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Long-time molecular diffusion, sedimentation and Taylor dispersion of a fluctuating cluster of interacting Brownian particles

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Generalized Taylor dispersion theory, incorporating so-called coupling effects, is used to calculate the transport properties of a single deformable 'chain' composed of hydrodynamically interacting rigid Brownian particles bound together by internal potentials and moving through an unbounded quiescent viscous fluid. The individual rigid particles comprising the flexible chain or cluster may each be of arbitrary shape, size and density, and are supposed 'joined' together to form the chain by a configuration-dependent internal potential V. Each particle separately undergoes translational and rotational Brownian motions; together, their relative motions give rise to a conformational or vibrational Brownian motion of the chain (in addition to a translational motion of the chain as a whole). Sufficient time is allowed for all accessible chain configurations to be sampled many times in consequence of this internal Brownian motion. As a result, an internal equilibrium Boltzmann probabilistic distribution of conformations derived from V effectively obtains.

In contrast with prior analyses of such chain transport phenomena, no *ad hoc* preaveraging hypotheses are invoked to effect the averaging of the input conformation-specific hydrodynamic mobility data. Rather, the calculation is effected rigorously within the usual (quasi-static) context of configuration-specific Stokes–Einstein equations.

Explicit numerical calculations serving to illustrate the general scheme are performed only for the simplest case, namely dumb-bells composed of identically sized spheres connected by a slack tether. In this context it is pointed out that prior calculations of flexible-body transport phenomena have failed to explicitly recognize the existence of a Taylor dispersion contribution to the long-time diffusivity of sedimenting deformable bodies. This fluctuation phenomenon is compounded of shape-sedimentation dispersion (arising as a consequence of the intrinsic geometrical anisotropy of the object) and size-sedimentation dispersion (arising from fluctuations in the instantaneous 'size' of the object). Whereas shape dispersion exists even for rigid objects, size dispersion is manifested only by flexible bodies. These two Taylor dispersion mechanisms are relevant to interpreting the non-equilibrium sedimentation–diffusion properties of monodisperse polymer molecules in solutions or suspensions.

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1. Introduction

Transport mechanics (Brenner & Condiff 1972, 1974) in systems composed of isolated rigid particles moving through a continuous fluid phase has been the subject of extensive theoretical studies for well over a century. Building upon the pioneering hydrodynamic investigations of Stokes (1851), who examined the 'slow' viscous translational motion of a spherical particle through a quiescent Newtonian fluid, a field has emerged which includes a strikingly rich variety of phenomena. Classified under the general title of 'low-Reynolds-number hydrodynamics' (Happel & Brenner 1983), this field incorporates such diverse areas as suspension rheology, sedimentation processes, translational and rotational Brownian motions and colloid science – as well as a multitude of other non-equilibrium fluid-particle phenomena.

In circumstances where the suspended objects are flexible, rather than rigid, progress has been limited, owing to the existence of several impediments. Not the least of these is the essentially pragmatic problem of dealing rigorously with the large number of degrees of freedom required to completely specify the instantaneous geometrical configuration of the flexible entity. A second related problem arises from the need to incorporate hydrodynamic interactions among the constituent rigid bodies making up the flexible body, and moving relative to one another. Usually, the first of these is dealt with within the more general framework of statistical mechanics (Landau & Lifshitz 1980) and kinetic theory (Bird *et al.* 1977), while the second is circumvented by either the complete neglect of hydrodynamic interactions, or by invoking lower-order approximations, such as the Burgers–Oseen interaction tensor with preaveraging (Kirkwood & Riseman 1948). This apparent necessity for introducing approximate hydrodynamic interaction calculations into the requisite analysis has not only hindered quantitative progress in calculations pertaining to specific models, but also the actual conceptual development of existing theories. Thus, a major aim of the present study is to provide a fresh impetus to the rigorous theoretical development of macromolecular (flexible body) transport mechanics by utilizing the newly developed framework of generalized Taylor dispersion theory (Brenner 1980, 1982*a*, *b*) to complement classical kinetic treatments (Bird *et al.* 1977) of macromolecular hydrodynamics. Our proposed framework allows both of the aforementioned difficulties to be surmounted (at least conceptually); specifically, all translational and orientational degrees of freedom of the individual constituent rigid particles comprising the cluster are retained, as too are all the requisite, many-body, configuration-specific, hydrodynamic phenomenological coefficients (grand resistance and mobility matrices).

The flexible-body model addressed herein is assumed to consist of a chain or cluster of rigid particles, not unlike the classical 'bead–spring' models of Rouse (1953) and Zimm (1956). However, in our treatment the constituent rigid particles are taken to be of finite size and to be of arbitrary shape; moreover, the configuration-specific internal potential that serves to join them together – thereby permitting collective identification of the cluster or chain as a single entity moving through physical space – is assumed arbitrary (rather than being limited, for example, by such restrictions as pairwise additivity) so long as the potential is sufficiently attractive at large particle separations to assure convergence of any subsequent integrals that arise in the theory. Other common models, such as the 'bead–rod' models of Kramers (1946) and Hassager (1974*a*, *b*), or those of 'segmentally flexible macromolecules' (Wegener 1982; Harvey, Mellado & Garcia de la Torre 1983; Garcia de la Torre, Mellado & Rodes 1985) can presumably be treated with appropriate choices of the potential,

although quantum-mechanical effects may unexpectedly arise (Rallison 1979) in effecting the transition from flexible to rigid form for the constraining potential.

In the realm of kinematics, any arbitrary motion of a rigid particle can be decomposed into a translation (of a locator point affixed to the particle) and a rigid-body rotation (about an axis through that point); however, the same is not true of the arbitrary motion of a flexible cluster of rigid bodies. Indeed, it is not *a priori* obvious which, if any, body-fixed geometrical point can best serve as a locator point for the chain 'position' in physical space. Points such as the centres of mass, volume, reaction (Brenner 1967), diffusion (Wegener 1985), or even an arbitrary point affixed to any one of the constituent rigid particles all appear to constitute equally reasonable candidates, although the ultimate physical results characterizing the long-time transport properties (Brenner & Pagitsas 1989) of the cluster as a whole must necessarily show themselves so be independent of the explicit choice made for the body-fixed chain locator point.

Another element of interest, particularly in problems pertaining to the sedimentation of flexible chains (Zimm 1982), is that although on average such a chain may possess a definite 'mean configuration', the chain may instantaneously exist in any one of an infinite number of other accessible geometrical configurations (with the probability of a specific configuration governed by a Boltzmann distribution, entailing the configuration-specific internal potential). For example, although on time average the flexible body may possess some definite symmetric shape, it does not generally possess this symmetry at all times, or indeed at any single instant of time. Since such deviations from the 'average' configuration normally create long-time secular or cumulative effects, the long-time physical properties of such a body can be expected in general to differ from those of its symmetric, preaveraged, rigid counterpart. To rigorously analyse secular effects arising from instantaneous deviations from the average, generalized Taylor dispersion theory (Brenner 1982*a*; Brenner & Pagitsas 1989) can be employed. Indeed, this paradigm has already been successfully used to investigate comparable sedimentation–dispersion phenomena in systems of rigid non-spherical particles (Brenner 1979, 1981). Upon incorporation of 'coupling' effects (Brenner 1982*b*), the generalized theory will be shown to be equally applicable to the macrotransport analysis of flexible clusters too.

Prediction of the conventional molecular diffusivity of flexible macromolecules (Wegener 1985; Haber & Brenner 1986), free of any sedimentation effects, is itself a challenging goal. Recently, Wegener (1985) and Haber & Brenner (1986) have independently recognized the important role of coupling between the translational, rotational and internal motions of flexible macromolecules. The former has shown via a perturbation analysis that the long-time macroscopic translational dispersivity of a flexible body is equal to the mean diffusivity of its (unique) centre of diffusion. Haber & Brenner (1986) have independently examined the same general problem within the Taylor–Aris (Taylor 1953; Aris 1956; Horn 1971) dispersion framework, performing detailed calculations for the case of a flexible dumb-bell.

Rheological implications (Bird *et al.* 1977) of our flexible-chain analysis will not be pursued here, but will rather be separately addressed elsewhere.

The organization of the remainder of this contribution is as follows. In the next section, generalized coupled dispersion theory (Brenner 1982*b*) is reviewed, followed in §3 by a general formulation of the flexible chain/cluster transport equation describing sedimentation within an otherwise quiescent fluid. Transformations detailed in §4 permit reduction of this scheme to a format identical with the canonical form (Brenner 1980, 1982*a*, *b*) of generalized Taylor dispersion theory. Section 5

derives explicit generic formulas for the long-time mean sedimentation velocity vector $\overline{U}^*$ and dispersivity dyadic $\overline{D}^*$ of the macromolecule through the fluid in terms of the prescribed configuration-specific phenomenological data – such data consisting of the multiparticle translational and rotational hydrodynamic mobility dyadics of the individual rigid bodies together with the internal potential-energy function. Sections 6 and 7 provide detailed numerical results for two specific examples, each involving so-called tethered dumb-bells. Finally, §8 furnishes a brief discussion of the implications of our results.

2. Generalized Taylor dispersion theory, including coupling

Generalized Taylor dispersion theory techniques (Brenner 1980, 1982*a*), incorporating coupling effects (Brenner 1982*b*), are briefly reviewed in this section. The latter theory provides a convenient framework for deriving long-time global evolution equations (Brenner & Pagitsas 1989) governing transport processes occurring in a general multidimensional space spanned by local (fast) and global (slow) variables, the former representing 'internal' degrees of freedom. Flexible-chain transport phenomena will subsequently prove to be analysable within this general framework, with the fast variables characterizing the instantaneous configuration (conformation) of the rigid bodies composing the chain.

Consider a multidimensional space (Brenner 1982*a*) composed of global variables $\boldsymbol{Q}$ and local variables $\boldsymbol{q}$, which are respectively 'slow' and 'fast' in the sense that equilibrium is rapidly established within $\boldsymbol{q}$-space whereas a non-equilibrium state permanently persists in $\boldsymbol{Q}$-space owing to its infinite extent. With

$$P \equiv P(\boldsymbol{Q}, \boldsymbol{q}, t \,|\, \boldsymbol{Q}', \boldsymbol{q}') \tag{2.1}$$

the conditional probability density for finding a Brownian 'tracer' at time t in an infinitesimal neighbourhood of point $(\boldsymbol{Q}, \boldsymbol{q})$, given its initial introduction (at $t = 0$) into the system at $(\boldsymbol{Q}', \boldsymbol{q}')$, the canonical transport equation for P adopts the form (Brenner 1980, 1982*a*)

$$\frac{\partial P}{\partial t} + \nabla_{\boldsymbol{Q}} \cdot \boldsymbol{J} + \nabla_{\boldsymbol{q}} \cdot \boldsymbol{j} = \delta(t)\, \delta(\boldsymbol{Q} - \boldsymbol{Q}')\, \delta(\boldsymbol{q} - \boldsymbol{q}'), \tag{2.2}$$

wherein $\nabla_{\boldsymbol{Q}}$ and $\nabla_{\boldsymbol{q}}$ are the respective global- and local-space gradient operators. In the presence of coupling effects (Brenner 1982*b*), the global and local flux densities required above are respectively given by the constitutive relations

$$\boldsymbol{J} = \boldsymbol{U}P - \boldsymbol{D}^{\boldsymbol{QQ}} \cdot \nabla_{\boldsymbol{Q}} P - \mathrm{e}^{-E} \boldsymbol{D}^{\boldsymbol{Qq}} \cdot \nabla_{\boldsymbol{q}} (\mathrm{e}^{E} P), \tag{2.3}$$

$$\boldsymbol{j} = \boldsymbol{u}P - \boldsymbol{D}^{\boldsymbol{qQ}} \cdot \nabla_{\boldsymbol{Q}} P - \mathrm{e}^{-E} \boldsymbol{D}^{\boldsymbol{qq}} \cdot \nabla_{\boldsymbol{q}} (\mathrm{e}^{E} P), \tag{2.4}$$

with $\boldsymbol{U}$ and $\boldsymbol{u}$ denoting global and local velocity fields, $\boldsymbol{D}^{\boldsymbol{QQ}}$ and $\boldsymbol{D}^{\boldsymbol{qq}}$ the global and local direct diffusion tensors, $\boldsymbol{D}^{\boldsymbol{qQ}}$ and $\boldsymbol{D}^{\boldsymbol{Qq}}$ the coupling or cross-diffusivities, and E the dimensionless local-space potential. Each of these phenomenological functions are assumed to be known functions of the fast variables $\boldsymbol{q}$, but independent of $\boldsymbol{Q}$. Furthermore, the symmetry relations (Brenner 1982*b*)

$$\boldsymbol{D}^{\boldsymbol{QQ}} = \boldsymbol{D}^{\boldsymbol{QQ}\dagger}, \quad \boldsymbol{D}^{\boldsymbol{qq}} = \boldsymbol{D}^{\boldsymbol{qq}\dagger}, \quad \boldsymbol{D}^{\boldsymbol{qQ}} = \boldsymbol{D}^{\boldsymbol{Qq}\dagger}, \tag{2.5}$$

are assumed to be obeyed by the diffusivity tensors, with $\dagger$ a transposition operator.

Together, (2.2)–(2.4) are to be solved for P subject to the pre-initial condition

$$P = 0 \quad (t < 0), \tag{2.6}$$

a no-flux condition on the local-space boundary,

$$\boldsymbol{n}\cdot\boldsymbol{j}=0 \quad \text{on } \partial\boldsymbol{q}_o, \tag{2.7a}$$

and the global attenuation-rate boundary condition

$$|\boldsymbol{Q}-\boldsymbol{Q}'|^m P\to 0 \quad \text{as } |\boldsymbol{Q}-\boldsymbol{Q}'|\to\infty \quad (m=0,1,2,\ldots), \tag{2.7b}$$

which assures convergence of all the moments of the distribution function. As such, it is readily seen that the required normalization property

$$\int_{\boldsymbol{Q}_\infty} \mathrm{d}\boldsymbol{Q} \int_{\boldsymbol{q}_o} \mathrm{d}\boldsymbol{q}\, P = 1 \quad (t>0) \tag{2.8}$$

is automatically satisfied by P. Here, $\boldsymbol{q}_o$ denotes the (bounded or closed) domain of the local space, and $\boldsymbol{Q}_\infty$ the (unbounded) range of the global coordinates (Brenner 1980).

Beginning with the above set of well-posed microtransport equations, generalized Taylor dispersion theory (Brenner & Pagitsas 1989) aims at deriving corresponding long-time macrotransport equations in $\boldsymbol{Q}$-space, from which all dependence upon the local degrees of freedom $\boldsymbol{q}$ has been eliminated. The focus of attention in that coarse-scale description is the purely global-space conditional probability density $\overline{P}$, defined as (Pagitsas, Nadim & Brenner 1986*a*, *b*; Nadim, Pagitsas & Brenner 1986)

$$\overline{P}(\boldsymbol{Q},t\,|\,\boldsymbol{Q}',\boldsymbol{q}') = \int_{\boldsymbol{q}_o} \mathrm{d}\boldsymbol{q}\, P. \tag{2.9}$$

An analysis of the type performed by Brenner (1982*b*) or Nadim *et al.* (1986) may be employed to show that for sufficiently long times, such that equilibrium has effectively been established within the local space (which long-time limit is designated by the superscript ∞), the latter satisfies the purely global-space transport equation

$$\frac{\partial\overline{P}^\infty}{\partial t} + \nabla_{\boldsymbol{Q}}\cdot\overline{\boldsymbol{J}}^\infty = \delta(t)\,\delta(\boldsymbol{Q}-\boldsymbol{Q}'), \tag{2.10}$$

with $\overline{P}^\infty \equiv \overline{P}^\infty(\boldsymbol{Q},t\,|\,\boldsymbol{Q}')$, wherein

$$\overline{\boldsymbol{J}}^\infty = \overline{\boldsymbol{U}}^*\overline{P}^\infty - \overline{\boldsymbol{D}}^*\cdot\nabla_{\boldsymbol{Q}}\overline{P}^\infty \tag{2.11}$$

is the long-time global flux density.

