generalized Taylor dispersion theory enables only asymptotic matching of the leading orders of the even moments, $\boldsymbol{M}_{2k}$ and $\boldsymbol{M}_{2k}^{\bullet}$, respectively, the resulting global model density $P^{\bullet}$ approximates the exact, local-space-averaged density $\bar{P}$ correctly to leading order. No modification of the model is possible that will improve the asymptotic approximation of $\bar{P}$ by $P^{\bullet}$ while simultaneously retaining a genuinely purely global model of the transport phenomena.

5. Relation to moment-gradient expansions

It appears desirable to clarify the relation between the present results and dispersion models deriving from moment-gradient expansions. These models, originally pioneered by Gill & Sankarasubramanian (1970, 1971) in the context of unidirectional tube flows, were recently applied more generally by Nadim *et al.* (1986*b*) to flows in the abstract $\boldsymbol{Q}_{\infty} \oplus \boldsymbol{q}_{o}$ phase space. The cornerstone underlying these schemes is the assumed existence of a 'separation-of-variables' expansion of the form

$$P(\boldsymbol{Q},\boldsymbol{q},t\,|\,\boldsymbol{q}') = \sum_{k=0}^{\infty} \boldsymbol{F}_k(\boldsymbol{q},t\,|\,\boldsymbol{q}')\,(\cdot)^k\,\nabla_Q^k \bar{P}(\boldsymbol{Q},t\,|\,\boldsymbol{q}'), \tag{5.1}$$

where, in the course of the derivation, the k-adic coefficients $\boldsymbol{F}_k$ are explicitly expressed in terms of $\boldsymbol{P}_j$ and $\boldsymbol{M}_j$ $(j = 0, 1, \ldots, k)$. Integration of (2.1) over $\boldsymbol{q}_o$, jointly with boundary condition (2.5), then leads to the local-space-averaged problem

$$\frac{\partial \bar{P}}{\partial t} + \nabla_Q \cdot \bar{\boldsymbol{J}} = 0 \tag{5.2}$$

and

$$\bar{\boldsymbol{J}} = \sum_{l=0}^{\infty} (-1)^l \boldsymbol{X}_{l+1}(t \mid \boldsymbol{q}') (\cdot)^l \nabla_Q^l \bar{P}(\boldsymbol{Q}, t \mid \boldsymbol{q}'), \tag{5.3}$$

in which the l-adic coefficients $\boldsymbol{X}_l(t \mid \boldsymbol{q}')$ possess the functional dependence indicated by their arguments. The local-space-averaged global flux vector $\bar{\boldsymbol{J}}$ is obtained from its definition in terms of the $\boldsymbol{q}_o$-space quadrature of $\boldsymbol{J}$ (cf. (2.2)) as

$$\bar{\boldsymbol{J}}(\boldsymbol{Q}, t \mid \boldsymbol{q}') = \int_{q_o} (\Delta \boldsymbol{U} P - \boldsymbol{D} \cdot \nabla_Q P) \, \mathrm{d}\boldsymbol{q}, \tag{5.4}$$

together with the assumed moment-gradient expansion (5.1).

Gill & Sankarasubramanian (1970, 1971) focus on obtaining an 'exact' solution of (5.2) and (5.3) valid for all $t > 0$. Towards this goal they truncate the series (5.3) immediately after the diffusion term $\boldsymbol{X}_2 \cdot \nabla_Q \bar{P}$, while retaining the dyadic $\boldsymbol{X}_2$ as a time-dependent phenomenological coefficient. Unlike the present formulation for a single Brownian tracer, their solution does not explicitly exhibit the indicated dependence of $\boldsymbol{X}_2(t \mid \boldsymbol{q}')$ upon the initial condition embodied in $\boldsymbol{q}'$. The latter is instead built into their development, which is restricted to the 'product' class,

$$f(\boldsymbol{Q}, \boldsymbol{q}) = f_1(\boldsymbol{Q}) f_2(\boldsymbol{q}), \tag{5.5}$$

of initial conditions (cf. (2.10)). For the sake of simplicity we select for comparison purposes an initial condition in which the solute is uniformly distributed over the tube cross-section and localized at $z = 0$, for which circumstances the asymptotic expansion (3.37) has already been obtained.

The comparable result of Gill & Sankarasubramanian (1971), recast in the present notation, is

$$\bar{\Pi}(\zeta, \tau) \sim \frac{D}{\bar{U} a^2 \tau^{\frac{1}{2}}} \left[Z^{(0)}(\zeta) - \frac{1}{720\tau} Z^{(2)}(\zeta) + O(\tau^{-2}) \right] \tag{5.6}$$

(cf. Appendix B). Comparison with (3.37) reveals that whereas both results agree to leading order as $\tau \to \infty$, they disagree insofar as the correction terms are concerned. Explicitly, the $O(\tau^{-\frac{1}{2}})$-term is missing altogether from the latter result – while, of the $O(\tau^{-1})$-terms, only the one involving $Z^{(2)}(\zeta)$ appears. Our resolution of this discrepancy serves to illuminate the inherent difference between the respective two schemes.

DeGance & Johns (1978*a*, *b*) provide a somewhat more rigorous basis for the (otherwise *ad hoc*) moment-gradient expansion in the case of unidirectional duct flows. They prove that the first $m+1$ Hermite total moments of $\bar{P}^{(m)}$ (the latter being the solution of (5.2) and (5.3), with (5.3) truncated at $l = m-1$) coincide with the corresponding moments of $\bar{P}$ for all $t > 0$.† (Similarly, truncation of (5.1) beyond

† Since $\bar{P}$ is determined by the totality of its moments (Reichl 1980), this result is insufficient to assure the accuracy of the approximation $\bar{P}^{(m)}$ associated with a specific finite truncation at $l = m-1$. Furthermore, it is well known (cf. Pawula 1967) that retention of any finite number of terms $l \geqslant 2$ in (5.3) can result in a physically unacceptable negative probability density $\bar{P}^{(m)} < 0$ for some combinations of parameters.

$k = m$ assures equality of the first $m+1$ local Hermite moments of the corresponding approximation $P^{(m)}$ with those of P, respectively, for all $t > 0$.) This criterion of equality is inherently different from that of our present scheme, which involves asymptotic matching for $t \to \infty$ of the leading orders of *all* the moments.

