TRANSPORT AND STATISTICAL MECHANICS OF FLEXIBLE CHAINS AND CLUSTERS OF BROWNIAN PARTICLES IN QUIESCENT VISCOUS FLUIDS

by

ALI NADIM

B.S., University of California at Davis
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M.S., Massachusetts Institute of Technology
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Certified by _____
Professor Howard Brenner
Thesis Supervisor

Accepted by _____
Professor William M. Deen
Committee for Graduate Students

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ABSTRACT

Generalized Taylor dispersion theory -- including so-called coupling effects -- is developed based upon a novel moment-gradient expansion technique, whereby the microscale probability density P is expressed as an infinite sum of global-space gradients of its corresponding macroscale density $\overline{P}$ multiplied by coefficients formed from its local and global moments. This general theory is then used to derive a scheme permitting calculation of the transport properties (i.e. mean velocity vector and dispersivity dyadic) of a single deformable chain composed of hydrodynamically-interacting rigid Brownian particles bound together by an internal potential 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 each separately undergoes translational and rotational Brownian motions. Together, their relative motions give rise to a configurational Brownian motion for the chain and thus, at long enough times for all accessible configurations to be sampled, an internal Boltzmann probabilistic distribution of conformations is obtained. In contrast with prior analyses of such chain transport phenomena, no ad hoc pre-averaging hypotheses are invoked to effect the averaging of the input configuration-specific hydrodynamic data.

Explicit numerical calculations are performed only for the simplest case of so-called tethered dumbbells. In this context, the size- and shape- fluctuation contributions to Taylor dispersion -- not recognized previously -- are shown to be significant in interpreting the nonequilibrium sedimentation-diffusion properties of polymer molecules in solution.

Thesis Supervisor: Professor Howard Brenner

Title: Willard Henry Dow Professor of Chemical Engineering

The moving finger writes; and, having writ,

Moves on: nor all your piety nor wit

Shall lure it back to cancel half a line,

Nor all your tears wash out a word of it.

- OMAR KHAYYAM, Rubaiyat (FitzGerald trans.)

To my father, Jafar,

my mother, Simin,

my sister, Nikou.

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PREFACE

This thesis consists of three essentially self-contained chapters, each with its own set of appropriate references. Chapter I serves as the thesis digest, providing both an introduction to and a summary of the main bulk of the thesis contained in the remaining chapters. It is meant to furnish a broad overview and point of reference for a reader who is not interested initially in all the details leading to the summarized results. Chapter II introduces a novel mathematical scheme--termed moment-gradient expansion--to obtain long-time and coarse-grained macrotransport equations starting with their more detailed fine-scale microtransport counterparts. Particular emphasis is paid to examining third and higher moments in the macrotransport process, proving a non-Gaussian global behavior contrary to what is generally assumed. In Chapter III, the above scheme is employed to develop generalized Taylor dispersion theory incorporating so-called coupling effects. The latter theory is then used to characterize the mean transport of a flexible chain or cluster composed of arbitrarily-shaped and -sized rigid Brownian particles, bound together by the agency of an internal configurational potential, and sedimenting through an unbounded quiescent viscous fluid. Explicit numerical results are also provided for the specific case of a tethered dumbbell. (Each chapter may be studied independently of the others.)

A. N.

Cambridge, MA

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CHAPTER I:

SCOPE

1. INTRODUCTION

Transport mechanics (Brenner and 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 and Brenner 1983), the latter 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 nonequilibrium fluid-particle transport 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 numbers 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 and 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 Burger-Oseen interaction tensors with preaveraging (Kirkwood and

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, 1982a, 1982b) 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 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 (1974a,b), or those of 'segmentally flexible macromolecules' (Harvey, Mellado and Garcia de la Torre 1983, Garcia de la Torre, Mellado and Rodes 1985, Wegener 1982) 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 centers 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 and Pagitsas 1987) of the cluster as a whole must necessarily show themselves to 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, pre-averaged rigid counterpart. To rigorously analyze secular effects arising from instantaneous deviations from the average, generalized Taylor dispersion theory (Brenner 1982a, Brenner & Pagitsas 1987) can be employed. Indeed this paradigm has already been successfully used to investigate comparable sedimentation-dispersion phenomena in systems of rigid nonspherical particles (Brenner 1979, 1981). Upon incorporation of "coupling" effects (Brenner 1982b), 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 and Brenner 1986), free of any sedimentation effects, is itself a challenging goal. Recently, Wegener (1985) and Haber and 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) center of diffusion. Haber and Brenner (1986) had independently examined the same general problem within the Taylor-Aris dispersion (Taylor 1953, Aris 1956, Horn

1971) framework, performing detailed calculations for the case of a flexible dumbbell.

In the next section, a summary of the pertinent results of generalized coupled Taylor dispersion theory are furnished, as obtained with the aid of a novel 'moment-gradient expansion' scheme. The applicability of the latter scheme to calculations of higher-order, nonGaussian terms in macrotransport processes is also discussed. Then, in Section 3, transport mechanics of flexible chains and clusters -- composed of rigid Brownian particles and sedimenting through an otherwise quiescent viscous fluid -- are reviewed. The results obtained through application of generalized coupled Taylor dispersion theory are outlined, and specific numerical calculations pertaining to simple tethered dumbbells presented.

2. GENERALIZED COUPLED TAYLOR DISPERSION THEORY

A significant portion of the effort required to understand the non-equilibrium behavior of suspensions of flexible chains must necessarily be devoted to first describing the transport of a single one of the flexible bodies within the phase-space codifying its internal and external configurations. In addition to the conventional convective and (direct) diffusive contributions, the transport of isolated flexible objects also entails indirect or coupling contributions, whereby probability density gradients in the internal space give rise to fluxes in the external space and conversely. In order to treat the effects of such coupling upon the macrotransport properties of the isolated body and (ultimately upon the macroscale properties of the suspension as a whole), the rigorous results of generalized Taylor dispersion theory (Brenner 1980, 1982a) -- including coupling effects (Brenner 1982b) -- will be employed. Accordingly, this section is devoted to reviewing the relevant results of the latter theory. Subsequently, in the next section, the theory will be applied to the important problem of Brownian diffusion and sedimentation of a flexible chain or cluster, composed of hydrodynamically-interacting rigid Brownian particles and moving through a quiescent viscous fluid.

The starting point of generalized Taylor dispersion theory is the canonical continuity equation (Brenner 1982b)

$$\partial P/\partial t + \nabla_{\underset{\sim}{Q}} \cdot \underset{\sim}{J} + \nabla_{\underset{\sim}{q}} \cdot \underset{\sim}{j} = \delta(t)\, \delta(\underset{\sim}{Q}-\underset{\sim}{Q}')\delta(\underset{\sim}{q}-\underset{\sim}{q}') \tag{2.1}$$

governing conservation and transport the conditional probability density $P(\underset{\sim}{Q},\underset{\sim}{q},t|\underset{\sim}{Q}',\underset{\sim}{q}')$ for a flexible 'tracer' to possess internal coordinates $\underset{\sim}{q}$ and external (physical-space) coordinates $\underset{\sim}{Q}$ at the instant t, given that at time t = 0 its respective $(\underset{\sim}{Q},\underset{\sim}{q})$ coordinates were $(\underset{\sim}{Q}',\underset{\sim}{q}')$. The local

(internal) and global (external) fluxes $\underset{\sim}{j}$ and $\underset{\sim}{J}$ are respectively assumed to be given by the constitutive expressions

$$\underset{\sim}{j} = \underset{\sim}{u}(\underset{\sim}{q})P - \underset{\approx}{D}^{qQ}(\underset{\sim}{q}) \cdot \underset{\sim}{\nabla}_{Q}P - e^{-E}\underset{\approx}{D}^{qq}(\underset{\sim}{q}) \cdot \underset{\sim}{\nabla}_{q}(e^{E}P), \tag{2.2}$$

$$\underset{\sim}{J} = \underset{\sim}{U}(\underset{\sim}{q})P - \underset{\approx}{D}^{QQ}(\underset{\sim}{q}) \cdot \underset{\sim}{\nabla}_{Q}P - e^{-E}\underset{\approx}{D}^{Qq}(\underset{\sim}{q}) \cdot \underset{\sim}{\nabla}_{q}(e^{E}P). \tag{2.3}$$

In addition to the usual <u>direct</u> contributions arising from convection and diffusion in each subspace (i.e., local and global), coupling effects between these subspaces have been included, as directly embodied in the existence of the coupling diffusivity $\underset{\approx}{D}^{qQ}$ (or its transpose $\underset{\approx}{D}^{Qq}$). The Fickian diffusivities $\underset{\approx}{D}^{QQ}$ and $\underset{\approx}{D}^{qq}$ are each assumed to be both symmetric and positive definite, as too is also the combination $\underset{\approx}{D}^{QQ} - \underset{\approx}{D}^{Qq} \cdot (\underset{\approx}{D}^{qq})^{-1} \cdot \underset{\approx}{D}^{qQ}$.

The conservation equation (2.1) is to be solved subject to appropriate attenuation-rate boundary conditions imposed as $|\underset{\sim}{Q}| \to \infty$ to assure convergence, a no-flux condition $\underset{\sim}{n} \cdot \underset{\sim}{j} = 0$ at the boundaries $\partial\underset{\sim}{q}_0$ of the local space, and the (pre-) initial condition $P = 0$ for $t < 0$. Application of a Lagrangian moment analysis to these equations reveals that the purely global transport of the tracer (i.e., from which transport process the internal degrees of freedom $\underset{\sim}{q}$ have been eliminated via integration) is characterized by two macrotransport coefficients, namely the mean tracer velocity vector through physical space,

$$\underset{\sim}{\bar{U}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \left[P_0^{\infty}\underset{\sim}{U} - e^{-E}\underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_{q}(e^{E}P_0^{\infty}) \right] , \tag{2.4}$$

and its physical-space dispersivity dyadic,

$$\underset{\approx}{\bar{D}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \{P_0^{\infty} \left[\underset{\approx}{D}^{QQ} - \underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_{q}\underset{\approx}{B} \right] + \left[P_0^{\infty}(\underset{\sim}{U} - \underset{\sim}{\bar{U}}^{*}) - e^{-E}\underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_{q}(e^{E}P_0^{\infty})\right]\underset{\approx}{E}\}. \tag{2.5}$$

The pair of coefficients $\bar{\underset{\sim}{U}}^*$ and $\bar{\underset{\approx}{D}}^*$ serves to describe the Q-space kinematical properties of the flexible cluster for times sufficiently long to have established a terminal state (equilibrium or quasisteady) within the internal space, a state that is independent of the initial internal configuration $\underset{\sim}{q}'$.

Calculation of these long-time macrotransport coefficients requires knowledge of the internal equilibrium density P_0^∞, satisfying (Brenner 1982b)

$$\underset{\sim}{\nabla}_q \cdot \left[\underset{\sim}{u} P_0^\infty - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \right] = 0 \ , \tag{2.6a}$$

$$\underset{\sim}{n} \cdot \left[\underset{\sim}{u} P_0^\infty - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \right] = 0 \text{ on } \partial\underset{\sim}{q}_0 , \tag{2.6b}$$

$$\int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \, P_0^\infty = 1 \ . \tag{2.6c}$$

Also required in (2.5) is the solution $\underset{\sim}{B}(\underset{\sim}{q})$ of the equations

$$\underset{\sim}{\nabla}_q \cdot \left[\underset{\sim}{u} P_0^\infty \underset{\sim}{B} - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty \underset{\sim}{B}) + P_0^\infty \underset{\approx}{D}^{qQ} \right] =$$

$$P_0^\infty (\underset{\sim}{U} - \bar{\underset{\sim}{U}}^*) - e^{-E} \underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \ , \tag{2.7a}$$

$$- P_0^\infty \underset{\sim}{n} \cdot \left[\underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q \underset{\sim}{B} - \underset{\approx}{D}^{qQ} \right] = \underset{\sim}{0} \text{ on } \partial\underset{\sim}{q}_0 \ , \tag{2.7b}$$

uniquely defining $\underset{\sim}{B}$ to within an irrelevant arbitrary additive constant vector.

Since only the long-time Q-space transport of the tracer is generally of interest in practice, the simplification afforded by being able to characterize the macrotransport process via only the two position-independent phenomenological coefficients (2.4) and (2.5) -- in place of the much larger set of $\underset{\sim}{q}$-dependent phenomenological coefficients appearing in (2.2)-(2.3) -- represents a major achievement of the general theory [albeit the

not inconsiderable effort perhaps necessary to actually solve (2.6) and (2.7)].

Moment-Gradient Expansion and Higher Order Moments

To effect the preceding derivations of the long-time mean velocity vector (2.4) and dispersivity dyadic (2.5), several existing techniques may be employed. These include Langrangian moment methods (Brenner 1980, 1982a, 1982b), projection operator methods (Pagitsas et al. 1986a), the multiple-time scale techniques (Pagitsas et al. 1986b) and the moment-gradient expansion scheme (Nadim et al. 1986). Of these, we will presently review the latter, together with its implications for moments of higher order and concomitant nonGaussian long-time behavior.

The moment-gradient expansion scheme represents a generalization of the ad hoc series expansion proposed by Gill and Sankarasubramanian (1970, 1971). It entails an expansion for the conditional probability density $P(\underset{\sim}{Q},\underset{\sim}{q},t|\underset{\sim}{Q}',\underset{\sim}{q}')$ of the form (Nadim et al. 1986)

$$P(\underset{\sim}{Q},\underset{\sim}{q},t|\underset{\sim}{Q}',\underset{\sim}{q}') = \sum_{j=0}^{\infty} \underset{\sim}{F}_j(\underset{\sim}{q},t|\underset{\sim}{q}')\ (\cdot)^j\ \underset{\sim}{\nabla}_{\underset{\sim}{Q}}^j\ P(\underset{\sim}{Q},t|\underset{\sim}{Q}',\underset{\sim}{q}'), \tag{2.8}$$

wherein the polyadic $\underset{\sim}{F}_j$ is a cartesian tensor of rank j, $(\cdot)^j$ denotes j scalar multiplications, and $\underset{\sim}{\nabla}_{\underset{\sim}{Q}}^j = \underset{\sim}{\nabla}_{\underset{\sim}{Q}}\underset{\sim}{\nabla}_{\underset{\sim}{Q}} \cdots \underset{\sim}{\nabla}_{\underset{\sim}{Q}}$ (j times). It may be shown (Nadim et al.) that the coefficients $\underset{\sim}{F}_j$ are related to respective local and total moments of P,

$$\underset{\sim}{P}_m(\underset{\sim}{q},t|\underset{\sim}{q}') \equiv \int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q}\ \underset{\sim}{Q}^m\ P \quad , \tag{2.9a}$$

$$\underset{\sim}{M}_m(t|\underset{\sim}{q}') \equiv \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \underset{\sim}{P}_m \quad , \tag{2.9b}$$

via the relations

$$F_0 = P_0 \simeq P_0^{\infty}(\underset{\sim}{q}) \quad , \tag{2.10a}$$

$$\underset{\sim}{F}_1 = -(\underset{\sim}{P}_1 - P_0\underset{\sim}{M}_1) \simeq -P_0^{\infty}\underset{\sim}{B}(\underset{\sim}{q}) \quad , \tag{2.10b}$$

$$\underset{\approx}{F}_2 = \frac{1}{2}[\underset{\approx}{P}_2 - 2\underset{\sim}{P}_1\underset{\sim}{M}_1 - P_0(\underset{\approx}{M}_2 - 2\underset{\sim}{M}_1\underset{\sim}{M}_1)] \simeq \frac{1}{2}P_0^{\infty}\underset{\approx}{H}(\underset{\sim}{q}) \quad , \tag{2.10c}$$

etc., the right-hand asymptotes being valid only in the limit $t\to\infty$. Each of these approaches a time- and $\underset{\sim}{q}'$-independent limit as $t\to\infty$, with P_0^{∞} and $\underset{\sim}{B}$ defined in (2.6) and (2.7), and with $\underset{\approx}{H}$ satisfying a similar local-space kinetic equation. The averaged probability $\overline{P}$ appearing in (2.8) is defined as

$$\overline{\underset{\sim}{P}}(\underset{\sim}{Q},t|\underset{\sim}{Q}',\underset{\sim}{q}') \equiv \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\; P(\underset{\sim}{Q},\underset{\sim}{q},t|Q',q') \quad . \tag{2.11}$$

The ultimate goal of generalized Taylor dispersion theory is to derive the long-time macrotransport equation governing $\overline{P}$, having eliminated all internal dependence from the latter by integration [cf. (2.11)]. Since the coefficients (2.10) ultimately become independent of $\underset{\sim}{q}'$, the same will be true of $\overline{P}$. Integration of (2.1) over the local-space domain $\underset{\sim}{q}_0$, followed by substitution of the moment-gradient expansion (2.8), eventually yields the equation

$$\partial\overline{P}/\partial t + \overline{\underset{\sim}{U}}^{*} \cdot \underset{\sim}{\nabla}_Q\overline{P} - \overline{\underset{\approx}{D}}^{*}(\cdot)^2\underset{\sim}{\nabla}_Q\underset{\sim}{\nabla}_Q\,\overline{P} + \overline{\underset{\approx}{E}}^{*}(\cdot)^3\underset{\sim}{\nabla}_Q\underset{\sim}{\nabla}_Q\underset{\sim}{\nabla}_Q\overline{P} + \ldots = 0 \tag{2.12}$$

governing the purely global-space transport for long times. Appearing in (2.12) are the constant mean phenomenological coefficients $\overline{\underset{\sim}{U}}^{*}$, $\overline{\underset{\approx}{D}}^{*}$, $\overline{\underset{\approx}{E}}^{*}$, etc. The first two of these can be identified as the mean velocity vector and Taylor dispersivity dyadic; these are to be calculated via the prescriptions (2.4) and (2.5). The third and higher-order coefficients -- multi-

plying the corresponding higher-order gradient terms in (2.12) -- are generally omitted. They govern temporal growth of the higher-order central moments of $\bar{P}$. Our scheme permits their explicit calculation, if desired. Just as $\underset{\sim}{\bar{U}}^*$ and $\underset{\approx}{\bar{D}}^*$ may be defined via their Langrangian definitions

$$\underset{\sim}{\bar{U}}^* \equiv \lim_{t\to\infty} \frac{d}{dt} \underset{\sim}{M}_1 \quad , \tag{2.13a}$$

$$\underset{\approx}{\bar{D}}^* \equiv \frac{1}{2} \lim_{t\to\infty} \frac{d}{dt} (\underset{\approx}{M}_2 - \underset{\sim}{M}_1\underset{\sim}{M}_1) \quad , \tag{2.13b}$$

so too may the triadic $\underset{\approx\approx}{\bar{E}}^*$ be defined as

$$\underset{\approx\approx}{\bar{E}}^* \equiv \frac{1}{6} \lim_{t\to\infty} \frac{d}{dt} \text{sym}(\underset{\approx\approx}{M}_3 - 3\underset{\sim}{M}_1\underset{\approx}{M}_2 + 2\underset{\sim}{M}_1\underset{\sim}{M}_1\underset{\sim}{M}_1) \quad . \tag{2.13c}$$

That $\underset{\approx\approx}{\bar{E}}^*$ does not vanish for long times, but rather tends to a constant, time-independent value, clearly demonstrates that the long-time mean probability density $\bar{P}$ is not strictly Gaussian. Gaussian behavior would demand vanishing of the third central moment, whereas (2.13c) demonstrates that this moment grows linearly in time -- at least for sufficiently long times.

This conclusion applies equally well to circumstances in which coupled transport effects are absent. Indeed, $\underset{\approx\approx}{\bar{E}}^*$ may be explicitly calculated in the simplest case of axial laminar flow in parallel plate (n=2) or circular cylindrical tube (n=3) geometries, yielding

$$\underset{\approx\approx}{\bar{E}}^* = \underset{\sim}{i}_\zeta\underset{\sim}{i}_\zeta\underset{\sim}{i}_\zeta\underset{\sim}{i}_\zeta \frac{\bar{V}^3 a^4}{D^2} \left[\frac{4(n-1)(5n^2+8n-45)}{(n+1)^2(n+3)^2(n+5)(n+7)(n+9)}\right] \quad , \tag{2.14}$$

with $\underset{\sim}{i}_\zeta$ a unit vector along the axis, $\bar{V}$ the area averaged Poiseuille velocity, a half the parallel plate separation distance or circular cylinder radius, and D the molecular diffusivity.

Such higher-order effects will not be considered in the next section,

aimed principally at obtaining the mean velocity vector $\overline{\underset{\sim}{U}}^*$ and dispersivity dyadic $\overline{\underset{\approx}{D}}^*$ for a flexible chain undergoing sedimentation in a viscous fluid.

3. BROWNIAN DIFFUSION AND SEDIMENTATION OF FLEXIBLE CHAINS AND CLUSTERS

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; as such, the conformation of the chain can (and does) vary with time.

Label the individual rigid particles with the index A (A = 0, 1, 2,...,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 each instant the complete configuration of the cluster is entirely determined by specification of the n+1 position vectors $\underset{\sim}{R}_A$ of the locator points O_A relative to an arbitrary space-fixed origin, and a comparable set of n+1 orientational triplets $\underset{\sim}{\phi}_A$ of each of the constituent particles.

Denote by

$$P(\underset{\sim}{R}_0,\ldots,\underset{\sim}{R}_n;\ \underset{\sim}{\phi}_0,\ldots,\underset{\sim}{\phi}_n,\ t|\underset{\sim}{R}'_0,\ldots,\underset{\sim}{R}'_n;\ \underset{\sim}{\phi}'_0,\ldots,\underset{\sim}{\phi}'_n) \tag{3.1}$$

the conditional probability density for finding the chain configuration in an infinitesimal neighborhood of $(\underset{\sim}{R}_0,\ldots\underset{\sim}{R}_n;\underset{\sim}{\phi}_0,\ldots,\underset{\sim}{\phi}_n)$ at time t, given that at time t=0 the chain possessed the corresponding primed configuration. The probability density P is chosen to satisfy the dual requirements

$$\int d\underset{\sim}{R}_0\ldots d\underset{\sim}{R}_n\ d\underset{\sim}{\phi}_0\ldots d\underset{\sim}{\phi}_n\ P = 1 \quad (t > 0) \quad , \tag{3.2a}$$

$$P = 0 \qquad (t < 0) \quad , \tag{3.2b}$$

in which the limits of integration extend over the entire physical- and orientational-space domains available for the configurational transport.