The constant convective and dispersive phenomenological coefficients $\overline{\boldsymbol{U}}^*$ and $\overline{\boldsymbol{D}}^*$ characterizing (Nadim *et al.* 1986; Pagitsas *et al.* 1986*a*, *b*) the long-time macrotransport process may be found upon quadrature of the integrals

$$\overline{\boldsymbol{U}}^* = \int_{\boldsymbol{q}_o} \mathrm{d}\boldsymbol{q}[P_0^\infty\,\boldsymbol{U} - \mathrm{e}^{-E}\boldsymbol{D}^{\boldsymbol{Q}\boldsymbol{q}}\cdot\nabla_{\boldsymbol{q}}(\mathrm{e}^E P_0^\infty)], \tag{2.12}$$

$$\overline{\boldsymbol{D}}^* = \int_{\boldsymbol{q}_o} \mathrm{d}\boldsymbol{q}\{P_0^\infty(\boldsymbol{D}^{\boldsymbol{Q}\boldsymbol{Q}} - \boldsymbol{D}^{\boldsymbol{Q}\boldsymbol{q}}\cdot\nabla_{\boldsymbol{q}}\boldsymbol{B}) + [P_0^\infty(\boldsymbol{U}-\overline{\boldsymbol{U}}^*) - \mathrm{e}^{-E}\boldsymbol{D}^{\boldsymbol{Q}\boldsymbol{q}}\cdot\nabla_{\boldsymbol{q}}(\mathrm{e}^E P_0^\infty)]\,\boldsymbol{B}\}, \tag{2.13}$$

derived (Brenner 1982*b*; Nadim 1986) from the generalized Taylor (1953)–Aris (1956) moment scheme via their asymptotic, long-time definitions

$$\int_{\boldsymbol{Q}_\infty} \mathrm{d}\boldsymbol{Q}(\boldsymbol{Q}-\boldsymbol{Q}')^m \int_{\boldsymbol{q}_o} \mathrm{d}\boldsymbol{q}\, P \sim \begin{cases} \overline{\boldsymbol{U}}^* t & (m=1), \\ \overline{\boldsymbol{U}}^*\overline{\boldsymbol{U}}^* t^2 + 2\overline{\boldsymbol{D}}^* t & (m=2), \end{cases}$$

valid as $t\to\infty$.

The respective local-space scalar and vector fields $P_0^\infty(\boldsymbol{q})$ and $\boldsymbol{B}(\boldsymbol{q})$ appearing in the latter integrands represent the solutions of the respective sets of equations (Brenner 1982*b*; Nadim 1986)

$$\boldsymbol{\nabla}_q\cdot[\boldsymbol{u}P_0^\infty - \mathrm{e}^{-E}\boldsymbol{D}^{qq}\cdot\boldsymbol{\nabla}_q(\mathrm{e}^E P_0^\infty)] = 0, \tag{2.14a}$$

$$\boldsymbol{n}\cdot[\boldsymbol{u}P_0^\infty - \mathrm{e}^{-E}\boldsymbol{D}^{qq}\cdot\boldsymbol{\nabla}_q(\mathrm{e}^E P_0^\infty)] = 0 \quad \text{on } \partial\boldsymbol{q}_o, \tag{2.14b}$$

$$\int_{q_o} \mathrm{d}\boldsymbol{q}\, P_0^\infty = 1, \tag{2.14c}$$

governing P_0^∞, and

$$\boldsymbol{\nabla}_q\cdot[\boldsymbol{u}P_0^\infty\boldsymbol{B} - \mathrm{e}^{-E}\boldsymbol{D}^{qq}\cdot\boldsymbol{\nabla}_q(\mathrm{e}^E P_0^\infty\boldsymbol{B}) + P_0^\infty\boldsymbol{D}^{qQ}] = P_0^\infty(\boldsymbol{U}-\overline{\boldsymbol{U}}^*) - \mathrm{e}^{-E}\boldsymbol{D}^{Qq}\cdot\boldsymbol{\nabla}_q(\mathrm{e}^E P_0^\infty), \tag{2.15a}$$

$$-P_0^\infty\boldsymbol{n}\cdot(\boldsymbol{D}^{qq}\cdot\boldsymbol{\nabla}_q\boldsymbol{B} - \boldsymbol{D}^{qQ}) = \boldsymbol{0} \quad \text{on } \partial\boldsymbol{q}_o, \tag{2.15b}$$

governing $\boldsymbol{B}$. The latter vector field is uniquely defined by this system of equations only to within a physically irrelevant additive vector constant (Brenner 1980, 1982*a*, *b*).

To complete the system of equations (2.10)–(2.11) we impose upon $\overline{P}^\infty$ a global-space attenuation condition analogous to (2.7*b*). Equations (2.10)–(2.11), governing the macrotransport of $\overline{P}^\infty$ and involving the mean velocity $\overline{\boldsymbol{U}}^*$ and dispersivity $\overline{\boldsymbol{D}}^*$ of the tracer as macroscale phenomenological coefficients, represent a coarse graining of their microtransport predecessors (2.2)–(2.4), involving the seven microscale phenomenological functions cited following (2.4). Subsequent sections address the explicit calculation of $\overline{\boldsymbol{U}}^*$ and $\overline{\boldsymbol{D}}^*$ for a flexible chain or cluster moving through three-dimensional space, $(x, y, z) \equiv \boldsymbol{Q}$.

3. General formulation of the flexible-chain transport equation

Consider a flexible cluster, synthesized by joining together $n+1$ rigid particles of arbitrary shapes via interparticle (internal) potentials. These potentials, which can be as elementary as simple tethers connecting pairs of particles, or as complex as one may wish to imagine, serve to permit collective identification of the $n+1$ rigid particles as a single identifiable entity – namely, a 'flexible chain'. Its 'flexibility' arises from the fact that its constituent rigid particles are free to translate and rotate relative to one another, subject to any configurational constraints imposed by the internal potential $E(\boldsymbol{q})$; as such, the conformation of the chain can (and does) vary with time. In order that the identification of the cluster as a single entity remain uniformly valid in time, it suffices to require that the diminution of the attractive portion of the internal potential with increasing separation between constituent rigid particles assure convergence of subsequent integrals that arise in our theory. Without further comment the validity of this condition will henceforth be assumed. (Note that the non-dimensional internal potential typically enters subsequent integrations in the form of a Boltzmann equilibrium factor $\exp(-E)$ multiplying the integrand.)

Label the individual rigid particles via the index A ($A = 0, 1, 2, \ldots, n$, for a total of $n+1$ particles), and denote by O_A an arbitrarily positioned particle 'locator point' rigidly affixed to particle A. At any instant the complete configuration (external 'position' and internal 'conformation') of the particle cluster is entirely determined by specification of the $n+1$ position vectors $\boldsymbol{R}_A$ of the locator points O_A (requiring $3(n+1)$ scalar coordinates) relative to an arbitrary space-fixed origin, and a comparable set of $n+1$ orientational triplets $\boldsymbol{\phi}_A$ (e.g. three Eulerian angles specifying the

orientation of particle A relative to a set of space-fixed rectangular Cartesian axes) of each of the constituent particles (requiring another $3(n+1)$ scalar coordinates). Note that the symbol $\boldsymbol{\phi}_A$ does not possess operational significance as a vector, whereas the infinitesimal rotation pseudovector $\delta\boldsymbol{\phi}_A$ (to appear later) does.

Denote by

$$P(\boldsymbol{R}_0,\ldots,\boldsymbol{R}_n;\boldsymbol{\phi}_0,\ldots,\boldsymbol{\phi}_n,t\,|\,\boldsymbol{R}'_0,\ldots,\boldsymbol{R}'_n;\boldsymbol{\phi}'_0,\ldots,\boldsymbol{\phi}'_n)\,\mathrm{d}\boldsymbol{R}_0\ldots\mathrm{d}\boldsymbol{R}_n\,\mathrm{d}\boldsymbol{\phi}_0\ldots\mathrm{d}\boldsymbol{\phi}_n \quad (3.1)$$

the conditional probability for finding the chain configuration within the elementary infinitesimal domain

$$\mathrm{d}\boldsymbol{R}_0\ldots\mathrm{d}\boldsymbol{R}_n\,\mathrm{d}\boldsymbol{\phi}_0\ldots\mathrm{d}\boldsymbol{\phi}_n \quad (3.2)$$

centred at $(\boldsymbol{R}_0,\ldots,\boldsymbol{R}_n;\boldsymbol{\phi}_0,\ldots,\boldsymbol{\phi}_n)$ at time t, given that at time $t=0$ the chain possessed the configuration $(\boldsymbol{R}'_0,\ldots,\boldsymbol{R}'_n;\boldsymbol{\phi}'_0,\ldots,\boldsymbol{\phi}'_n)$. The probability density P is chosen to satisfy the normalization condition

$$\int\mathrm{d}\boldsymbol{R}_0\ldots\mathrm{d}\boldsymbol{R}_n\,\mathrm{d}\boldsymbol{\phi}_0\ldots\mathrm{d}\boldsymbol{\phi}_n\,P=1 \quad (t>0), \quad (3.3)$$

along with (2.6), in which the limits of integration extend over the entire physical- and orientational-space domains available for the external and internal configurational transport. (Subsequently, we will introduce no-flux boundary conditions that assure the conservation of probability density implied by (3.3).)

The conservation equation governing the detailed configurational transport of the flexible cluster through a fluid continuum is of the general form

$$\frac{\partial P}{\partial t}+\sum_{A=0}^{n}\left(\frac{\partial}{\partial\boldsymbol{R}_A}\cdot\boldsymbol{J}[\boldsymbol{R}_A]+\frac{\partial}{\partial\boldsymbol{\phi}_A}\cdot\boldsymbol{j}[\boldsymbol{\phi}_A]\right)=\delta(t)\prod_{A=0}^{n}\delta(\boldsymbol{R}_A-\boldsymbol{R}'_A)\,\delta(\boldsymbol{\phi}_A-\boldsymbol{\phi}'_A), \quad (3.4)$$

in which, more explicitly,

$$\frac{\partial}{\partial\boldsymbol{R}_A}\equiv\left(\frac{\partial}{\partial\boldsymbol{R}_A}\right)_{\boldsymbol{R}_C;\,\boldsymbol{\phi}_B},\quad \frac{\partial}{\partial\boldsymbol{\phi}_A}\equiv\left(\frac{\partial}{\partial\boldsymbol{\phi}_A}\right)_{\boldsymbol{R}_B;\,\boldsymbol{\phi}_C}, \quad (3.5a,b)$$

where $B=0,1,\ldots,n$ and $C=0,1,\ldots,A-1,A+1,\ldots,n$. The derivatives defined in (3.5) are the respective physical- and orientational-space gradients of particle A. Since an infinitesimal rotation is a (pseudo) vector, (3.5b) possesses appropriate operational significance as a vector operator (Brenner & Condiff 1972). The Dirac delta function source term product appearing on the right-hand side of (3.4) arises from the instantaneous introduction of the flexible chain (possessing the indicated primed configuration) into the fluid at $t=0$, together with the unit normalization (3.3). The configuration-specific physical- and orientational-space vector flux densities $\boldsymbol{J}[\boldsymbol{R}_A]$ and $\boldsymbol{j}[\boldsymbol{\phi}_A]$ of particle A will be assumed to possess the respective convective–diffusive constitutive forms

$$\boldsymbol{J}[\boldsymbol{R}_A]=\dot{\boldsymbol{R}}_A\,P-\sum_{B=0}^{n}\left(\boldsymbol{D}[\boldsymbol{R}_A\,|\,\boldsymbol{R}_B]\cdot\frac{\partial P}{\partial\boldsymbol{R}_B}+\boldsymbol{D}[\boldsymbol{R}_A\,|\,\boldsymbol{\phi}_B]\cdot\frac{\partial P}{\partial\boldsymbol{\phi}_B}\right), \quad (3.6a)$$

$$\boldsymbol{j}[\boldsymbol{\phi}_A]=\dot{\boldsymbol{\phi}}_A\,P-\sum_{B=0}^{n}\left(\boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_B]\cdot\frac{\partial P}{\partial\boldsymbol{R}_B}+\boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B]\cdot\frac{\partial P}{\partial\boldsymbol{\phi}_B}\right). \quad (3.6b)$$

The (non-Brownian) translational and angular velocity vectors of particle A, respectively defined as

$$\dot{\boldsymbol{R}}_A\overset{\text{def}}{=}\frac{\delta\boldsymbol{R}_A}{\delta t},\quad \dot{\boldsymbol{\phi}}_A\overset{\text{def}}{=}\frac{\delta\boldsymbol{\phi}_A}{\delta t}, \quad (3.7a,b)$$

will be assumed given by the low-Reynolds-number constitutive relations (Brenner 1964; Happel & Brenner 1983)

$$\dot{\boldsymbol{R}}_A = \sum_{B=0}^{n} (\boldsymbol{M}[\boldsymbol{R}_A \,|\, \boldsymbol{R}_B]\cdot\boldsymbol{F}_B + \boldsymbol{M}[\boldsymbol{R}_A \,|\, \boldsymbol{\phi}_B]\cdot\boldsymbol{T}_B), \tag{3.8a}$$

$$\dot{\boldsymbol{\phi}}_A = \sum_{B=0}^{n} (\boldsymbol{M}[\boldsymbol{\phi}_A \,|\, \boldsymbol{R}_B]\cdot\boldsymbol{F}_B + \boldsymbol{M}[\boldsymbol{\phi}_A \,|\, \boldsymbol{\phi}_B]\cdot\boldsymbol{T}_B), \tag{3.8b}$$

where $\boldsymbol{F}_B$ and $\boldsymbol{T}_B$ are the (non-hydrodynamic and non-Brownian) force and torque (the latter about point O_B), respectively, exerted on particle B. Typically, these contain both interparticle and external contributions. The mobility dyadics $\boldsymbol{M}[A \,|\, B]$ appearing in (3.8) are functionally dependent only upon the internal configuration (conformation) of the flexible body (i.e. the orientations and relative positions of all of the rigid constituent particles of which it is composed). The arguments of each, shown in square brackets, concisely serve to distinguish the several physical possibilities; for example, those mobilities $\boldsymbol{M}[\boldsymbol{R}_A \,|\, \boldsymbol{\phi}_B]$ and $\boldsymbol{M}[\boldsymbol{\phi}_A \,|\, \boldsymbol{R}_B]$ possessing mixed physical- and orientational-space arguments arise from coupling between respective rotational and translational motions (not necessarily referring to motions of the *same* particle – i.e. B may or may not be equal to A). The mobilities $\boldsymbol{M}[A \,|\, B]$ are closely related to the comparable Brownian diffusivity dyadics $\boldsymbol{D}[A \,|\, B]$ appearing in (3.6) via the multibody configuration-specific Stokes–Einstein relations (Brenner 1967)

$$\boldsymbol{D}[A \,|\, B] = kT\boldsymbol{M}[A \,|\, B]. \tag{3.9}$$

In principle, the configuration-specific mobilities $\boldsymbol{M}[A \,|\, B]$ may be found by solving the $(n+1)$-particle Stokes flow problem (for that specific geometric configuration) for which only one of the $n+1$ particles translates or rotates (but does not do both simultaneously) in an otherwise quiescent fluid, while all the other n particles neither translate nor rotate.‡ Equation (3.9) then provides the requisite molecular diffusivities $\boldsymbol{D}[A \,|\, B]$.