The origin of the difference between the respective asymptotic expansions of $\bar{\Pi}(\zeta, \tau)$ is now clear. The solution of Gill & Sankarasubramanian gives $\boldsymbol{M}_2$ correctly for all $t > 0$. For $t \to \infty$ this, in turn, assures matching of the dominant asymptotic behaviour for all $\boldsymbol{M}_{2k}$ (and, concomitantly, that of $\bar{P}$ and $\bar{\Pi}$ too). This accounts for the agreement of the respective leading-order terms of (3.37) and (5.6). As is evident from the present derivation, the $O(\tau^{-\frac{1}{2}})$ first-order correction term originates in the leading asymptotic behaviour of the odd moments $\boldsymbol{M}_{2k+1}$, and thus cannot be accounted for by the Gill & Sankarasubramanian asymptotic approximation scheme. From the $O(\tau^{-1})$-terms, we find in (5.6) only $-Z^{(2)}(\zeta)/720\tau$, whose source is $\boldsymbol{M}_2$. The remaining $O(\tau^{-1})$-terms appear for the first time in $\boldsymbol{M}_4$ and $\boldsymbol{M}_6$, respectively, and hence are not to be found in (5.6).

We now turn to yet another aspect of the dispersion models resulting from moment-gradient expansions. As $t \to \infty$ the coefficients of (5.3) are known (cf. Gill & Sankarasubramanian 1970, 1971; Nadim *et al.* 1986*b*) to approach (using the present notation and frame of reference) the respective $\boldsymbol{q}'$-independent constant limits

$$\boldsymbol{X}_1 = \boldsymbol{0}, \quad \boldsymbol{X}_2 = \boldsymbol{D}^*, \quad \boldsymbol{X}_3 = \boldsymbol{D}_3^*, \ldots \tag{5.7}$$

exponentially rapidly. Consequently, it was implied (Chatwin 1972; Nadim *et al.* 1986*b*) that the accuracy of the purely global macrotransport model $P^{\bullet}$ for $\bar{P}$ could be improved through replacement of the original constitutive equation (4.2) by its 'non-truncated generalization'

$$\bar{\boldsymbol{J}}^{\bullet} = \sum_{l=0}^{\infty} (-1)^l \boldsymbol{X}_{l+1}^* (\cdot)^l \nabla_Q^l P^{\bullet}, \tag{5.8}$$

where the constant phenomenological l-adic coefficients $\boldsymbol{X}_l^*$ are the respective long-time limits of $\boldsymbol{X}_l$ $(l = 0, 1, 2, \ldots)$. This proposal appears to conflict with the conclusion drawn in §4.

In order to clarify this point we consider the cumulant expansion

$$\tilde{\bar{P}}(\omega, t \mid \boldsymbol{q}') = \exp\left[\sum_{n=1}^{\infty} \frac{(\mathrm{i}\boldsymbol{\omega})^n}{n!} (\cdot)^n \boldsymbol{C}_n(t \mid \boldsymbol{q}')\right] \tag{5.9}$$

in what follows. Perform the Fourier transform of the macrotransport equation (5.2) and make use of the proposed gradient expansion (5.3) together with the identity inverse to (3.19) to obtain

$$\frac{\partial \tilde{\bar{P}}}{\partial t} - \sum_{l=1}^{\infty} \boldsymbol{X}_l(t \mid \boldsymbol{q}') (\cdot)^l (\mathrm{i}\boldsymbol{\omega})^l \tilde{\bar{P}} = 0. \tag{5.10}$$

Introduction of the cumulant expansion (5.9) into the latter shows, provided the moment-gradient expansion exists, that its coefficients are related to the cumulants via the expressions

$$\boldsymbol{X}_m(t \mid \boldsymbol{q}') = \frac{1}{m!} \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{C}_m(t \mid \boldsymbol{q}') \quad (m = 1, 2, 3, \ldots). \tag{5.11}$$

Utilize the relations existing between the cumulants and the total moments (Abramowitz & Stegun 1968) together with the foregoing asymptotic results (3.14) and (3.15) to obtain

$$\left.\begin{aligned} \boldsymbol{C}_1 &= \boldsymbol{M}_1 \sim \boldsymbol{A}(\boldsymbol{q}')+\exp(t\,|\,\boldsymbol{q}'), \\ \boldsymbol{C}_2 &= \boldsymbol{M}_2-\boldsymbol{M}_1\boldsymbol{M}_1 \sim 2[\boldsymbol{D}^*t+\boldsymbol{A}_2^{(1)}+\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')-\tfrac{1}{2}\boldsymbol{A}^2(\boldsymbol{q}')]+\exp(t\,|\,\boldsymbol{q}'), \\ \boldsymbol{C}_3 &= \boldsymbol{M}_3-3[\boldsymbol{M}_1\boldsymbol{M}_2]^s+2\boldsymbol{M}_1^3 \sim 3!\boldsymbol{D}_3^*t+\boldsymbol{A}_3(\boldsymbol{q}')+\exp(t\,|\,\boldsymbol{q}'), \\ \boldsymbol{C}_4 &= \boldsymbol{M}_4-3[\boldsymbol{M}_2^2]^s-4[\boldsymbol{M}_1\boldsymbol{M}_3]^s+12[\boldsymbol{M}_1^2\boldsymbol{M}_2]^s-6\boldsymbol{M}_1^4 \sim 4!\boldsymbol{D}_4^*t+\boldsymbol{A}_4(\boldsymbol{q}')+\exp(t\,|\,\boldsymbol{q}'). \end{aligned}\right\} \tag{5.12}$$

Thus, according to (5.11), the coefficients $\boldsymbol{X}_n$ do indeed attain their respective invariant limits, namely (5.7), exponentially rapidly. However, the probability density $\bar{P}$ depends upon the cumulants themselves, and not merely upon their asymptotic growth rates; accordingly, the effect of the $O(1)$, $\boldsymbol{q}'$-dependent terms appearing in the respective right-hand sides of (5.12) does not vanish in the limit as $t \to \infty$. This leads us to reiterate our main conclusion, namely that no systematic improvement of the purely global model $P^{\bullet}$ can be achieved through the addition of higher-order gradient terms to the constitutive equation for $\boldsymbol{J}^{\bullet}$.