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

$$\frac{\partial P}{\partial t} + \sum_{A=0}^{n} \left(\frac{\partial}{\partial \underset{\sim}{R}_A} \cdot \underset{\sim}{J}[\underset{\sim}{R}_A] + \frac{\partial}{\partial \underset{\sim}{\phi}_A} \cdot \underset{\sim}{j}[\underset{\sim}{\phi}_A] \right) = \delta(t) \prod_{A=0}^{n} \delta(\underset{\sim}{R}_A - \underset{\sim}{R}_A') \, \delta(\underset{\sim}{\phi}_A - \underset{\sim}{\phi}_A') \quad , \tag{3.3}$$

The configuration-specific physical- and orientational-space vector flux densities $\underset{\sim}{J}[\underset{\sim}{R}_A]$ and $\underset{\sim}{j}[\underset{\sim}{\phi}_A]$ of particle A will be assumed to possess the respective convective-diffusive constitutive forms

$$\underset{\sim}{J}[\underset{\sim}{R}_A] = \dot{\underset{\sim}{R}}_A P - \sum_{B=0}^{n} \{ \underset{\approx}{D}[\underset{\sim}{R}_A | \underset{\sim}{R}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{R}_B} + \underset{\approx}{D}[\underset{\sim}{R}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{\phi}_B} \} \quad , \tag{3.4a}$$

$$\underset{\sim}{j}[\underset{\sim}{\phi}_A] = \dot{\underset{\sim}{\phi}}_A P - \sum_{B=0}^{n} \{ \underset{\approx}{D}[\underset{\sim}{\phi}_A | \underset{\sim}{R}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{R}_B} + \underset{\approx}{D}[\underset{\sim}{\phi}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{\phi}_B} \} \quad , \tag{3.4b}$$

in which

$$\dot{\underset{\sim}{R}}_A = - \sum_{B=0}^{n} \{ \underset{\approx}{M}[\underset{\sim}{R}_A | \underset{\sim}{R}_B] \cdot \frac{\partial V}{\partial \underset{\sim}{R}_B} + \underset{\approx}{M}[\underset{\sim}{R}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial V}{\partial \underset{\sim}{\phi}_B} \} \quad , \tag{3.5a}$$

$$\dot{\underset{\sim}{\phi}}_A = - \sum_{B=0}^{n} \{ \underset{\approx}{M}[\underset{\sim}{\phi}_A | \underset{\sim}{R}_B] \cdot \frac{\partial V}{\partial \underset{\sim}{R}_B} + \underset{\approx}{M}[\underset{\sim}{\phi}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial V}{\partial \underset{\sim}{\phi}_B} \} \quad . \tag{3.5b}$$

The configuration-specific mobility dyadics $\underset{\approx}{M}[A|B]$ and diffusivity dyadics $\underset{\approx}{D}[A|B]$ are functionally dependent only upon the internal configuration of the cluster; they are closely related to one another via the multibody configuration-specific Stokes-Einstein relations (Brenner 1967)

$$\underset{\approx}{D}[A|B] = kT \, \underset{\approx}{M}[A|B] \quad . \tag{3.6}$$

The potential $V(\underset{\sim}{R}_0, \ldots, \underset{\sim}{R}_n; \underset{\sim}{\phi}_0, \ldots, \underset{\sim}{\phi}_n)$ appearing in (3.5) is also

assumed to be a known function of the internal configuration, to which potential is added a further contribution arising from a constant external force $\underset{\sim}{F}$ (e.g., gravity) causing sedimentation of the chain [cf. (3.9)].

Subject to appropriate boundary and initial conditions, equation (3.3) for P may be solved 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, a much more physically useful and concise description is that of the transport through physical space of the flexible body as a whole, viewed as the sole object of interest. Attainment of this goal requires that we assign a single locator point to the flexible cluster as a definable entity, and focus exclusively on the stochastic trajectory of that point through ordinary three-dimensional (i.e.,physical) space. All other coordinates, aside from the three required to specify the position of that locator point in physical space, are then assigned the role of specifying the internal conformation of the chain. Our eventual goal is thus to eliminate from the transport equation all the internal degrees of freedom, at least for sufficiently long times to assure that equilibrium with respect to internal conformation has effectively been attained.

Equations (3.3) - (3.5), by themselves, effect no definite decomposition of the internal variables into respective local (internal) and global (external) sets. As this classification is prerequisite in applying to particular problems the results of coupled generalized Taylor dispersion theory given in Section 2, we will presently effect an appropriate trans-

formation permitting this classification to be made.

Local/Global Form of the Equations

Our ansatz consists of recognizing that for long times the choice of locator point for the flexible cluster is irrelevant; that is, any and all choices of chain locator point suffice equally well for identifying the location of the flexible body in physical space. In the long run, all such points behave alike as regards their net translational motions in physical space. As such, we are free to choose any point O_0 rigidly affixed to particle A=0 as the locator point of the flexible cluster. Denote by $\underset{\sim}{Q}$ the position vector of this point, so that

$$\underset{\sim}{Q} \equiv \underset{\sim}{R}_0 \quad , \tag{3.7}$$

spanning the entire global (physical) space available for chain transport. Consider the local variables $\underset{\sim}{q}$ to consist of the set

$$\underset{\sim}{q} \equiv (\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_n \; , \; \phi_0, \phi_1, \ldots, \phi_n) \equiv (\underset{\sim}{r}^n, \phi^{n+1}) \quad . \tag{3.8a}$$

in which

$$\underset{\sim}{r}_a \equiv \underset{\sim}{R}_a - \underset{\sim}{R}_0 \qquad (a = 1,2, \ldots, n) \tag{3.8b}$$

are the position vectors of the remaining points O_a relative to the designated point O_0.

Effecting the transformation of coordinates from $(\underset{\sim}{R}_0, \ldots, R_n; \phi_0, \ldots, \phi_n)$ to $(\underset{\sim}{Q}, \underset{\sim}{q})$ -- as represented by (3.7) and (3.8) -- into (3.3) - (3.5), in conjunction with the assumed decomposition of V into the global • local form

$$V = -\underset{\sim}{F} \cdot \underset{\sim}{R}_0 + kT \; E(\underset{\sim}{r}^n, \phi^{n+1}) \quad , \tag{3.9}$$

(with $\underset{\sim}{F}$ a constant external force vector), ultimately yields the global/local form

$$\partial P/\partial t + \underset{\sim}{\nabla}_Q \cdot \underset{\sim}{J} + [\![\underset{\sim}{\nabla}_q]\!]^\dagger \cdot [\![\underset{\sim}{j}]\!] = \delta(t)\delta(\underset{\sim}{Q} - \underset{\sim}{Q}')\delta(\underset{\sim}{q} - \underset{\sim}{q}') \quad , \tag{3.10}$$

of the conservation equation for P, in which

$$[\![\underset{\sim}{\nabla}_q]\!]^\dagger \equiv [\![\partial/\partial \underset{\sim}{r}_1^\dagger \ldots \partial/\partial \underset{\sim}{r}_n^\dagger \quad \partial/\partial \underset{\sim}{\phi}_0^\dagger \ldots \partial/\partial \underset{\sim}{\phi}_n^\dagger]\!] \quad , \tag{3.11}$$

$$[\![\underset{\sim}{j}]\!] = [\![\underset{\sim}{u}]\!] P - [\![\underset{\approx}{D}^{qQ}]\!] \cdot \underset{\sim}{\nabla}_Q P - e^{-E} [\![\underset{\approx}{D}^{qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] (e^E P) \quad , \tag{3.12}$$

and

$$\underset{\sim}{J} = \underset{\sim}{U} P - \underset{\approx}{D}^{QQ} \cdot \underset{\sim}{\nabla}_Q P - e^{-E} [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] (e^E P) \quad . \tag{3.13}$$

In the above, the double-bracketed quantities are partitioned matrices, whose individual elements are themselves vectors or dyadics. The phenomenological coefficients appearing in (3.12) and (3.13) are defined as follows:

(i) Local velocity matrix $[\![\underset{\sim}{u}]\!]$:

$$[\![\underset{\sim}{u}]\!] = \begin{bmatrix\!\!\![} \underset{\sim}{u}[\underset{\sim}{r}_a] \\ \underset{\sim}{u}[\underset{\sim}{\phi}_A] \end{bmatrix\!\!\!]} \quad , \tag{3.14a}$$

with

$$\underset{\sim}{u}[\underset{\sim}{r}_a] = \{\underset{\approx}{M}[\underset{\sim}{R}_a|\underset{\sim}{R}_0] - \underset{\approx}{M}[\underset{\sim}{R}_0|\underset{\sim}{R}_0]\} \cdot \underset{\sim}{F} \quad , \tag{3.14b}$$

$$\underset{\sim}{u}[\underset{\sim}{\phi}_A] = \underset{\approx}{M}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_0] \cdot \underset{\sim}{F} \quad ; \tag{3.14c}$$

(ii) Coupling diffusivity matrices $[\![\underset{\approx}{D}^{qQ}]\!]$ and $[\![\underset{\approx}{D}^{Qq}]\!]$:

$$[\![\underset{\approx}{D}^{qQ}]\!] = [\![\underset{\approx}{D}^{Qq}]\!]^\dagger = \begin{bmatrix\!\!\![} \underset{\approx}{D}^{qQ}[\underset{\sim}{r}_a] \\ \underset{\approx}{D}^{qQ}[\underset{\sim}{\phi}_A] \end{bmatrix\!\!\!]} \quad , \tag{3.15a}$$

with

$$\underset{\approx}{D}^{qQ}[\underset{\sim}{r}_a] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_o] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \quad , \tag{3.15b}$$

$$\underset{\approx}{D}^{qQ}[\underset{\sim}{\phi}_A] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_o] \quad ; \tag{3.15c}$$

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

$$[\![\ \underset{\approx}{D}^{qq}\ ]\!] = \left[\!\!\left[\begin{array}{cc} \underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{r}_b] & \underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{\phi}_A] \\ \underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{r}_a] & \underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] \end{array} \right]\!\!\right] \quad , \tag{3.16a}$$

in which

$$\underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{r}_b] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_b] - \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_o] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_b] + \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \ , \tag{3.16b}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{\phi}_A] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{\phi}_A] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{\phi}_A] \quad , \tag{3.16c}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{r}_a] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_a] - \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_o] = \underset{\approx}{D}^{qq\dagger}[\underset{\sim}{r}_a|\underset{\sim}{\phi}_A] \quad , \tag{3.16d}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] \quad ; \tag{3.16e}$$

(iv) Global velocity vector $\underset{\sim}{U}$:

$$\underset{\sim}{U} \equiv \underset{\approx}{M}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \cdot \underset{\sim}{F} \quad ; \tag{3.17}$$

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

$$\underset{\approx}{D}^{QQ} \equiv \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \quad . \tag{3.18}$$

Equations (3.10), (3.12), and (3.13) are identical to the canonical forms of the equations of generalized coupled Taylor dispersion theory (2.1) - (2.3) albeit the more complex appearance of their partitioned-matrix phenomenological coefficients. As such, the results (2.4) and (2.5) are directly applicable in this circumstance.

Results

For completeness, explicit expressions for the mean velocity vector $\overline{\underset{\sim}{U}}^*$ and dispersivity dyadic $\overline{\underset{\approx}{D}}^*$ of the flexible chain sedimenting through an otherwise quiescent viscous fluid are now presented. These correspond identically to equations (2.4) and (2.5) of Section 2, namely

$$\overline{\underset{\sim}{U}}^* = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\{P_0^\infty \underset{\sim}{U} - e^{-E} [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] (e^E P_0^\infty)\} \quad , \tag{3.19}$$

and

$$\overline{\underset{\approx}{D}}^* = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\{P_0^\infty [\, \underset{\approx}{D}^{QQ} - [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] \underset{\approx}{B} \,]$$

$$+ [P_0^\infty (\underset{\sim}{U} - \overline{\underset{\sim}{U}}^*) - e^{-E} [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] (e^E P_0^\infty)] \underset{\approx}{B}\} \quad , \tag{3.20}$$

The requisite local fields P_0^∞ and $\underset{\approx}{B}$ appearing above are to be obtained by solving equations equivalent to (2.6) and (2.7).

Expressions (3.19) and (3.20) represent the major results of our analysis. Together with identification from existing data of the phenomenological coefficients required therein, as given by (3.14) - (3.18), they permit rigorous calculation of the long-time mean sedimentation velocity vector $\overline{\underset{\sim}{U}}^*$ and dispersivity dyadic $\overline{\underset{\approx}{D}}^*$ for any flexible chain or cluster composed of rigid Brownian constituent particles bound together via internal potentials.

Example

As an example consider the sedimentation-dispersion problem for the tethered dumbbell depicted in Fig 1. The latter consists of two identical rigid spherical particles of radii $\underline{a}$, each denser than its surrounding fluid by an amount corresponding to a mass difference $|\Delta m|$. A tether of

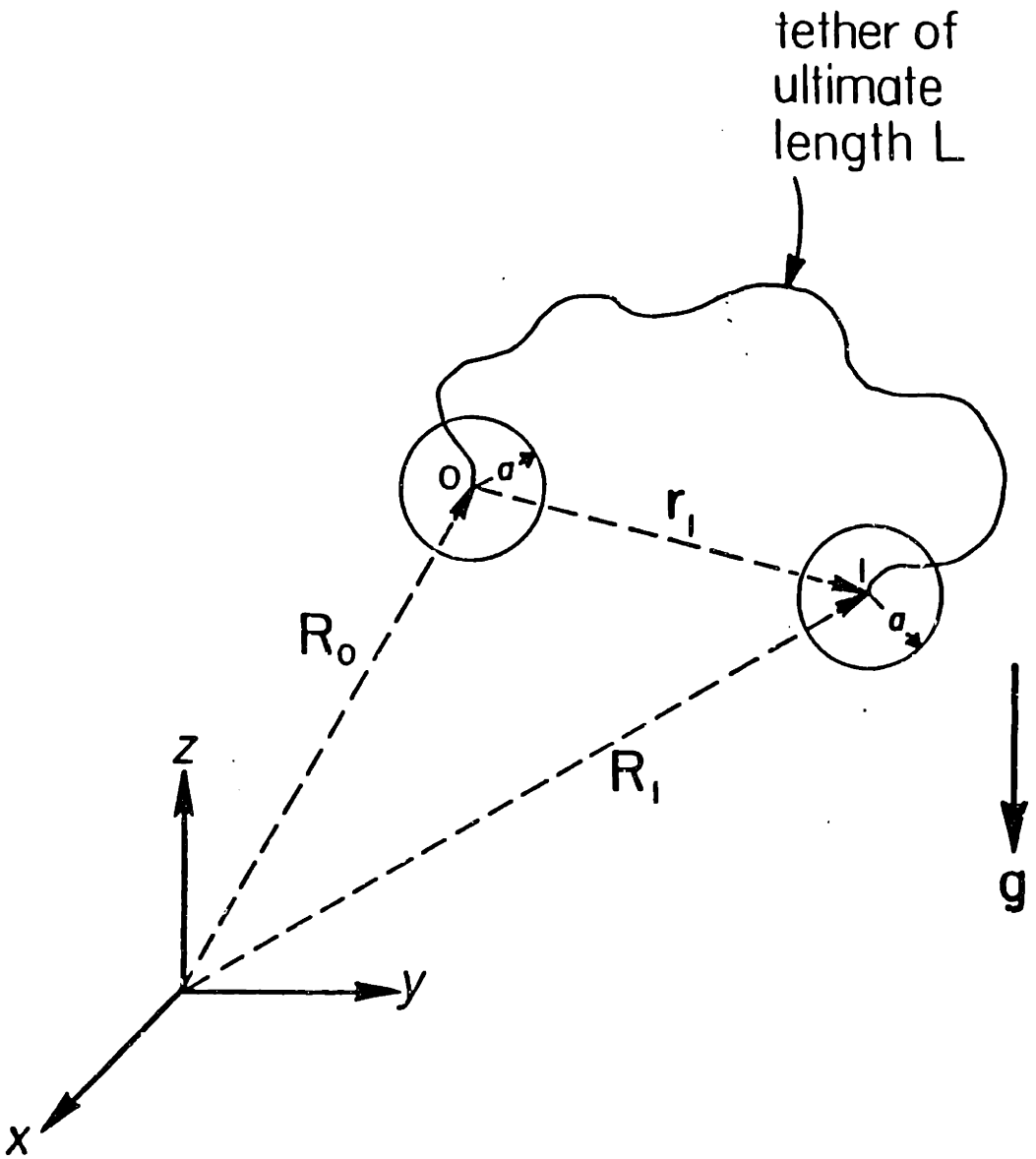

Fig. 1. Tethered dumbbell.

ultimate extensibility L is assumed to connect their geometric centers. The total sedimentation force acting on the dumbbell is here

$$\underset{\sim}{F} = 2|\Delta m|\underset{\sim}{g} = F\hat{\underset{\sim}{F}} \quad , \tag{3.21}$$

with $\hat{\underset{\sim}{F}}$ a unit vector along gravity field vector $\underset{\sim}{g}$. If the dimensionless tether length to sphere radius ratio is denoted by

$$\chi = L/a \quad , \tag{3.22}$$

and the Langevin parameter (embodying the ratio of gravitational to thermal energies of the dumbbell) designated as

$$\gamma = Fa/kT \quad , \tag{3.23}$$

the final results of the foregoing analysis may be summarized by the explicit relations

$$\underset{\sim}{\bar{U}}^{*}/\,(M_{\infty}F) = \hat{\bar{M}}\,\hat{\underset{\sim}{F}} \tag{3.24}$$

and

$$\underset{\approx}{\bar{D}}^{*}/D_{\infty} = \hat{D}_{\parallel}\,\hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}} + \hat{D}_{\perp}(\underset{\approx}{I} - \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}}) \quad , \tag{3.25a}$$

in which

$$\hat{D}_{\parallel} = \hat{\bar{M}} + \gamma^{2}(\hat{\alpha} + \hat{\beta}/5) \quad , \tag{3.25b}$$

$$\hat{D}_{\perp} = \hat{\bar{M}} + \gamma^{2}(3\hat{\beta}/20) \quad . \tag{3.25c}$$

Here,

$$M_{\infty} = (12\pi\mu a)^{-1} \quad , \quad D_{\infty} = kT\,M_{\infty} \tag{3.26a,b}$$

with μ the fluid viscosity.

The functions $\hat{\bar{M}}$, $\hat{\alpha}$ and $\hat{\beta}$ appearing in (3.24) - (3.25) are dependant only upon χ. These have been calculated numerically, using as input data the hydrodynamic calculations of Jeffrey and Onishi (1984) and Batchelor (1976). Calculated results for these coefficients are embodied in Figs. 2-4.

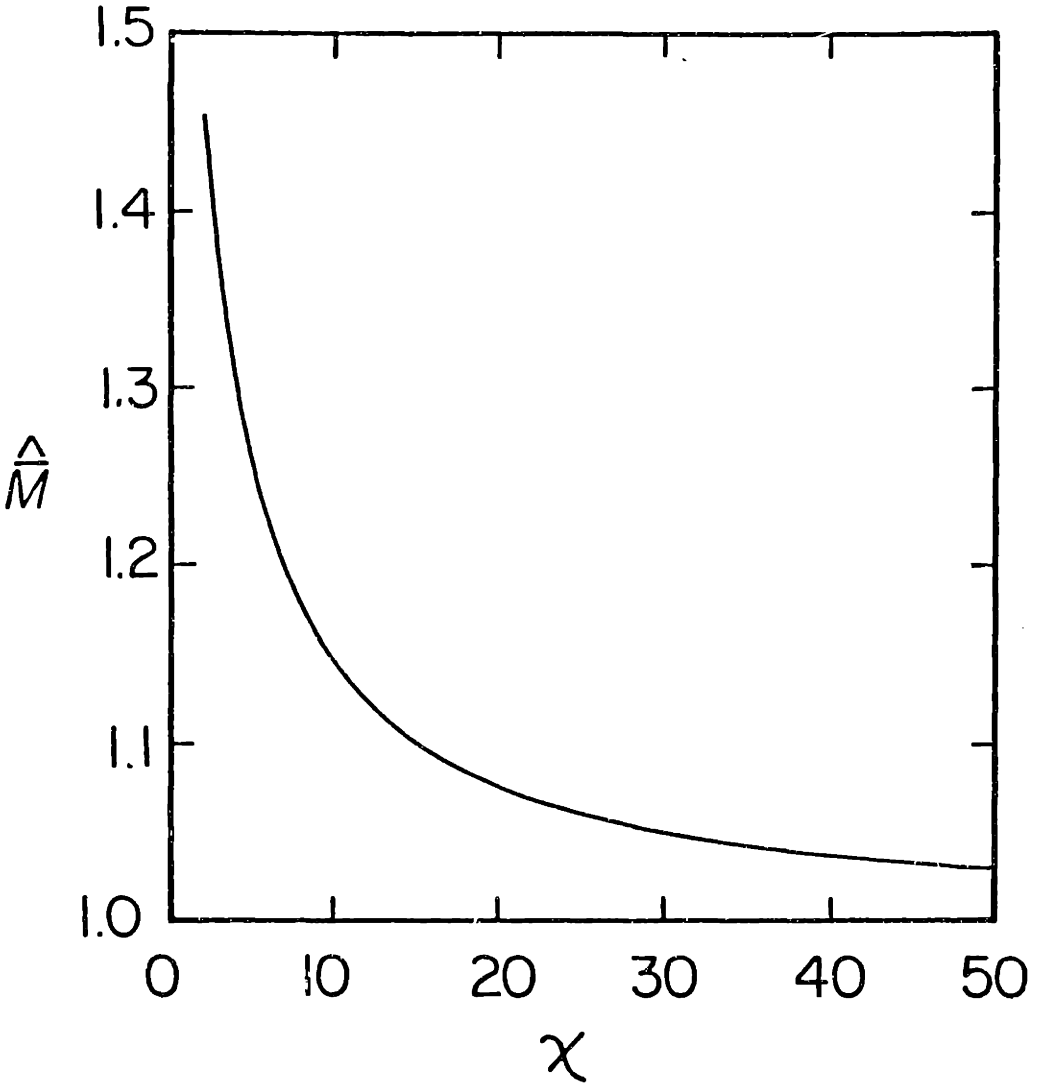

Fig. 2. (a) Mean nondimensional mobility $\hat{\bar{M}}$ vs nondimensional tether length χ.