The forces and torques $\boldsymbol{F}_B$ and $\boldsymbol{T}_B$ appearing in (3.8) are assumed derivable from a potential $V(\boldsymbol{R}_0, \ldots, \boldsymbol{R}_n; \boldsymbol{\phi}_0, \ldots, \boldsymbol{\phi}_n)$:

$$\boldsymbol{F}_B = -\frac{\partial V}{\partial \boldsymbol{R}_B}, \quad \boldsymbol{T}_B = -\frac{\partial V}{\partial \boldsymbol{\phi}_B}, \tag{3.10a,b}$$

in which circumstances (3.8) adopts the form

$$\dot{\boldsymbol{R}}_A = -\sum_{B=0}^{n} \left(\boldsymbol{M}[\boldsymbol{R}_A \,|\, \boldsymbol{R}_B]\cdot\frac{\partial V}{\partial \boldsymbol{R}_B} + \boldsymbol{M}[\boldsymbol{R}_A \,|\, \boldsymbol{\phi}_B]\cdot\frac{\partial V}{\partial \boldsymbol{\phi}_B}\right), \tag{3.11a}$$

$$\dot{\boldsymbol{\phi}}_A = -\sum_{B=0}^{n} \left(\boldsymbol{M}[\boldsymbol{\phi}_A \,|\, \boldsymbol{R}_B]\cdot\frac{\partial V}{\partial \boldsymbol{R}_B} + \boldsymbol{M}[\boldsymbol{\phi}_A \,|\, \boldsymbol{\phi}_B]\cdot\frac{\partial V}{\partial \boldsymbol{\phi}_B}\right). \tag{3.11b}$$

Equation (3.4), supplemented with the constitutive flux expressions (3.6), in conjunction with (3.11), furnishes the convective–diffusive equation governing the detailed configurational transport of the isolated flexible chain in $(\boldsymbol{R}_0, \ldots, \boldsymbol{R}_n; \boldsymbol{\phi}_0, \ldots, \boldsymbol{\phi}_n)$-space. All the material, configuration-specific, phenomenological dyadics required therein (mobilities and diffusivities) will henceforth be assumed known

‡ More properly, that experiment would furnish the comparable intrinsic hydrodynamic resistance dyadics $\boldsymbol{K}[A \,|\, B]$, whose elements collectively comprise the so-called grand resistance matrix (Happel & Brenner 1983). Inversion of the latter would then yield the required 'grand' mobility matrix.

functions of the specified configuration, obtainable by solving the appropriate low-Reynolds-number hydrodynamic problems (Brenner 1964; Happel & Brenner 1983) cited. These dyadics satisfy the symmetry relationships (Brenner 1964)

$$\boldsymbol{M}^{\dagger}[\boldsymbol{R}_A\,|\,\boldsymbol{R}_B] = \boldsymbol{M}[\boldsymbol{R}_B\,|\,\boldsymbol{R}_A], \quad \boldsymbol{M}^{\dagger}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B] = \boldsymbol{M}[\boldsymbol{\phi}_B\,|\,\boldsymbol{\phi}_A],$$
$$\boldsymbol{M}^{\dagger}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_B] = \boldsymbol{M}[\boldsymbol{R}_B\,|\,\boldsymbol{\phi}_A], \quad (3.12a\text{–}c)$$

in consequence of the Lorentz reciprocal theorem (Happel & Brenner 1983). The configuration-specific potential-energy function V required in (3.11) will also be assumed known.

The boundary conditions to be imposed upon the probability density P, consistent with the necessary conservation statement (3.3), are the usual zero normal-flux conditions existing at the physical- and orientational-space 'boundaries' (cf. §2, as well as Haber & Brenner 1986). Subject to the foregoing boundary conditions and the pre-initial condition (2.6), the governing equation (3.4) for P may be solved so as to obtain an exact description of the configurational transport process; however, such a detailed resolution of the problem is not ordinarily the ultimate objective of interest. Indeed, for large n, such a description would be overwhelmingly detailed. Rather, if the flexible object is to be viewed as an entity unto itself – modelling, for instance a polymer chain, macromolecule, or cluster – a much more physically useful and concise description is that of transport through physical space of the flexible body as a whole, viewed as the sole object of interest – free from the detailed translational and rotational motions of its individual constituent rigid members.

Attainment of this goal requires that we assign a particular locator point to the flexible object as a definable entity, and focus exclusively on the stochastic convective–diffusive trajectory of that point through ordinary three-dimensional physical space. Only three scalar coordinates (e.g. the position vector of its locator point) are required to localize the flexible cluster in this space at each instant of time. The remaining $6n+3$ scalar coordinates then serve to specify the internal configuration or conformation of the flexible chain. Specifically, our eventual goal is to eliminate from the transport equation the internal degrees of freedom, at least for times sufficiently long to assure that equilibrium (or steady state) with respect to conformation has been attained (but yet sufficiently short such that no comparable terminal state of affairs prevails with respect to position in three-dimensional physical space). This task will be accomplished by adopting the formalism of generalized Taylor dispersion theory, including coupling effects (Brenner 1982*b*), as reviewed in the preceding section.

Equations (3.4), (3.6) and (3.11), by themselves, effect no definite decomposition of the independent variables into respective local (internal) and global (external) variables. As this classification is a prerequisite to applying the results of §2, the next section will be devoted to effecting this choice, as well as subsequently casting the governing equations of this section into a form directly amenable to generalized Taylor dispersion analysis. The latter is accomplished by a concomitant decomposition of the dependent variables into forms demanded by the local/global classification of the independent variables (i.e. coordinates). That such a transformation is possible is an immediate consequence of the ansatz that, for long times, the choice of locator point for the flexible body is irrelevant. Specifically, any and all choices of chain locator point rigidly affixed to any one of the constituent particles can serve equally well for identifying the 'position' of the flexible body in physical space; for in the long run, each and every constituent particle comprising the flexible body

necessarily behaves alike as regards its net translational motion through physical space. (Were this not the case, the concept of the cluster as a single identifiable entity would be devoid of physical meaning.) While the centres of mass or volume of the flexible body are the common choices made for chain locator point in earlier studies by others, in fact any point will suffice equally well in the long run. A formal proof of such invariance to the choice of chain-fixed locator point is available elsewhere (Nadim 1986).

4. Local/global form of the flexible-chain microtransport equation

Motivated by the aforementioned ansatz, choose any point O_0 rigidly affixed to particle $A = 0$ as the locator point of the flexible cluster. Denote by $\boldsymbol{Q}$ the position vector of this point, so that

$$\boldsymbol{Q} \equiv \boldsymbol{R}_0. \tag{4.1}$$

This vector thus spans the entire global (physical) space available for transport of the flexible object, at least in the case where no boundaries are present.‡ The set of coordinates necessary for specifying the internal configuration or conformation of the flexible chain consists of $3(n+1)$ scalar orientational coordinates arising from the $n+1$ orientational triplets $\boldsymbol{\phi}_0, \boldsymbol{\phi}_1, \ldots, \boldsymbol{\phi}_n$ (hereinafter designated collectively as $\boldsymbol{\phi}^{n+1}$) and the $3n$ scalar positional coordinates arising from the n relative position vectors

$$\boldsymbol{r}_a \overset{\text{def}}{=} \boldsymbol{R}_a - \boldsymbol{R}_0 \tag{4.2}$$

of the remaining points $O_a (a = 1, 2, \ldots, n)$ with respect to point O_0. Note that whereas the majuscule particle-labelling indices $A, B, \ldots$ previously employed range over the integers from 0 to n, minuscule indices $a, b, \ldots$ vary only from 1 to n. The local space is thus spanned by the $6n+3$ scalar coordinates

$$\boldsymbol{q} \equiv (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{\phi}_0, \boldsymbol{\phi}_1, \ldots, \boldsymbol{\phi}_n) \equiv (\boldsymbol{r}^n, \boldsymbol{\phi}^{n+1}). \tag{4.3}$$

Define the new gradient operators

$$\boldsymbol{\nabla}_Q \equiv \left(\frac{\partial}{\partial \boldsymbol{Q}}\right)_{\boldsymbol{r}_a, \boldsymbol{\phi}_A}, \tag{4.4a}$$

$$\frac{\partial}{\partial \boldsymbol{r}_a} \equiv \left(\frac{\partial}{\partial \boldsymbol{r}_a}\right)_{\boldsymbol{Q}, \boldsymbol{r}_b (\neq \boldsymbol{r}_a), \boldsymbol{\phi}_A}, \quad \frac{\partial}{\partial \boldsymbol{\phi}_A} \equiv \left(\frac{\partial}{\partial \boldsymbol{\phi}_A}\right)_{\boldsymbol{Q}, \boldsymbol{r}_a, \boldsymbol{\phi}_B (\neq \boldsymbol{\phi}_A)}. \tag{4.4b,c}$$

It is readily established that the orientational gradient (4.4c) is identical with its earlier counterpart (3.5b); hence, the same symbol is used unambiguously for both. On the other hand, (3.5a) is related to (4.4a, b) via the relations

$$\frac{\partial}{\partial \boldsymbol{R}_0} = \boldsymbol{\nabla}_Q - \sum_{a=1}^{n} \frac{\partial}{\partial \boldsymbol{r}_a}, \qquad \frac{\partial}{\partial \boldsymbol{R}_a} = \frac{\partial}{\partial \boldsymbol{r}_a} \tag{4.5a,b}$$

‡ We will consistently assume this to be the case in what follows. The case where boundaries girdling the physical-space flow are present is easily handled by reassigning one or two of the three scalar coordinates comprising $\boldsymbol{R}_0$ to the status of local rather than global coordinates. For example, in the case where the flexible body moves within a circular cylindrical tube, of the three circular cylindrical coordinates (r, ϕ, z) comprising $\boldsymbol{R}_0$, only the z-coordinate is to be chosen as global. The remaining two coordinates (r, ϕ), each of which is respectively bounded, are then to be classified as being local in character.

($a = 1, 2, \ldots, n$). The transformation of coordinates from $(\boldsymbol{R}^{n+1}, \boldsymbol{\phi}^{n+1})$ to $(\boldsymbol{Q}, \boldsymbol{q}) \equiv (\boldsymbol{Q}, \boldsymbol{r}^n, \boldsymbol{\phi}^{n+1})$ in (3.4), together with the corresponding interpretation of the conditional probability (cf. (3.1))

$$P(\boldsymbol{Q}, \boldsymbol{r}^n, \boldsymbol{\phi}^{n+1}, t \,|\, \boldsymbol{Q}', \boldsymbol{r}'^n, \boldsymbol{\phi}'^{n+1})\, \mathrm{d}\boldsymbol{Q}\, \mathrm{d}\boldsymbol{r}^n\, \mathrm{d}\boldsymbol{\phi}^{n+1}, \tag{4.6}$$

results in the microtransport equation

$$\frac{\partial P}{\partial t} + \nabla_Q \cdot \boldsymbol{J} + \sum_{a=1}^{n} \frac{\partial}{\partial \boldsymbol{r}_a} \cdot \boldsymbol{j}[\boldsymbol{r}_a] + \sum_{A=0}^{n} \frac{\partial}{\partial \boldsymbol{\phi}_A} \cdot \boldsymbol{j}[\boldsymbol{\phi}_A]$$

$$= \delta(t)\, \delta(\boldsymbol{Q} - \boldsymbol{Q}') \prod_{a=1}^{n} \delta(\boldsymbol{r}_a - \boldsymbol{r}'_a) \prod_{A=0}^{n} \delta(\boldsymbol{\phi}_A - \boldsymbol{\phi}'_A). \tag{4.7}$$

(It can be shown (Nadim 1986) that the volume element appearing in (4.6) is identical with that in (3.1), (3.2).) The global flux density vector $\boldsymbol{J}$ appearing above is given in symbolic-functional form by the expression

$$\boldsymbol{J} \equiv \boldsymbol{J}[\boldsymbol{R}_0], \tag{4.8}$$

whereas the local translational flux vector densities $\boldsymbol{j}[\boldsymbol{r}_a]$ are given by [cf. (3.6a)]

$$\boldsymbol{j}[\boldsymbol{r}_a] \equiv \boldsymbol{J}[\boldsymbol{R}_a] - \boldsymbol{J}[\boldsymbol{R}_0] \tag{4.9}$$

($a = 1, 2, \ldots, n$). On the other hand, the local orientational flux densities $\boldsymbol{j}[\boldsymbol{\phi}_A]$ are unchanged from (3.6b).

The potential function V appearing in (3.10) may be decomposed into the sum

$$V = -\boldsymbol{F} \cdot \boldsymbol{R}_0 + kTE(\boldsymbol{r}^n, \boldsymbol{\phi}^{n+1}), \tag{4.10}$$

(wherein $\boldsymbol{F} = \text{const.}$), with its global portion $-\boldsymbol{F} \cdot \boldsymbol{R}_0$ assumed to arise from the action of a uniform external field $\boldsymbol{F}$ (e.g. gravity, causing sedimentation of the flexible chain). The constant vector $\boldsymbol{F} = -\nabla_Q V$ represents the total external force acting on the flexible body. The internal contribution to the potential is also assumed to be explicitly known, and of the non-dimensional functional form $E(\boldsymbol{r}^n, \boldsymbol{\phi}^{n+1})$.

Utilize (4.10) and effect the transformation (4.5) in the constitutive flux equations (3.6a, b). In conjunction with (3.9) this yields the following expressions:

(i) global flux density,

$$\begin{aligned} \boldsymbol{J} = {} & \boldsymbol{M}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0] \cdot \boldsymbol{F}P - \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0] \cdot \nabla_Q P \\ & - \sum_{a=1}^{n} \mathrm{e}^{-E} (\boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_a] - \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0]) \cdot \frac{\partial (\mathrm{e}^E P)}{\partial \boldsymbol{r}_a} \\ & - \sum_{A=0}^{n} \mathrm{e}^{-E}\, \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{\phi}_A] \cdot \frac{\partial (\mathrm{e}^E P)}{\partial \boldsymbol{\phi}_A}; \end{aligned} \tag{4.11}$$

(ii) local translational flux densities,

$$\begin{aligned} \boldsymbol{j}[\boldsymbol{r}_a] = {} & (\boldsymbol{M}[\boldsymbol{R}_a \,|\, \boldsymbol{R}_0] - \boldsymbol{M}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0]) \cdot \boldsymbol{F}P - (\boldsymbol{D}[\boldsymbol{R}_a \,|\, \boldsymbol{R}_0] - \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0]) \cdot \nabla_Q P \\ & - \sum_{b=1}^{n} \mathrm{e}^{-E} (\boldsymbol{D}[\boldsymbol{R}_a \,|\, \boldsymbol{R}_b] - \boldsymbol{D}[\boldsymbol{R}_a \,|\, \boldsymbol{R}_0] - \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_b] + \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{R}_0]) \cdot \frac{\partial (\mathrm{e}^E P)}{\partial \boldsymbol{r}_b} \\ & - \sum_{A=0}^{n} \mathrm{e}^{-E} (\boldsymbol{D}[\boldsymbol{R}_a \,|\, \boldsymbol{\phi}_A] - \boldsymbol{D}[\boldsymbol{R}_0 \,|\, \boldsymbol{\phi}_A]) \cdot \frac{\partial (\mathrm{e}^E P)}{\partial \boldsymbol{\phi}_A}; \end{aligned} \tag{4.12}$$

(iii) local rotational flux densities,

$$\begin{aligned}\boldsymbol{j}[\boldsymbol{\phi}_A] = \boldsymbol{M}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0]\cdot\boldsymbol{F}P - \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0]\cdot\boldsymbol{\nabla}_Q P \\ - \sum_{a=1}^{n} \mathrm{e}^{-E}(\boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_a] - \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0])\cdot\frac{\partial(\mathrm{e}^{E}P)}{\partial \boldsymbol{r}_a} \\ - \sum_{B=0}^{n} \mathrm{e}^{-E}\,\boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B]\cdot\frac{\partial(\mathrm{e}^{E}P)}{\partial \boldsymbol{\phi}_B}.\end{aligned} \tag{4.13}$$

Equation (4.7) together with (4.11)–(4.13) represents the exact microtransport equation governing the detailed stochastic motion of the flexible chain through $(\boldsymbol{Q}\oplus\boldsymbol{q})$-space. In order to apply the results of §2 dealing with generalized Taylor dispersion analyses (Brenner 1982*b*) – with the ultimate goal in mind of eliminating the local-space dependence – additional notational changes must be effected, namely from vector-dyadic to partitioned-matrix form.