A further comment seems warranted since it appears paradoxical that the higher-order invariants $\boldsymbol{X}_n^*$ can be defined, and nevertheless not serve to improve the approximation of $\bar{P}$ by $P^{\bullet}$. In resolving this paradox it should be borne in mind that these invariants are based on the asymptotic rates of change of the cumulants (and, hence, of the total moments). As such, they represent a Lagrangian description of the movement of the Brownian tracer in the global subspace. On the other hand, the proposed incorporation of these invariants as phenomenological coefficients in the constitutive relation governing the purely global model represents a Eulerian description of the macrotransport process. The irreconcilability of these alternative descriptions, as embodied in our negative conclusions, represents yet another manifestation of the fact that the Lagrangian view represents the more fundamental of the two in the present macrotransport context; that is, whereas Eulerian and Lagrangian views are completely interchangeable in the *exact*, microtransport description of the transport process, they are no longer formally equivalent in the *approximate* or coarse-grained, macrotransport description of this same process. In our opinion, failure to appreciate the ramifications of this fundamental disparity is ubiquitous in the non-equilibrium statistical-mechanics literature concerned with coarse-graining schemes!

I.F. is grateful to the Bantrell Foundation for a postdoctoral fellowship administered by the Massachusetts Institute of Technology. H.B. was supported by the National Science Foundation and the US Army Research Office.

Appendix A. Long-time asymptotic expansions of $\boldsymbol{P}_m$

Tedious calculations deriving from (3.10) and (3.11) eventually lead to the following expansions of the local moments:

Even orders ($m = 2k$):

$$\begin{aligned}\boldsymbol{P}_{2k}(\boldsymbol{q},t\,|\,\boldsymbol{q}') \sim P_0^\infty(\boldsymbol{q})\Big\{&\frac{(2k)!}{k!}[(\boldsymbol{D}^*t)^k]^s+\frac{(2k)!}{(k-1)!}[(\boldsymbol{D}^*t)^{k-1}\{\boldsymbol{A}_2^{(1)}+\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')+\boldsymbol{B}(\boldsymbol{q})\boldsymbol{A}(\boldsymbol{q}')\\ &+\boldsymbol{B}_2(\boldsymbol{q})\}]^s+\frac{(2k)!}{(k-2)!}[(\boldsymbol{D}^*t)^{k-2}\{\boldsymbol{D}_4^*+\boldsymbol{D}_3^*\boldsymbol{A}(\boldsymbol{q}')+\boldsymbol{D}_3^*\boldsymbol{B}(\boldsymbol{q})\}t]^s\\ &+\frac{(2k)!}{2(k-3)!}[(\boldsymbol{D}^*t)^{k-3}(\boldsymbol{D}_3^*t)^2]^s+O(t^{k-2})\Big\}\quad (k=0,1,2,\ldots);\end{aligned}\tag{A 1}$$

Odd orders ($m = 2k+1$):†

$$\begin{aligned}&\boldsymbol{P}_{2k+1}(\boldsymbol{q},t\,|\,\boldsymbol{q}')\\ &\sim P_0^\infty(\boldsymbol{q})\Big\{\frac{(2k+1)!}{k!}[(\boldsymbol{D}^*t)^k\{\boldsymbol{A}(\boldsymbol{q}')+\boldsymbol{B}(\boldsymbol{q})\}]^s+\frac{(2k+1)!}{(k-1)!}[(\boldsymbol{D}^*t)^{k-1}\boldsymbol{D}_3^*t]^s\\ &+\boldsymbol{A}_{2k+1}(\boldsymbol{q}')t^{k-1}+\frac{(2k+1)!}{(k-1)!}[(\boldsymbol{D}^*t)^{k-1}\{\boldsymbol{B}(\boldsymbol{q})\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')+\boldsymbol{B}(\boldsymbol{q})\boldsymbol{A}_2^{(1)}\\ &+\boldsymbol{B}_2(\boldsymbol{q})\boldsymbol{A}(\boldsymbol{q}')+\boldsymbol{B}_3(\boldsymbol{q})\}]^s+\frac{(2k+1)!}{(k-2)!}[(\boldsymbol{D}^*t)^{k-2}\{\boldsymbol{B}(\boldsymbol{q})\boldsymbol{D}_4^*+\boldsymbol{B}(\boldsymbol{q})\boldsymbol{D}_3^*\boldsymbol{A}(\boldsymbol{q}')+\boldsymbol{B}_2(\boldsymbol{q})\boldsymbol{D}_3^*\}t]^s\\ &+\frac{(2k+1)!}{2(k-3)!}[\boldsymbol{B}(\boldsymbol{q})(\boldsymbol{D}_3^*t)^2(\boldsymbol{D}^*t)^{k-3}]^s+O(t^{k-2})\Big\}\quad (k=0,1,2,\ldots).\end{aligned}\tag{A 2}$$

Appearing in the preceding pair of expansions are the following functions and constants:

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

$$P_0^\infty(\boldsymbol{q})\boldsymbol{B}(\boldsymbol{q})=\lim_{t\to\infty}\int_0^t\int_{q_0}p(\boldsymbol{q},t_1\,|\,\boldsymbol{q}_1)P_0^\infty(\boldsymbol{q}_1)\Delta\boldsymbol{U}(\boldsymbol{q}_1)\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1,\tag{A 4}$$

$$\boldsymbol{D}^*=\int_{q_0}P_0^\infty(\boldsymbol{q}_1)[\boldsymbol{D}(\boldsymbol{q}_1)+\Delta\boldsymbol{U}(\boldsymbol{q}_1)\boldsymbol{B}(\boldsymbol{q}_1)]^s\,\mathrm{d}\boldsymbol{q}_1,\tag{A 5}$$

$$P_0^\infty(\boldsymbol{q})\boldsymbol{B}_2(\boldsymbol{q})=\lim_{t\to\infty}\int_0^t\int_{q_0}p(\boldsymbol{q},t_1\,|\,\boldsymbol{q}_1)P_0^\infty(\boldsymbol{q}_1)\{\boldsymbol{D}(\boldsymbol{q}_1)+[\Delta\boldsymbol{U}(\boldsymbol{q}_1)\boldsymbol{B}(\boldsymbol{q}_1)]^s\}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1,\tag{A 6}$$