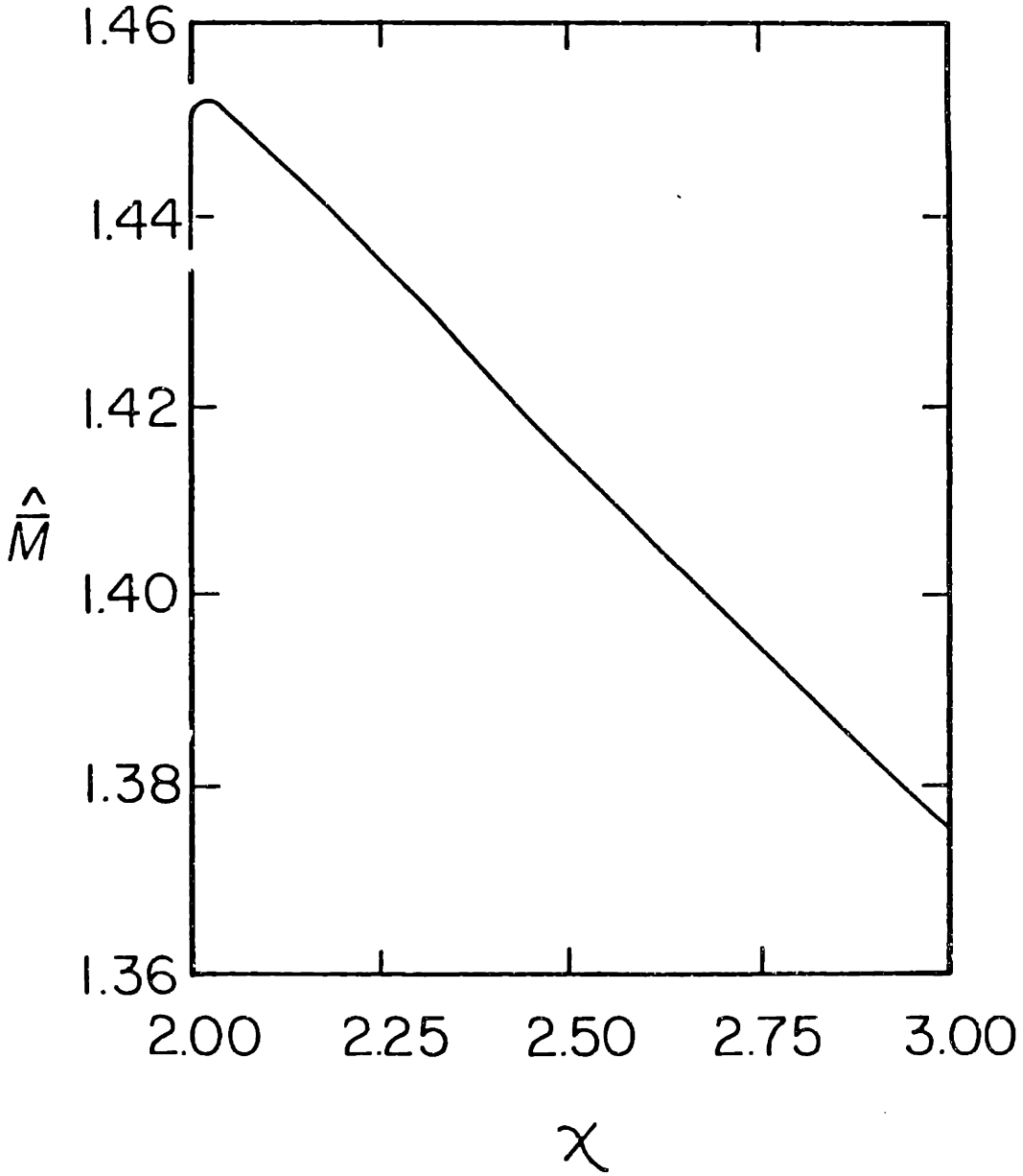

Fig. 2. (b) Enlargement of the near-touching range $2 \leq \chi \leq 3$.

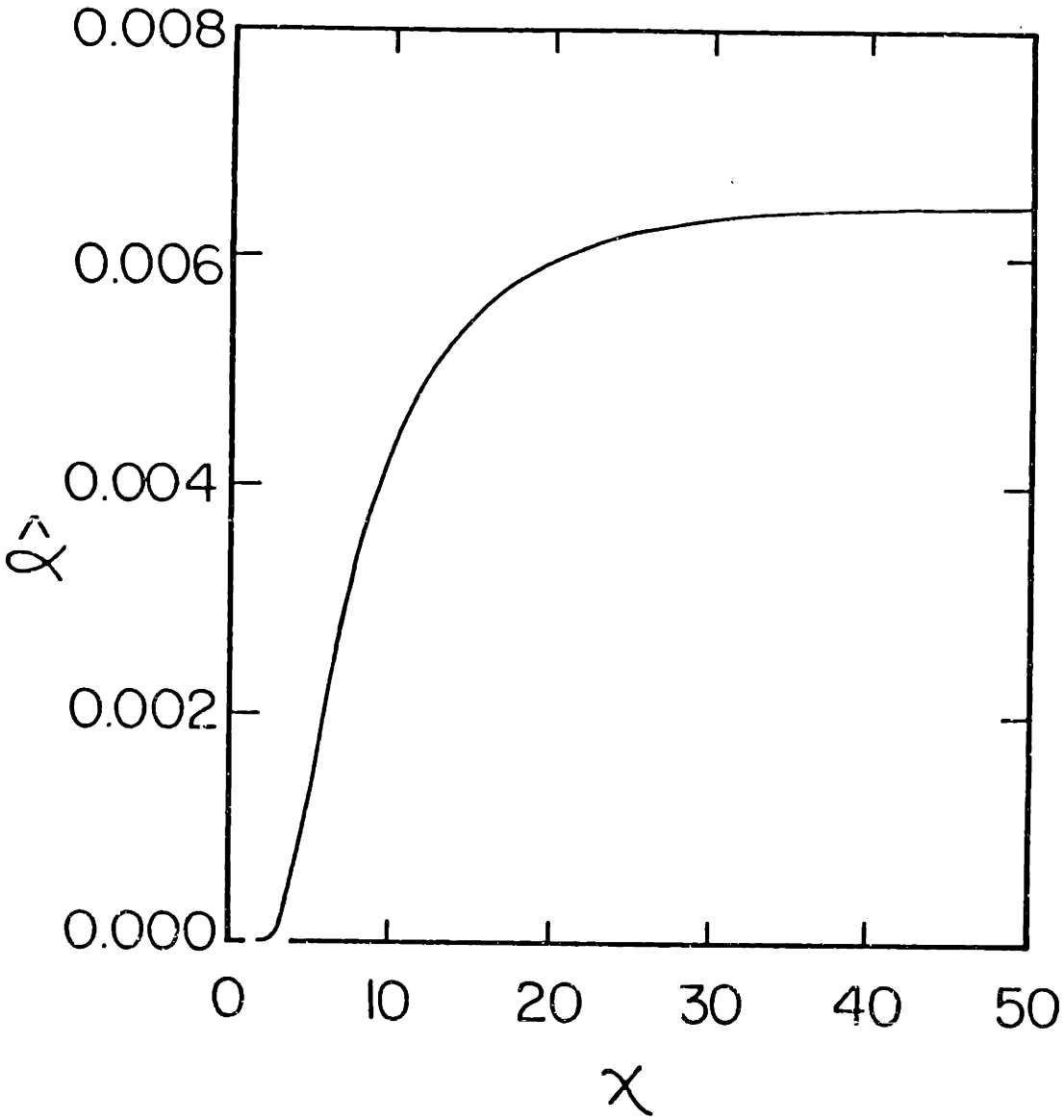

Fig. 3 Taylor dispersivity coefficient $\hat{\alpha}$ vs nondimensional tether length χ.

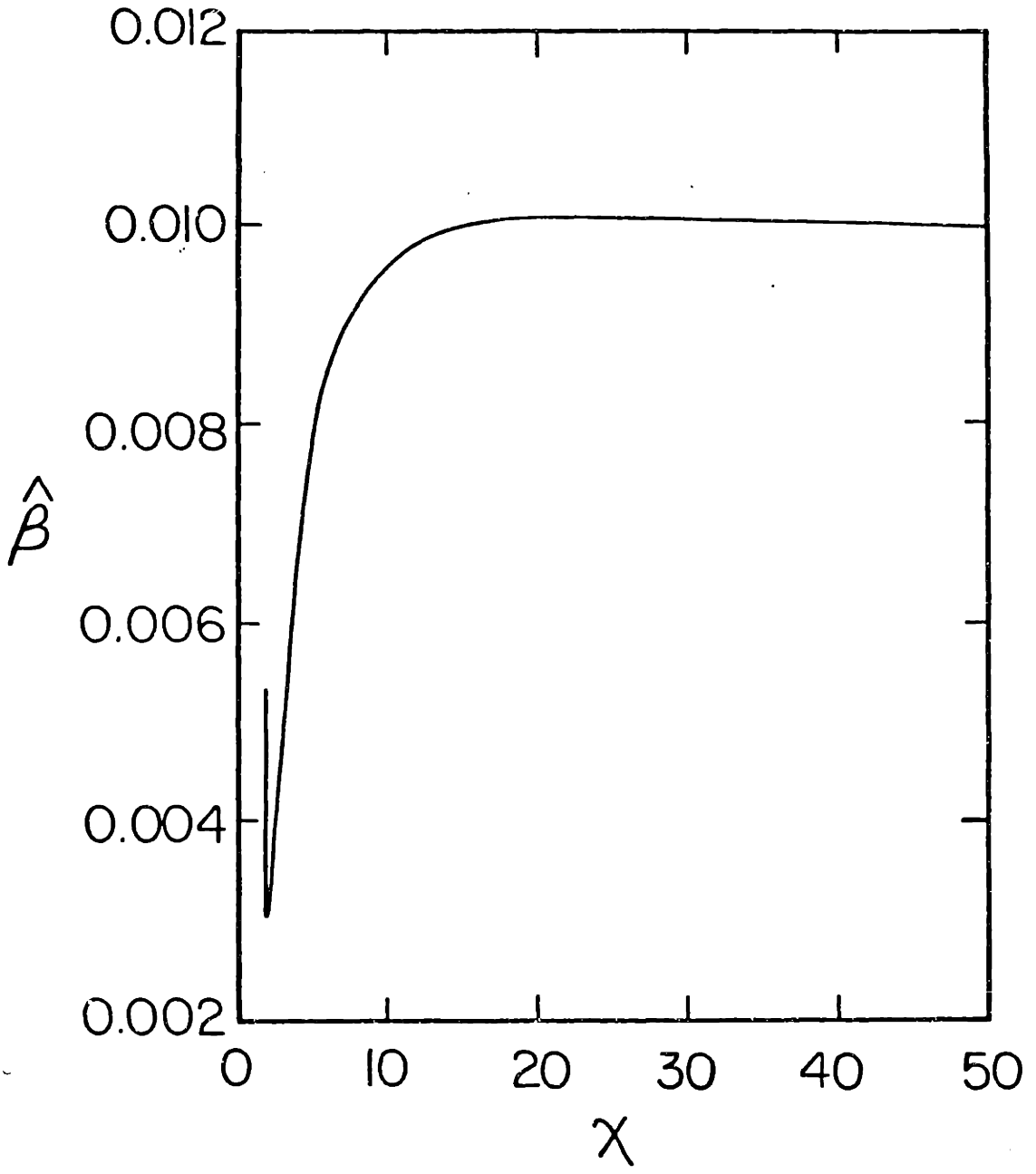

Fig. 4. (a) Taylor dispersivity coefficient $\hat{\beta}$ vs nondimensional tether length χ.

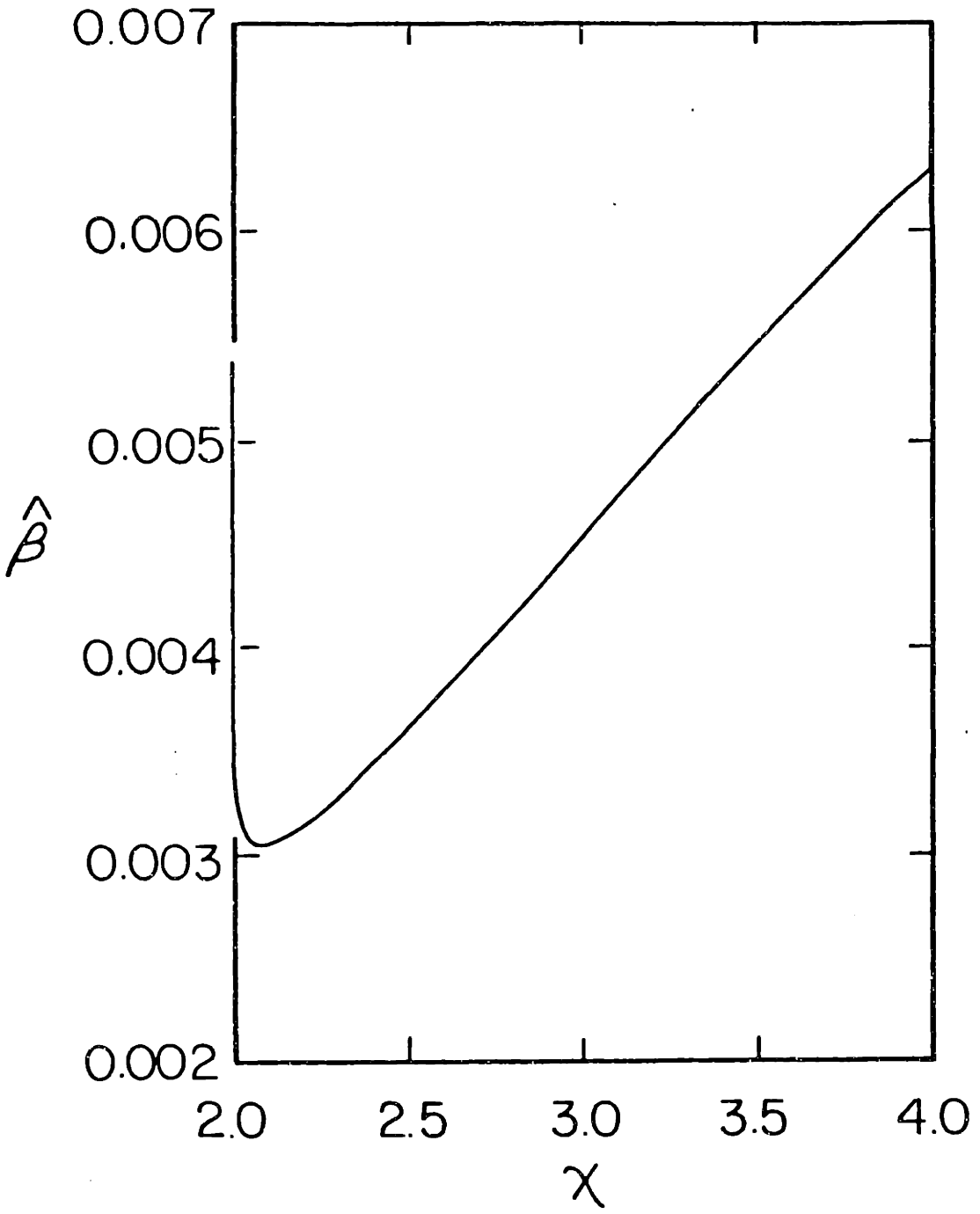

Fig. 4. (b) Enlargement of the near-touching range $2 \leq \chi \leq 4$.

Summary

A general scheme has been provided which permits 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 nonzero sizes and of the hydrodynamic interactions among the individual rigid particles comprising the flexible chain. No ad hoc pre-averaging approximations have been invoked to bring the calculations to fruition. Explicit numerical results are given for tethered dumbbells.

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CHAPTER II:

HIGHER ORDER MOMENTS IN MACROTRANSPORT PROCESSES

ABSTRACT

A novel moment-gradient expansion scheme, expressing the microscale probability density P as an infinite sum of global-space gradients of its corresponding macroscale density $\bar{P}$ multiplied by coefficients formed from its local and total moments, is employed to derive an asymptotic long-time macrotransport equation from its more detailed microtransport predecessor. Particular emphasis is paid to third- and higher-order gradient terms in the expansion. These are shown to result in non-Gaussian behavior of the macroscale probability density $\bar{P}$ governing convective-diffusive transport processes.

I. INTRODUCTION

The recent generalization[1,2] of Taylor dispersion phenomena[3-5] to situations in which the convective-molecular diffusion solute transport processes occur in an abstract multidimensional space $\underline{Q} \oplus \underline{q}$, composed of local or internal coordinates $\underline{q}$ and global or physical-space coordinates $\underline{Q}$, has extended the applicability of Taylor dispersion analyses greatly beyond their original focus upon unidirectional duct flows. Indeed, problems as varied as the sedimentation-dispersion of non-spherical Brownian particles,[6,7] dispersion accompanying solute flow through spatially-periodic porous media,[8] and momentum transport occurring in spatially-periodic suspensions of neutrally buoyant particles[9] have been analyzed within this generalized Taylor dispersion framework, culminating in development of the general area of Macrotransport Processes.[10]

The main principles[2] underlying the macrotransport analysis may be recapitulated as follows: A detailed conservation equation is written for the transport of a passive Brownian tracer initially introduced at an arbitrary point $(\underline{Q},\underline{q}')$ of the $(\underline{Q},\underline{q})$ space. Together with appropriate constitutive expressions (containing prescribed $\underline{q}$-dependent phenomenological coefficients) for the flux in each subspace, and respective no-flux and attenuation conditions prevailing on their boundaries, this system of microtransport equations exactly governs the detailed convective-diffusion process. Evolution equations are then derived for the mean temporal displacement of the tracer (i.e. the first moment of the tracer distribution function) in the global space, along with its mean-square displacement about that mean (second central moment). Asymptotic evaluation of these displacements for long times then furnishes explicit expressions for the mean

global-space velocity vector and dispersivity dyadic of the tracer as the respective coefficients of the linear growth terms (in time) of the moments. The 'two-coefficient' macrotransport description thereby provided of the purely physical $\underline{Q}$-space transport, based upon use of this mean tracer velocity and dispersivity, represents a much more tractable account of the transport process than does its more detailed microtransport counterpart -- one from which the independent internal degrees of freedom $\underline{q}$ have been removed.

In recent contributions[11,12] aimed at providing a rational (i.e. perturbative) mathematical basis for otherwise ad hoc generalized Taylor dispersion analyses, it was pointed out that terms beyond the conventional first- and second-order central moments of the mean or macroscopic distribution[2] persist for long times, indicating that the long-time distribution is not strictly a travelling Gaussian. The existence of such higher-order terms has hitherto been studied only in the simple context of unidirectional flows;[13-15] furthermore, the theoretical effort pertaining to these terms has heretofore been focussed primarily only on interpreting the short-time behavior of this distribution and the higher-order temporal corrections thereto.

Herein we undertake a systematic study the properties of such third- and higher-order moments, paying particular attention to the asymptotic forms of these moments for long times. In the process, the relationship between the moment method of generalized Taylor dispersion theory[1,5,16] and the series expansion proposed by Gill and Sankarasubramanian[14] is clarified. Concurrently, a new scheme is introduced for deriving the asymptotic, global-space, macrotransport equation.

This paper is organized as follows: In the next section a generic

series expansion is provided, permitting the normalized probability density function $P(\underline{Q},\underline{q})$ to be expanded in terms of the products of its moments with the global gradients of the mean probability density $\bar{P}(\underline{Q})$, obtained by integration of P over the local space $\underline{q}$. In section 3 the conservation and constitutive equations governing the detailed microtransport process are used in conjunction with the moment-gradient expansion to obtain the macrotransport equation governing the temporal evolution of $\bar{P}$ in $\underline{Q}$ space. Section 4 is devoted to a derivation of the time-asymptotic form of this macrotransport description, including higher-order global gradients beyond the second. Finally, in section 5, the general scheme is illustrated via the problem of Taylor dispersion accompanying Poiseuille flow within an $\underline{n}$-dimensional hypercircular cylinder. This is solved up to third-order terms, contemporaneously reproducing known dispersion results for laminar flow within a circular cylinder (n=3) and between parallel plates (n=2) for these particular dimensionalities.

II. MOMENT-GRADIENT EXPANSION

Consider a probability density function $P(\underset{\sim}{Q},\underset{\sim}{q})$, defined over the bounded local space $\underset{\sim}{q} \in \underset{\sim}{q}_o$ and unbounded global space $\underset{\sim}{Q} \in \underset{\sim}{Q}_\infty$, and satisfying the normalization requirement

$$\int_{\underset{\sim}{q}_o} d\underset{\sim}{q} \int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q}\ P(\underset{\sim}{Q},\underset{\sim}{q}) = 1 \ . \tag{2.1}$$

[Of course, in particular circumstances P may depend on other independent variables too (such as t and $\underset{\sim}{q}'$ in subsequent sections). However, in the interests of generality these are here explicitly suppressed from the argument of P.] Define the mth local moment of P as[2]

$$\underset{\sim}{P}_m(\underset{\sim}{q}) = \int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q}\ \underset{\sim}{Q}^m\ P(\underset{\sim}{Q},\underset{\sim}{q}) \ , \tag{2.2}$$

as well as the mth total moment,

$$\underset{\sim}{M}_m = \int_{\underset{\sim}{q}_o} d\underset{\sim}{q}\ \underset{\sim}{P}_m(\underset{\sim}{q}) \ , \tag{2.3}$$

each such polyadic being an mth rank tensor in $\underset{\sim}{Q}_\infty$. Furthermore, denote by

$$\overline{P}(\underset{\sim}{Q}) = \int_{\underset{\sim}{q}_o} d\underset{\sim}{q}\ P(\underset{\sim}{Q},\underset{\sim}{q}) \tag{2.4}$$

the average of P over the local space.