Towards that end, let the local flux column vector $[\![\boldsymbol{j}]\!]$ be given in the partitioned matrix form

$$[\![\boldsymbol{j}]\!]^{\dagger} = [\![\boldsymbol{j}^{\dagger}[\boldsymbol{r}_1]\ldots\boldsymbol{j}^{\dagger}[\boldsymbol{r}_n]\boldsymbol{j}^{\dagger}[\boldsymbol{\phi}_0]\ldots\boldsymbol{j}^{\dagger}[\boldsymbol{\phi}_n]]\!] \quad \{1\times(6n+3)\}, \tag{4.14a}$$

whose individual row-vector elements $\boldsymbol{j}^{\dagger}[\ ]$ are themselves 1×3 matrices whose three scalar elements are the three components of the vector $\boldsymbol{j}[\ ]$. Double square brackets serve to indicate that the entity they surround is not a simple vector (or later a dyadic), but rather a partitioned matrix, whose matrix elements are 'vectors' (1×3 or 3×1 matrices) or 'dyadics' (3×3 matrices). Numbers following a definition denote the size of the equivalent matrix representation with *scalar* entries. Equation (4.14*a*) may be compactly abbreviated as

$$[\![\boldsymbol{j}]\!] = \left[\!\!\left[\begin{matrix}\boldsymbol{j}[\boldsymbol{r}_a]\\ \boldsymbol{j}[\boldsymbol{\phi}_A]\end{matrix}\right]\!\!\right] \{(6n+3)\times 1\}, \tag{4.14b}$$

wherein $$[\![\boldsymbol{j}[\boldsymbol{r}_a]]\!] = \left[\!\!\left[\begin{matrix}\boldsymbol{j}[\boldsymbol{r}_1]\\ \vdots\\ \boldsymbol{j}[\boldsymbol{r}_n]\end{matrix}\right]\!\!\right] \{3n\times 1\}, \quad [\![\boldsymbol{j}[\boldsymbol{\phi}_A]]\!] = \left[\!\!\left[\begin{matrix}\boldsymbol{j}[\boldsymbol{\phi}_0]\\ \vdots\\ \boldsymbol{j}[\boldsymbol{\phi}_n]\end{matrix}\right]\!\!\right] \{(3n+3)\times 1\},$$

whose individual column vector elements $\boldsymbol{j}[\ ]$ are the 3×1 transposed matrices of $\boldsymbol{j}^{\dagger}[\ ]$. This notation readily generalizes to partitioned matrices whose elements are 'dyadics' (i.e. 3×3 matrices) rather than 'vectors'. In this connection the generic identity

$$[\![\boldsymbol{\alpha}\,\boldsymbol{\beta}]\!]^{\dagger} = \left[\!\!\left[\begin{matrix}\boldsymbol{\alpha}^{\dagger}\\ \boldsymbol{\beta}^{\dagger}\end{matrix}\right]\!\!\right]$$

obtains for matrix elements $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ of any rank.

Represent the local gradient operator $[\![\boldsymbol{\nabla}_q]\!]$ as the partitioned matrix

$$[\![\boldsymbol{\nabla}_q]\!]^{\dagger} = \left[\!\!\left[\frac{\partial^{\dagger}}{\partial \boldsymbol{r}_1}\cdots\frac{\partial^{\dagger}}{\partial \boldsymbol{r}_n}\,\frac{\partial^{\dagger}}{\partial \boldsymbol{\phi}_0}\cdots\frac{\partial^{\dagger}}{\partial \boldsymbol{\phi}_n}\right]\!\!\right] \{1\times(6n+3)\}. \tag{4.15}$$

As such, the microtransport equation (4.7) may be written in the convenient hybrid vector/matrix form

$$\frac{\partial P}{\partial t} + \boldsymbol{\nabla}_Q\cdot\boldsymbol{J} + [\![\boldsymbol{\nabla}_q]\!]^{\dagger}\cdot[\![\boldsymbol{j}]\!] = \delta(t)\,\delta(\boldsymbol{Q}-\boldsymbol{Q}')\,\delta(\boldsymbol{q}-\boldsymbol{q}'), \tag{4.16}$$

in which an obvious definition has been adopted for $\delta(\boldsymbol{q}-\boldsymbol{q}')$. The local flux density 'vector' $[\![\boldsymbol{j}]\!]$ is found by combining (4.12) and (4.13) to obtain

$$[\![\boldsymbol{j}]\!] = [\![\boldsymbol{u}]\!]P - [\![\boldsymbol{D}^{qQ}]\!]\cdot\boldsymbol{\nabla}_Q P - \mathrm{e}^{-E}[\![\boldsymbol{D}^{qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^{E}P), \tag{4.17}$$

whereas the global flux vector (4.11) is given in the present notation by the expression

$$\boldsymbol{J} = \boldsymbol{U}P - \boldsymbol{D}^{QQ}\cdot\boldsymbol{\nabla}_Q P - \mathrm{e}^{-E}[\![\boldsymbol{D}^{Qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^{E}P). \tag{4.18}$$

Appearing in (4.17) and (4.18) are the following phenomenological coefficients:
(i) Local velocity matrix $[\![\boldsymbol{u}]\!]$:

$$[\![\boldsymbol{u}]\!] = \left[\!\!\left[\begin{array}{c}\boldsymbol{u}[\boldsymbol{r}_a]\\ \boldsymbol{u}[\boldsymbol{\phi}_A]\end{array}\right]\!\!\right]\{(6n+3)\times 1\}, \tag{4.19a}$$

with‡

$$\boldsymbol{u}[\boldsymbol{r}_a] = \{\boldsymbol{M}[\boldsymbol{R}_a\,|\,\boldsymbol{R}_0] - \boldsymbol{M}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_0]\}\cdot\boldsymbol{F} \tag{4.19b}$$

and

$$\boldsymbol{u}[\boldsymbol{\phi}_A] = \boldsymbol{M}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0]\cdot\boldsymbol{F}; \tag{4.19c}$$

(ii) Coupling diffusivity matrix $[\![\boldsymbol{D}^{qQ}]\!]$:

$$[\![\boldsymbol{D}^{qQ}]\!] = \left[\!\!\left[\begin{array}{c}\boldsymbol{D}^{qQ}[\boldsymbol{r}_a]\\ \boldsymbol{D}^{qQ}[\boldsymbol{\phi}_A]\end{array}\right]\!\!\right]\{(6n+3)\times 3\}, \tag{4.20a}$$

with

$$\boldsymbol{D}^{qQ}[\boldsymbol{r}_a] = \boldsymbol{D}[\boldsymbol{R}_a\,|\,\boldsymbol{R}_0] - \boldsymbol{D}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_0] \tag{4.20b}$$

and

$$\boldsymbol{D}^{qQ}[\boldsymbol{\phi}_A] = \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0]; \tag{4.20c}$$

(iii) Local diffusivity matrix $[\![\boldsymbol{D}^{qq}]\!]$:

$$[\![\boldsymbol{D}^{qq}]\!] = \left[\!\!\left[\begin{array}{cc}\boldsymbol{D}^{qq}[\boldsymbol{r}_a\,|\,\boldsymbol{r}_b] & \boldsymbol{D}^{qq}[\boldsymbol{r}_a\,|\,\boldsymbol{\phi}_A]\\ \boldsymbol{D}^{qq}[\boldsymbol{\phi}_A\,|\,\boldsymbol{r}_a] & \boldsymbol{D}^{qq}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B]\end{array}\right]\!\!\right]\{(6n+3)\times(6n+3)\}, \tag{4.21a}$$

in which

$$\boldsymbol{D}^{qq}[\boldsymbol{r}_a\,|\,\boldsymbol{r}_b] = \boldsymbol{D}[\boldsymbol{R}_a\,|\,\boldsymbol{R}_b] - \boldsymbol{D}[\boldsymbol{R}_a\,|\,\boldsymbol{R}_0] - \boldsymbol{D}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_b] + \boldsymbol{D}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_0], \tag{4.21b}$$

$$\boldsymbol{D}^{qq}[\boldsymbol{r}_a\,|\,\boldsymbol{\phi}_A] = \boldsymbol{D}[\boldsymbol{R}_a\,|\,\boldsymbol{\phi}_A] - \boldsymbol{D}[\boldsymbol{R}_0\,|\,\boldsymbol{\phi}_A], \tag{4.21c}$$

$$\boldsymbol{D}^{qq}[\boldsymbol{\phi}_A\,|\,\boldsymbol{r}_a] = \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_a] - \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{R}_0] = \boldsymbol{D}^{qq\dagger}[\boldsymbol{r}_a\,|\,\boldsymbol{\phi}_A], \tag{4.21d}$$

$$\boldsymbol{D}^{qq}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B] = \boldsymbol{D}[\boldsymbol{\phi}_A\,|\,\boldsymbol{\phi}_B]. \tag{4.21e}$$

It is easily established that the square matrix (4.21*a*) is symmetric;
(iv) Global velocity vector $\boldsymbol{U}$:

$$\boldsymbol{U} \equiv \boldsymbol{M}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_0]\cdot\boldsymbol{F}\,\{3\times 1\}; \tag{4.22}$$

(v) Global diffusivity dyadic $\boldsymbol{D}^{QQ}$:

$$\boldsymbol{D}^{QQ} \equiv \boldsymbol{D}[\boldsymbol{R}_0\,|\,\boldsymbol{R}_0]\,\{3\times 3\}; \tag{4.23}$$

(vi) Transposed coupling diffusivity matrix $[\![\boldsymbol{D}^{Qq}]\!]$:

$$[\![\boldsymbol{D}^{Qq}]\!] = [\![\boldsymbol{D}^{qQ}]\!]^{\dagger}\,\{3\times(6n+3)\}, \tag{4.24}$$

with the right-hand side explicitly defined in (4.20).

Each of the six phenomenological matrices (4.19)–(4.24) are well-defined functions of the conformation $\boldsymbol{q}$, and are all calculable once the $n+1$ multibody hydrodynamic

‡ No confusion should result from using identical symbols such as $\boldsymbol{u}[\ ]$ in both the matrix-vector mode, as in (4.19*a*), and the literal vector mode, as in (4.19*b*) and (4.19*c*).

interaction problem is solved. They further satisfy all the necessary symmetry conditions outlined in §2. Despite their complex appearance (and generally large numbers of degrees of freedom), they render the forms of the detailed microtransport equation (4.16) and constitutive flux expressions (4.17) and (4.18) identical in appearance with the corresponding canonical equations of generalized coupled Taylor dispersion theory outlined in §2.

5. Macrotransport coefficients

Having transformed the detailed equations governing the configurational transport process into the canonical forms of coupled generalized Taylor dispersion theory, the formal results for the long-time mean velocity vector and dispersivity dyadic of the flexible chain may now be given explicitly.

5.1. *Mean velocity vector* $\overline{\boldsymbol{U}}^*$

Following (2.12), the expression for the mean velocity vector of the flexible body, sedimenting through the viscous fluid under the action of the external force $\boldsymbol{F}$ (cf. (4.10)), adopts the hybrid vector/matrix form

$$\overline{\boldsymbol{U}}^* = \int_{q_o} \mathrm{d}\boldsymbol{q}\{P_0^\infty \boldsymbol{U} - \mathrm{e}^{-E}[\![\boldsymbol{D}^{Qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^E P_0^\infty)\}, \tag{5.1}$$

in which the volume element $\mathrm{d}\boldsymbol{q}$ represents $\mathrm{d}\boldsymbol{r}^n\,\mathrm{d}\boldsymbol{\phi}^{n+1}$. The quantities $\boldsymbol{U}$, $[\![\boldsymbol{D}^{Qq}]\!]$, E and $[\![\boldsymbol{\nabla}_q]\!]$ appearing in the integrand are respectively given by (4.22), (4.24), (4.10) and (4.15). The local equilibrium density $P_0^\infty(\boldsymbol{q}) \equiv P_0^\infty(\boldsymbol{r}^n, \boldsymbol{\phi}^{n+1})$, required above, represents the solution of the pair of equations (cf. (2.14))

$$[\![\boldsymbol{\nabla}_q]\!]^\dagger\cdot\{[\![\boldsymbol{u}]\!]P_0^\infty - \mathrm{e}^{-E}[\![\boldsymbol{D}^{qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^E P_0^\infty)\} = 0, \tag{5.2a}$$

$$\int_{q_o} \mathrm{d}\boldsymbol{q}\, P_0^\infty = 1, \tag{5.2b}$$

wherein, rather than specifying explicitly posed boundary conditions, any such required conditions are incorporated into the potential E (in a manner similar to so-called 'hard-sphere' potential interactions) and/or the phenomenological coefficients. Coefficients $[\![\boldsymbol{u}]\!]$ and $[\![\boldsymbol{D}^{qq}]\!]$, required above, are given explicitly by (4.19) and (4.21).

5.2. *Dispersivity dyadic* $\overline{\boldsymbol{D}}^*$

Corresponding to (2.13), the flexible-body long-time dispersivity dyadic is

$$\overline{\boldsymbol{D}}^* = \int_{q_o} \mathrm{d}\boldsymbol{q}\{P_0^\infty(\boldsymbol{D}^{QQ} - [\![\boldsymbol{D}^{Qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!]\boldsymbol{B}) + [P_0^\infty(\boldsymbol{U} - \overline{\boldsymbol{U}}^*) - \mathrm{e}^{-E}[\![\boldsymbol{D}^{Qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^E P_0^\infty)]\boldsymbol{B}\}, \tag{5.3}$$

with $\boldsymbol{D}^{QQ}$ given by (4.23). The global-space vector field $\boldsymbol{B}(\boldsymbol{q})$, defined over the local space $\boldsymbol{q}_o$, may be obtained (cf. (2.15)) upon solving the equation

$$[\![\boldsymbol{\nabla}_q]\!]^\dagger\cdot\{[\![\boldsymbol{u}]\!]P_0^\infty\boldsymbol{B} - \mathrm{e}^{-E}[\![\boldsymbol{D}^{qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^E P_0^\infty \boldsymbol{B}) + P_0^\infty[\![\boldsymbol{D}^{qQ}]\!]\}$$
$$= P_0^\infty(\boldsymbol{U} - \overline{\boldsymbol{U}}^*) - \mathrm{e}^{-E}[\![\boldsymbol{D}^{Qq}]\!]\cdot[\![\boldsymbol{\nabla}_q]\!](\mathrm{e}^E P_0^\infty), \tag{5.4}$$

subject to appropriate 'boundary' behaviour built into the phenomenological coefficients and/or potential. The $\boldsymbol{B}$-field is uniquely determined only to within an arbitrary additive constant vector.