$$\begin{aligned}\boldsymbol{A}_2^{(1)}=\lim_{t\to\infty}\Big\{&\int_0^t\int_0^{t_1}\int_{q_0}\int_{q_0}[\Delta\boldsymbol{U}(\boldsymbol{q}_1)\Delta\boldsymbol{U}(\boldsymbol{q}_2)]^sP_0^\infty(\boldsymbol{q}_2)\,p(\boldsymbol{q}_1,t_1-t_2\,|\,\boldsymbol{q}_2)\\ &\times\mathrm{d}\boldsymbol{q}_2\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1-t\int_{q_0}P_0^\infty(\boldsymbol{q}_1)[\Delta\boldsymbol{U}(\boldsymbol{q}_1)\boldsymbol{B}(\boldsymbol{q}_1)]^s\,\mathrm{d}\boldsymbol{q}_1\Big\},\end{aligned}\tag{A 7}$$

$$\begin{aligned}\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')=\lim_{t\to\infty}\int_0^t\int_{q_0}\Big\{&\boldsymbol{D}(\boldsymbol{q}_1)\,p(\boldsymbol{q}_1,t_1\,|\,\boldsymbol{q}')+\int_0^{t_1}\int_{q_0}[\Delta\boldsymbol{U}(\boldsymbol{q}_1)\Delta\boldsymbol{U}(\boldsymbol{q}_2)]^s\\ &\times p(\boldsymbol{q}_1,t_1-t_2\,|\,\boldsymbol{q}_2)\,p(\boldsymbol{q}_2,t_2\,|\,\boldsymbol{q}')\Big\}\,\mathrm{d}\boldsymbol{q}_2\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1,\end{aligned}\tag{A 8}$$

† In the interests of brevity the right-hand side of (A 2) does not explicitly display *all* of the second-order $O(t^{k-1})$ terms in $\boldsymbol{P}_{2k+1}$ (the first-order $O(t^k)$ terms being those occupying the first line of (A 2)). Rather, only those terms needed to obtain the second-order terms of $\boldsymbol{P}_{2k}$ in (A 1) (when use is made of (3.10)) are explicitly presented in (A 2).

$$\boldsymbol{D}_3^* = \int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,[\boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1) + \Delta \boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1)]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1, \tag{A 9}$$

$$P_0^\infty(\boldsymbol{q})\,\boldsymbol{B}_3(\boldsymbol{q}) = \lim_{t\to\infty}\left\{\int_0^t \int_{q_o} p(\boldsymbol{q}, t-t_1\,|\,\boldsymbol{q}_1)\,P_0^\infty(\boldsymbol{q}_1)\,[\Delta \boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1) + \boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}(\boldsymbol{q}_1)]^{\mathrm{s}} \right.$$
$$\left. \times\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_1 - \int_0^t \int_0^{t_1} \int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,p(\boldsymbol{q}, t-t_2\,|\,\boldsymbol{q}_1)\,[\Delta \boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{D}^*]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}t_2\,\mathrm{d}t_1\right\} \tag{A 10}$$

and
$$\boldsymbol{D}_4^* = \int_{q_o} P_0^\infty(\boldsymbol{q}_1)\,[\Delta \boldsymbol{U}(\boldsymbol{q}_1)\,\boldsymbol{B}_3(\boldsymbol{q}_1) + \boldsymbol{D}(\boldsymbol{q}_1)\,\boldsymbol{B}_2(\boldsymbol{q}_1)]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}_1. \tag{A 11}$$

The indicial terms $\boldsymbol{A}_{2k+1}(\boldsymbol{q}')$ are functions solely of $\boldsymbol{q}'$. Moreover, any term appearing in $\boldsymbol{P}_{2k}$ or $\boldsymbol{P}_{2k+1}$ which corresponds to a negative power of t should be replaced by an exponentially small term. Inductive arguments may be invoked to straightforwardly verify the preceding results.

It is advantageous in applications to express each of the coefficients of the preceding asymptotic expansions in an alternative form as as to enable its calculation without explicit *a priori* knowledge of the time- and initial-condition-dependent function $p(\boldsymbol{q}, t\,|\,\boldsymbol{q}')$ appearing in (3.11). Towards this end, the fields $P_0^\infty(\boldsymbol{q})$, $\boldsymbol{B}(\boldsymbol{q})$, $\boldsymbol{B}_2(\boldsymbol{q})$ and $\boldsymbol{B}_3(\boldsymbol{q})$ will be represented as the respective solutions of a sequence of appropriate boundary-value problems. These, in turn, are formulated as follows: (i) substitute the asymptotic expansion (A 1) or (A 2) for $\boldsymbol{P}_m$ into both the differential equation (3.5) and boundary condition (3.7), while neglecting terms known to become exponentially small for $t\to\infty$; (ii) complete the formulation by making use of the normalization relations (3.12) in conjunction with the respective definitions of the various fields given above.

This scheme results in the following sequence of boundary-value problems defining each of the four requisite fields:

(i) $P_0^\infty(\boldsymbol{q})$:

$$\boldsymbol{\nabla}_q \cdot (\boldsymbol{u}P_0^\infty - \boldsymbol{d}\cdot\boldsymbol{\nabla}_q P_0^\infty) = 0, \tag{A 12a}$$

$$\hat{\boldsymbol{n}} \cdot (\boldsymbol{u}P_0^\infty - \boldsymbol{d}\cdot\boldsymbol{\nabla}_q P_0^\infty) = 0 \quad \text{on } \partial \boldsymbol{q}_o, \tag{A 12b}$$

and
$$\int_{q_o} P_0^\infty\,\mathrm{d}\boldsymbol{q} = 1; \tag{A 12c}$$

(ii) $\boldsymbol{B}(\boldsymbol{q})$:

$$\boldsymbol{\nabla}_q \cdot [\boldsymbol{u}P_0^\infty \boldsymbol{B} - \boldsymbol{d}\cdot\boldsymbol{\nabla}_q(P_0^\infty \boldsymbol{B})] = \Delta \boldsymbol{U} P_0^\infty, \tag{A 13a}$$

$$P_0^\infty\,\hat{\boldsymbol{n}}\cdot\boldsymbol{d}\cdot\boldsymbol{\nabla}_q \boldsymbol{B} = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o, \tag{A 13b}$$

and
$$\int_{q_o} P_0^\infty \boldsymbol{B}\,\mathrm{d}\boldsymbol{q} = \boldsymbol{0}; \tag{A 13c}$$