Our generalization of the *ad hoc* series expansion proposed by Gill and Sankarasubramanian[14] entails an expansion of the form

$$P(\underline{Q},\underline{q}) = \sum_{j=0}^{\infty} \underline{F}_j(\underline{q})(\cdot)^j \nabla_{\underline{Q}}^j \bar{P}(\underline{Q})$$

$$= F_0(\underline{q})\bar{P} + \underline{F}_1(\underline{q})\cdot\nabla_{\underline{Q}}\bar{P} + \underline{\underline{F}}_2(\underline{q})(\cdot)^2\nabla_{\underline{Q}}\nabla_{\underline{Q}}\bar{P} + \cdots , \qquad (2.5)$$

wherein the polyadic $\underline{F}_j$ is a tensor of rank j; $(\cdot)^j$ denotes j scalar multiplications in the order prescribed by the "nesting convention" of Chapman and Cowling;[17] and $\nabla_{\underline{Q}}^j = \nabla_{\underline{Q}}\nabla_{\underline{Q}}\cdots\nabla_{\underline{Q}}$ (j times), in which $\nabla_{\underline{Q}} = (\partial/\partial\underline{Q})_{\underline{q}}$ is the global-space gradient operator. We shall furnish a proof of this expansion (heretofore lacking even in the one-dimensional case), and in the process explicitly relate the tensor coefficients $\underline{F}_j(\underline{q})$ to the moments (2.2) and (2.3).

To that end, define the global-space Fourier transform

$$P(\underline{k},\underline{q}) = \int_{\underline{Q}_\infty} d\underline{Q}\, \exp(i\underline{k}\cdot\underline{Q})\, P(\underline{Q},\underline{q}) \qquad (2.6)$$

of $P(\underline{Q},\underline{q})$. Similarly, the transform of the average (2.4) is

$$\bar{P}(\underline{k}) = \int_{\underline{Q}_\infty} d\underline{Q}\, \exp(i\underline{k}\cdot\underline{Q})\, \bar{P}(\underline{Q}) = \int_{\underline{q}_o} d\underline{q}\, P(\underline{k},\underline{q}) . \qquad (2.7)$$

Taylor series expansion of the exponential appearing in (2.6) considered in conjunction with (2.2) yields

$$P(\underline{k},\underline{q}) = \sum_{n=0}^{\infty} (n!)^{-1}(i\underline{k})^n(\cdot)^n \underline{P}_n(\underline{q}) . \qquad (2.8)$$

Substitute the latter into the RHS of (2.7) and make use of (2.3) to obtain

$$\bar{P}(\underline{k}) = 1 + \sum_{n=1}^{\infty} (n!)^{-1} (i\underline{k})^n (\cdot)^n \underline{M}_n \quad . \tag{2.9}$$

That $M_0 = 1$ is a consequence of (2.1).

Divide (2.8) by (2.9) and expand the denominator via the binomial theorem to establish that

$$\frac{P(\underline{k},\underline{q})}{\bar{P}(\underline{k})} = \left[\sum_{n=0}^{\infty} (n!)^{-1} (i\underline{k})^n (\cdot)^n \underline{P}_n(\underline{q})\right]\left[1 + \sum_{j=1}^{\infty} (-1)^j S^j(\underline{k})\right] \quad , \tag{2.10}$$

in which

$$S(\underline{k}) = \sum_{n=1}^{\infty} (n!)^{-1} (i\underline{k})^n (\cdot)^n \underline{M}_n \quad . \tag{2.11}$$

Expand the RHS of (2.10) in powers of ik to obtain

$$\frac{P(\underline{k},\underline{q})}{\bar{P}(\underline{k})} = P_0 + (i\underline{k})\cdot(\underline{P}_1 - P_0\underline{M}_1) + (2!)^{-1}(i\underline{k})^2(\cdot)^2[\underline{\underline{P}}_2 - 2\underline{P}_1\underline{M}_1 - P_0(\underline{\underline{M}}_2 - 2\underline{M}_1\underline{M}_1)] \tag{2.12}$$

$$+ (3!)^{-1}(i\underline{k})^3(\cdot)^3[\underline{\underline{\underline{P}}}_3 - 3\underline{\underline{P}}_2\underline{M}_1 - 3\underline{P}_1(\underline{\underline{M}}_2 - 2\underline{M}_1\underline{M}_1) - P_0(\underline{\underline{\underline{M}}}_3 - 6\underline{M}_1\underline{\underline{M}}_2 + 6\underline{M}_1\underline{M}_1\underline{M}_1)] + \ldots \quad .$$

Multiply both sides of the latter by $\bar{P}(\underline{k})$ and invert the Fourier transform to derive an expression of the form (2.5), wherein the required coefficients are explicitly identified as

$$F_0 = P_0 \quad . \tag{2.13a}$$

$$\underset{\sim}{F}_1 = -(\underset{\sim}{P}_1 - P_0\underset{\sim}{M}_1) \ , \tag{2.13b}$$

$$\underset{\approx}{F}_2 = \frac{1}{2}\left[\underset{\approx}{P}_2 - 2\underset{\sim}{P}_1\underset{\sim}{M}_1 - P_0(\underset{\approx}{M}_2 - 2\underset{\sim}{M}_1\underset{\sim}{M}_1)\right] \ , \tag{2.13c}$$

$$\underset{\approx\approx}{F}_3 = -\frac{1}{6}\left[\underset{\approx\approx}{P}_3 - 3\underset{\approx}{P}_2\underset{\sim}{M}_1 - 3\underset{\sim}{P}_1(\underset{\approx}{M}_2 - 2\underset{\sim}{M}_1\underset{\sim}{M}_1) - P_0(\underset{\approx\approx}{M}_3 - 6\underset{\sim}{M}_1\underset{\approx}{M}_2 + 6\underset{\sim}{M}_1\underset{\sim}{M}_1\underset{\sim}{M}_1)\right] \ , \tag{2.13d}$$

etc. These polyadic coefficients -- regarded as cartesian tensors -- may, without loss of generality, be completely symmetrized with respect to interchange of any pairs of tensor indices, since they appear in (2.5) et seq. only in the role of fully contracted scalar products with the completely symmetric tensor $\nabla^j_{\sim Q}\overline{P}$.

Equation (2.5) represents a generalized moment-gradient expansion whose coefficients $\underset{\sim}{F}_j(\underset{\sim}{q})$ involve various combinations of local and total moments of the density function. Since partial differential equations and boundary conditions governing these moments are available,[2] and since these are solvable in appropriate circumstances to which Taylor dispersion schemes apply, the latter expansion can be employed to derive the Q-space conservation and constitutive equations governing transport of the average quantity $\overline{P}(\underset{\sim}{Q})$, as will be demonstrated in the next section.

A sufficient condition guaranteeing validity of the expansion (2.5) is that the Fourier transforms (2.6)-(2.7) exist (i.e. possess convergent integrals) and that the series representation (2.10) be valid (requiring $|S(\underset{\sim}{k})| < 1$). These necessitate, inter alia, that the probability density function P decay sufficiently fast as $|\underset{\sim}{Q}| \to \infty$.

When the latter condition obtains, the coefficients (2.13) may also be found successively [once an expansion of the form (2.5) is assumed] upon multiplying (2.5) by $\underset{\sim}{Q}^n$ (n=0,1,2,..., successively) and integrating over the infinite domain $\underset{\sim}{Q}_\infty$. Identical results are thereby obtained.

III. MACROTRANSPORT ANALYSIS

The detailed microtransport equation governing the conditional probability density $P(\underline{Q},\underline{q},t|\underline{q}')$ that the tracer locator point be situated at the position $(\underline{Q},\underline{q})$ at time t, given its initial introduction at t=0 into the flowing fluid at the position $(\underline{0},\underline{q}')$, consists[2] of the conservation equation

$$\partial P/\partial t + \nabla_{\underline{Q}}\cdot\underline{J} + \nabla_{\underline{q}}\cdot\underline{j} = \delta(\underline{Q})\delta\underline{q}-\underline{q}')\delta(t) \ , \tag{3.1}$$

together with the constitutive equations

$$\underline{J} = \underline{U}(\underline{q})P - \underline{\underline{D}}(\underline{q})\cdot\nabla_{\underline{Q}}P \tag{3.2}$$

and

$$\underline{j} = \underline{u}(\underline{q})P - e^{-E(\underline{q})}\underline{\underline{d}}(\underline{q})\cdot\nabla_{\underline{q}}(e^{E(\underline{q})}P) \tag{3.3}$$

for the global and local fluxes respectively.

Subject to the no-flux condition

$$\underline{n}\cdot\underline{j} = 0 \quad \text{on} \quad \partial\underline{q}_o \tag{3.4}$$

on the local-space boundary $\partial\underline{q}_o$, the global-space attenuation requirement

$$P \to 0 \quad \text{as} \quad |\underline{Q}| \to \infty \tag{3.5}$$

far from the initial source, and the pre-initial condition

$$P = 0 \quad \text{for} \quad t < 0 \ , \tag{3.6}$$

P is readily shown to satisfy the normalization condition

$$\int_{\underline{q}_o} d\underline{q} \int_{\underline{Q}_\infty} d\underline{Q} \; P = 1 \quad (t > 0) \ . \tag{3.7}$$

Define[2] the respective local and total moments of P as

$$\underline{P}_m(\underline{q},t|\underline{q}') = \int_{\underline{Q}_\infty} d\underline{Q} \; \underline{Q}^m \; P \ , \tag{3.8}$$

$$\underline{M}_m(t|\underline{q}') = \int_{\underline{q}_o} d\underline{q} \; \underline{P}_m \ , \tag{3.9}$$

(m=0,1,2,...). Further, denote by $\bar{P}$ the 'average' value of P over the local space, namely

$$\bar{P}(\underline{Q},t|\underline{q}') = \int_{\underline{q}_o} d\underline{q} \; P(\underline{Q},\underline{q},t|\underline{q}') \ . \tag{3.10}$$

The macrotransport counterpart, governing $\bar{P}$, of the microtransport equations (3.1)-(3.6), governing P, represents a completely global-space version of the latter equations (at least in the asymptotic limit of long times), from which all dependence upon the internal independent variables $\underline{q}$ (including 'memory' of the initial position $\underline{q}'$) has been eliminated. Such a global description can be derived via a number of alternative schemes, including a Lagrangian moment method,[1,2] a projection-operator technique,[11] and a multiple time scale analysis.[12] Here, we shall develop yet another scheme, one deriving from the existence of the moment-gradient expansion

(2.5). The utility of our technique resides in the fact that it provides the macrotransport equation directly, eliminating the need for additional definitions of mean velocity and dispersivity based upon the asymptotic linear growth of the total moments in time. At the same time, it renders explicit the economy of conceptual and algebraic detail heretofore only implicit in the original method of moments.[1,2]

The approach is as follows: Inasmuch as the conditional probability density $P(\underline{Q},\underline{q},t|\underline{q}')$ satisfies the necessary stipulations outlined in section 2 at any instant $t > 0$, this density may be expanded in the form (2.5) -- with coefficients $\underline{F}_n = \underline{F}_n(\underline{q},t|\underline{q}')$ now functionally dependent upon the indicated arguments, and given explicitly by (2.13) (with the moments therein now also dependent upon the additional independent variables t and $\underline{q}'$). Explicitly,

$$P = F_0\bar{P} + \underline{F}_1\cdot\nabla_{\underline{Q}}\bar{P} + \underline{\underline{F}}_2(\cdot)^2\nabla_{\underline{Q}}\nabla_{\underline{Q}}\bar{P} + \ldots \ . \tag{3.11}$$

Application of $\nabla_{\underline{Q}}$ to both sides of the above further yields

$$\nabla_{\underline{Q}}P = F_0\nabla_{\underline{Q}}\bar{P} + \underline{F}_1\cdot\nabla_{\underline{Q}}\nabla_{\underline{Q}}\bar{P} + \underline{\underline{F}}_2(\cdot)^2\nabla_{\underline{Q}}\nabla_{\underline{Q}}\nabla_{\underline{Q}}\bar{P} + \ldots \ . \tag{3.12}$$

Integrate (3.1) over the local domain $\underline{q}_o$ to obtain the macrotransport conservation equation

$$\partial\bar{P}/\partial t + \nabla_{\underline{Q}}\cdot\bar{\underline{J}} = \delta(\underline{Q})\delta(t) \ , \tag{3.13}$$

in which use was made of the local-space divergence theorem together with the

boundary condition (3.4). Appearing above is the mean or total flux

$$\bar{\underline{J}} \overset{\text{def.}}{=} \int_{\underline{q}_o} d\underline{q}\ \underline{J} = \int_{\underline{q}_o} d\underline{q}\ [\underline{U}(\underline{q})P - \underline{\underline{D}}(\underline{q})\cdot\nabla_Q P] \ . \tag{3.14}$$

In order that (3.13) adopt a functional macrotransport form, we must express $\bar{\underline{J}}$ as an explicit functional of the global density $\bar{P}$. This step can readily be achieved by use of the moment-gradient expansion (3.11). Substitute the latter along with (3.12) into the RHS of (3.14), and collect together terms of equal order in the respective gradients of $\bar{P}$ to obtain

$$\bar{\underline{J}} = \bar{\underline{U}}(t|\underline{q}')\bar{P} - \bar{\underline{\underline{D}}}(t|\underline{q}')\cdot\nabla_Q\bar{P} + \bar{\underline{\underline{\underline{E}}}}(t|\underline{q}')(\cdot)^2\nabla_Q\nabla_Q\bar{P} + \ \ldots \ , \tag{3.15}$$

where the time-dependent transport coefficients governing the global-space transport of $\bar{P}$ are identified as

$$\bar{\underline{U}}(t|\underline{q}') = \int_{\underline{q}_o} d\underline{q}\ \underline{U}(\underline{q})F_0(\underline{q},t|\underline{q}') \ , \tag{3.16}$$

$$\bar{\underline{\underline{D}}}(t|\underline{q}') = -\text{sym}\int_{\underline{q}_o} d\underline{q}\ [\underline{U}(\underline{q})\underline{F}_1(\underline{q},t|\underline{q}') - \underline{\underline{D}}(\underline{q})F_0(\underline{q},t|\underline{q}')] \ , \tag{3.17}$$

$$\bar{\underline{\underline{\underline{E}}}}(t|\underline{q}') = \text{sym}\int_{\underline{q}_o} d\underline{q}\ [\underline{U}(\underline{q})\underline{\underline{F}}_2(\underline{q},t|\underline{q}') - \underline{\underline{D}}(\underline{q})\underline{F}_1(\underline{q},t|\underline{q}')] \ , \tag{3.18}$$

etc. The operation designated as "sym" denotes symmetrization with respect to all tensorial indices -- a procedure that entails no loss of generality for reasons outlined earlier.

The conservation equation (3.13), together with constitutive equation (3.15) and phenomenological coefficients (3.16) *et seq.*, represents the *exact* global-space macrotransport equation, valid for all time. The requisite

phenomenological coefficients (3.16)-(3.18), etc. can be obtained by solving the system[2] of equations governing the moments (3.8) and (3.9). Circumstances requiring knowledge of only the first few coefficients of (3.15) obviously demand computation of only the first few moments of P. Furthermore, for sufficiently long times, the global-space transport coefficients (3.6) et seq. all tend (exponentially rapidly) to time-independent values that are also independent of the initial position $\underline{q}'$ -- facts that will be demonstrated in section 4. In that asymptotic limit the macrotransport description is then fully independent of the internal degrees of freedom $\underline{q}$ and $\underline{q}'$.

Only the first two terms of (3.15) are normally retained at the 'Taylor dispersion' level of description, and then only in the $t \to \infty$ limit. Here, however, the third-rank tensor coefficient $\bar{E}_{ijk}$ in (3.15) will also be calculated (albeit only in the long-time limit) to illustrate the computational scheme, as well as to establish the relative order-of-magnitude correction to the classical Taylor dispersion result occasioned by the existence of this third-order contribution. Fourth- and higher-order terms can similarly be calculated if desired.

Appearing in (3.16) et seq. are the functions $\underline{F}_n$ identified explicitly in (2.13). Equations governing the local moments $\underline{P}_m$, knowledge of which is required to calculate the $\underline{F}_n$, are available[2] for all orders m. For our purposes, however, we only require those for m=0,1 and 2. Explicitly, these obey the following equations:

$$m=0: \qquad \partial P_0/\partial t + \nabla_{\underline{q}} \cdot \underline{j}_0 = \delta(\underline{q}-\underline{q}')\delta(t) \ , \tag{3.19a}$$

$$dM_0/dt = \delta(t) \ ; \tag{3.19b}$$

$$m=1: \qquad \partial \underline{P}_1/\partial t + \nabla_{\underline{q}} \cdot \underline{\underline{j}}_1 = \underline{U}\, P_0 \ , \tag{3.20a}$$

$$d\underline{M}_1/dt = \int_{\underline{q}_o} d\underline{q}\ \underline{U} P_0 \ ; \tag{3.20b}$$

$$m=2: \qquad \partial \underline{\underline{P}}_2/\partial t + \nabla_{\underline{q}} \cdot \underline{\underline{\underline{j}}}_2 = 2\ \mathrm{sym}(\underline{\underline{D}} P_0 + \underline{\underline{U}} \underline{P}_1) \ , \tag{3.21a}$$

$$d\underline{\underline{M}}_2/dt = 2\ \mathrm{sym} \int_{\underline{q}_o} d\underline{q}\ (\underline{\underline{D}} P_0 + \underline{\underline{U}} \underline{P}_1) \ . \tag{3.21b}$$

The local flux densities $\underline{j}_m$ appearing above are defined as

$$\underline{j}_m = \underline{\underline{u}} \underline{P}_m - e^{-E} \underline{\underline{d}} \cdot \nabla_{\underline{q}} (e^{E} P_m) \tag{3.22}$$

for m=0,1,2,... . Each of the local moment equations (3.19)-(3.21) is to be solved subject to the no-flux condition

$$\underline{n} \cdot \underline{j}_m = \underline{0} \quad \text{on} \quad \partial \underline{q}_o \ , \tag{3.23}$$

and the trivial pre-initial condition $\underline{P}_m = \underline{0}$ for $t < 0$, deriving from (3.6).

Knowledge of these $\underline{P}_m$ in conjunction with (2.13) and (3.16) permits the global-space cartesian tensor phenomenological coefficients $\bar{U}_i$, $\bar{D}_{ij}$, $\bar{E}_{ijk}$, etc. to be calculated for all times. Asymptotic forms of these transport coefficients, free of dependence upon the initial local-space position $\underline{q}'$, are established in the next section.

IV. ASYMPTOTIC ANALYSIS

For times $t > 0$, Eq. (3.19b) possesses the solution

$$M_0 = 1 \ . \tag{4.1}$$

As $t \to \infty$, the zeroth local moment $P_0(\underline{q},t|\underline{q}')$ exponentially rapidly approaches a t- and $\underline{q}'$-independent limit,[2] $P_0^\infty(\underline{q})$, satisfying

$$\nabla_{\underline{q}} \cdot \underline{j}_0^\infty = 0 \ , \tag{4.2a}$$

$$\underline{n} \cdot \underline{j}_0^\infty = 0 \quad \text{on } \partial q_o \ , \tag{4.2b}$$

and, in consequence of (4.1), the normalization condition

$$\int_{q_o} d\underline{q} \ P_0^\infty(\underline{q}) = 1 \ . \tag{4.2c}$$

In (4.2), $\underline{j}_0^\infty$ is defined as in (3.22), but with $P_0^\infty(\underline{q})$ substituted for P_m. Using (2.13a) and (3.16), the long-time limit of the mean velocity vector (3.16) can readily be identified as

$$\underline{\bar{U}}^* = \lim_{t\to\infty} \underline{\bar{U}}(t|\underline{q}') = \int_{q_o} d\underline{q} \ \underline{U}(\underline{q}) \ P_0^\infty(\underline{q}) \ , \tag{4.3}$$

in agreement with previous calculations.[2] (Here, and subsequently, an asterisk generically denotes the long-time limit of the phenomenological macrotransport coefficient to which it is affixed.)