For completeness we also provide explicit forms for boundary conditions (2.14*b*) and (2.15*b*) in a formulation that includes a conventional treatment of boundaries. If the scalar equation

$$s(\boldsymbol{r}^n, \boldsymbol{\phi}^{n+1}) = 0 \tag{5.5}$$

represents an explicit parameterization of the local-space boundary $\partial \boldsymbol{q}_o$ (with $s < 0$ within, and $s > 0$ outside of $\partial \boldsymbol{q}_o$), the unit outward-drawn normal 'vector' $[\![\boldsymbol{n}]\!]$ will be given by

$$[\![\boldsymbol{n}]\!] = ([\![\boldsymbol{\nabla}_q]\!]^\dagger s \cdot [\![\boldsymbol{\nabla}_q]\!] s)^{-\frac{1}{2}} [\![\boldsymbol{\nabla}_q]\!] s. \tag{5.6}$$

In this formulation, (5.2*a*, *b*) are to be supplemented by the zero-normal-flux condition (cf. (2.14*b*))

$$[\![\boldsymbol{n}]\!]^\dagger \cdot \{[\![\boldsymbol{u}]\!] P_0^\infty - \mathrm{e}^{-E}[\![\boldsymbol{D}^{qq}]\!] \cdot [\![\boldsymbol{\nabla}_q]\!] (\mathrm{e}^E P_0^\infty)\} = 0 \quad \text{on } \partial \boldsymbol{q}_o, \tag{5.7}$$

whereas (5.4) is to be solved subject to (cf. (2.15*b*))

$$-P_0^\infty [\![\boldsymbol{n}]\!]^\dagger \cdot ([\![\boldsymbol{D}^{qq}]\!] \cdot [\![\boldsymbol{\nabla}_q]\!] \boldsymbol{B} - [\![\boldsymbol{D}^{qQ}]\!]) = \boldsymbol{0} \quad \text{on } \partial \boldsymbol{q}_o. \tag{5.8}$$

5.3. '*Molecular dispersion*' $\overline{\boldsymbol{D}}^{\mathrm{M}}$ *in the absence of sedimentation*

This subsection provides solutions of the above sets of equations for circumstances in which the global external force $\boldsymbol{F}$ giving rise to sedimentation of the flexible chain is absent. Thus, chain transport occurs solely as a result of the coupled translational and rotational Brownian motions of its constituent rigid particles. With $\boldsymbol{F} = \boldsymbol{0}$ it may be anticipated that $\overline{\boldsymbol{U}}^* = \boldsymbol{0}$, a fact which will be proved shortly. As such, the long-time transport is characterized solely by $\overline{\boldsymbol{D}}^*$, whose explicit form will now be calculated.

Upon setting $\boldsymbol{F} = \boldsymbol{0}$, the phenomenological coefficients $[\![\boldsymbol{u}]\!]$ and $\boldsymbol{U}$ are found to vanish identically (cf. (4.19) and (4.22)). Equations (5.2*a*, *b*) therefore possess the unique (Brenner 1982*b*) solution

$$P_0^\infty = W^{-1} \mathrm{e}^{-E}, \quad W = \int_{q_o} \mathrm{d}\boldsymbol{q}\, \mathrm{e}^{-E}, \tag{5.9a, b}$$

(which also satisfies (5.7)). Substitution of (5.9) into (5.1), in conjunction with the vanishing of $\boldsymbol{U}$, thereby demonstrates that

$$\overline{\boldsymbol{U}}^* = \boldsymbol{0}, \tag{5.10}$$

as expected.

Under these conditions (5.4) adopts the simple form

$$-[\![\boldsymbol{\nabla}_q]\!]^\dagger \cdot \{P_0^\infty ([\![\boldsymbol{D}^{qq}]\!] \cdot [\![\boldsymbol{\nabla}_q]\!] \boldsymbol{B} - [\![\boldsymbol{D}^{qQ}]\!])\} = \boldsymbol{0}, \tag{5.11}$$

thereby requiring that

$$[\![\boldsymbol{\nabla}_q]\!] \boldsymbol{B} = [\![\boldsymbol{D}^{qq}]\!]^{-1} \cdot [\![\boldsymbol{D}^{qQ}]\!] \tag{5.12}$$

(which also satisfies (5.8)), with $[\![\boldsymbol{D}^{qq}]\!]^{-1}$ the matrix inverse of $[\![\boldsymbol{D}^{qq}]\!]$ (itself a $(6n+3) \times (6n+3)$ matrix). Examination of (5.3) suggests that since the terms multiplying $\boldsymbol{B}$ in the integrand vanish, no need exists to solve (5.12) explicitly for $\boldsymbol{B}$ in the present case. Substitution of (5.12) into (5.3) immediately yields the long-time 'molecular dispersivity' dyadic (in hybrid dyadic/matrix form)

$$\overline{\boldsymbol{D}}^{\mathrm{M}} = \int_{q_o} \mathrm{d}\boldsymbol{q}\, P_0^\infty (\boldsymbol{D}^{QQ} - [\![\boldsymbol{D}^{Qq}]\!] \cdot [\![\boldsymbol{D}^{qq}]\!]^{-1} \cdot [\![\boldsymbol{D}^{qQ}]\!]) \tag{5.13}$$

of the flexible chain. Note that this expression differs from an averaged molecular diffusivity for the body. In particular, although no net external force was assumed

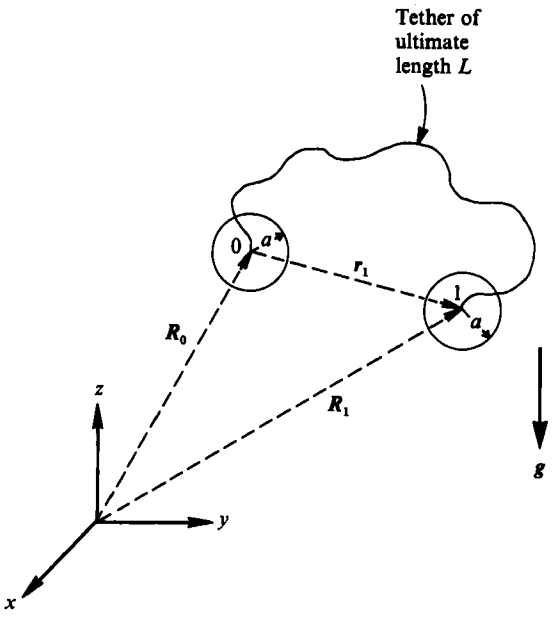

FIGURE 1. Tethered dumb-bell.

to exist, no such assumption was made regarding external 'couples' tending to confer upon the flexible body a particular orientation. The resulting 'molecular dispersivity' (5.13) may indeed be anisotropic, as will prove to be the case for the non-sedimenting, but 'loaded', flexible dumb-bell described in §7.

6. Sedimentation of a flexible dumb-bell

The general multiparticle analysis developed in preceding sections will be applied in this section to the two-body problem arising from the sedimentation and diffusion of a flexible Brownian dumb-bell in an otherwise quiescent viscous fluid.

As in figure 1, consider a dumb-bell composed of two identical rigid spherical particles, numbered 0 and 1, of radii a, whose geometric centres – possessing respective position vectors $\boldsymbol{R}_0, \boldsymbol{R}_1$ – are chosen as their respective locator points. Each of the constituent spheres is assumed to be homogeneous, possessing a density higher than that of the surrounding fluid. Denote by $|\Delta m|$ the difference between its *en vacuo* mass and that of the displaced fluid. In a gravity field of vector strength $\boldsymbol{g}$, the combined gravitational–buoyancy portion of the dumb-bell potential is thus found to be

$$-|\Delta m|\,\boldsymbol{g}\cdot\boldsymbol{R}_0-|\Delta m|\,\boldsymbol{g}\cdot\boldsymbol{R}_1=-2|\Delta m|\,\boldsymbol{g}\cdot\boldsymbol{R}_0-|\Delta m|\,\boldsymbol{g}\cdot\boldsymbol{r}_1, \tag{6.1}$$

where, in accordance with (4.2),

$$\boldsymbol{r}_1=\boldsymbol{R}_1-\boldsymbol{R}_0. \tag{6.2}$$

The total potential of the flexible dumb-bell is obtained by adding to (6.1) the additional (internal) conformational potential $kT\hat{E}(\boldsymbol{r}_1)$, which we assume to depend only upon the internal vector $\boldsymbol{r}_1$, but not upon the orientations of either of the individual spheres. This yields (cf. (4.10))

$$V=-\boldsymbol{F}\cdot\boldsymbol{R}_0+kTE(\boldsymbol{r}_1), \tag{6.3a}$$

in which we identify the total external force,

$$\boldsymbol{F} = 2|\Delta m|\,\boldsymbol{g}, \tag{6.3b}$$

and total internal potential,

$$kTE(\boldsymbol{r}_1) = kT\hat{E}(\boldsymbol{r}_1) - |\Delta m|\,\boldsymbol{g}\cdot\boldsymbol{r}_1. \tag{6.3c}$$

The latter contains contributions from the purely conformational potential as well as from the 'internal' portion of the gravitational–buoyancy potential.

As a joint consequence of the choices of the sphere centres as individual sphere locator points, the assumed homogeneity of each of the spheres (resulting in the absence of external torques about their centres), and the assumed independence of the conformational potential upon the orientations $(\boldsymbol{\phi}_0, \boldsymbol{\phi}_1)$ of the constituent spheres, it may be shown that the latter orientations play a superfluous role in the analysis (since all the phenomenological microtransport coefficients appearing in the theory are necessarily independent of $(\boldsymbol{\phi}_0, \boldsymbol{\phi}_1)$). As such, it is convenient to eliminate these internal variables at the outset by simply integrating the fundamental conservation equation (4.16) over the orientational degrees of freedom.‡ This yields a greatly simplified set of microtransport equations governing the probability density $P(\boldsymbol{R}_0, \boldsymbol{r}_1, t\,|\,\boldsymbol{R}_0', \boldsymbol{r}_1')$, with $\boldsymbol{R}_0$ spanning the global space (cf. (4.1)), i.e.

$$\boldsymbol{Q} \equiv \boldsymbol{R}_0, \tag{6.4}$$

and with the vector $\boldsymbol{r}_1$ serving as the sole local coordinate (cf. (4.3)), i.e.

$$\boldsymbol{q} \equiv \boldsymbol{r}_1. \tag{6.5}$$

This simplification eliminates the prior necessity for a hybrid matrix/dyadic form of the basic microtransport equations; in fact, the following 'equivalence' relations obtain (cf. (4.15), (4.19)–(4.24)):

$$[\![\nabla_{\boldsymbol{Q}}]\!] = \nabla_{\boldsymbol{r}_1}, \quad [\![\boldsymbol{u}]\!] = (\boldsymbol{M}_{10} - \boldsymbol{M}_{00})\cdot\boldsymbol{F}, \quad [\![\boldsymbol{D}^{\boldsymbol{qQ}}]\!] = \boldsymbol{D}_{10} - \boldsymbol{D}_{00}, \tag{6.6a–c}$$

$$[\![\boldsymbol{D}^{\boldsymbol{qq}}]\!] = \boldsymbol{D}_{11} - \boldsymbol{D}_{10} - \boldsymbol{D}_{01} + \boldsymbol{D}_{00} \equiv 2(\boldsymbol{D}_{00} - \boldsymbol{D}_{10}), \tag{6.6d}$$

$$\boldsymbol{U} = \boldsymbol{M}_{00}\cdot\boldsymbol{F}, \quad \boldsymbol{D}^{\boldsymbol{QQ}} = \boldsymbol{D}_{00}, \quad [\![\boldsymbol{D}^{\boldsymbol{Qq}}]\!] = \boldsymbol{D}_{01} - \boldsymbol{D}_{00} = \boldsymbol{D}_{10} - \boldsymbol{D}_{00}, \tag{6.6e–g}$$

wherein the right-hand sides of each of the above expressions are either vectors or dyadics. In writing these relations we have introduced the simplified notation

$$\boldsymbol{M}[\boldsymbol{R}_A\,|\,\boldsymbol{R}_B] \equiv \boldsymbol{M}_{AB}, \quad \boldsymbol{D}[\boldsymbol{R}_A\,|\,\boldsymbol{R}_B] \equiv \boldsymbol{D}_{AB}, \tag{6.7}$$

since, in the absence of orientational variables, no confusion can result in the course of interpreting the right-hand sides of these expressions. Furthermore, in (6.6*d*, *g*) use was made of the identities

$$\boldsymbol{D}_{01} = \boldsymbol{D}_{10}(\boldsymbol{M}_{01} = \boldsymbol{M}_{10}), \quad \boldsymbol{D}_{11} = \boldsymbol{D}_{00}(\boldsymbol{M}_{11} = \boldsymbol{M}_{00}). \tag{6.8a, b}$$

These low-Reynolds-number identities obtain when the two spheres composing the dumb-bell are identical (Brenner 1964; Brenner & O'Neill 1972; Jeffrey & Onishi 1984).

The equivalence relations (6.6) will now be employed to specialize the general results of §5 to the present sedimenting flexible-dumb-bell problem.

‡ This is possible since the phenomenological coefficients appearing in each of the constitutive flux expressions are presently independent of $\boldsymbol{\phi}_A$.

6.1. *Mean settling velocity vector* $\overline{\boldsymbol{U}}^*$

Equations (5.2) for $P_0^\infty(\boldsymbol{r}_1)$ here adopt the respective forms

$$\nabla_{r_1}\cdot[(\boldsymbol{M}_{10}-\boldsymbol{M}_{00})\cdot\boldsymbol{F}P_0^\infty-2\mathrm{e}^{-E}(\boldsymbol{D}_{00}-\boldsymbol{D}_{10})\cdot\nabla_{r_1}(\mathrm{e}^E P_0^\infty)]=0, \tag{6.9a}$$

$$\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 P_0^\infty = 1, \tag{6.9b}$$

in which $\boldsymbol{F}$ and E are given by (6.3b, c), and the symbol τ_{r_1} denotes the entire domain accessible to $\boldsymbol{r}_1$. Their solution is the Boltzmann distribution

$$P_0^\infty = W^{-1}\exp[-\hat{E}(\boldsymbol{r}_1)], \tag{6.10a}$$

with $\hat{E}$ the conformational potential and W the normalization constant

$$W=\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-\hat{E}). \tag{6.10b}$$

$\hat{E}$ is assumed to contain, *inter alia*, the so-called hard-sphere repulsive potential contribution, preventing interpenetration of the spheres. For the tethered dumb-bell depicted in figure 1, $\hat{E}$ thus adopts the form

$$\hat{E}(\boldsymbol{r}_1)=\begin{cases}\infty & (|\boldsymbol{r}_1|<2a),\\ 0 & (2a\leqslant|\boldsymbol{r}_1|\leqslant L),\\ \infty & (L<|\boldsymbol{r}_1|),\end{cases} \tag{6.11}$$

with L the tether length. To verify that (6.10) is indeed the solution of (6.9), note that with P_0^∞ given by (6.10) the following identity prevails:

$$\mathrm{e}^{-E}\nabla_{r_1}(\mathrm{e}^E P_0^\infty) = -\frac{P_0^\infty \boldsymbol{F}}{2kT}. \tag{6.12}$$

Substitution of the latter into (6.9a) followed by use of the Stokes–Einstein relation (3.9) shows that the term within square brackets in (6.9a) vanishes identically, thereby confirming the solution (6.10).

Equation (5.1) here adopts the form (cf. (6.6a, e, g))

$$\overline{\boldsymbol{U}}^* = \int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1[P_0^\infty \boldsymbol{M}_{00}\cdot\boldsymbol{F}-\mathrm{e}^{-E}(\boldsymbol{D}_{10}-\boldsymbol{D}_{00})\cdot\nabla_{r_1}(\mathrm{e}^E P_0^\infty)]. \tag{6.13}$$

With use of (6.10) and (6.12) this becomes

$$\overline{\boldsymbol{U}}^* = \left[W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-\hat{E})\boldsymbol{M}\right]\cdot\boldsymbol{F}, \tag{6.14}$$

in which

$$\boldsymbol{M} \overset{\text{def}}{\equiv} \tfrac{1}{2}(\boldsymbol{M}_{00}+\boldsymbol{M}_{10}). \tag{6.15}$$

The mobility dyadics appearing in the latter are known functions of the centre-to-centre displacement vector $\boldsymbol{r}_1$ (Batchelor 1976; Jeffrey & Onishi 1984; Kim & Mifflin 1985). As a result of the inherent symmetry of the dumb-bell geometry, all of the phenomenological transport dyadics and, hence, $\boldsymbol{M}$ may be written in the body-fixed, transversely isotropic form (Brenner 1964)

$$\boldsymbol{M} = M_\parallel \boldsymbol{ee}+M_\perp(\boldsymbol{I}-\boldsymbol{ee}), \tag{6.16}$$

with $\boldsymbol{e}$ a unit vector in the direction of $\boldsymbol{r}_1$, and with the scalar functions $M_\parallel$ and $M_\perp$ dependent only upon the scalar magnitude r of $\boldsymbol{r}_1$:

$$|\boldsymbol{r}_1| = r, \quad \boldsymbol{r}_1 = r\boldsymbol{e}. \tag{6.17}$$

Explicitly, these are given in the notation of Jeffrey & Onishi (1984) as

$$M_\parallel = (12\pi\mu a)^{-1}(x_{11}^a + x_{12}^a), \quad M_\perp = (12\pi\mu a)^{-1}(y_{11}^a + y_{12}^a), \tag{6.18a,b}$$

with the dimensionless functions x_{11}^a, x_{12}^a, y_{11}^a and y_{12}^a furnished by these authors in their §§8 and 9. (Note that whereas we have numbered our spheres 0 and 1, theirs are labelled 1 and 2; moreover, their sphere radius-ratio parameter $\lambda = a_2/a_1$ is here equal to unity, while their non-dimensional sphere centre-separation parameter s here becomes $s = r/a$.) Numerical evaluation of (6.14) will subsequently be carried out for the tethered dumb-bell case (6.11). However, no conceptual difficulties exist in contemplating comparable calculations for other, more complex, conformational potentials – for example a Hookean spring connecting the sphere centres.