(iii) $\boldsymbol{B}_2(\boldsymbol{q})$:

$$\boldsymbol{\nabla}_q \cdot [\boldsymbol{u}P_0^\infty \boldsymbol{B}_2 - \boldsymbol{d}\cdot\boldsymbol{\nabla}_q(P_0^\infty \boldsymbol{B}_2)] = [\Delta \boldsymbol{U} P_0^\infty \boldsymbol{B}]^{\mathrm{s}} + P_0^\infty(\boldsymbol{D} - \boldsymbol{D}^*), \tag{A 14a}$$

$$P_0^\infty\,\hat{\boldsymbol{n}}\cdot\boldsymbol{d}\cdot\boldsymbol{\nabla}_q \boldsymbol{B}_2 = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o, \tag{A 14b}$$

and
$$\int_{q_o} P_0^\infty \boldsymbol{B}_2\,\mathrm{d}\boldsymbol{q} = \boldsymbol{0}; \tag{A 14c}$$

(iv) $\boldsymbol{B}_3(\boldsymbol{q})$:

$$\nabla_q \cdot [\boldsymbol{u} P_0^\infty \boldsymbol{B}_3 - \boldsymbol{d} \cdot \nabla_q (P_0^\infty \boldsymbol{B}_3)] = [\Delta U P_0^\infty \boldsymbol{B}_2]^s + [(\boldsymbol{D} - \boldsymbol{D}^*) P_0^\infty \boldsymbol{B}]^s - P_0^\infty \boldsymbol{D}_3^*, \tag{A 15a}$$

$$P_0^\infty \hat{\boldsymbol{n}} \cdot \boldsymbol{d} \cdot \nabla_q \boldsymbol{B}_3 = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o, \tag{A 15b}$$

and

$$\int_{q_o} P_0^\infty \boldsymbol{B}_3 \, \mathrm{d}\boldsymbol{q} = \boldsymbol{0}. \tag{A 15c}$$

It is an immediate corollary of the foregoing formulation that the coefficients $\boldsymbol{D}^*$, $\boldsymbol{D}_3^*$, and $\boldsymbol{D}_4^*$, respectively defined by (A 5), (A 9) and (A 11), may be calculated without first determining $p(\boldsymbol{q}, t \,|\, \boldsymbol{q}')$.

We now turn to express $\boldsymbol{A}(\boldsymbol{q}')$, $\boldsymbol{A}_2^{(1)}$ and $\boldsymbol{A}_2^{(2)}(\boldsymbol{q}')$. Following Smith (1981*b*), observe that for $t \to \infty$

$$\int_0^t (P_0 - P_0^\infty) \, \mathrm{d}t_1 = \int_0^t p(\boldsymbol{q}, t_1 \,|\, \boldsymbol{q}') \, \mathrm{d}t_1 \sim P_0^\infty(\boldsymbol{q}) \, a(\boldsymbol{q} \,|\, \boldsymbol{q}') + \exp \tag{A 16}$$

(cf. (3.11) *et seq.*). Upon integrating over the initial- and boundary-value problem posed for P_0, (3.5)–(3.8) for $m = 0$, and neglecting terms that are known to become exponentially small as $t \to \infty$, the function $a(\boldsymbol{q} \,|\, \boldsymbol{q}')$ is found to satisfy the following system of equations:

$$\nabla_q \cdot [\boldsymbol{u} P_0^\infty a - \boldsymbol{d} \cdot \nabla_q (P_0^\infty a)] = \delta(\boldsymbol{q} - \boldsymbol{q}') - P_0^\infty(\boldsymbol{q}), \tag{A 17a}$$

$$P_0^\infty \hat{\boldsymbol{n}} \cdot \boldsymbol{d} \cdot \nabla_q a = 0 \quad \text{on } \partial \boldsymbol{q}_o \tag{A 17b}$$

and

$$\int_{q_o} P_0^\infty(\boldsymbol{q}_1) \, a(\boldsymbol{q}_1 \,|\, \boldsymbol{q}') \, \mathrm{d}\boldsymbol{q}_1 = 0. \tag{A 17c}$$

Upon changing the integration order in (A 3) we thereby obtain

$$\boldsymbol{A}(\boldsymbol{q}') = \int_{q_o} \Delta U(\boldsymbol{q}_1) \, P_0^\infty(\boldsymbol{q}_1) \, a(\boldsymbol{q}_1 \,|\, \boldsymbol{q}') \, \mathrm{d}\boldsymbol{q}_1. \tag{A 18}$$

In a similar manner, from (A 2) for $k = 0$ one obtains for $t \to \infty$

$$\int_0^t [P_1 - P_0^\infty(\boldsymbol{A} + \boldsymbol{B})] \, \mathrm{d}t_1 \sim P_0^\infty(\boldsymbol{q}) \, \boldsymbol{a}_1(\boldsymbol{q} \,|\, \boldsymbol{q}') + \exp, \tag{A 19}$$

where $\boldsymbol{a}_1$ is governed by the boundary-value problem

$$\nabla_q \cdot [\boldsymbol{u} P_0^\infty \boldsymbol{a}_1 - \boldsymbol{d} \cdot \nabla_q (P_0^\infty \boldsymbol{a}_1)] = -P_0^\infty(\boldsymbol{A} + \boldsymbol{B}) + \Delta U P_0^\infty a \tag{A 20a}$$

and

$$P_0^\infty \hat{\boldsymbol{n}} \cdot \boldsymbol{d} \cdot \nabla_q \boldsymbol{a}_1 = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o, \tag{A 20b}$$

which determines $\boldsymbol{a}_1$ only to within an arbitrary additive constant vector. (This indeterminacy has no effect in the sequel.)