Calculation of the long-time limit of the dispersivity dyadic (3.17)

requires knowledge of the time-asymptotic form of the vector $\underline{F}_1$ defined in (2.13b). Subject to a posteriori verification, assume the asymptotic form of $\underline{P}_1$ to be

$$\underline{P}_1^{\infty}(\underline{q},t) = P_0^{\infty}(\underline{q})[\underline{M}_1^{\infty}(t) + \underline{B}(\underline{q})] \ , \tag{4.4}$$

wherein $\underline{M}_1^{\infty}$ satisfies [cf. (3.20b)]

$$d\underline{M}_1^{\infty}/dt = \int_{\underline{q}_0} d\underline{q}\ \underline{U}\ P_0^{\infty} = \overline{\underline{U}}^{*} \ , \text{ say.} \tag{4.5}$$

The test form (4.4) is motivated by (2.13b) together with the anticipated asymptotic time independence of $\underline{F}_1$. Substitute (4.4) and (4.5) into (3.20) to obtain the equation

$$\underline{\nabla}_q\cdot[\underline{u}\ P_0^{\infty}\underline{B} - e^{-E}\underline{\underline{d}}\cdot\underline{\nabla}_q(e^{E}\ P_0^{\infty}\underline{B})] = P_0^{\infty}(\underline{U} - \overline{\underline{U}}^{*}) \tag{4.6a}$$

governing the time-independent $\underline{B}(\underline{q})$ vector field appearing in (4.4). This is to be solved for $\underline{B}$ subject to the boundary condition [derivable from (3.23)]

$$P_0^{\infty}\underline{n}\cdot\underline{\underline{d}}\cdot\underline{\nabla}_q\underline{B} = \underline{0} \quad \text{on } \partial\underline{q}_o \ , \tag{4.6b}$$

and the normalization requirement

$$\int_{\underline{q}_o} d\underline{q}\ P_0^{\infty}(\underline{q})\underline{B}(\underline{q}) = \underline{0} \ , \tag{4.6c}$$

obtained by integration of (4.4) over $\underline{q}_o$. [Note that in consequence of (4.6c), $\underline{B}(\underline{q})$ is uniquely determined. This fact contrasts with the original treatment,[2] where $\underline{B}$ was identified only to within an arbitrary additive constant; this minor change results from a slight modification in the definition of $\underline{B}$ herein adopted [cf. (4.4).] Inasmuch as the solution of (4.6) exists and is unique, the assumed asymptotic form (4.4) is confirmed *a posteriori*. As such, the function $\underline{F}_1$ tends to the time-independent limit

$$\underline{F}_1^{\infty}(\underline{q}) = -P_0^{\infty}(\underline{q})\underline{E}(\underline{q}) , \tag{4.7}$$

whence the long-time dispersivity dyadic adopts the form

$$\bar{\underline{\underline{D}}}^{*} = \text{sym} \int_{\underline{q}_o} d\underline{q} \, [\underline{\underline{D}}(\underline{q})P_0^{\infty}(\underline{q}) + \underline{U}(\underline{q})\underline{B}(\underline{q})P_0^{\infty}(\underline{q})] . \tag{4.8}$$

Finally, calculation of $\bar{\underline{\underline{E}}}$ from (3.18) for long times requires determination of the long-time limit of $\underline{\underline{F}}_2$, and hence of $\underline{\underline{P}}_2$. Guided by the form (2.13c), and anticipating that $\underline{\underline{F}}_2$ eventually becomes time-independent, we assume the following asymptotic trial function form:

$$\underline{\underline{P}}_2^{\infty}(\underline{q},t) = \text{sym}\{P_0^{\infty}[\underline{\underline{M}}_2^{\infty} + 2\underline{B}\underline{M}_1^{\infty} + \underline{\underline{H}}(\underline{q})]\} , \tag{4.9}$$

with

$$d\underline{\underline{M}}_2^{\infty}/dt = 2 \, \text{sym} \int_{\underline{q}_o} d\underline{q} \, (\underline{\underline{D}}P_0^{\infty} + \underline{U}\underline{P}_1^{\infty}) = 2 \, \text{sym}(\bar{\underline{\underline{D}}}^{*} + \bar{\underline{U}}^{*}\underline{M}_1^{\infty}) , \tag{4.10}$$

from (3.21b). Substitute (4.9) and (4.10) into (3.21a) to obtain

$$\nabla_{\underline{q}} \cdot [\underline{u}P_0^{\infty}\underline{\underline{H}} - e^{-E}\underline{\underline{d}} \cdot \nabla_{\underline{q}}(e^{E}P_0^{\infty}\underline{\underline{H}})] = 2P_0^{\infty}(\underline{\underline{D}} - \bar{\underline{\underline{D}}}^{*}) + 2P_0^{\infty}\underline{B}(\underline{U} - \bar{\underline{U}}^{*}) \tag{4.11a}$$

as the equation governing the dyadic $\underset{\approx}{H}(\underset{-}{q})$ field. Here, the symmetrization operator has been deleted from both sides for clarity. Equation (4.11a) is to be solved so as to jointly satisfy the boundary condition

$$P_0^{\infty}\underset{-}{n}\cdot\underset{\approx}{d}\cdot\nabla_{\underset{-}{q}}\underset{\approx}{H} = \underset{\approx}{0} \quad \text{on } \partial\underset{-}{q}_o \tag{4.11b}$$

and normalization requirement

$$\int_{\underset{-}{q}_o} d\underset{-}{q}\; P_0^{\infty}\underset{\approx}{H} = \underset{\approx}{0} \; . \tag{4.11c}$$

That a solution $\underset{\approx}{H}(\underset{-}{q})$ of Eqs. (4.11) exists provides a posteriori confirmation of the assumed form (4.9). Equation (2.13c) then shows that $\underset{\approx}{F}_2$ attains the asymptotic limiting form

$$\underset{\approx}{F}_2^{\infty}(\underset{-}{q}) = \frac{1}{2}\, P_0^{\infty}(\underset{-}{q})\underset{\approx}{H}(\underset{-}{q}) \; . \tag{4.12}$$

In turn, substitution of the latter and (4.7) into (3.18) yields

$$\overline{\underset{\approx}{E}}^{*} = \text{sym} \int_{\underset{-}{q}_o} d\underset{-}{q}\; (\underset{\approx}{D}\underset{\approx}{B}P_0^{\infty} + \frac{1}{2}\,\underset{\approx}{U}\underset{\approx}{H}P_0^{\infty}) \tag{4.13}$$

in the long-time limit.

This process can obviously be extended to obtain comparable (long-time) formulas for all higher-order phenomenological macrotransport coefficients. In the absence of any compelling current need for this information, their calculation will not be undertaken here.

To recapitulate, the long-time macrotransport equation governing $\overline{P}$ is

[cf. (3.13) and (3.15)]

$$\partial \bar{P}/\partial t + \bar{\underline{U}}^* \cdot \nabla_{\underline{Q}} \bar{P} - \bar{\underline{\underline{D}}}^* (\cdot)^2 \nabla_{\underline{Q}} \nabla_{\underline{Q}} \bar{P} + \bar{\underline{\underline{\underline{E}}}}^* (\cdot)^3 \nabla_{\underline{Q}} \nabla_{\underline{Q}} \nabla_{\underline{Q}} \bar{P} + \ldots = 0 , \qquad (4.14a)$$

with

$$\bar{\underline{U}}^* = \int_{\underline{q}_o} d\underline{q}\, P_0^\infty \underline{U} , \qquad (4.14b)$$

$$\bar{\underline{\underline{D}}}^* = \text{sym} \int_{\underline{q}_o} d\underline{q}\, P_0^\infty (\underline{U}\underline{B} + \underline{\underline{D}}) , \qquad (4.14c)$$

$$\bar{\underline{\underline{\underline{E}}}}^* = \text{sym} \int_{\underline{q}_o} d\underline{q}\, P_0^\infty (\tfrac{1}{2}\, \underline{U}\underline{\underline{H}} + \underline{\underline{D}}\underline{B}) , \qquad (4.14d)$$

etc., wherein P_0^∞, $\underline{B}$ and $\underline{\underline{H}}$ are the respective solutions of Eqs. (4.2), (4.6) and (4.11). Although the actual time dependence of the phenomenological coefficients (together with memory effects) has not been explicitly examined here, previous studies[1,11,14] have shown their approach to the constant time-independent values displayed above to be exponentially rapid, with a relaxation time of the order of the local-space equilibration time, ℓ^2/d, where ℓ and d are respectively a characteristic local-space length and molecular diffusivity.

V. EXAMPLE

We consider here the problem of Taylor dispersion occurring during generalized 'Poiseuille' flow through an (n-1) dimensional hypercircular cylinder[18] of radius r = a, where

$$r^2 = x_1^2 + x_2^2 + \ldots + x_{n-1}^2 , \qquad (|r| \leq a)$$

is the hypercircular cylindrical polar distance from the cylinder axis. By addressing this multidimensional problem we are able to treat simultaneously the two main cases n = 2 and 3 of physical interest, corresponding respectively to transport between flat parallel plates ($-a \leq r \leq a$; $r = x_1$) and within a circular cylinder ($0 \leq r \leq a$; $r^2 = x_1^2 + x_2^2$). The Poiseuille velocity profile for flow within the hypercylinder is[18] $\underset{\sim}{U} = \underset{\sim}{i}_z U(r)$, with

$$U(r) = \frac{1}{2}(n+1)\bar{V}\left[1 - \left(\frac{r}{a}\right)^2\right] , \qquad (5.1)$$

in which $\bar{V}$ is the area-averaged velocity over the (n-1)-dimensional cross-sectional space $|r| \leq a$, and $z = x_n$ is the cartesian coordinate along the hypercylinder axis; $\underset{\sim}{i}_z$ is a unit vector in the z direction. For our purposes the unbounded global coordinate $\underset{\sim}{Q}$ is identified with the single variable z ($-\infty < z < \infty$), whereas the bounded local coordinates $\underset{\sim}{q}$ are identified as the set of n-1 cartesian coordinates $(x_1, x_2, \ldots, x_{n-1})$.

Denote by $\underset{\sim}{\nabla}_{n-1} = (\partial/\partial x_1, \partial/\partial x_2, \ldots, \partial/\partial x_{n-1}) = \underset{\sim}{\nabla}_q$ the (n-1)-dimensional gradient operator in the cross-sectional subspace of the hypercylinder. For $t > 0$ the microtransport equation is thus given in hypercircular cylindrical coordinates by the convective-diffusion equation

$$\frac{\partial P}{\partial t} + U(r)\frac{\partial P}{\partial z} = D\left[\nabla^2_{n-1} + \frac{\partial^2}{\partial z^2}\right]P \ , \tag{5.2}$$

in which[18]

$$\nabla^2_{n-1} = \frac{1}{r^{n-2}}\ \frac{\partial}{\partial r}\left[r^{n-2}\ \frac{\partial}{\partial r}\right] .$$

We have eliminated from the latter Laplacian the derivatives of the azimuthal angles[18] $\phi_1,\phi_2,\ldots,\phi_{n-1}$ $(-\pi \le \phi_j \le \pi)$ in the cross-sectional subspace that would otherwise have appeared. In doing so we are generalizing the arguments of Brenner and Gaydos[19] for the case n=3 by eliminating a priori these 'dead' azimuthal degrees of freedom from the complete probability density $P(r,\phi_1,\phi_2,\ldots,\phi_{n-2},z)$, replacing the latter by P(r,z) -- modulo a multiplicative factor of $\pi^{(n-1)/2}/\Gamma\left[\frac{1}{2}(n+1)\right]$ [cf. (5.4b)], where Γ is the gamma function.

The first step of the Taylor dispersion calculation requires that we solve equations (4.2), which in present circumstances adopt the forms

$$\nabla^2_{n-1}P^{\infty}_0 = 0 \ , \tag{5.3a}$$

$$-D\ \partial P^{\infty}_0/\partial r = 0 \quad \text{at } r=a \ , \tag{5.3b}$$

$$\int_A dA\ P^{\infty}_0 = 1 \ , \tag{5.3c}$$

wherein D is the (constant) molecular diffusivity and $A = \underset{\sim}{q}_o$ denotes the cross-sectional domain of the hypercylinder. The solution of the latter equations is the constant

$$P_0^{\infty} = W^{-1} , \tag{5.4a}$$

with W the normalization constant

$$W = \int_A dA = \pi^{(n-1)/2} a^{n-1} / \Gamma\left[\tfrac{1}{2}(n+1)\right] . \tag{5.4b}$$

From (5.1) one can now immediately calculate the mean velocity (4.14b) of the tracer to be

$$\bar{\underline{U}}^* = \underline{i}_z \bar{U}^* , \tag{5.5a}$$

in which

$$\bar{U}^* = \int_A dA \, W^{-1} U(r) = \bar{V} , \tag{5.5b}$$

in accord with expectations; that is, in present circumstances the tracer necessarily possesses the same mean velocity $\bar{V}$ as the fluid.

Calculation of the dispersivity (4.14c) requires solving Eqs. (4.6) for $\underline{B}(r, \phi_1, \phi_2, \ldots, \phi_{n-2}, z)$. Subject to <u>a posteriori</u> verification, assume the solution to be of the form $\underline{B} = \underline{i}_z B(r)$ (with no azimuthal dependence). This yields the following set of equations governing the scalar B field:

$$-\frac{D}{r^{n-2}} \frac{d}{dr}\left[r^{n-2} \frac{dB}{dr}\right] = \bar{V}\left[\frac{n-1}{2} - \frac{n+1}{2}\left(\frac{r}{a}\right)^2\right] , \tag{5.6a}$$

$$dB/dr = 0 \quad \text{at } r=a \ , \tag{5.6b}$$

$$\int_0^a dr\, r^{n-2} B = 0 \ . \tag{5.6c}$$

These are readily solved to obtain

$$B = \frac{\bar{V} a^2}{8D} \left[\left(\frac{r}{a}\right)^4 - 2\left(\frac{r}{a}\right)^2 + \frac{(n-1)(n+5)}{(n+1)(n+3)} \right] . \tag{5.7}$$

That a unique solution exists serves to confirm the assumed trial solution for $\underset{\sim}{B}$.

Substitution of (5.7) into (4.14c) yields, upon evaluation of the requisite integrals appropriate to the hypercylinder geometry,

$$\underset{\approx}{\bar{D}}^* = \underset{\sim}{i}_z \underset{\sim}{i}_z \bar{D}^* \ , \tag{5.8a}$$

in which

$$\bar{D}^* = D + \frac{\bar{V}^2 a^2}{D} \frac{2(n-1)}{(n+1)(n+3)(n+5)} \ . \tag{5.8b}$$

This expression for the dispersivity reproduces the well-known Taylor-Aris dispersion results for flat plates[20] (n=2) and circular cylinders[5] (n=3).

Calculation of the third-order phenomenological coefficient $\underset{\approx\approx}{\bar{E}}^*$ requires the solution of Eqs. (4.11) for the dyadic field $\underset{\approx}{H}$. The trial solution $\underset{\approx}{H} = \underset{\sim}{i}_z \underset{\sim}{i}_z H(r)$ defining the scalar field H then yields the following scalar counterparts of this system of equations:

$$\frac{1}{\xi^{n-2}}\frac{d}{d\xi}\left(\xi^{n-2}\frac{dH}{d\xi}\right) = -\frac{\bar{V}^2a^4}{8D^2}\left[(n+1)\xi^6 - (3n+1)\xi^4 + \frac{(n-1)(3n+11)}{(n+3)}\xi^2 - \frac{(n-1)(n^3+9n^2+15n-57)}{(n+1)(n+3)(n+5)}\right], \tag{5.9a}$$

$$dH/d\xi = 0 \quad \text{at } \xi = 1, \tag{5.9b}$$

$$\int_0^1 d\xi\, \xi^{n-2}H(\xi) = 0, \tag{5.9c}$$

where $\xi = r/a$. This trio of equations possesses the (unique) solution

$$H = \frac{\bar{V}^2a^4}{16D^2}\left[\frac{n+1}{4(n+5)}\xi^8 - \frac{3n+1}{3(n+3)}\xi^6 + \frac{(n-1)(3n+11)}{2(n+3)(n+1)}\xi^4 - \frac{n^3+9n^2+15n-57}{(n+1)(n+3)(n+5)}\xi^2 + C_n\right], \tag{5.10a}$$

with the integration constant C_n defined as

$$C_n = (n-1)\left[\frac{n^3+9n^2+15n-57}{(n+1)^2(n+3)(n+5)} - \frac{(n-1)(3n+11)}{2(n+3)^2(n+1)} + \frac{3n+1}{3(n+3)(n+5)} - \frac{n+1}{4(n+5)(n+7)}\right]. \tag{5.10b}$$

Substitute (5.10) into (4.14d). Upon performing the requisite integration, and after considerable reduction, we obtain the expression

$$\underset{\approx}{\bar{E}}^* = \underset{-z-z-z}{i\,i\,i}\,\bar{E}^*, \tag{5.11a}$$

in which

$$\bar{E}^* = \frac{\bar{V}^3 a^4}{D^2}\left[\frac{4(n-1)(5n^2+8n-45)}{(n+1)^2(n+3)^2(n+5)(n+7)(n+9)}\right] . \qquad (5.11b)$$

This formula points up a change of algebraic sign between the parallel plate and circular cylinder cases. Thus, upon denoting the bracketed numerical factor in (5.11b) by $\alpha(n)$, we obtain $\alpha(2) = -4/17325$ for parallel plate and $\alpha(3) = 1/2880$ for circular cylindrical geometries. These values accord with the respective results of Refs. 11 and 14.

Our analysis shows that the long-time macrotransport equation governing Taylor dispersion during Poiseuille flow through a hypercircular cylinder is

$$\frac{\partial \bar{P}}{\partial t} + \bar{U}^* \frac{\partial \bar{P}}{\partial z} - \bar{D}^* \frac{\partial^2 \bar{P}}{\partial z^2} + \bar{E}^* \frac{\partial^3 \bar{P}}{\partial z^3} + \ldots = 0 , \qquad (5.12)$$

with scalar coefficients $\bar{U}^*$, $\bar{D}^*$ and $\bar{E}^*$ given respectively by Eqs. (5.5b), (5.8b) and (5.11b). Scaling the z coordinate with a 'macroscopic' length L shows the ratio of third- to second-derivative terms in (5.12) to be of order Pe a/L, with Pe = $\bar{V}a/D$ the Peclet number based upon the duct radius a. Thus, third- and higher-order derivatives in (5.12) may be neglected in the limit $a/L \to 0$, provided that Pe = O(1) with respect to the latter parameter.

VI. DISCUSSION

As an alternative to the moment-gradient expansion, the Lagrangian method of moments can equally well furnish the phenomenological transport coefficients (4.14b,c,d). The long-time macrotransport coefficients $\underline{\bar{U}}^*$ and $\underline{\underline{\bar{D}}}^*$ are defined in this moment scheme[2] as

$$\underline{\bar{U}}^* = \lim_{t\to\infty} \frac{d\underline{M}_1}{dt} , \tag{6.1}$$

$$\underline{\underline{\bar{D}}}^* = \frac{1}{2} \lim_{t\to\infty} \frac{d}{dt}(\underline{\underline{M}}_2 - \underline{M}_1\underline{M}_1) , \tag{6.2}$$

respectively representing coefficients for linear growth in time of the first total moment and the second central total moment. The equivalent momental definition for $\underline{\underline{\underline{\bar{E}}}}^*$, though not previously given, is readily derived as

$$\underline{\underline{\underline{\bar{E}}}}^* = \frac{1}{6} \lim_{t\to\infty} \frac{d}{dt} \text{sym}(\underline{\underline{\underline{M}}}_3 - 3\underline{M}_1\underline{\underline{M}}_2 + 2\underline{M}_1\underline{M}_1\underline{M}_1) . \tag{6.3}$$

This triadic coefficient represents the temporal linear long-time growth term of the third central total moment. That $\underline{\underline{\underline{\bar{E}}}}^*$ does not vanish for long times, but rather tends to a constant time-independent value, clearly demonstrates that the long-time mean probability density $\bar{P}$ [e.g. $\bar{P}(z,t)$ in the hypercylinder case] is not strictly Gaussian. Gaussian behavior would demand vanishing of the third central moment; in contrast, we have shown here that this moment does not vanish, but rather grows linearly in time -- at least for sufficiently long times.

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CHAPTER III:

TRANSPORT MECHANICS OF FLEXIBLE CHAINS AND CLUSTERS COMPOSED OF RIGID BROWNIAN PARTICLES IN QUIESCENT VISCOUS FLUIDS

ABSTRACT

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. In consequence, 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 pre-averaging hypotheses are invoked to effect the averaging of the input conformation-specific hydrodynamic mobility data. Rather, the calculation is effected rigorously within the usual (quasistatic) context of configuration-specific Stokes-Einstein equations.

Explicit numerical calculations serving to illustrate the general scheme are performed only for the simplest case, namely dumbbells 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 nonequilibrium sedimentation-diffusion properties of monodisperse polymer molecules in solutions or suspensions.

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), the latter 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 nonequilibrium 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 numbers 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

Burger-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, 1982a, 1982b) 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 (1974a,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 centers 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 1987) of the cluster as a whole must necessarily show themselves to 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, pre-averaged, rigid counterpart. To rigorously analyze secular effects arising from instantaneous deviations from the average, generalized Taylor dispersion theory (Brenner 1982a, Brenner & Pagitsas 1987) can be employed. Indeed, this paradigm has already been successfully used to investigate comparable sedimentation-dispersion phenomena in systems of rigid nonspherical particles (Brenner 1979, 1981). Upon incorporation of "coupling" effects (Brenner 1982b), 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) center 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 dumbbell.

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 1982b) will be developed in the context of current needs, with the aid of the so-called moment-gradient expansion technique (Nadim et al. 1986). Section 3 furnishes a general formulation of the flexible chain/cluster transport equation describing sedimentation within an otherwise quiescent fluid. Transformations detailed in Section 4 permit reduction of this scheme to a format identical with the canonical form (Brenner 1980, 1982a,b) of generalized Taylor dispersion theory. Section 5 derives explicit generic formulas for the long-time mean sedimentation velocity vector $\overline{\underset{\sim}{U}}^{*}$ and dispersivity dyadic $\overline{\underset{\approx}{D}}^{*}$ 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 and the internal potential-energy function. Sections 6 and 7 provide detailed numerical results for two specific examples, each involving so-called tethered dumbbells. Finally, Section 8 furnishes, inter alia, proof of the invariance of the values obtained for $\overline{\underset{\sim}{U}}^{*}$ and $\overline{\underset{\approx}{D}}^{*}$ to the explicit choice of chain-fixed locator point.

2. TENSORIAL FORMULATION OF GENERALIZED TAYLOR DISPERSION THEORY INCORPORATING COUPLING

Generalized Taylor dispersion theory techniques (Brenner 1980, 1982a), incorporating coupling effects (Brenner 1982b), are reviewed in this section. Particular emphasis is paid to the tensorial formulation of the governing equations and boundary conditions. The latter endeavor, representing a continuation of the prior analysis of Haber & Brenner (1986), is meant to render the existing symbolic forms of these equations (Brenner 1980, 1982a,b) operational. Explicitly, the scheme provides literal forms for the required conservation and constitutive equations in a general tensorial representation of the multidimensional transport process in an arbitrary (generally nonorthogonal) curvilinear coordinate system. This invariant tensorial formulation is particularly valuable when dealing with transport of flexible chains, since the latter possess a large number of internal degrees of freedom (Haber & Brenner 1986, Bird et al. 1977); moreover, such generalized coordinate formulations must often be employed (Bird et al. 1977) to describe the configurational (conformational) chain transport process. Although our analysis is eventually applicable to a broader class of transport mechanisms, we shall mainly be concerned with (and, hence, motivated by) the problem of the sedimentation, molecular diffusion and Taylor dispersion of isolated flexible chains in an otherwise quiescent fluid medium.