6.2. *Pure molecular diffusivity* $\overline{\boldsymbol{D}}^{\mathrm{M}}$

Although this section is focused on dispersive effects accompanying sedimentation, it is instructive to consider first the simpler circumstance where sedimentation is absent ($\boldsymbol{F} = \boldsymbol{0}$), so that the only transport mechanism is molecular diffusion of the flexible dumb-bell. The internal Boltzmann equilibrium probability density (6.10) obviously remains unchanged as $\boldsymbol{F} \to \boldsymbol{0}$, establishing the validity of (6.10) even in the absence of sedimentation. In this limit, the sedimentation velocity (6.14) vanishes, whence the purely molecular contribution to the dumb-bell dispersivity adopts the form (cf. (5.13))

$$\begin{aligned}\overline{\boldsymbol{D}}^{\mathrm{M}} &= W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-\hat{E})[\boldsymbol{D}_{00} - \tfrac{1}{2}(\boldsymbol{D}_{10} - \boldsymbol{D}_{00})\cdot(\boldsymbol{D}_{00} - \boldsymbol{D}_{10})^{-1}\cdot(\boldsymbol{D}_{10} - \boldsymbol{D}_{00})], \\ &\equiv W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-\hat{E})\boldsymbol{D}, \end{aligned} \tag{6.19}$$

with

$$\boldsymbol{D} \overset{\text{def}}{\equiv} \tfrac{1}{2}(\boldsymbol{D}_{00} + \boldsymbol{D}_{10}) \equiv kT\boldsymbol{M}. \tag{6.20}$$

These results point to the interesting conclusion that if the quantity within square brackets in (6.14) is interpreted as a 'mean' dumb-bell mobility dyadic (and denoted by $\overline{\boldsymbol{M}}$, as in (6.22)), then the Stokes–Einstein-type relationship $\overline{\boldsymbol{D}}^{\mathrm{M}} = kT\overline{\boldsymbol{M}}$ obtains between the mean molecular dispersivity (6.19) and the mean mobility.

6.3. *Sedimentation dispersivity* $\overline{\boldsymbol{D}}^{*}$

We here resume calculation of the dumb-bell dispersivity dyadic $\overline{\boldsymbol{D}}^{*}$ for the case $\boldsymbol{F} \neq \boldsymbol{0}$, incorporating coupling effects arising from interactions between the translational–rotational–vibrational Brownian motions of the dumb-bell and its instantaneous configuration-dependent sedimentation velocity $\boldsymbol{U}$.

Using the equivalence relations (6.6) together with the identity (6.12), the required $\boldsymbol{B}(\boldsymbol{r}_1)$-field is found to satisfy (cf. (5.4))

$$\nabla_{r_1}\cdot[-2P_0^\infty(\boldsymbol{D}_{00} - \boldsymbol{D}_{10})\cdot\nabla_{r_1}\boldsymbol{B} + P_0^\infty(\boldsymbol{D}_{10} - \boldsymbol{D}_{00})] = P_0^\infty(\boldsymbol{M} - \overline{\boldsymbol{M}})\cdot\boldsymbol{F}, \tag{6.21}$$

with $\boldsymbol{M}$ given by (6.15) and $\overline{\boldsymbol{M}}$ defined as the term within square brackets in (6.14), namely

$$\overline{\boldsymbol{M}} = W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-\hat{E})\boldsymbol{M}. \tag{6.22}$$

The decomposition

$$\boldsymbol{B}(\boldsymbol{r}_1) \overset{\text{def}}{=} -\tfrac{1}{2}\boldsymbol{r}_1 + \boldsymbol{B}'(\boldsymbol{r}_1) \tag{6.23}$$

together with the definition

$$\boldsymbol{d} \overset{\text{def}}{\equiv} 2(\boldsymbol{D}_{00} - \boldsymbol{D}_{10}) \tag{6.24}$$

furnishes the following equation governing $\boldsymbol{B}'$:

$$-\boldsymbol{\nabla}_{r_1}\cdot(P_0^{\infty}\,\boldsymbol{d}\cdot\boldsymbol{\nabla}_{r_1}\boldsymbol{B}') = P_0^{\infty}(\boldsymbol{M}-\overline{\boldsymbol{M}})\cdot\boldsymbol{F}. \tag{6.25}$$

Were explicit recognition to be given to the boundary condition (5.8) imposed on $\boldsymbol{B}$, (6.25) would be supplemented by the boundary condition

$$-P_0^{\infty}\,\boldsymbol{n}\cdot\boldsymbol{d}\cdot\boldsymbol{\nabla}_{r_1}\boldsymbol{B}' = \boldsymbol{0} \quad \text{on } \partial\tau_{r_1}, \tag{6.26}$$

with $\boldsymbol{n}$ the outwardly directed unit normal vector on the boundary $\partial\tau_{r_1}$ of $\boldsymbol{r}_1$ space, were the latter space indeed bounded.

The dyadic $\boldsymbol{d}$ possesses the transversely isotropic decomposition

$$\boldsymbol{d} = d_{\parallel}\,\boldsymbol{ee} + d_{\perp}(\boldsymbol{I}-\boldsymbol{ee}), \tag{6.27}$$

with the r-dependent scalar coefficients $d_{\parallel}$ and $d_{\perp}$ related to the dimensionless functions of Jeffrey & Onishi (1984) via the relations

$$d_{\parallel} = \frac{kT}{3\pi\mu a}(x_{11}^a - x_{12}^a), \quad d_{\perp} = \frac{kT}{3\pi\mu a}(y_{11}^a - y_{12}^a). \tag{6.28a,b}$$

Equation (6.25) is most conveniently solved (Brenner 1979, 1981) by introducing a body-fixed dyadic field $\boldsymbol{b}(\boldsymbol{r}_1)$, defined by the relation

$$\boldsymbol{B}'(\boldsymbol{r}_1) = \boldsymbol{b}(\boldsymbol{r}_1)\cdot\boldsymbol{F} \tag{6.29}$$

(to which definition of $\boldsymbol{b}$ may be added a physically irrelevant, arbitrary, additive constant vector, which we shall here take to be zero without loss of generality). Substitution into (6.25), followed by mutual cancellation of the 'arbitrary' space-fixed vector $\boldsymbol{F}$ from both sides of the resulting equation, yields

$$\boldsymbol{\nabla}_{r_1}\cdot(P_0^{\infty}\,\boldsymbol{d}\cdot\boldsymbol{\nabla}_{r_1}\boldsymbol{b}) = P_0^{\infty}(\overline{\boldsymbol{M}}-\boldsymbol{M}). \tag{6.30}$$

This exclusively body-fixed inhomogeneous equation governs the dyadic field $\boldsymbol{b}$.

Further simplifications result from confining subsequent attention in this section to circumstances where the conformational potential $\hat{E}(\boldsymbol{r}_1)$ depends only upon the scalar magnitude r (cf. (6.17)) of $\boldsymbol{r}_1$, but not upon the direction $\boldsymbol{e}$ of the latter vector. (An example where this is not the case will be considered in the next section.) Consequently, since the volume element $\mathrm{d}\boldsymbol{r}_1$ may be represented as

$$\mathrm{d}\boldsymbol{r}_1 = r^2\,\mathrm{d}r\,\mathrm{d}^2\boldsymbol{e}, \tag{6.31a}$$

with $\mathrm{d}^2\boldsymbol{e}$ ($\equiv \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$) an element of solid angle on the surface of a unit sphere S_1 (Brenner 1979), several of the required multidimensional integrations (e.g. (6.10b), (6.14), (6.19)) may be partially performed. In particular, it is found that

$$W = 4\pi\omega, \quad \omega \equiv \int_{r=0}^{\infty} \mathrm{d}r\,r^2\exp[-\hat{E}(r)], \tag{6.31b,c}$$

since

$$\oint_{S_1} \mathrm{d}^2\boldsymbol{e} = 4\pi. \tag{6.32}$$

Furthermore, upon substitution of (6.31*b*) and (6.16) into (6.22), we find after performing the resulting S_1 integration that the dyadic $\overline{\boldsymbol{M}}$ adopts the isotropic form

$$\overline{\boldsymbol{M}} = \boldsymbol{I}\overline{M}, \quad \overline{M} = \frac{1}{3\omega}\int_{r=0}^{\infty} \mathrm{d}r\, r^2 \exp(-\hat{E})(M_{\parallel}+2M_{\perp}). \tag{6.33a,b}$$

In obtaining (6.33*a*), use was made of the dyadic identity (Brenner 1979)

$$(4\pi)^{-1}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\,\boldsymbol{e}\boldsymbol{e} = \tfrac{1}{3}\boldsymbol{I}. \tag{6.34}$$

Equations (6.33*a*) and (6.16) combine to yield

$$\overline{\boldsymbol{M}}-\boldsymbol{M} = [\overline{M}-\tfrac{1}{3}(M_{\parallel}+2M_{\perp})]\boldsymbol{I}-\tfrac{2}{3}(M_{\parallel}-M_{\perp})\boldsymbol{P}_2(\boldsymbol{e}), \tag{6.35}$$

with the dyadic

$$\boldsymbol{P}_2(\boldsymbol{e}) = \tfrac{1}{2}(3\boldsymbol{e}\boldsymbol{e}-\boldsymbol{I}) \tag{6.36a}$$

the polyadic surface spherical harmonic of degree 2 (Brenner 1964, 1979, 1981). This possesses the useful property that, with $\nabla_e^2 \equiv \nabla_e\cdot\nabla_e$,

$$\nabla_e^2\boldsymbol{P}_2(\boldsymbol{e}) = -6\boldsymbol{P}_2(\boldsymbol{e}), \tag{6.36b}$$

in which ∇_e is the gradient operator on S_1 (Brenner & Condiff 1972; Brenner 1979), being related to ∇_{r_1} via the expression

$$\nabla_{r_1} = \frac{1}{r}\nabla_e + \boldsymbol{e}\frac{\partial}{\partial r}. \tag{6.37}$$

Introduction of (6.35) into (6.30) yields

$$\nabla_{r_1}\cdot(\mathrm{e}^{-\hat{E}}\boldsymbol{d}\cdot\nabla_{r_1}\boldsymbol{b}) = \mathrm{e}^{-\hat{E}}[\overline{M}-\tfrac{1}{3}(M_{\parallel}+2M_{\perp})]\boldsymbol{I}-\tfrac{2}{3}\mathrm{e}^{-\hat{E}}(M_{\parallel}-M_{\perp})\boldsymbol{P}_2(\boldsymbol{e}). \tag{6.38}$$

The form of the forcing term on the right-hand side of the preceding equation suggests a trial solution of the form

$$\boldsymbol{b}(\boldsymbol{r}_1) = f(r)\boldsymbol{I}+g(r)\boldsymbol{P}_2(\boldsymbol{e}). \tag{6.39}$$

Substitute (6.39) into the governing equation (6.38) and employ the identities (Brenner & Condiff 1972)

$$\boldsymbol{e}\cdot\nabla_e = 0, \quad \nabla_e\boldsymbol{e} = \boldsymbol{I}-\boldsymbol{e}\boldsymbol{e}, \quad \nabla_e\cdot\boldsymbol{e} = 2, \tag{6.40a–c}$$

together with (6.36*b*), to obtain the resulting pair of ordinary differential equations

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\mathrm{e}^{-\hat{E}}d_{\parallel}\frac{\mathrm{d}f}{\mathrm{d}r}\right) = \mathrm{e}^{-\hat{E}}[\overline{M}-\tfrac{1}{3}(M_{\parallel}+2M_{\perp})], \tag{6.41a}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\mathrm{e}^{-\hat{E}}d_{\parallel}\frac{\mathrm{d}g}{\mathrm{d}r}\right)-\frac{6}{r^2}\mathrm{e}^{-\hat{E}}d_{\perp}g = -\tfrac{2}{3}\mathrm{e}^{-\hat{E}}(M_{\parallel}-M_{\perp}), \tag{6.42a}$$

respectively governing the unknown scalar fields $f(r)$ and $g(r)$. For these specific circumstances in which the tethered potential (6.11) is adopted it proves more convenient to restrict attention to the domain $2a \leqslant r \leqslant L$ (outside of which P_0^{∞} vanishes) in the course of solving these equations. Boundary condition (6.26) can then be shown to require that

$$d_{\parallel}\frac{\mathrm{d}f}{\mathrm{d}r} = 0 \quad \text{at } r = 2a, L, \tag{6.41b}$$

$$d_{\parallel}\frac{\mathrm{d}g}{\mathrm{d}r} = 0 \quad \text{at } r = 2a, L. \tag{6.42b}$$

Equations (6.41) and (6.42) are simple ordinary differential equations, whose solutions can readily be obtained via standard numerical analyses. (Note that the phenomenological coefficients appearing therein are not themselves known in analytical form (Batchelor 1976; Jeffrey & Onishi 1984; Kim & Mifflin 1985), thereby precluding analytical solutions of these equations.) Upon their solution the $\boldsymbol{B}$-field will be fully known, adopting the form (cf. (6.23), (6.29), (6.39))

$$\boldsymbol{B}(\boldsymbol{r}_1) = -\tfrac{1}{2}\boldsymbol{r}_1 + [f(r)\boldsymbol{I} + g(r)\boldsymbol{P}_2(\boldsymbol{e})]\cdot\boldsymbol{F}. \tag{6.43}$$

Upon use of (6.6) and (6.12) the dispersivity dyadic (5.3) becomes

$$\overline{\boldsymbol{D}}^* = W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1\, \mathrm{e}^{-\hat{E}}\{[\boldsymbol{D}_{00} - (\boldsymbol{D}_{10} - \boldsymbol{D}_{00})\cdot\nabla_{r_1}\boldsymbol{B}] + (\boldsymbol{M} - \overline{\boldsymbol{M}})\cdot\boldsymbol{F}\boldsymbol{B}\}. \tag{6.44}$$

The contribution of the $-\frac{1}{2}\boldsymbol{r}_1$ term appearing in (6.43) to the value of (6.44) arises solely from the square-bracketed term in the integrand of the latter, this contribution being identical with the so-called molecular portion (6.19) of the dispersivity. The contribution from the remaining part of the integrand in (6.44) vanishes in consequence of the polyadic integral identities

$$\frac{1}{4\pi}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\,\boldsymbol{e}\boldsymbol{e}\ldots\boldsymbol{e}\boldsymbol{e} = \boldsymbol{0}, \tag{6.45}$$

valid for any *odd* number of multiples of $\boldsymbol{e}$ occurring in the integrand.