Making use of the definitions of $\boldsymbol{a}_1$ and ΔU of (A 19), (2.7) and (3.13), respectively, and of the expression (3.10) for $\boldsymbol{P}_1$ in conjunction with the decomposition (3.11) for P_0, it is readily verified through comparison with the definitions (A 7) and (A 8) that

$$\boldsymbol{A}_2^{(1)} + \boldsymbol{A}_2^{(2)}(\boldsymbol{q}') = \int_{q_o} P_0^\infty(\boldsymbol{q}_1) [\Delta U(\boldsymbol{q}_1) \, \boldsymbol{a}_1(\boldsymbol{q}_1 \,|\, \boldsymbol{q}') + \boldsymbol{D}(\boldsymbol{q}_1) \, a(\boldsymbol{q}_1 \,|\, \boldsymbol{q}')]^s \, \mathrm{d}\boldsymbol{q}_1. \tag{A 21}$$

(Since, in all of the expressions for the various moments, $\boldsymbol{A}_2^{(1)}$ and $\boldsymbol{A}_2^{(2)}$ appear only in the combination $\boldsymbol{A}_2^{(1)} + \boldsymbol{A}_2^{(2)}$, no need exists for explicit expressions for each separately.) Thus, the required asymptotic expansion is rendered independent of explicit knowledge of $p(\boldsymbol{q},t\,|\,\boldsymbol{q}')$.

In those special circumstances where the local-space velocity field $\boldsymbol{u}$ is derivable from a scalar potential, namely

$$\boldsymbol{u}(q) = -\boldsymbol{d}\cdot\nabla_q E, \tag{A 22}$$

an eigenfunction series representation of $p(\boldsymbol{q},t\,|\,\boldsymbol{q}')$ of the form (Dill & Brenner 1983*b*)

$$p(\boldsymbol{q},t\,|\,\boldsymbol{q}') = \exp\left[E(\boldsymbol{q}')\right] \sum_{n=1}^{\infty} X_n(\boldsymbol{q}')X_n(\boldsymbol{q})\exp(\lambda_n t)$$

can be utilized to readily verify the pair of 'reciprocal' relations

$$A(\boldsymbol{q}') = \boldsymbol{B}(\boldsymbol{q}'), \tag{A 23}$$

$$\boldsymbol{A}_2^{(2)}(\boldsymbol{q}') = \boldsymbol{B}_2(\boldsymbol{q}'), \tag{A 24}$$

together with the identity

$$\boldsymbol{A}_2^{(1)} = -\int_{q_0} P_0^{\infty}\,\boldsymbol{BB}\,\mathrm{d}\boldsymbol{q}. \tag{A 25}$$

In applications, (A 22) occurs most commonly in those situations for which $\boldsymbol{u} = \boldsymbol{0}$ identically.

Appendix B. The asymptotic expansion of the classical Taylor problem

B.1. *Expansion* (3.24)

The expansion of $P_0(r,\vartheta,t\,|\,r',\vartheta')$ into an eigenfunction series in terms of Bessel functions of the first kind in r and trigonometric functions in ϑ was given by Aris (1956). Thus, in principle, the coefficients of the asymptotic expansion for $\bar{P}$ could be evaluated by direct substitution followed by quadratures of (A 3)–(A 11). However, it proves far more convenient to use the alternative procedure embodied in (A 12)–(A 25). Straightforward calculations then yield

$$P_0^{\infty} = \frac{1}{\pi a^2}, \tag{B 1}$$

$$\Delta\boldsymbol{U} = \boldsymbol{e}_z\Delta U, \quad \Delta U = \bar{U}(1-2\chi^2); \tag{B 2}$$

$$\boldsymbol{B} = \boldsymbol{e}_z B, \quad B = \frac{\bar{U}a^2}{8D}(\chi^4-2\chi^2+\tfrac{2}{3}); \tag{B 3}$$

$$\boldsymbol{A} = \boldsymbol{e}_z A, \quad A = B(\chi');\dagger \tag{B 4}$$

$$\boldsymbol{D}^* = \boldsymbol{e}_z^2 D^*, \quad D^* = D+\frac{\bar{U}^2a^2}{48D}; \tag{B 5}$$

$$\boldsymbol{A}_2^{(1)} = \boldsymbol{e}_z^2 A_2^{(1)}, \quad A_2^{(1)} = -\frac{\bar{U}^2a^4}{720D^2}; \tag{B 6}$$

$$\boldsymbol{B}_2 = \boldsymbol{e}_z^2 B_2, \quad B_2 = \frac{\bar{U}^2a^4}{32D^2}(\tfrac{1}{8}\chi^8-\tfrac{5}{9}\chi^6+\tfrac{5}{6}\chi^4-\tfrac{1}{2}\chi^2+\tfrac{31}{360}); \tag{B 7}$$

$$\boldsymbol{A}_2^{(2)} = \boldsymbol{e}_z^2 A_2^{(2)}, \quad A_2^{(2)} = B_2(\chi'); \tag{B 8}$$

† Since $\boldsymbol{u} = \boldsymbol{0}$ in the present example, the requirement (A 22) is trivially satisfied.

$$\boldsymbol{D}_3^* = \boldsymbol{e}_z^3 D_3^*, \quad D_3^* = -\frac{\bar{U}^3 a^4}{2880 D^2}; \tag{B 9}$$

$$\boldsymbol{B}_3 = \boldsymbol{e}_z^3 B_3, \quad B_3 = \frac{\bar{U}^3 a^6}{4608 D^3}\left(\tfrac{1}{4}\chi^{12} - \tfrac{89}{50}\chi^{10} + 5\chi^8 - 7\chi^6 + \tfrac{91}{20}\chi^4 - \tfrac{7}{10}\chi^2 - \tfrac{109}{700}\right); \tag{B 10}$$

$$\boldsymbol{D}_4^* = \boldsymbol{e}_z^4 D_4^*, \quad D_4^* = -\frac{41}{2580480}\frac{\bar{U}^4 a^6}{D^3}. \tag{B 11}$$

The functions B, B_2 and B_3 coincide with the respective functions $g^{(1)}$, $g^{(2)}$ and $g^{(3)}$ of Chatwin (1970).