Consider a set of independent curvilinear coordinates ζ^I (I=1,2,...,N; with N the total number of degrees of freedom) required to completely specify the configuration of the flexible chain or cluster (i.e., the

physical-space positions and orientations of each of its constituent rigid particles). Define $\mathcal{F}$ to be the Rayleigh dissipation function (Rayleigh 1945, Brenner 1965, 1967), so that $2\mathcal{F}$ is the rate of dissipation of mechanical energy (per unit time per unit volume of configuration space) resulting from motion of the flexible chain through the otherwise quiescent fluid. At small Reynolds numbers the latter is a homogeneous quadratic function of the generalized velocities $\dot{\zeta}^I$, leading to the relation (Gans 1928, Brenner 1965)

$$2\mathcal{F} = g_{IJ}\dot{\zeta}^I\dot{\zeta}^J \tag{2.1}$$

(summation convention; I,J = 1,2,...,N), which may be regarded as the definition of the set of metrical coefficients g_{IJ}. It is clear that g_{IJ} may be taken to be symmetric in its two indices (Landau & Lifshitz 1980, §121) without loss of generality. Furthermore, since the dissipation function is always nonegative (Brenner 1965), we may conclude from (2.1) that g_{IJ} is a nonegative-definite form. Functionally, g_{IJ} will generally depend upon the coordinates ζ^I but not upon the corresponding velocities $\dot{\zeta}^I$; g_{IJ} will also be assumed not to depend explicitly upon the time t. Upon further assuming that the chain possesses a velocity-independent configuration-specific potential energy $\mathcal{V}(\zeta^1,\ldots,\zeta^N)$, then in the quasistatic low-Reynolds-number (i.e., inertialess) limit the Lagrangian equations of motion governing the chain motions are (Brenner 1965)

$$\frac{\partial\mathcal{F}}{\partial\dot{\zeta}^I} + \frac{\partial\mathcal{V}}{\partial\zeta^I} = 0 \quad , \tag{2.2}$$

representing an instantaneous balance between the respective hydrodynamic (dissipative) and conservative (nondissipative) forces.

Let g^{IJ} denote the inverse of g_{IJ}, defined such that

$$g^{IK}g_{KJ} = g_{JK}g^{KI} = \delta^I_J \quad , \tag{2.3}$$

with δ^I_J the Kroneker delta. Simultaneous solution of Eqs. (2.1) and (2.2) for $\dot{\zeta}^I$ (Brenner 1965) thereby yields

$$\dot{\zeta}^I = - g^{IJ}\partial\mathcal{V}/\partial\zeta^J \quad . \tag{2.4}$$

Derivation of an explicit transport equation for the flexible chain necessitates defining a metric space within which the transport process takes place. In turn, this necessitates an appropriate choice of metric tensor, serving to define the distance $|ds|$ between two neighboring points in the space. Such a tensor must be symmetric and positive definite, reflecting the positivity of $(ds)^2$. In circumstances for which the kinetic energy (i.e., inertia) of both chain and fluid are negligible, the most appropriate choice for the latter metric is g_{IJ} (Gans 1928, Brenner 1965, 1967, Haber & Brenner 1986), being based upon the dissipation function $\mathcal{F}$. Thus, we write

$$(ds)^2 = g_{IJ}d\zeta^I d\zeta^J \quad . \tag{2.5}$$

Comparison with (2.1) yields

$$(ds)^2 = 2\mathcal{F}(dt)^2 \quad , \tag{2.6}$$

which is indeed nonegative.[1] As such, the g_{IJ} represent the covariant components of the metric tensor, whereas the g^{IJ} are its corresponding contravariant components. As usual, denote by

$$g = \det|g_{IJ}| > 0 \tag{2.7}$$

the determinant of the metric tensor. The latter is a relative scalar of weight 2 (and not a true scalar, cf. Butkov 1968).

With the Riemannian space defined by (2.5), the invariant volume element in that space is given by (Synge & Schild 1949)

$$\sqrt{g}\, d\zeta^1 d\zeta^2 \ldots d\zeta^N \quad . \tag{2.8}$$

We shall denote by

$$P(\zeta^1,\ldots,\zeta^N,t|\zeta'^1,\ldots,\zeta'^N)\ \sqrt{g}\, d\zeta^1 \ldots d\zeta^N \tag{2.9a}$$

the conditional probability for finding the chain configuration within the infinitesimal 'volume' $\sqrt{g}d\zeta^1 d\zeta^2 \ldots d\zeta^N$ centered at the point $(\zeta^1,\ldots,\zeta^N)$ at time t, given that at time t=0 the chain was introduced into the fluid with configuration $(\zeta'^1,\ldots,\zeta'^N)$. The conditional probability density P will be chosen as to satisfy the normalization condition

$$\int P\sqrt{g}\, d\zeta^1 \ldots d\zeta^N = \begin{cases} 1 & \text{for } t>0 \\ 0 & \text{for } t<0 \end{cases} , \tag{2.9b}$$

where the integration extends over the entire domain spanned by the curvilinear coordinates ζ^I.

With J^I the contravariant components of the flux density vector $\underset{\sim}{J}$ of the probability density, the conservation equation for P takes the form (Brenner 1967)

$$\frac{\partial P}{\delta t} + \frac{1}{\sqrt{g}} \frac{\partial}{\partial \zeta^I} (\sqrt{g} J^I) = \frac{\delta(t)}{\sqrt{g}} \prod_{I=1}^{N} \delta(\zeta^I - \zeta'^I) \ . \tag{2.10}$$

The right-hand product of Dirac delta functions is a source term, representing introduction of the chain with its initial primed configuration into the fluid at t=0. The constitutive expression for the flux vector is assumed to consist of respective convective and diffusive contributions, and hence to be of the classical piggy-back/Fickian form (Brenner 1967)

$$J^I = \dot{\zeta}^I P - D^{IJ} \partial P/\partial \zeta^J \quad , \tag{2.11}$$

wherein $\partial P/\partial \zeta^I \equiv P,_I$ are the covariant components of the vector gradient of

P. The contravariant components D^{IJ} of the configuration-specific chain molecular diffusion tensor are assumed to be given by the generalized Stokes-Einstein relation (Brenner 1967)

$$D^{IJ} = kT\, g^{IJ} , \tag{2.12}$$

with k the Boltzmann constant and T the absolute temperature. Equation (2.12) derives from the fact that the conjugate metric g^{IJ} is identical to the Stokes mobility tensor, for -- as in (2.4) -- it serves as the phenomenological or material proportionality tensor linearly relating the generalized velocity vector $\dot{\zeta}^I$ to the generalized external force vector $-\partial \mathcal{V}/\partial \zeta^J$ acting on the chain.

In order to adapt existing Taylor dispersion techniques to the chain transport problem, we must identify which of the coordinates ζ^I are to be understood as <u>global</u> and which as <u>local</u> (Brenner 1980, 1982a,b). The domain of the global (external, slow) coordinates is infinite in extent, whereas the domain of the local (internal, fast) coordinates is typically (but not necessarily) bounded, closed, cyclic, or otherwise of finite extent. More fundamentally, equilibration of the probability density is assumed to occur within the "local" space on a relatively fast time scale, one considerably shorter than times of 'macroscopic' physical interest, while no such equilibrium state obtains within the "global" space on the latter time scale. Generalized Taylor dispersion theory provides a convenient framework for deriving macrotransport equations (Brenner & Pagitsas 1987) governing the purely global-space transport process, from which has been eliminated all dependence upon the local degrees of freedom. Such a description, which represents a much more wieldy account of the global transport process than its detailed N-dimensional microtransport

counterpart, will be valid for times longer than the local-space equilibration time.

Of the N coordinates ζ^I, let the first three be the Cartesian coordinates of an arbitrarily-selected, three-dimensional, physical-space 'chain locator point' within, or affixed to, the flexible chain. Rename these coordinates as Q^i (i = 1, 2, 3); explicitly,

$$Q^1 = \zeta^1 \ , \ Q^2 = \zeta^2 \ , \ Q^3 = \zeta^3 \ . \tag{2.13}$$

The Q^i, which span the unbounded range $(-\infty, \infty)$, constitute the global variables in the sense (and notation) of generalized Taylor dispersion theory. The remaining N-3 curvilinear coordinates are then designated as local variables q^α (α = 4, 5,..., N), and renamed explicitly as

$$q^4 = \zeta^4 \ , \ q^5 = \zeta^5 \ , \ldots , \ q^N = \zeta^N \ . \tag{2.14}$$

All second-rank tensors, either covariant or contravariant, may be correspondingly partitioned into the generic matrix form

$$[a(IJ)] = \begin{bmatrix} a(ij) & a(i\beta) \\ a(\alpha j) & a(\alpha\beta) \end{bmatrix} \ , \tag{2.15}$$

wherein (and throughout this section) the majuscule and miniscule Roman and Greek indices respectively span the following ranges:

$$\begin{aligned} &I, J, K, \ldots = 1, 2, \ldots, N \ ; \\ &i, j, k, \ldots = 1, 2, 3 \ ; \\ &\alpha, \beta, \gamma, \ldots = 4, 5, \ldots, N \ . \end{aligned} \tag{2.16}$$

[In more general circumstances, where chain transport occurs within a partially-bounded physical space domain -- e.g., within an infinitely long

cylinder or channel -- only one or two, rather than all three, of the coordinates appearing in (2.13) will actually constitute the global coordinates. In that case the ranges of i, j,... and α, β,... will differ from those cited above, but the subsequent analysis will itself be unaffected.] Since a pure translation ($Q^i \to Q^i + \Delta Q^i$) of the chain locator point (while holding its internal configuration fixed) will not change the chain's physical-space mobility or diffusivity tensor, it will hereafter be assumed that the metric tensors g_{IJ} and g^{IJ} depend only upon the local coordinates q^α, being independent of Q^i. This same property will be enjoyed by the determinant (2.7).

The governing equation (2.10) may be rewritten in the more explicit global/local form

$$\frac{\partial P}{\partial t} + \frac{\partial J^i}{\partial Q^i} + \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^\alpha} (\sqrt{g}\, j^\alpha) = \delta(t) \prod_{i=1}^{3} \delta(Q^i - Q'^i) \frac{1}{\sqrt{g}} \prod_{\alpha=4}^{N} \delta(q^\alpha - q'^\alpha) \ , \quad (2.17)$$

where, consistent with prior notation (Brenner 1982a,b), the lower case symbol j^α identifies the contravariant components of the local flux-density vector. In the purely symbolic notation of Brenner (1982a,b) the latter is formally equivalent to

$$\frac{\partial P}{\partial t} + \underset{\sim}{\nabla}_Q \cdot \underset{\sim}{J} + \underset{\sim}{\nabla}_q \cdot \underset{\sim}{j} = \delta(t)\, \delta(\underset{\sim}{Q} - \underset{\sim}{Q}')\, \delta(\underset{\sim}{q} - \underset{\sim}{q}') \ , \quad (2.17')$$

representing an invariant vector or matrix form of the tensor relation (2.17). Whereas (2.17) is wholly operational, (2.17') is purely symbolic in content. Hereafter, at appropriate stages in the analysis, we shall provide corresponding 'invariant' forms of the subsequent tensor equations in order to make explicit the connection with prior invariant notation, which has been exclusively employed in all earlier contributions concerned

with generalized Taylor dispersion theory. The corresponding equation number will merely have a prime superscript affixed, as in Eq. (2.17'), but will generally not be commented upon explicitly.

The potential $\mathcal{V}(\zeta^I)$ will be assumed to possess the global/local decomposition

$$\mathcal{V} = - F_i Q^i + kT\, E(q^\alpha) \quad , \tag{2.18}$$

with F_i the constant (i.e., ζ^I-independent) covariant components of some external vector force (typically gravity) causing sedimentation of the chain, and E the dimensionless internal configurational potential. The flux expression (2.11), in conjunction with (2.4) and (2.12), then yields the explicit contravariant forms of the global and local flux as

$$J^i = U^i P - D^{ij} \frac{\partial P}{\partial Q^i} - e^{-E} D^{i\alpha} \frac{\partial (e^E P)}{\partial q^\alpha} \quad , \tag{2.19}$$

$$\underset{\sim}{J} = \underset{\sim}{U}\, P - \underset{\approx}{D}^{QQ} \cdot \underset{\sim}{\nabla}_Q P - e^{-E}\, \underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_q (e^E P) \quad ; \tag{2.19'}$$

and

$$j^\alpha = u^\alpha P - D^{\alpha i} \frac{\partial P}{\partial Q^i} - e^{-E}\, D^{\alpha\beta} \frac{\partial (e^E P)}{\partial q^\beta} \quad , \tag{2.20}$$

$$\underset{\sim}{j} = \underset{\sim}{u}\, P - \underset{\approx}{D}^{qQ} \cdot \underset{\sim}{\nabla}_Q P - e^{-E}\, \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q\, (e^E P) \quad . \tag{2.20'}$$

The respective global and local velocity components U^i and u^α in (2.19) and (2.20) are defined via the relations

$$U^i = g^{ij} F_j \quad , \tag{2.21}$$

$$u^\alpha = g^{\alpha j} F_j \quad . \tag{2.22}$$

Each of these velocities, as well as the transport coefficients D^{ij}, $D^{i\alpha}$,

$D^{\alpha i}$, $D^{\alpha\beta}$ and potential E, depend only upon the local-space coordinates. These configuration-specific molecular diffusivity tensors are assumed to obey the symmetry relations (Brenner 1982b)

$$D^{ij} = D^{ji} \; ; \quad D^{\alpha\beta} = D^{\beta\alpha} \; ; \quad D^{i\alpha} = D^{\alpha i} \; . \tag{2.23}$$

Equation (2.17), to which is adjoined the constitutive flux expressions (2.19) and (2.20), is to be solved subject to the pre-initial condition

$$P = 0 \quad \text{for} \quad t < 0 \; , \tag{2.24}$$

the global attenuation condition

$$\left|Q^i - Q'^i\right|^m P \to 0 \quad \text{as} \quad \left|Q^i - Q'^i\right| \to \infty \quad (m=0,1,2, \ldots) \; , \tag{2.25}$$

and a no-flux condition on the local-space boundary. To formulate the latter explicitly, suppose that the local-space boundary ∂q_0, say, is expressed by the functional relation

$$s(q^4, \ldots, q^N) = 0 \; , \tag{2.26}$$

with $s < 0$ within, and $s > 0$ outside this local-space boundary. The outwardly-drawn unit 'normal' vector to the latter domain is thus given in covariant form as

$$n_\alpha = \left| \frac{\partial s}{\partial q^\alpha} \right|^{-1} \frac{\partial s}{\partial q^\alpha} \; , \tag{2.27a}$$

with

$$\left| \frac{\partial s}{\partial q^\alpha} \right| \equiv \left(g^{\alpha\beta} \frac{\partial s}{\partial q^\alpha} \frac{\partial s}{\partial q^\beta} \right)^{1/2} . \tag{2.27b}$$

The zero normal-flux boundary condition prevailing on the local-space boundary thus adopts the explicit form

$$n_\alpha \, j^\alpha = 0 \quad \text{on} \quad s(q^4, \ldots, q^N) = 0 \quad , \tag{2.28}$$

$$\underset{\sim}{n} \cdot \underset{\sim}{j} = 0 \quad \text{on} \quad \partial \underset{\sim}{q}_0 \quad , \tag{2.28'}$$

where, in prior invariant notation, $\underset{\sim}{q}_0$ denotes the local-space domain, and $\partial \underset{\sim}{q}_0$ its boundary; (following past notation, $\underset{\sim}{Q}_\infty$ will correspondingly denote the unbounded global-space domain.) In some cases, the local-space may itself be unbounded or closed upon itself; there, appropriate attenuation-rate or singlevaluedness and continuity criteria will respectively be imposed in lieu of (2.28). It is also possible (and indeed at times more convenient) to eliminate the need for the explicit no-flux conditions (2.28) by incorporating physically equivalent behavior into the local-space phenomenological coefficients $\underset{\sim}{u}$, $\underset{\approx}{D}^{qQ}$, $\underset{\approx}{D}^{qq}$ and E themselves (e.g., by allowing E to become infinitely repulsive in regions lying beyond the accessible local-space domain). Such techniques are best illustrated later, in the context of specific physical examples.

Integration of (2.17) over the entire global-local domain, in conjunction with (2.24), (2.25) and (2.28), together with the generalized divergence theorem (Aris 1962), demonstrates that the unit normalization condition

$$\int_{Q_\infty^i} dQ^1 dQ^2 dQ^3 \int_{q_0^\alpha} \sqrt{g} \, dq^4 \ldots dq^N \, P = 1 \quad (t > 0) \quad , \tag{2.29}$$

$$\int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q} \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \, P = 1 \qquad (t > 0) \quad , \tag{2.29'}$$

demanded of the probability is indeed satisfied.

The governing configurational conservation equation (2.17), together with the flux expressions (2.19) and (2.20), the pre-initial condition

(2.24), the global-space attenuation requirement (2.25), the local-space no-flux boundary condition (2.28) and, of course, the given phenomenological data, may (in principle) be solved explicitly to obtain the normalized conditional probability density P for all times. Such meticulously detailed information -- whether analytical or numerical -- is, however, rarely of interest as an end unto itself; rather, in practice, one is normally concerned only with the global - (i.e., physical-) space transport process, and then only for times sufficiently long to effectively achieve local-space equilibration. Generalized Taylor dispersion theory (Brenner 1980, 1982a, 1982b) provides a simple, but rigorous, framework for extracting the projected, purely global-space, transport equations directly from the above set of microtransport equations. In the subsequent analysis we shall instead apply a moment-gradient expansion technique (Nadim et al. 1986) to derive these global-space macrotransport equations. This scheme provides an alternate derivation, complementary either to that of Brenner (1982b), or to alternative projection operator (Pagitsas et al. 1986a) or multiple time-scale (Pagitsas et al. 1986b) schemes for effecting this 'course graining'. As the requisite derivation is most transparently presented in invariant notation, the invariant form of the equation will hereafter be given first, followed -- when necessary -- by the equivalent tensorial form.

The moment-gradient expansion scheme entails a series expansion of $P(\underset{\sim}{Q},\underset{\sim}{q},t|\underset{\sim}{Q},\underset{\sim}{q}')$ in terms of global gradients of the average global density,

$$\bar{P}(\underset{\sim}{Q},t|\underset{\sim}{Q}',\underset{\sim}{q}') = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ P \ , \qquad (2.30')$$

with coefficients derived from successively higher-order moments of the

density P. When truncated at second-order terms, this expansion has the explicit form (Nadim et al. 1986)

$$P = P_0 \overline{P} - (\underset{\sim}{P}_1 - P_0 \underset{\sim}{M}_1) \cdot \underset{\sim}{\nabla}_Q \overline{P} + \ldots , \tag{2.31'}$$

wherein the local and total moments appearing herein as coefficients are defined via the respective relations

$$\underset{\sim}{P}_m(\underset{\sim}{q},t|\underset{\sim}{q}') = \int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q}\ (\underset{\sim}{Q}-\underset{\sim}{Q}')^m\ P \quad , \tag{2.32'}$$

$$\underset{\sim}{M}(t|\underset{\sim}{q}') = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \underset{\sim}{P}_m \ , \tag{2.33'}$$

($m = 0,1,2,\ldots$). That the preceding moments are independent of $\underset{\sim}{Q}'$ is an immediate consequence of the fact that P depends functionally only upon the global-space positional difference $\underset{\sim}{Q} - \underset{\sim}{Q}'$, rather than upon $\underset{\sim}{Q}$ and $\underset{\sim}{Q}'$ separately. Indeed, in previous expositions, $\underset{\sim}{Q}'$ was chosen to be zero without loss of generality (Brenner 1980, 1982a, 1982b, Nadim et al. 1986).