On the other hand, the remaining term of (6.43) contributes to the dispersivity only as a consequence of the last term within the curly brackets in (6.44), this being the so-called 'convective' contribution $\overline{\boldsymbol{D}}^{\mathrm{C}}$ to the dispersivity. Thus, the total dispersivity of the sedimenting dumb-bell becomes

$$\overline{\boldsymbol{D}}^* = \overline{\boldsymbol{D}}^{\mathrm{M}} + \overline{\boldsymbol{D}}^{\mathrm{C}}, \tag{6.46}$$

with the molecular contribution given by (6.19) – here taking the isotropic form (cf. (6.20), (6.22), (6.33))

$$\overline{\boldsymbol{D}}^{\mathrm{M}} = \boldsymbol{I}\overline{D}^{\mathrm{M}} = \boldsymbol{I}kT\overline{M}, \tag{6.47}$$

and the 'convective' contribution given by

$$\overline{\boldsymbol{D}}^{\mathrm{C}} = \boldsymbol{F}\cdot\left[W^{-1}\int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1\, \mathrm{e}^{-\hat{E}}(\boldsymbol{M} - \overline{\boldsymbol{M}})(f\boldsymbol{I} + g\boldsymbol{P}_2)\right]\cdot\boldsymbol{F}. \tag{6.48}$$

Substitute (6.35) into (6.48) and use the dyadic surface spherical harmonic orthogonality condition

$$\frac{1}{4\pi}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\,\boldsymbol{P}_2(\boldsymbol{e}) = \boldsymbol{0} \tag{6.49}$$

(since $P_0(\boldsymbol{e}) = 1$), to obtain

$$\overline{\boldsymbol{D}}^{\mathrm{C}} = \alpha\boldsymbol{F}\boldsymbol{F} + \beta\boldsymbol{F}\cdot\boldsymbol{T}\cdot\boldsymbol{F}. \tag{6.50}$$

Here, the tetradic $\boldsymbol{T}$ is defined as

$$\boldsymbol{T} = \frac{1}{4\pi}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\,\boldsymbol{P}_2(\boldsymbol{e})\,\boldsymbol{P}_2(\boldsymbol{e}), \tag{6.51}$$

whereas the dimensional scalar constants α and β are given by

$$\alpha = -\frac{1}{\omega}\int_0^\infty \mathrm{d}r\, r^2 \mathrm{e}^{-\hat{E}}[\overline{M} - \tfrac{1}{3}(M_\parallel + 2M_\perp)]f(r), \tag{6.52}$$

$$\beta = \frac{2}{3\omega}\int_0^\infty \mathrm{d}r\, r^2 \mathrm{e}^{-\hat{E}}(M_\parallel - M_\perp)\, g(r). \tag{6.53}$$

Expression (6.52) for α may be written in a more convenient form upon multiplying both sides of (6.41*a*) by $r^2 f$ and integrating by parts; this eventually yields

$$\alpha = \frac{1}{\omega}\int_0^\infty \mathrm{d}r\, r^2 \mathrm{e}^{-\hat{E}}\, d_\parallel \left(\frac{\mathrm{d}f}{\mathrm{d}r}\right)^2. \tag{6.54}$$

The tetradic $\boldsymbol{T}$ integral (6.51) can be evaluated explicitly (Brenner 1979; Haber & Brenner 1984), yielding the explicit Cartesian tensor form

$$T_{ijkl} = \tfrac{1}{20}[3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 2\delta_{ij}\delta_{kl}]. \tag{6.55}$$

Consequently,

$$\boldsymbol{F}\cdot\boldsymbol{T}\cdot\boldsymbol{F} = \tfrac{1}{20}F^2[4\hat{\boldsymbol{F}}\hat{\boldsymbol{F}} + 3(\boldsymbol{I} - \hat{\boldsymbol{F}}\hat{\boldsymbol{F}})], \tag{6.56}$$

in which $F = |\boldsymbol{F}|$ and

$$\hat{\boldsymbol{F}} = \frac{\boldsymbol{F}}{F} \tag{6.57}$$

is a unit vector in the direction of $\boldsymbol{F}$. Finally, substitute (6.56) into (6.50) and add the resulting expression to (6.47) to obtain the transversely isotropic dispersivity dyadic

$$\overline{\boldsymbol{D}}^* = \overline{D}_\parallel^*\,\hat{\boldsymbol{F}}\hat{\boldsymbol{F}} + \overline{D}_\perp^*(\boldsymbol{I} - \hat{\boldsymbol{F}}\hat{\boldsymbol{F}}), \tag{6.58a}$$

wherein

$$\overline{D}_\parallel^* = \overline{D}^{\mathrm{M}} + (\alpha + \tfrac{1}{5}\beta)F^2, \quad \overline{D}_\perp^* = \overline{D}^{\mathrm{M}} + \tfrac{3}{20}\beta F^2. \tag{6.58b,c}$$

6.4. *Tethered, hard-sphere dumb-bell calculations*

In this subsection the requisite integrals appearing above will be explicitly evaluated for circumstances in which the conformational dumb-bell potential is given by (6.11). The tether itself is assumed to be massless and of ultimate (i.e. inextensible) length L (figure 1).

The requisite calculations involve evaluation of the mobility constant $\overline{M}$, which furnishes the sedimentation velocity through (6.14), (6.22) and (6.33), and the mean molecular dispersivity through (6.47). Also required are the constants α and β, which provide the convective contributions to the dispersivity through (6.50) or (6.58). The latter convective calculations necessitate solving (6.41) and (6.42) for the respective scalar functions $f(r)$ and $g(r)$.

Denote by

$$M_\infty \equiv (12\pi\mu a)^{-1}, \quad D_\infty \equiv (12\pi\mu a)^{-1}\, kT \tag{6.59a,b}$$

the respective 'non-hydrodynamically interacting' dumb-bell mobility and diffusivity coefficients. These admit of the pair of non-dimensionalizations

$$\frac{\overline{D}^{\mathrm{M}}}{D_\infty} = \frac{\overline{M}}{M_\infty} \equiv \hat{\overline{M}}, \tag{6.60}$$

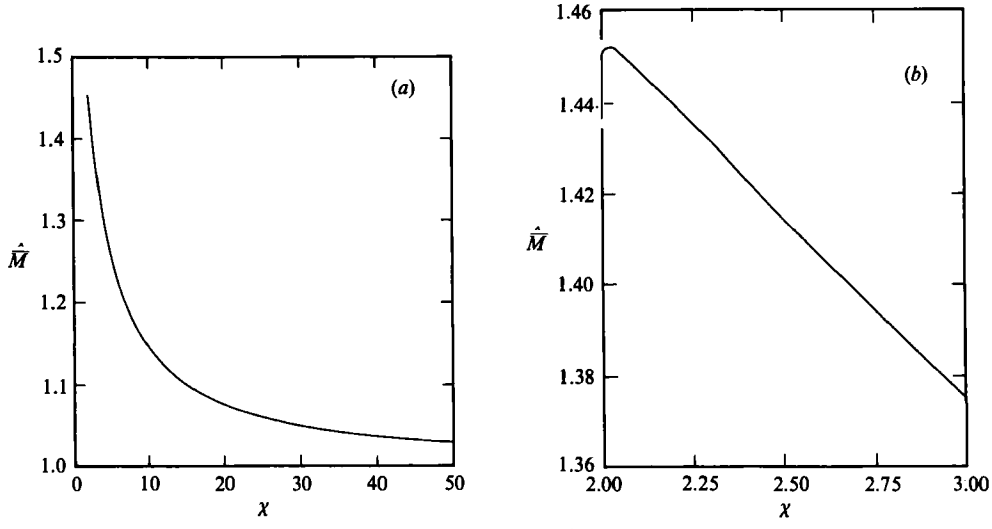

FIGURE 2. (*a*) Mean non-dimensional mobility $\hat{\bar{M}}$ *vs.* non-dimensional tether length χ; (*b*) enlargement of the near-touching range $2 \leqslant \chi \leqslant 3$.

involving the dimensionless normalized mobility coefficient (cf. (6.33*b*), (6.18), (6.31*c*))

$$\hat{\bar{M}}(\chi) = (3\hat{\omega})^{-1} \int_2^{\chi} \mathrm{d}s\, s^2(\hat{M}_{\parallel} + 2\hat{M}_{\perp}), \tag{6.61a}$$

wherein

$$\hat{M}_{\parallel}(s) = \frac{M_{\parallel}}{M_{\infty}} = x_{11}^a + x_{12}^a, \quad \hat{M}_{\perp}(s) = \frac{M_{\perp}}{M_{\infty}} = y_{11}^a + y_{12}^a, \tag{6.61b,c}$$

and

$$\hat{\omega}(\chi) = \int_2^{\chi} \mathrm{d}s\, s^2 = \tfrac{1}{3}(\chi^3 - 8). \tag{6.62}$$

In the above

$$\chi \equiv \frac{L}{a} \quad (\chi \geqslant 2), \tag{6.63}$$

$$s = \frac{r}{a} \quad (2 \leqslant s \leqslant \chi). \tag{6.64}$$

Define the additional non-dimensional functions

$$d_{\parallel}(s) = \frac{d_{\parallel}}{D_{\infty}} = 4(x_{11}^a - x_{12}^a), \quad \hat{d}_{\perp}(s) = \frac{d_{\perp}}{D_{\infty}} = 4(y_{11}^a - y_{12}^a). \tag{6.65a,b}$$

Then, with the dimensionless counterparts of f and g defined as

$$\hat{f}(s) = \frac{kTf}{a^2}, \quad \hat{g}(s) = \frac{kTg}{a^2}, \tag{6.66a,b}$$

(6.41*a*) and (6.42*a*) respectively become

$$\frac{1}{s^2}\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2\hat{d}_{\parallel}\frac{\mathrm{d}\hat{f}}{\mathrm{d}s}\right) = \hat{\bar{M}} - \tfrac{1}{3}(\hat{M}_{\parallel} + 2\hat{M}_{\perp}), \tag{6.67a}$$

$$\frac{1}{s^2}\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2\hat{d}_{\parallel}\frac{\mathrm{d}\hat{g}}{\mathrm{d}s}\right) - \frac{6}{s^2}\hat{d}_{\perp}\hat{g} = -\tfrac{2}{3}(\hat{M}_{\parallel} - \hat{M}_{\perp}). \tag{6.68a}$$

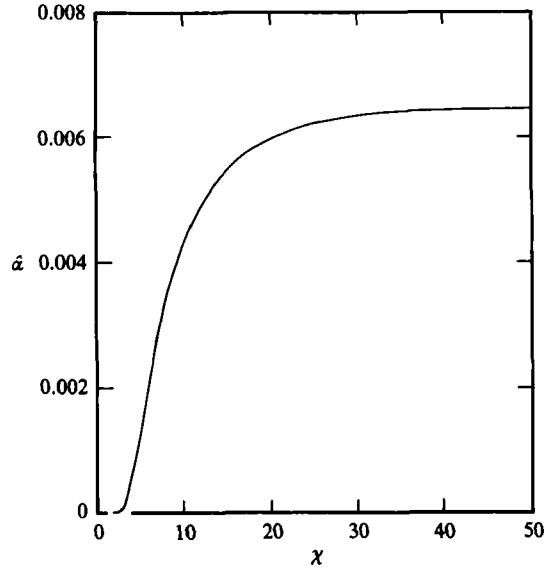

FIGURE 3. Taylor dispersivity coefficient $\hat{\alpha}$ *vs.* non-dimensional tether length χ.

These are to be solved in the region $2 < s < \chi$ subject to the no-flux conditions (cf. (6.41*b*), (6.42*b*))

$$\hat{d}_{\parallel} \frac{\mathrm{d}\hat{f}}{\mathrm{d}s} = 0 \quad \text{at } s = 2, \chi, \tag{6.67b}$$

$$\hat{d}_{\parallel} \frac{\mathrm{d}\hat{g}}{\mathrm{d}s} = 0 \quad \text{at } s = 2, \chi. \tag{6.68b}$$

Equations (6.67*a*, *b*) possess the first integral

$$\frac{\mathrm{d}\hat{f}(s)}{\mathrm{d}s} = [s^2 \hat{d}_{\parallel}(s)]^{-1} \int_2^s \mathrm{d}s'\, s'^2 \{\bar{\hat{M}} - \tfrac{1}{3}[\hat{M}_{\parallel}(s') + 2\hat{M}_{\perp}(s')]\}. \tag{6.69}$$

Define the non-dimensional Langevin parameter

$$\gamma = \frac{Fa}{kT}, \tag{6.70}$$

embodying the ratio of gravitational to thermal energies of the dumb-bell, to obtain

$$\frac{\alpha F^2}{D_\infty} = \gamma^2 \hat{\alpha}, \tag{6.71}$$

$$\frac{\beta F^2}{D_\infty} = \gamma^2 \hat{\beta}, \tag{6.72}$$

wherein

$$\hat{\alpha}(\chi) = \frac{1}{\hat{\omega}} \int_2^\chi \mathrm{d}s\, s^2 \hat{d}_{\parallel} \left(\frac{\mathrm{d}\hat{f}}{\mathrm{d}s}\right)^2 \tag{6.73a}$$

and

$$\hat{\beta}(\chi) = \frac{2}{3\hat{\omega}} \int_2^\chi \mathrm{d}s\, s^2 (\hat{M}_{\parallel} - \hat{M}_{\perp}) \hat{g}. \tag{6.73b}$$

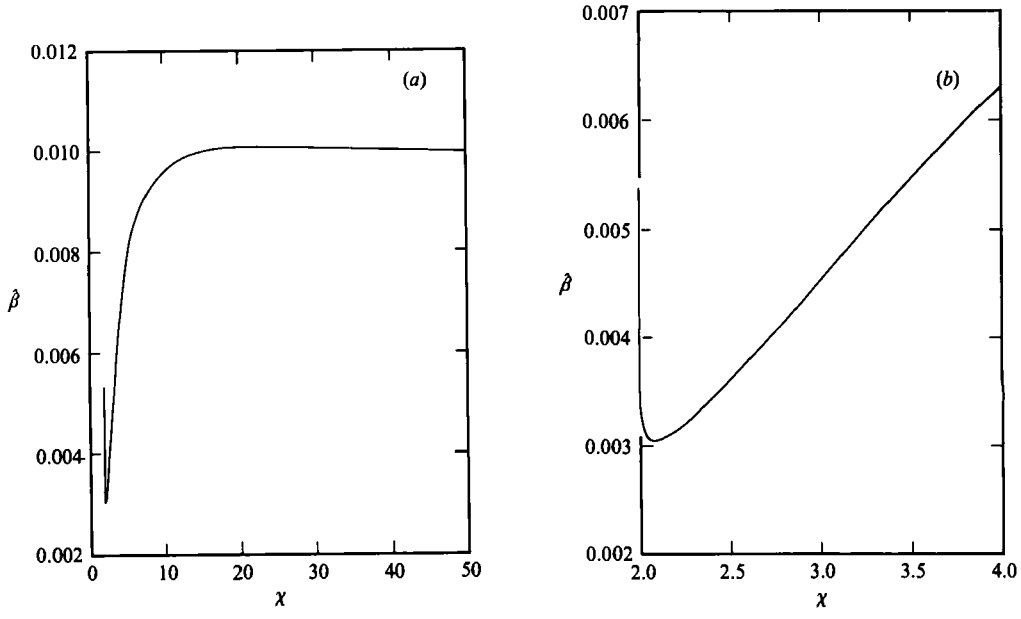

FIGURE 4. (*a*) Taylor dispersivity coefficient $\hat{\beta}$ *vs.* non-dimensional tether length χ; (*b*) enlargement of the near-touching range $2 \leqslant \chi \leqslant 4$.