B.2. *Gill & Sankarasubramanian's* (1971) *expansion*, (5.6)

The comparable result of Gill & Sankarasubramanian (1971) for this case (their equations (57) and (58), recast in the present notation) is

$$\bar{\Pi}(z,t) = \frac{1}{2(\pi\xi)^{\frac{1}{2}}}\exp\left(-\frac{z^2}{4\xi}\right), \tag{B 12}$$

where
$$\xi = \int_0^t X_2(t_1)\,\mathrm{d}t_1. \tag{B 13}$$

As $t \rightarrow \infty$ we obtain (their (1970) equation (23), again in present notation)

$$\xi \sim D^* t + L + \exp. \tag{B 14}$$

Substitute the latter into (B 12) and transform from (z,t) to the non-dimensional variables (ζ, τ) (cf. (3.33)) to obtain

$$\bar{\Pi}(\zeta,\tau) \sim \frac{D}{\bar{U}a^2 \tau^{\frac{1}{2}}}\left[Z^{(0)}(\zeta) + \frac{D^2 L}{\bar{U}^2 a^4 \tau} Z^{(2)}(\zeta) + O(\tau^{-2})\right]. \tag{B 15}$$

The time-independent quantity L could, in principle, be evaluated by summing an appropriate infinite series of Bessel functions and their eigenvalues. It is, however, much simpler to effect its calculation via the alternative methods of Appendix A by making use of relevant results of Nadim *et al.* (1986*b*), namely

$$\begin{aligned}\xi = \int_0^t \boldsymbol{X}_2(t_1\,|\,\boldsymbol{q}')\,\mathrm{d}t_1 &= -\int_0^t\int_{q_0} [\boldsymbol{F}_1(\boldsymbol{q},t_1\,|\,\boldsymbol{q}')\,\Delta\boldsymbol{U}(\boldsymbol{q}) - F_0(\boldsymbol{q},t_1\,|\,\boldsymbol{q}')\,\boldsymbol{D}(\boldsymbol{q})]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}\,\mathrm{d}t_1\\ &= \int_0^t\int_{q_0} [\boldsymbol{P}_1(\boldsymbol{q},t_1\,|\,\boldsymbol{q}')\,\Delta\boldsymbol{U}(\boldsymbol{q}) + P_0(\boldsymbol{q},t_1\,|\,\boldsymbol{q}')\,\boldsymbol{D}(\boldsymbol{q})]^{\mathrm{s}}\,\mathrm{d}\boldsymbol{q}\,\mathrm{d}t_1\\ &\quad - \int_0^t [\boldsymbol{M}_1(t_1\,|\,\boldsymbol{q}')\int_{q_0} P_0(\boldsymbol{q},t_1\,|\,\boldsymbol{q}')\,\Delta\boldsymbol{U}(\boldsymbol{q})\,\mathrm{d}\boldsymbol{q}]^{\mathrm{s}}\,\mathrm{d}t_1.\end{aligned} \tag{B 16}$$

Integration of (3.10) over $\boldsymbol{q}_o$ while using the normalization condition (3.12) shows that the first term on the right-hand side of the latter equation is $\frac{1}{2}\boldsymbol{M}_2(t\,|\,\boldsymbol{q}')$. Similarly, integration of (3.5), in conjunction with the boundary condition (3.7), shows the remaining term to be $\frac{1}{2}\boldsymbol{M}_1^2(t\,|\,\boldsymbol{q}')$. Hence,

$$\xi = \tfrac{1}{2}(\boldsymbol{M}_2 - \boldsymbol{M}_1\boldsymbol{M}_1). \tag{B 17}$$

In the present example, $\boldsymbol{\xi} = \boldsymbol{e}_z^2 \xi$ and $\boldsymbol{M}_m = \boldsymbol{e}_z^m M_m$, where

$$M_m = \int_{-\infty}^{\infty} z^m \bar{\Pi}(z,t)\,\mathrm{d}z = (2D^*t)^{(m+1)/2} \int_{-\infty}^{\infty} \zeta^m \bar{\Pi}(\zeta,\tau)\,\mathrm{d}\zeta. \tag{B 18}$$

Use of the long-time asymptotic expansion (3.37) of $\bar{\Pi}(\zeta,\tau)$ thereby yields

$$\xi \sim D^*t + A_2^{(1)} + \exp. \tag{B 19}$$

Comparison with (B 14) reveals that $L = A_2^{(1)}$. Substitution of the explicit formula (B 6) for the latter constant into (B 15) thereby yields (5.6).

REFERENCES

ABRAMOWITZ, M. & STEGUN, I. A. 1968 *Handbook of Mathematical Functions*. Dover.

ADLER, P. M. & BRENNER, H. 1984 Transport processes in spatially periodic capillary networks II. Taylor dispersion with mixing vertices. *PhysicoChem. Hydrodyn.* **5**, 269–285.

ARIS, R. 1956 On the dispersion of solute in a fluid flowing through a tube. *Proc. R. Soc. Lond.* A **235**, 67–77.

BRENNER, H. 1979 Taylor dispersion in systems of sedimenting nonspherical Brownian particles: I. Homogeneous, centrosymmetric, axisymmetric particles. *J. Colloid Interface Sci.* **71**, 189–208.

BRENNER, H. 1980*a* A general theory of Taylor dispersion phenomena. *PhysicoChem. Hydrodyn.* **1**, 91–123.

BRENNER, H. 1980*b* Dispersion resulting from flow through spatially periodic porous media. *Phil. Trans. R. Soc. Lond.* A **297**, 81–133.

BRENNER, H. 1981 Taylor dispersion in systems of sedimenting nonspherical Brownian particles II. Homogeneous ellipsoidal particles. *J. Colloid Interface Sci.* **80**, 548–588.

BRENNER, H. 1982*a* A general theory of Taylor dispersion phenomena II. An extension. *PhysicoChem. Hydrodyn.* **3**, 139–157.

BRENNER, H. 1982*b* A general theory of Taylor dispersion phenomena IV. Direct coupling effects. *Chem. Engng Commun.* **18**, 355–379.

BRENNER, H. & ADLER, P. M. 1982 Dispersion resulting from flow through spatially periodic porous media II. Surface and intraparticle transport. *Phil. Trans. R. Soc. Lond.* A **307**, 149–200.

BRENNER, H. & GAYDOS, L. J. 1977 The constrained Brownian movement of spherical particles in cylindrical pores of comparable radius: Models of the diffusive and convective transport of solute molecules in membranes and porous media. *J. Colloid Interface Sci.* **58**, 312–356.

BRENNER, H., NADIM, A. & HABER, S. 1987 Long-time molecular diffusion, sedimentation and Taylor dispersion of a fluctuating cluster of interacting Brownian particles. *J. Fluid Mech.* **183**, 511–542.

CHAPMAN, S. & COWLING, T. G. 1961 *The Mathematical Theory of Non-Uniform Gases*, 2nd edn. Cambridge University Press.