The equations governing the temporal evolution of the $\underset{\sim}{P}_m$ can be readily derived by differentiating (2.32') and (2.33') with respect to time. For long times, when local-space equilibrium prevails, the following asymptotic limits obtain (Brenner 1982b, Nadim et al. 1986):

$$P_0(\underset{\sim}{q},t|\underset{\sim}{q}') \to P_0^\infty(\underset{\sim}{q}) \quad , \tag{2.34'}$$

$$\underset{\sim}{P}_1 - P_0\underset{\sim}{M}_1 \ \to \ P_0^\infty(\underset{\sim}{q})\underset{\sim}{B}(\underset{\sim}{q}) \quad . \tag{2.35'}$$

Appearing above are the local equilibrium distribution $P_0^\infty(\underset{\sim}{q})$ and the so-called $\underset{\sim}{B}$ field, which is a global-space vector field, functionally dependent only upon the local-space configuration $\underset{\sim}{q}$. These two fields are

respectively found by solving the following sets of equations: (i) for $P_0^\infty(\underset{\sim}{q})$,

$$\underset{\sim}{\nabla}_q \cdot \left[\underset{\sim}{u} P_0^\infty - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \right] = 0 \quad , \tag{2.36a'}$$

$$\underset{\sim}{n} \cdot \left[\underset{\sim}{u} P_0^\infty - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \right] = 0 \quad \text{on } \partial \underset{\sim}{q}_0 \ , \tag{2.36b'}$$

$$\int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \, P_0^\infty = 1 \quad ; \tag{2.36c'}$$

equivalently, in tensor notation,

$$\frac{1}{\sqrt{g}} \frac{\partial}{\partial q^\alpha} \{ \sqrt{g} \left[u^\alpha P_0^\infty - e^{-E} D^{\alpha\beta} \frac{\partial (e^E P_0^\infty)}{\partial q^\beta} \right] \} = 0 \quad , \tag{2.36a}$$

$$n_\alpha \left[u^\alpha P_0^\infty - e^{-E} D^{\alpha\beta} \frac{\partial (e^E P_0^\infty)}{\partial q^\beta} \right] = 0 \quad \text{on} \quad s = 0 \quad , \tag{2.36b}$$

$$\int_{q_0^\alpha} \sqrt{g} \, dq^1 \ldots dq^N P_0^\infty = 1 \quad . \tag{2.36c}$$

(ii) For $\underset{\sim}{B}(\underset{\sim}{q})$,

$$\underset{\sim}{\nabla}_q \cdot \left[\underset{\sim}{u} P_0^\infty \underset{\sim}{B} - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty \underset{\sim}{B}) + P_0^\infty \underset{\approx}{D}^{qQ} \right] =$$

$$P_0^\infty (\underset{\sim}{U} - \underset{\sim}{\bar{U}}^*) - e^{-E} \underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \quad , \tag{2.37a'}$$

$$-P_0^\infty \underset{\sim}{n} \cdot (\underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q \underset{\sim}{B} - \underset{\approx}{D}^{qQ}) = \underset{\sim}{0} \qquad \text{on } \partial q_0 \ , \tag{2.37b'}$$

$$\int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \, P_0^\infty \underset{\sim}{B} = \underset{\sim}{0} \quad , \tag{2.37c'}$$

wherein

$$\underset{\sim}{\bar{U}}^* \equiv \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \left[P_0^\infty \underset{\sim}{U} - e^{-E} \underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty) \right] \quad . \tag{2.38'}$$

In tensor notation these take the forms

$$\frac{1}{\sqrt{g}}\frac{\partial}{\partial q^{\alpha}}\left\{\sqrt{g}\left[u^{\alpha}P_0^{\infty}B^{i}-e^{-E_D}D^{\alpha\beta}\frac{\partial(e^{E}P_0^{\infty}B^{i})}{\partial q^{\beta}}+P_0^{\infty}D^{\alpha i}\right]\right\}=$$

$$P_0^{\infty}(U^{i}-\bar{U}^{*i})-e^{-E_D}D^{i\beta}\frac{\partial(e^{E}P_0^{\infty})}{\partial q^{\beta}} \quad , \tag{2.37a}$$

$$-P_0^{\infty}n_{\alpha}\left(\mathfrak{D}^{\alpha\beta}\frac{\partial B^{i}}{\partial q^{\beta}}-D^{\alpha i}\right)=0 \quad , \tag{2.37b}$$

$$\int_{q_0^{\alpha}}\sqrt{g}\;dq^{4}\ldots dq^{N}\,P_0^{\infty}B^{i}=0 \quad , \tag{2.37c}$$

with

$$\underset{\sim}{\bar{U}}^{*i}\equiv\int_{q_0^{\alpha}}\sqrt{g}\;dq^{4}\ldots dq^{N}\left[P_0^{\infty}U^{i}-e^{-E_D}D^{i\alpha}\frac{\partial(e^{E}P_0^{\infty})}{\partial q^{\alpha}}\right] . \tag{2.38}$$

To obtain the purely global-space macrotransport equation for the global density $\bar{P}$ [cf. (2.30')], it is necessary to integrate (2.17) over the local-space domain $\underset{\sim}{q}_0$. In conjunction with the local-space divergence theorem and the no-flux boundary condition (2.28), this yields the exact equation

$$\frac{\partial\bar{P}}{\partial t}+\frac{\partial\bar{J}^{i}}{\partial Q^{i}}=\delta(t)\prod_{i=1}^{3}\delta(Q^{i}-Q'^{i}) , \tag{2.39}$$

in which

$$\bar{J}^{i}=\int_{q_0^{\alpha}}\sqrt{g}\;dq^{4}\ldots dq^{N}\,J^{i} \quad . \tag{2.40}$$

To express $\underset{\sim}{\bar{J}}$ in terms of $\bar{P}$, substitute (2.19) into the last equation, and expand P appearing in the integrand thereof in accordance with (2.31'), permitting removal of terms involving $\bar{P}$ from beneath the integral sign. The long-time limit [cf. (2.34'), (2.35')] of the resulting expression is thus found to be

$$\underset{\sim}{\overline{J}}^{\infty} \simeq \underset{\sim}{\overline{U}}^{*}\overline{P} - \underset{\approx}{\overline{D}}^{*} \cdot \underset{\sim}{\nabla}_{Q}\overline{P} \ , \tag{2.41'}$$

$$\overline{J}^{\infty i} \simeq \overline{U}^{*i}\,\overline{P} - \overline{D}^{*ij}\,\frac{\partial \overline{P}}{\partial Q^{j}} \ , \tag{2.41}$$

at least up to first-order gradient terms in $\overline{P}$ (Nadim et al. 1986).

The expansion for the mean velocity $\underset{\sim}{\overline{U}}^{*}$ required in (2.41') is that given in (2.38), while the required Taylor dispersivity dyadic $\underset{\approx}{\overline{D}}^{*}$ is found to be given by

$$\underset{\approx}{\overline{D}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \left[P_0^{\infty}\underset{\approx}{D}^{QQ} + P_0^{\infty}\underset{\sim}{U}\underset{\sim}{B} - e^{-E}\underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_{q}(e^{E}P_0^{\infty}\,\underset{\sim}{B})\ \right] \ , \tag{2.42'}$$

$$\overline{D}^{*ij} = \int_{q_0^{\alpha}} \sqrt{g}\ dq^{4}\ldots dq^{N}\left[P_0^{\infty}D^{ij} + P_0^{\infty}U^{i}B^{j} - e^{-E}D^{i\alpha}\,\frac{\partial(e^{E}P_0^{\infty}B^{j})}{\partial q^{\alpha}}\right] . \tag{2.42}$$

Alternatively, (2.42') may be written as

$$\underset{\approx}{\overline{D}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\left\{P_0^{\infty}\left(\underset{\approx}{D}^{QQ} - \underset{\approx}{D}^{Qq}\cdot\underset{\sim}{\nabla}_{q}\underset{\sim}{B}\right) + \left[P_0^{\infty}(\underset{\sim}{U}-\underset{\sim}{\overline{U}}^{*}) - e^{-E}\underset{\approx}{D}^{Qq} \cdot \underset{\sim}{\nabla}_{q}(e^{E}P_0^{\infty})\right]\underset{\sim}{B}\right\}, \tag{2.43'}$$

in which (2.37c') was used to subtract the product $P_0^{\infty}\underset{\sim}{\overline{U}}^{*}\underset{\sim}{B}$ from the integrand. In this form, addition of an arbitrary constant $\underset{\sim}{Q}$-space vector to $\underset{\sim}{B}$ leaves $\underset{\approx}{\overline{D}}^{*}$ unaffected; hence, it suffices to obtain the value of $\underset{\sim}{B}$ only to within an arbitrary additive constant. Thus, if (2.43') is used, condition (2.37c') no longer need be imposed upon $\underset{\sim}{B}$, since the latter condition can always be satisfied by adding to $\underset{\sim}{B}$ an appropriate constant vector.

To recapitulate, the long-time macrotransport equation governing the global-space transport of $\overline{P}^{\infty}(\underset{\sim}{Q} - \underset{\sim}{Q}',t)$ [i.e., the long-time limit of $\overline{P}(\underset{\sim}{Q},t|\underset{\sim}{Q}',\underset{\sim}{q}')$] adopts the simple form

$$\partial\overline{P}^{\infty}/\partial t + \underset{\sim}{\nabla}_{Q} \cdot \underset{\sim}{\overline{J}}^{\infty} = 0 \ , \tag{2.44'}$$

$$\partial \overline{P}^{\infty}/\partial t + \partial \overline{J}^{\infty i}/\partial Q^{i} = 0 \ , \tag{2.44}$$

in which the long-time global flux density vector is given by (2.41). Expressions for the mean velocity vector and dispersivity dyadic appearing in the latter are, in turn, given respectively by (2.38) and (2.42) [or (2.43')].

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 $E(\underset{\sim}{q})$ [cf. (2.18)]; 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 nondimensional 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,...,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 $\underset{\sim}{R}_A$ 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 $\underset{\sim}{\phi}_A$ (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 $\underset{\sim}{\phi}_A$ does not possess operational significance as a vector, whereas the infinitesimal rotation pseudovector $\delta\underset{\sim}{\phi}_A$ (to appear later) does.

Denote by

$$P(\underset{\sim}{R}_0,\ldots,\underset{\sim}{R}_n;\ \underset{\sim}{\phi}_0,\ldots,\underset{\sim}{\phi}_n,\ t|\underset{\sim}{R}'_0,\ldots,\underset{\sim}{R}'_n;\ \underset{\sim}{\phi}'_0,\ldots,\underset{\sim}{\phi}'_n)\ d\underset{\sim}{R}_0\ldots d\underset{\sim}{R}_n\ d\underset{\sim}{\phi}_0\ldots d\underset{\sim}{\phi}_n \qquad (3.1)$$

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

$$d\underset{\sim}{R}_0\ldots d\underset{\sim}{R}_n\ d\underset{\sim}{\phi}_0\ldots d\underset{\sim}{\phi}_n \qquad (3.2)$$

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

$$\int d\underset{\sim}{R}_0\ldots d\underset{\sim}{R}_n\ d\underset{\sim}{\phi}_0\ldots d\underset{\sim}{\phi}_n\ P = 1 \quad (t > 0) \quad , \qquad (3.3a)$$

along with

$$P = 0 \quad (t < 0) \quad , \qquad (3.3b)$$

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 (3.3a).]

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

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

in which, more explicitly,

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

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

where B = 0,1,...,n and C = 0,1,...,A-1,A+1,...,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 RHS 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 (3.3a). The configuration-specific physical- and orientational-space vector flux densities $\underset{\sim}{J}[\underset{\sim}{R}_A]$ and $\underset{\sim}{j}[\underset{\sim}{\phi}_A]$ of particle A will be assumed to possess the respective convective-diffusive constitutive forms

$$\underset{\sim}{J}[\underset{\sim}{R}_A] = \dot{\underset{\sim}{R}}_A P - \sum_{B=0}^{n} \{ \underset{\approx}{D}[\underset{\sim}{R}_A | \underset{\sim}{R}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{R}_B} + \underset{\approx}{D}[\underset{\sim}{R}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{\phi}_B} \} \quad , \tag{3.6a}$$

$$\underset{\sim}{j}[\underset{\sim}{\phi}_A] = \dot{\underset{\sim}{\phi}}_A P - \sum_{B=0}^{n} \{ \underset{\approx}{D}[\underset{\sim}{\phi}_A | \underset{\sim}{R}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{R}_B} + \underset{\approx}{D}[\underset{\sim}{\phi}_A | \underset{\sim}{\phi}_B] \cdot \frac{\partial P}{\partial \underset{\sim}{\phi}_B} \} \quad , \tag{3.6b}$$

The (nonBrownian) translational and angular velocity vectors of particle A, respectively defined as

$$\dot{\underset{\sim}{R}}_A \overset{\text{def.}}{=} \delta \underset{\sim}{R}_A / \delta t \quad , \tag{3.7a}$$

$$\dot{\underset{\sim}{\phi}}_A \overset{\text{def.}}{=} \delta \underset{\sim}{\phi}_A / \delta t \quad , \tag{3.7b}$$

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

$$\dot{\underset{\sim}{R}}_A = \sum_{B=0}^{n} \{ \underset{\approx}{M}[\underset{\sim}{R}_A | \underset{\sim}{R}_B] \cdot \underset{\sim}{F}_B + \underset{\approx}{M}[\underset{\sim}{R}_A | \underset{\sim}{\phi}_B] \cdot \underset{\sim}{T}_B \} \quad , \tag{3.8a}$$

$$\dot{\underset{\sim}{\phi}}_A = \sum_{B=0}^{n} \{ \underset{\approx}{M}[\underset{\sim}{\phi}_A | \underset{\sim}{R}_B] \cdot \underset{\sim}{F}_B + \underset{\approx}{M}[\underset{\sim}{\phi}_A | \underset{\sim}{\phi}_B] \cdot \underset{\sim}{T}_B \} \quad , \tag{3.8b}$$

where $\underset{\sim}{F}_B$ and $\underset{\sim}{T}_B$ are the (nonhydrodynamic and nonBrownian) 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 $\underset{\approx}{M}[A|B]$ appearing in (3.8) are functionally dependent only upon the <u>internal</u> configuration (conformation) of the flexible body (i.e., the orientations and <u>relative</u> 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 $\underset{\approx}{M}[\underset{\sim}{R}_A | \underset{\sim}{\phi}_B]$ and $\underset{\approx}{M}[\underset{\sim}{\phi}_A | \underset{\sim}{R}_B]$ possessing mixed physical- and orientational-space arguments arise from coupling between respective rotational and translational motions (not necessarily referring to motions of the <u>same</u> particle -- i.e., B may or may not be equal to A). The mobilities $\underset{\approx}{M}[A|B]$ are closely related to the comparable Brownian diffusivity dyadics $\underset{\approx}{D}[A|B]$ appearing in (3.6) via the multibody configuration-specific Stokes-Einstein relations (Brenner 1967)

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

In principle, the configuration-specific mobilities $\underset{\sim}{\underset{\sim}{M}}[A|B]$ may be found by solving the (n+1)-particle Stokes flow problem (for that specific geometric configuration) for which only <u>one</u> 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.[2] Equation (3.9) then provides the requisite molecular diffusivities $\underset{\sim}{\underset{\sim}{D}}[A|B]$.

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

$$\underset{\sim}{F}_B = -\,\partial V/\partial \underset{\sim}{R}_B \quad , \tag{3.10a}$$

$$\underset{\sim}{T}_B = -\,\partial V/\partial \underset{\sim}{\phi}_B \quad , \tag{3.10b}$$

in which circumstances (3.8) adopts the form

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

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

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 $(\underset{\sim}{R}_0,\ldots,\underset{\sim}{R}_n;\ \underset{\sim}{\phi}_0,\ldots,\underset{\sim}{\phi}_n)$ space. All the material, configuration-specific, phenomenological dyadics required therein (mobilities and diffusivities) will henceforth be assumed known 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)

$$\underset{\sim}{\underset{\sim}{M}}^{\dagger}[\underset{\sim}{R}_A|\underset{\sim}{R}_B] = \underset{\sim}{\underset{\sim}{M}}[\underset{\sim}{R}_B|\underset{\sim}{R}_A] \quad , \tag{3.12a}$$

$$\underset{\approx}{M}^{\dagger}[\underset{\sim}{\Phi}_A|\underset{\sim}{\Phi}_B] = \underset{\approx}{M}[\underset{\sim}{\Phi}_B|\underset{\sim}{\Phi}_A] \quad , \tag{3.12b}$$

$$\underset{\approx}{M}^{\dagger}[\underset{\sim}{\Phi}_A|\underset{\sim}{R}_B] = \underset{\approx}{M}[\underset{\sim}{R}_B|\underset{\sim}{\Phi}_A] \quad , \tag{3.12c}$$

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 (3.3a), are the usual zero normal-flux conditions existing at the physical- and orientational-space 'boundaries' (cf. Section 2, as well as Haber & Brenner 1986). These will not be explicitly written down in full generality at this point, although we shall now address several common possibilities. Consider, for instance, *a* constituent particle situated sufficiently far from its neighbors and from any bounding walls (if indeed any are present) such that, with its locator point held fixed, <u>all</u> orientations are accessible (i.e., there exists no possible rotation about its locator point that would bring it into contact with any of its neighbors or with the walls). In such circumstances the orientational domain accessible to the particle then consists of the entire three-dimensional orientational-space available to an isolated rigid body, namely a 'closed' space (of volume $8\pi^2$) with no boundaries (Brenner 1979, 1981). As such, no boundary condition need be imposed upon the orientational transport of the particle other than the requirement that the probability density be single-valued throughout the entire domain. On the other hand, when a constituent particle is close to one or more of its neighbors, or to bounding walls, rotational motion about its locator point may be restricted. In that case one of several possible alternative, but physically equivalent, viewpoints may be adopted. One

possibility is to regard the orientational domain as being bounded, and consequently to adopt zero normal-flux conditions at its boundary [as given explicitly in (2.28)]. A convenient alternative viewpoint is to regard the orientational-space as consisting of the entire closed space (of volume $8\pi^2$) referred to previously, and, at the same time, to define the phenomenological transport coefficients or the interparticle (internal) potential in such a manner as to incorporate into these material functions the appropriate kinematics or physics of the interparticle interactions. A simple and common example of the latter entails use of the so-called "hard-sphere" potential in circumstances for which the constituent particles are rigid impenetrable spheres. We will most often adopt the second viewpoint, since it is more general, and hence more adaptable towards extending the present theory to nontrivial circumstances, such as those encountered for which the constituent particles may themselves be flexible.

An entirely analogous point of view will be adopted in regard to the physical-space boundary conditions. (Indeed, the hard-sphere potential example really constitutes an illustration of the latter.) The only remaining aspect of the physical-space domain to be addressed arises from the fact that it is unbounded in extent. As such, the appropriate conditions to be imposed at infinity (far from the initial location of the chain in space, and for large separations between constituent particles) are attenuation conditions that guarantee convergence of all subsequent integrals (e.g., the probability moments) arising in the theory. Finally, it is noteworthy that although attention is presently focused on transport of the chain within an unbounded fluid domain, no conceptual difficulties arise in the comparable treatment of transport problems in laterally-

confined geometries (e.g., channels or ducts). In such circumstances the lateral physical coordinates spanning the 'cross section' of the confined domain must be treated as local rather than global, with the transport coefficients (diffusivity and mobility dyadics) and internal potential now regarded as being dependent upon both the chain conformation and chain proximity to the confining wall.

Subject to the foregoing boundary conditions and the pre-initial condition (3.3b), 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 1982b), 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 prerequisite to applying the results of Section 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 motions 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 centers 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. Indeed, in Section 8, we formally prove this primitive intuitive idea, by demonstrating invariance to the choice of chain-fixed locator point of our physical results pertaining to the transport properties of the cluster as a whole.

4. LOCAL/GLOBAL FORM OF THE 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. (We will subsequently verify that our long-time results are indeed independent of this arbitrary choice of locator point. In fact, the explicit choice of which of the n+1 constituent particles is identified as the 'zeroth' particle is obviously arbitrary, much less which point affixed to a given particle is selected as origin.) Denote by $\underset{\sim}{Q}$ the position vector of this point, so that

$$\underset{\sim}{Q} \equiv \underset{\sim}{R}_0 \quad . \tag{4.1}$$

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.[3] 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 $\underset{\sim}{\phi}_0$, $\underset{\sim}{\phi}_1$, ..., $\underset{\sim}{\phi}_n$ (hereafter designated collectively as $\underset{\sim}{\phi}^{n+1}$) and the 3n scalar positional coordinates arising from the n relative position vectors

$$\underset{\sim}{r}_a \overset{\text{def.}}{=} \underset{\sim}{R}_a - \underset{\sim}{R}_0 \tag{4.2}$$

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

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

Define the new gradient operators

$$\underset{\sim}{\nabla}_Q \equiv (\partial/\partial \underset{\sim}{Q})_{\underset{\sim}{r}_a, \underset{\sim}{\phi}_A} \quad , \tag{4.4a}$$

$$\partial/\partial \underset{\sim}{r}_a \equiv (\partial/\partial \underset{\sim}{r}_a)_{\underset{\sim}{Q}, \underset{\sim}{r}_b (\neq \underset{\sim}{r}_a), \underset{\sim}{\phi}_A} \quad , \tag{4.4b}$$

$$\partial/\partial \underset{\sim}{\phi}_A \equiv (\partial/\partial \underset{\sim}{\phi}_A)_{\underset{\sim}{Q}, \underset{\sim}{r}_a, \underset{\sim}{\phi}_B (\neq \underset{\sim}{\phi}_A)} \quad . \tag{4.4c}$$

It is readily established that the latter orientational gradient is identical to 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

$$\partial/\partial \underset{\sim}{R}_0 = \underset{\sim}{\nabla}_Q - \sum_{a=1}^{n} \partial/\partial \underset{\sim}{r}_a \tag{4.5a}$$

and

$$\partial/\partial \underset{\sim}{R}_a = \partial/\partial \underset{\sim}{r}_a \tag{4.5b}$$

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

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

results in the microtransport equation

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

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

[It is demonstrated in Appendix A that the volume element appearing in (4.6) is identical to that in (3.1), (3.2).] The global flux density vector $\underset{\sim}{J}$ appearing above is given in symbolic-functional form by the expression

$$\underset{\sim}{J} \equiv \underset{\sim}{J}[R_0] \quad , \tag{4.8}$$

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

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

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

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

$$V = -\underset{\sim}{F} \cdot \underset{\sim}{R}_0 + kT\, E(\underset{\sim}{r}^n, \underset{\sim}{\phi}^{n+1}) \quad , \tag{4.10}$$

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

Utilize (4.10) and effect the transformation (4.5) in the constitutive flux equations (3.6a) - (3.6b). In conjunction with (4.9) this yields the following expression: (i) global flux density,

$$\underset{\sim}{J} = \underset{\approx}{M}[\underset{\sim}{R}_0|\underset{\sim}{R}_0] \cdot \underset{\sim}{F}\, P - \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_0] \cdot \underset{\sim}{\nabla}_Q P$$

$$- \sum_{a=1}^{n} e^{-E} \{\underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_a] - \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_0]\} \cdot \partial(e^E P)/\partial \underset{\sim}{r}_a$$

$$- \sum_{A=0}^{n} e^{-E}\, \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{\phi}_A] \cdot \partial(e^E P)/\partial \underset{\sim}{\phi}_A \quad ; \tag{4.11}$$

(ii) local translational flux densities,

$$\underset{\sim}{j}[\underset{\sim}{r}_a] = \{\underset{\approx}{M}[\underset{\sim}{R}_a|\underset{\sim}{R}_0] - \underset{\approx}{M}[\underset{\sim}{R}_0|\underset{\sim}{R}_0]\} \cdot \underset{\sim}{F}\, P - \{\underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_0] - \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_0]\} \cdot \underset{\sim}{\nabla}_Q P$$

$$- \sum_{b=1}^{n} e^{-E} \{\underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_b] - \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_0] - \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_b] + \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{R}_0]\} \cdot \partial(e^E P)/\partial \underset{\sim}{r}_b$$

$$- \sum_{A=0}^{n} e^{-E} \{\underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{\phi}_A] - \underset{\approx}{D}[\underset{\sim}{R}_0|\underset{\sim}{\phi}_A]\} \cdot \partial(e^E P)/\partial \underset{\sim}{\phi}_A \quad , \tag{4.12}$$

(iii) local rotational flux densities,

$$\underset{\sim}{j}[\underset{\sim}{\phi}_A] = \underset{\approx}{M}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_0] \cdot \underset{\sim}{F}\, P - \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_0] \cdot \underset{\sim}{\nabla}_Q P$$

$$- \sum_{a=1}^{n} e^{-E} \{\underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_a] - \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_0]\} \cdot \partial(e^E P)/\partial \underset{\sim}{r}_a$$

$$- \sum_{B=0}^{n} e^{-E}\, \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] \cdot \partial(e^E P)/\partial \underset{\sim}{\phi}_B \quad . \tag{4.13}$$

Equation (4.7) together with (4.11) - (4.13) represents the exact microtransport equation governing the detailed stochastic motion of the flexible chain through $\underset{\sim}{Q} \bullet \underset{\sim}{q}$ space. In order to apply the results of Section 2 dealing with generalized Taylor dispersion analyses (Brenner 1982b) -- 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 $[\![\, \underset{\sim}{j} \,]\!]$ be given in

the partitioned matrix form

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

whose individual row vector elements $\underset{\sim}{j}^{\dagger}[\ ]$ are themselves 1×3 matrices whose three scalar elements are the three components of the vector $\underset{\sim}{j}[\ ]$. 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 <u>scalar</u> entries. Equation (4.14a) may be compactly abbreviated as

$$[\![\ \underset{\sim}{j}\ ]\!] = \left[\!\!\left[\begin{array}{c} \underset{\sim}{j}[\underset{\sim}{r}_a] \\ \underset{\sim}{j}[\underset{\sim}{\varphi}_A] \end{array}\right]\!\!\right] \qquad \{(6n+3)\times 1\} \quad , \tag{4.14b}$$

wherein

$$[\![\ \underset{\sim}{j}[\underset{\sim}{r}_a]\ ]\!] = \left[\!\!\left[\begin{array}{c} \underset{\sim}{j}[\underset{\sim}{r}_1] \\ \vdots \\ \underset{\sim}{j}[\underset{\sim}{r}_n] \end{array}\right]\!\!\right] \{3n\times 1\} \ , \ [\![\ \underset{\sim}{j}[\underset{\sim}{\varphi}_A]\ ]\!] = \left[\!\!\left[\begin{array}{c} \underset{\sim}{j}[\underset{\sim}{\varphi}_0] \\ \vdots \\ \underset{\sim}{j}[\underset{\sim}{\varphi}_n] \end{array}\right]\!\!\right] \{(3n+3)\times 1\},$$

whose individual column vector elements $\underset{\sim}{j}[\ ]$ are the 3×1 transposed matrices of $\underset{\sim}{j}^{\dagger}[\ ]$. 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

$$[\![\ \underset{\sim}{\alpha}\ \underset{\sim}{\beta}\ ]\!]^{\dagger} = \left[\!\!\left[\begin{array}{c} \underset{\sim}{\alpha}^{\dagger} \\ \underset{\sim}{\beta}^{\dagger} \end{array}\right]\!\!\right]$$

obtains for matrix elements $\underset{\sim}{\alpha}$ and $\underset{\sim}{\beta}$ of any rank. In Eq. (4.14b) and subsequent equations, observe again that minuscule indices a, b,... range

from 1 to n, whereas majuscule indices range from 0 to n.