Thus, the dimensionless total dumb-bell dispersivity dyadic is given by (cf. (6.58*a–c*))

$$\frac{\overline{\boldsymbol{D}}^*}{D_\infty} = \frac{\overline{D}_\parallel^*}{D_\infty}\hat{\boldsymbol{F}}\hat{\boldsymbol{F}} + \frac{\overline{D}_\perp^*}{D_\infty}(\boldsymbol{I} - \hat{\boldsymbol{F}}\hat{\boldsymbol{F}}), \tag{6.74a}$$

in which

$$\frac{\overline{D}_\parallel^*}{D_\infty} = \hat{\overline{M}} + \gamma^2(\hat{\alpha} + \tfrac{1}{5}\hat{\beta}), \quad \frac{\overline{D}_\perp^*}{D_\infty} = \hat{\overline{M}} + \tfrac{3}{20}\gamma^2\hat{\beta}. \tag{6.74b,c}$$

Moreover, the dimensionless mean dumb-bell velocity vector is

$$\frac{\overline{\boldsymbol{U}}^*}{M_\infty F} = \hat{\overline{M}}\hat{\boldsymbol{F}}. \tag{6.75}$$

The three scalar constants $\hat{\overline{M}}$, $\hat{\alpha}$ and $\hat{\beta}$, required above, are functions only of the dimensionless tether-length parameter χ. We have evaluated them numerically, our results being summarized in figures 2–4. The requisite input mobility data for the calculations were principally those of Jeffrey & Onishi (1984). For $s \leqslant 2.015$ and $s \geqslant 4.0$, their respective 'nearly-touching' and 'widely-separated' asymptotic analytical formulas were employed to calculate the required transport coefficients; for intermediate values of s, their numerically tabulated data, as well as that of Batchelor (1976), were used in conjunction with a second-order interpolation scheme (Abramawitz & Stegun 1972). The ordinary differential equation (6.68) was solved via a finite-difference scheme (Hornbeck 1975).

Figure 2(*a*, *b*) furnishes $\hat{\overline{M}}$ *vs.* χ. For touching spheres ($\chi = 2$), $\hat{\overline{M}}$ attains the limiting value 1.437, decreasing monotonically (after a slight initial increase) to an asymptotic value of 1.0 as $\chi \to \infty$. Figure 3 summarizes the variation of $\hat{\alpha}$ with χ. The latter is zero for the touching-spheres case $\chi = 2$, undergoes a rapid initial increase for increasing values of χ, and finally attains an asymptotic value of $\frac{1}{160}$. Figure 4(*a*, *b*) shows the dependence of $\hat{\beta}$ upon χ. For *touching* spheres,

$\hat{\beta} = 5.33 \times 10^{-3}$, decreasing rapidly to a minimum at $\chi \approx 2.09$, generally increasing thereafter to an eventual asymptotic limit of $\frac{1}{96}$. (The pair of limiting $\chi = 2, \infty$ results cited above were not part of the numerical calculations; rather, they were analytically calculated by appropriate asymptotic schemes.) The extreme χ-dependent behaviour of $\hat{\overline{M}}$ *and* $\hat{\beta}$ near $\chi = 2$ is a manifestation of the singular behaviour of the mobility functions (Jeffrey & Onishi 1984) for touching spheres. That $\hat{\alpha}$ and $\hat{\beta}$ attain constant non-zero limiting values as $\chi \to \infty$ indicates that, even with no potential interactions other than hard-sphere repulsion (e.g. no tether or spring), the effect of the second sphere upon the dispersivity of a sedimenting dumb-bell is always manifested – at least for times sufficiently long for the two spheres to have sampled all accessible relative configurations. Of course, this characteristic time also increases with χ.

7. Diffusion of an inhomogeneously weighted, neutrally buoyant dumb-bell in a gravity field

As a second application we consider the tethered dumb-bell discussed in the previous section for circumstances wherein the dumb-bell is neutrally buoyant as a whole, while – of the two individually homogeneous spheres comprising the dumb-bell – one is denser than the fluid by an amount corresponding to a particle/displaced fluid mass difference $|\Delta m|$, the other being less dense by precisely this same amount. Since $\boldsymbol{F} = \boldsymbol{0}$, the dumb-bell does not suffer net sedimentation as a whole. Consequently, its mean motion may still be described as pure Brownian diffusion, albeit with an anisotropic diffusivity. For definiteness, choose sphere 0 to be the lighter one; hence, on average, the centre of sphere 1 will be found to lie vertically below that of sphere 0. (On average, it is physically evident that the tether will generally be stretched to its limit, and hence will be maintained in a state of tension.) Such a flexible body will be termed a 'loaded' dumb-bell.

The gravitational–buoyancy portion of the potential for such a body is

$$|\Delta m|\, \boldsymbol{g}\cdot\boldsymbol{R}_0 - |\Delta m|\, \boldsymbol{g}\cdot\boldsymbol{R}_1 = -|\Delta m|\, \boldsymbol{g}\cdot\boldsymbol{r}_1, \tag{7.1}$$

whence the total dumb-bell potential here takes the form

$$V = kTE(\boldsymbol{r}_1) \equiv kT\hat{E}(\boldsymbol{r}_1) - |\Delta m|\, \boldsymbol{g}\cdot\boldsymbol{r}_1, \tag{7.2}$$

with $\hat{E}(\boldsymbol{r}_1)$ the internal conformational potential, given by (6.11) for the present tethered case. Since no net external force is now exerted on the dumb-bell (i.e. $\boldsymbol{F} = \boldsymbol{0}$), the results presented at the end of §5 remain applicable, whence it may be immediately concluded that (cf. (5.10))

$$\overline{\boldsymbol{U}}^* = \boldsymbol{0}, \tag{7.3}$$

confirming the absence of sedimentation of the dumb-bell as a whole.

The equilibrium density $P_0^\infty(\boldsymbol{r}_1)$ is given by (5.9), here taking the explicit form

$$P_0^\infty(\boldsymbol{r}_1) = W^{-1} \exp[-E(\boldsymbol{r}_1)], \quad W = \int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp[-E(\boldsymbol{r}_1)], \tag{7.4a,b}$$

with $E(\boldsymbol{r}_1)$ defined in (7.2). Substitution of (7.4) into (5.13), in conjunction with use of the equivalence relations (6.6*c, d, f, g*), yields the mean 'molecular' dispersivity

$$\overline{\boldsymbol{D}}^{\mathrm{M}} = W^{-1} \int_{\tau_{r_1}} \mathrm{d}\boldsymbol{r}_1 \exp(-E)\, \boldsymbol{D} \tag{7.5}$$

of the loaded dumb-bell, in which the configuration-specific molecular diffusivity $\boldsymbol{D}$ is identical with that defined in (6.20). Explicit evaluation of (7.5) requires use of the identities

$$(4\pi)^{-1}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\exp(\boldsymbol{v}\cdot\boldsymbol{e}) = v^{-1}\sinh v, \tag{7.6a}$$

$$(4\pi)^{-1}\oint_{S_1} \mathrm{d}^2\boldsymbol{e}\,\boldsymbol{ee}\exp(\boldsymbol{v}\cdot\boldsymbol{e}) = \hat{\boldsymbol{v}}\hat{\boldsymbol{v}}[(v^{-1}+3v^{-3})\sinh v - 3v^{-2}\cosh v] + \boldsymbol{I}(v^{-2}\cosh v - v^{-3}\sinh v), \tag{7.6b}$$

wherein $\boldsymbol{v} = \hat{\boldsymbol{v}}v$ is any constant vector of magnitude $v = |\boldsymbol{v}|$ in the direction of the unit vector $\hat{\boldsymbol{v}}$.

Upon noting that (cf. (6.16), (6.18), (6.20), (6.61*b*, *c*))

$$\frac{\boldsymbol{D}}{D_\infty} = \boldsymbol{ee}\hat{M}_\parallel + (\boldsymbol{I}-\boldsymbol{ee})\hat{M}_\perp, \tag{7.7}$$

and upon defining the Langevin parameter λ for the present case to be

$$\lambda \equiv \frac{|\Delta m|\,ga}{kT}, \tag{7.8}$$

the identities (7.6*a*, *b*) may be used to obtain the dimensionless form of (7.5) (with D_∞ given by (6.59*b*)) as

$$\frac{\overline{\boldsymbol{D}}^{\mathrm{M}}}{D_\infty} = \boldsymbol{I}A + \hat{\boldsymbol{g}}\hat{\boldsymbol{g}}B \equiv (\boldsymbol{I}-\hat{\boldsymbol{g}}\hat{\boldsymbol{g}})A + \hat{\boldsymbol{g}}\hat{\boldsymbol{g}}(A+B), \tag{7.9}$$

with components A and B respectively given by

$$A(\chi,\lambda) = \frac{1}{\hat{W}}\int_2^\chi \left\{(\hat{M}_\parallel - \hat{M}_\perp)\left[\frac{\cosh\lambda s}{(\lambda s)^2} - \frac{\sinh\lambda s}{(\lambda s)^3}\right] + \hat{M}_\perp\frac{\sinh\lambda s}{\lambda s}\right\} s^2\,\mathrm{d}s, \tag{7.10a}$$

$$B(\chi,\lambda) = \frac{1}{\hat{W}}\int_2^\chi \left\{(\hat{M}_\parallel - \hat{M}_\perp)\left[\left(\frac{1}{\lambda s}+\frac{3}{(\lambda s)^3}\right)\sinh\lambda s - \frac{3\cosh\lambda s}{(\lambda s)^2}\right]\right\} s^2\,\mathrm{d}s, \tag{7.10b}$$

wherein

$$\hat{W} = \lambda^{-3}(\chi\lambda\cosh\chi\lambda - \sinh\chi\lambda - 2\lambda\cosh 2\lambda + \sinh 2\lambda). \tag{7.10c}$$

Dimensionless scalars A and B depend functionally only upon the non-dimensional parameters χ and λ, the latter being the Langevin parameter (7.8) measuring the ratio of the orienting gravitational potential energy $|\Delta m|\,ga$ to the disorienting thermal energy kT, while the former is defined in (6.63). Analogously to the calculations of the preceding section, the evaluation of (7.10*a*–*c*) must be performed numerically, although such calculations now require only straightforward quadrature. Moreover, for large values of λ (i.e. large mass inhomogeneities, leading to perfect alignment of the dumb-bell dipole parallel to the gravitational field) the quadratures can be performed analytically, leading to the following asymptotic limiting values:

$$A \sim \hat{M}_\perp(\chi) + O(\chi\lambda)^{-2}, \quad B \sim [\hat{M}_\parallel(\chi) - \hat{M}_\perp(\chi)][1 - 2(\chi\lambda)^{-1} + O(\chi\lambda)^{-2}], \tag{7.11a, b}$$

valid when $\chi\lambda \gg 1$. Moreover, for touching spheres ($\chi = 2$), the limiting forms of (7.10) are found by a straightforward application of L'Hospital's rule to be

$$A(2,\lambda) = \hat{M}_\perp(2) + [\hat{M}_\parallel(2) - \hat{M}_\perp(2)]\left[\frac{2\lambda\coth 2\lambda - 1}{(2\lambda)^2}\right], \tag{7.12a}$$

$$B(2,\lambda) = [\hat{M}_\parallel(2) - \hat{M}_\perp(2)]\left\{1 - 3\left[\frac{2\lambda\coth 2\lambda - 1}{(2\lambda)^2}\right]\right\}. \tag{7.12b}$$

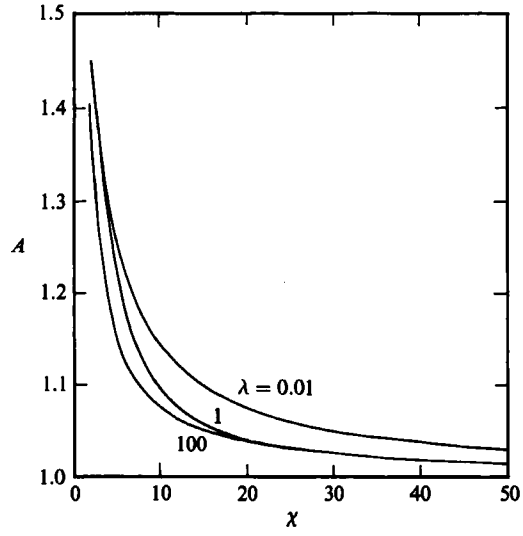

FIGURE 5. Isotropic Taylor dispersion coefficient A *vs.* non-dimensional tether length χ at various Langevin parameters λ for the loaded dumb-bell.

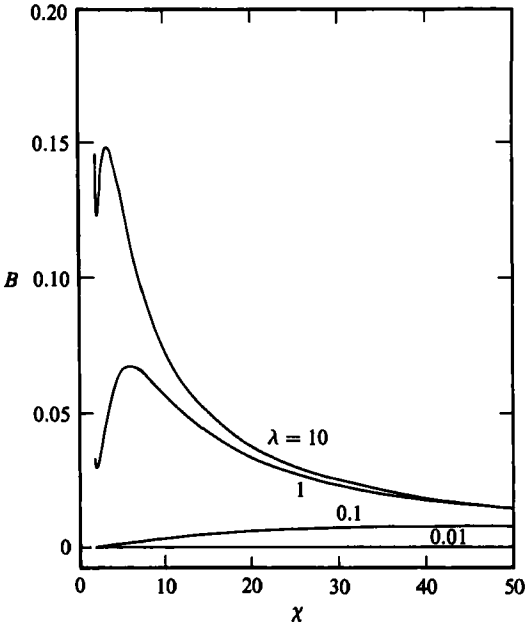

FIGURE 6. Anisotropic Taylor dispersion coefficient B *vs.* non-dimensional tether length χ at various Langevin parameters λ for the loaded dumb-bell.

Figures 5 and 6 present A and B *vs.* χ at parametric values of λ. In the limit $\lambda = 0$, where the gravitational orienting force is relatively small, the isotropic portion A of the dispersivity is identical with the function $\hat{M}$ of the previous section. Increasing λ generally tends to decrease A, though not to a major extent. In contrast, the coefficient B of the anisotropic term vanishes at $\lambda = 0$, but increases substantially with increasing λ (at fixed values of χ).

8. Discussion

8.1. *Size-fluctuation dispersion and preaveraging approximations*

Having created an exact standard against which approximate calculations may be compared, questions may now be quantitatively addressed regarding the accuracy of *ad hoc* preaveraging techniques, whereby the flexible sedimenting chain is replaced by an equivalent 'average' rigid geometric object for purposes of computing its 'average' hydrodynamic resistance properties. Our calculations clearly indicate the non-existence of any simple rigorous relation which would *a priori* allow a 'preaveraged' hypothetical rigid body to be constructed – one exhibiting the same mean velocity and dispersivity as the original flexible chain. This effect is particularly dramatic as regards calculation of the Taylor dispersivity contribution (an effect hitherto not considered (cf. Zimm 1982)) in examining the merits of preaveraging approximations. For example, in the case of a rigid homogeneous dumb-bell undergoing sedimentation, the term corresponding to $f(r)$ in (6.39) can be shown to be completely absent (cf. Brenner 1979), whence no contribution comparable to $\hat{\alpha}$ in the dispersivity (cf. (6.74*b*), (6.73*a*)) would be surmized by any preaveraging scheme. Figures 3 and 4 indicate that the latter coefficient can be comparable in magnitude with the contribution $\hat{\beta}$, which continues to exist (albeit with some modifications) even for rigid non-spherical bodies. In this context, it is perhaps useful to coin the descriptive designation 'size-fluctuation dispersion' for this phenomenon, representing the contribution to the Taylor dispersivity over and above that possible for an anisotropic rigid structure (Brenner 1979, 1981). In fact, such a dispersive contribution would be present even if the flexible body were always spherical in shape (like a bubble) but could suffer Brownian 'fluctuations' in its instantaneous radius (Brenner & Mauri 1988).

8.2. *Summary*

A general scheme has been provided permitting rigorous calculations of the long-time macrotransport coefficients characterizing the mean translational velocity vector and Taylor dispersivity dyadic of flexible chains and clusters of rigid Brownian particles, sedimenting under the influence of a uniform external force within otherwise quiescent viscous fluids. The constituent rigid particles may be of arbitrary shapes and sizes, and mutually interact via arbitrary configuration-specific internal potentials. Full account is taken of the non-zero sizes and of the hydrodynamic interactions among the individual rigid particles comprising the flexible chain. Our formulas are free of any preaveraging approximations. Explicit examples are given only for dumb-bells, since these are currently the only multi-particle objects for which complete configuration-specific hydrodynamic interaction data are available over the entire range of geometrically accessible conformations.

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