CHATWIN, P. C. 1970 The approach to normality of the concentration distribution of a solute in a solvent flowing along a straight pipe. *J. Fluid Mech.* **43**, 321–357.

CHATWIN, P. C. 1972 The cumulants of the distribution of concentration of a solute dispersing in solvent flowing through a tube. *J. Fluid Mech.* **51**, 63–67.

CHATWIN, P. C. & SULLIVAN, P. J. 1982 The effect of aspect ratio on longitudinal diffusivity in rectangular channels. *J. Fluid Mech.* **120**, 347–358.

DEGANCE, A. E. & JOHNS, L. E. 1978*a* The theory of dispersion of chemically active solutes in a rectilinear flow field. *Appl. Sci. Res.* **34**, 189–225.

DEGANCE, A. E. & JOHNS, L. E. 1978*b* On the dispersion coefficients for Poiseuille flow in a circular cylinder. *Appl. Sci. Res.* **34**, 227–258.

DEGANCE, A. E. & JOHNS, L. E. 1985 The theory of dispersion of chemically active solutes in a rectilinear flow field: The vector problem. *Appl. Sci. Res.* **42**, 55–88.

DILL, L. H. & BRENNER, H. 1982*a* A general theory of Taylor dispersion phenomena III. Surface transport. *J. Colloid Interface Sci.* **85**, 101–117.

DILL, L. H. & BRENNER, H. 1982*b* A general theory of Taylor dispersion phenomena V. Time-periodic convection. *PhysicoChem. Hydrodyn.* **3**, 267–292.

DILL, L. H. & BRENNER, H. 1983*a* Dispersion resulting from flow through spatially periodic porous media III. Time-periodic processes. *PhysicoChem. Hydrodyn.* **4**, 279–302.

DILL, L. H. & BRENNER, H. 1983*b* A general theory of Taylor dispersion phenomena VI. Langevin methods. *J. Colloid Interface Sci.* **93**, 343–365.

DOSHI, M. R., DAIYA, P. M. & GILL, W. N. 1978 Three-dimensional laminar dispersion in open and closed rectangular conduits. *Chem. Engng Sci.* **33**, 795–804.

DUNGAN, S. R. & BRENNER, H. 1988 Sedimentation and dispersion of nonneutrally buoyant Brownian particles in cellular circulatory flows simulating local fluid agitation. *Phys. Rev. A* **38**, 3601–3608.

GAJDOS, L. J. & BRENNER, H. 1978 Flow field fractionation: Extensions to non-spherical particles and wall effects. *Sep. Sci. Technol.* **13**, 215–240.

GILL, W. N. & SANKARASUBRAMANIAN, R. 1970 Exact analysis of unsteady convective-diffusion. *Proc. R. Soc. Lond.* A **316**, 341–350.

GILL, W. N. & SANKARASUBRAMANIAN, R. 1971 Dispersion of a nonuniform slug in time-dependent flow. *Proc. R. Soc. Lond.* A **322**, 101–117.

MAURI, R. & BRENNER, H. 1989 Rheological properties of suspensions determined by momentum tracer methods (to be published).

MAVROVOUNIOTIS, G. M. & BRENNER, H. 1988 Dispersion of Brownian spheres in cylindrical pores. *J. Colloid Interface Sci.* **124**, 269–283.

NADIM, H. & BRENNER, H. 1989 Longtime nonpreaveraged diffusion and sedimentation properties of flexible Brownian dumbbells. *Physicochem. Hydrodyn.* (in press).

NADIM, A., COX, R. G. & BRENNER, H. 1986*a* Taylor dispersion in concentrated suspensions of rotating cylinders. *J. Fluid Mech.* **164**, 185–215.

NADIM, A., PAGITSAS, M. & BRENNER, H. 1986*b* Higher-order moments in macrotransport processes. *J. Chem. Phys.* **85**, 5238–5245.

PAWULA, R. F. 1967 Approximation of the linear Boltzmann equation by the Fokker–Planck equation. *Phys. Rev.* **162**, 186–188.

REICHL, L. E. 1980 *A Modern Course in Statistical Physics*, p. 143. University of Texas Press.

SANKARASUBRAMANIAN, R. & GILL, W. N. 1973 Unsteady convective-diffusion with interphase mass transfer. *Proc. R. Soc. Lond.* A **333**, 115–132.

SHAPIRO, M. & BRENNER, H. 1986 Taylor dispersion of chemically reactive species: Irreversible first-order reactions in bulk and on boundaries. *Chem. Engng Sci.* **41**, 1417–1433.

SHAPIRO, M. & BRENNER, H. 1987*a* Chemically reactive generalized Taylor dispersion phenomena. *AIChE J.* **33**, 1155–1167.

SHAPIRO, M. & BRENNER, H. 1987*b* Green's function formalism in generalized Taylor dispersion theory. *Chem. Engng Commun.* **55**, 19–27.

SHAPIRO, M. & BRENNER, H. 1988 Dispersion of a chemically reactive solute in a spatially periodic model of a porous medium. *Chem. Engng. Sci.* **43**, 551–571.

SHAPIRO, M. & BRENNER, H. 1989 Dispersion/reaction model of aerosol filtration by porous filters. *J. Aerosol Sci.* (submitted).

SHAPIRO, M., ORON, A. & GUTFINGER, C. 1989 Electrostatic precipitation of charged particles from a turbulent flow between coaxial cylinders. *J. Colloid Interface Sci.* (in press).

SMITH, R. 1981*a* A delay-diffusion description for contaminant dispersion. *J. Fluid Mech.* **105**, 469–486.

SMITH, R. 1981*b* The importance of discharge siting upon contaminant dispersion in narrow rivers and estuaries. *J. Fluid Mech.* **108**, 43–53.

SMITH, R. 1985 When and where to put a discharge in an oscillatory flow. *J. Fluid Mech.* **153**, 479–499.

SMITH, R. 1987*a* Diffusion in shear flows made easy: the Taylor limit. *J. Fluid Mech.* **175**, 201–214.

SMITH, R. 1987*b* Shear dispersion looked at from a new angle. *J. Fluid Mech.* **182**, 447–466.

TAYLOR, G. I. 1953 Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond.* A **219**, 186–203.

TAYLOR, G. I. 1954 Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. R. Soc. Lond.* A **225**, 473–477.