Represent the local gradient operator $[\![\nabla_q]\!]$ as the partitioned matrix

$$[\![\nabla_q]\!]^\dagger \equiv [\![\partial/\partial \underset{\sim}{r}_1^\dagger \ldots \partial/\partial \underset{\sim}{r}_n^\dagger \quad \partial/\partial \underset{\sim}{\phi}_0^\dagger \ldots \partial/\partial \underset{\sim}{\phi}_n^\dagger]\!] \quad \{1\times(6n+3)\} \quad . \tag{4.15}$$

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

$$\partial P/\partial t + \nabla_Q \cdot \underset{\sim}{J} + [\![\nabla_q]\!]^\dagger \cdot [\![\underset{\sim}{j}]\!] = \delta(t)\delta(\underset{\sim}{Q} - \underset{\sim}{Q}')\delta(\underset{\sim}{q} - \underset{\sim}{q}') \quad , \tag{4.16}$$

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

$$[\![\underset{\sim}{j}]\!] = [\![\underset{\sim}{u}]\!] P - [\![\underset{\approx}{D}^{qQ}]\!] \cdot \nabla_Q P - e^{-E} [\![\underset{\approx}{D}^{qq}]\!] \cdot [\![\nabla_q]\!] (e^E P) \quad , \tag{4.17}$$

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

$$\underset{\sim}{J} = \underset{\sim}{U} P - \underset{\approx}{D}^{QQ} \cdot \nabla_Q P - e^{-E} [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\nabla_q]\!] (e^E P) \quad . \tag{4.18}$$

Appearing in (4.17) and (4.18) are the following phenomenological coefficients:

(i) Local velocity matrix $[\![\underset{\sim}{u}]\!]$:

$$[\![\underset{\sim}{u}]\!] = \begin{bmatrix\![} \underset{\sim}{u}[\underset{\sim}{r}_a] \\ \underset{\sim}{u}[\underset{\sim}{\phi}_A] \end{bmatrix\!]} \qquad \{(6n+3)\times 1\} \quad , \tag{4.19a}$$

with[4]

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

and

$$\underset{\sim}{u}[\underset{\sim}{\phi}_A] = \underset{\approx}{M}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_0]\cdot\underset{\sim}{F} \quad ; \tag{4.19c}$$

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

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

with

$$\underset{\approx}{D}^{qQ}[\underset{\sim}{r}_a] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_o] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \tag{4.20b}$$

and

$$\underset{\approx}{D}^{qQ}[\underset{\sim}{\phi}_A] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_o] \quad ; \tag{4.20c}$$

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

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

in which

$$\underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{r}_b] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_b] - \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{R}_o] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_b] + \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \quad , \tag{4.21b}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{r}_a|\underset{\sim}{\phi}_A] = \underset{\approx}{D}[\underset{\sim}{R}_a|\underset{\sim}{\phi}_A] - \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{\phi}_A] \quad , \tag{4.21c}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{r}_a] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_a] - \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{R}_o] = \underset{\approx}{D}^{qq\dagger}[\underset{\sim}{r}_a|\underset{\sim}{\phi}_A] \quad , \tag{4.21d}$$

$$\underset{\approx}{D}^{qq}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] = \underset{\approx}{D}[\underset{\sim}{\phi}_A|\underset{\sim}{\phi}_B] \quad . \tag{4.21e}$$

It is easily established that the square matrix (4.21a) is symmetric;

(iv) Global velocity vector $\underset{\sim}{U}$:

$$\underset{\sim}{U} \equiv \underset{\approx}{M}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \cdot \underset{\sim}{F} \qquad \{3\times 1\} \quad ; \tag{4.22}$$

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

$$\underset{\approx}{D}^{QQ} \equiv \underset{\approx}{D}[\underset{\sim}{R}_o|\underset{\sim}{R}_o] \qquad \{3\times 3\} \quad ; \tag{4.23}$$

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

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

with the RHS explicitly defined in (4.20).

Each of the six phenomenological matrices (4.19) - (4.24) are well-defined functions of the conformation $\underset{\sim}{q}$, and are all calculable once the n+1 multibody hydrodynamic interaction problem is solved. They further satisfy all the necessary symmetry conditions outlined in Section 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 to the 'primed' forms of the canonical equations of generalized coupled Taylor dispersion theory outlined in Section 2.

5. RESULTS

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.

Mean velocity vector

As in (2.38'), the mean velocity vector of the flexible body, sedimenting through the viscous fluid under the action of the external force $\underset{\sim}{F}$ [cf. (4.10)], adopts the hybrid vector/matrix form

$$\overline{\underset{\sim}{U}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \{P_0^{\infty} \underset{\sim}{U} - e^{-E} [\![\underset{\approx}{D}^{Qq}]\!] \cdot [\![\underset{\sim}{\nabla}_q]\!] (e^{E} P_0^{\infty})\} \quad , \tag{5.1}$$

in which the volume element $d\underset{\sim}{q}$ represents $d\underset{\sim}{r}^n d\underset{\sim}{\phi}^{n+1}$. The quantities $\underset{\sim}{U}$, $[\![\underset{\approx}{D}^{Qq}]\!]$, E and $[\![\underset{\sim}{\nabla}_q]\!]$ appearing in the integrand are respectively given by (4.22), (4.24), (4.10) and (4.15). The local equilibrium density $P_0^{\infty}(\underset{\sim}{q}) \equiv P_0^{\infty}(\underset{\sim}{r}^n, \underset{\sim}{\phi}^{n+1})$, required above, represents the solution of the pair of equations [cf. (2.36')]

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

$$\int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \; P_0^{\infty} = 1 \quad , \tag{5.2b}$$

wherein, rather than specifying explicitly-posed boundary conditions, any such required conditions must be incorporated into the potential E and/or

the phenomenological coefficients. Coefficients $[\![\, \underset{\sim}{u} \,]\!]$ and $[\![\, \underset{\approx}{D}^{qq} \,]\!]$, required above, are given explicitly by (4.19) and (4.21).

Mean dispersivity dyadic

Corresponding to (2.43'), the flexible-body long-time dispersivity dyadic is

$$\overline{\underset{\approx}{D}}^{*} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \{ P_0^{\infty} \left(\underset{\approx}{D}^{QQ} - [\![\, \underset{\approx}{D}^{Qq} \,]\!] \cdot [\![\, \underset{\sim}{\nabla}_q \,]\!] \underset{\approx}{B} \right)$$

$$+ \left[P_0^{\infty} (\underset{\sim}{U} - \overline{\underset{\sim}{U}}^{*}) - e^{-E} [\![\, \underset{\approx}{D}^{Qq} \,]\!] \cdot [\![\, \underset{\sim}{\nabla}_q \,]\!] (e^{E} P_0^{\infty}) \right] \underset{\approx}{B} \} \quad , \qquad (5.3)$$

with $\underset{\approx}{D}^{QQ}$ given by (4.23). The global-space vector field $\underset{\sim}{B}(\underset{\sim}{q})$, defined over the local space $\underset{\sim}{q}_0$, may be obtained [cf. (2.37')] upon solving the equation

$$[\![\, \underset{\sim}{\nabla}_q \,]\!]^{\dagger} \cdot \{ [\![\, \underset{\sim}{u} \,]\!] P_0^{\infty} \underset{\approx}{B} - e^{-E} [\![\, \underset{\approx}{D}^{qq} \,]\!] \cdot [\![\, \underset{\sim}{\nabla}_q \,]\!] (e^{E} P_0^{\infty} \underset{\approx}{B}) + P_0^{\infty} [\![\, \underset{\approx}{D}^{qQ} \,]\!] \} =$$

$$P_0^{\infty} (\underset{\sim}{U} - \overline{\underset{\sim}{U}}^{*}) - e^{-E} [\![\, \underset{\approx}{D}^{Qq} \,]\!] \cdot [\![\, \underset{\sim}{\nabla}_q \,]\!] (e^{E} P_0^{\infty}) \quad , \qquad (5.4)$$

subject to appropriate 'boundary' behavior built into the phenomenological coefficients and/or potential, which would be equivalent to (2.37b') if explicit account were to be taken of any existing orientational- or physical-space boundaries. Since (5.3) is based upon the alternate formulation (2.43'), no integral requirement of the form (2.37c') need be imposed upon $\underset{\sim}{B}$; accordingly, the latter is uniquely determined only to within an arbitrary additive constant vector.

For completeness we also provide explicit forms of boundary conditions (2.36b') and (2.37b') in a formulation that includes a conventional treatment of boundaries. If the scalar equation

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

represents an explicit parameterization of the local-space boundary ∂q_0, (with $s<0$ within and $s>0$ outside of ∂q_0), the unit outward-drawn normal 'vector' $[\![\ \underset{\sim}{n}\ ]\!]$ will be given by

$$[\![\ \underset{\sim}{n}\ ]\!] = \left([\![\ \underset{\sim}{\nabla}_q\ ]\!]^{\dagger} s \cdot [\![\ \underset{\sim}{\nabla}_q\ ]\!] s \right)^{-1/2} [\![\ \underset{\sim}{\nabla}_q\ ]\!] s \quad . \tag{5.6}$$

In this formulation, equations (5.2a,b) are to supplemented by the zero normal-flux condition [cf. (2.36b')]

$$[\![\ \underset{\sim}{n}\ ]\!]^{\dagger} \cdot \{ [\![\ \underset{\sim}{u}\ ]\!] P_0^{\infty} - e^{-E} [\![\ \underset{\approx}{D}^{qq}\ ]\!] \cdot [\![\ \underset{\sim}{\nabla}_q\ ]\!] (e^{E} P_0^{\infty}) \} = 0 \text{ on } \partial q_0 \ , \tag{5.7}$$

whereas equation (5.4) is to be solved subject to [cf. (2.37b')]

$$-P_0^{\infty} [\![\ \underset{\sim}{n}\ ]\!]^{\dagger} \cdot \{ [\![\ \underset{\approx}{D}^{qq}\ ]\!] \cdot [\![\ \underset{\sim}{\nabla}_q\ ]\!] \underset{\approx}{B} - [\![\ \underset{\approx}{D}^{qQ}\ ]\!] \} = \underset{\sim}{0} \quad \text{on } \partial q_0 \ , \tag{5.8}$$

'Molecular dispersion' in the absence of sedimentation

This subsection provides solutions of the above sets of equations for circumstances in which the global external force $\underset{\sim}{F}$ 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 $\underset{\sim}{F} = \underset{\sim}{0}$ it may be anticipated that $\overline{\underset{\sim}{U}}^{*} = \underset{\sim}{0}$, a fact which will be proved shortly. As such, the long-time transport is characterized solely by $\overline{\underset{\approx}{D}}^{*}$, whose explicit form will now be calculated.

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

$$P_0^{\infty} = e^{-E}/W \quad , \tag{5.9a}$$

with

$$W = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\; e^{-E} \quad , \tag{5.9b}$$

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

$$\overset{\rightarrow}{\underset{\sim}{U}}^{*} = \underset{\sim}{0} \quad , \tag{5.10}$$

as expected.

Under these conditions eq. (5.4) adopts the simple form

$$-\left[\!\left[\underset{\sim}{\nabla}_q \right]\!\right]^{\dagger} \cdot \{P_0^{\infty}\Big(\left[\!\left[\underset{\approx}{D}^{qq} \right]\!\right] \cdot \left[\!\left[\underset{\sim}{\nabla}_q \right]\!\right] \underset{\approx}{B} - \left[\!\left[\underset{\approx}{D}^{qQ} \right]\!\right] \Big)\} = \underset{\sim}{0} \quad , \tag{5.11}$$

thereby requiring that

$$\left[\!\left[\underset{\sim}{\nabla}_q \right]\!\right] \underset{\approx}{B} = \left[\!\left[\underset{\approx}{D}^{qq} \right]\!\right]^{-1} \cdot \left[\!\left[\underset{\approx}{D}^{qQ} \right]\!\right] \tag{5.12}$$

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

$$\overset{\rightarrow}{\underset{\approx}{D}}^{M} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\; P_0^{\infty}\{ \underset{\approx}{D}^{QQ} - \left[\!\left[\underset{\approx}{D}^{Qq} \right]\!\right] \cdot \left[\!\left[\underset{\approx}{D}^{qq} \right]\!\right]^{-1} \cdot \left[\!\left[\underset{\approx}{D}^{qQ} \right]\!\right] \} \tag{5.13}$$

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 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 nonsedimenting, but 'loaded', flexible dumbbell described in Section 7.

6. SEDIMENTATION OF A FLEXIBLE DUMBBELL

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 dumbbell in an otherwise quiescent viscous fluid.

As in Fig. 1, consider a dumbbell composed of two identical rigid spherical particles, numbered 0 and 1, of radii a, whose geometric centers -- possessing respective position vectors $\underset{\sim}{R}_0$, $\underset{\sim}{R}_1$ -- 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 $\underset{\sim}{g}$, the combined gravitational-buoyancy portion of the dumbbell potential is thus found to be

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

where, in accordance with (4.2),

$$\underset{\sim}{r}_1 = \underset{\sim}{R}_1 - \underset{\sim}{R}_0 \quad . \tag{6.2}$$

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

$$V = - \underset{\sim}{F} \cdot \underset{\sim}{R}_0 + kT\, E(\underset{\sim}{r}_1) \quad , \tag{6.3a}$$

in which we identify the total external force,

$$\underset{\sim}{F} = 2|\Delta m| \underset{\sim}{g} \quad , \tag{6.3b}$$

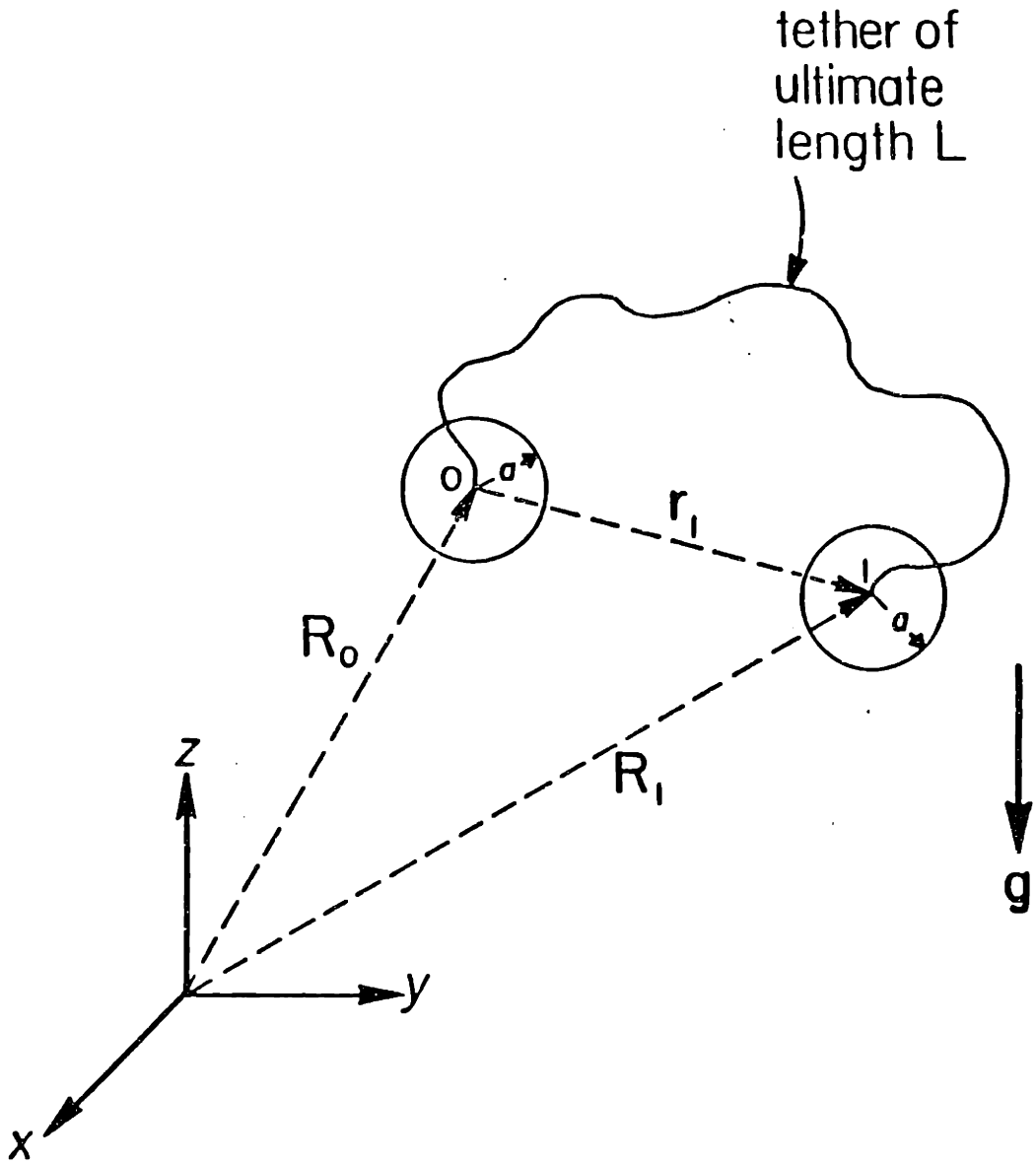

Fig. 1. Tethered dumbbell.

and total internal potential,

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

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 centers as individual sphere locator points, the assumed homogeneity of each of the spheres (resulting in the absence of external torques about their centers) and the assumed independence of the conformational potential upon the orientations $(\underset{\sim}{\phi}_0,\underset{\sim}{\phi}_1)$ 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 $(\underset{\sim}{\phi}_0,\underset{\sim}{\phi}_1)$]. 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.[5] This yields a greatly simplified set of microtransport equations governing the probability density $P(\underset{\sim}{R}_0,\underset{\sim}{r}_1,t|\underset{\sim}{R}_0',\underset{\sim}{r}_1')$, with $\underset{\sim}{R}_0$ spanning the global space [cf. (4.1)], i.e.,

$$\underset{\sim}{Q} \equiv \underset{\sim}{R}_0 \quad , \tag{6.4}$$

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

$$\underset{\sim}{q} \equiv \underset{\sim}{r}_1 \quad . \tag{6.5}$$

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

$$[\![\underset{\sim}{\nabla} q]\!] = \underset{\sim}{\nabla} r_1 \quad , \tag{6.6a}$$

$$[\![\underset{\sim}{u}]\!] = (\underset{\approx}{M}_{10} - \underset{\approx}{M}_{00}) \cdot \underset{\sim}{F} \quad , \tag{6.6b}$$

$$[\![\underset{\approx}{D}^{qQ}]\!] = \underset{\approx}{D}_{10} - \underset{\approx}{D}_{00} \quad , \tag{6.6c}$$

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

$$\underset{\sim}{U} = \underset{\approx}{M}_{00} \cdot \underset{\sim}{F} \quad , \tag{6.6e}$$

$$\underset{\approx}{D}^{QQ} = \underset{\approx}{D}_{00} \quad , \tag{6.6f}$$

$$[\![\underset{\approx}{D}^{Qq}]\!] = \underset{\approx}{D}_{01} - \underset{\approx}{D}_{00} = \underset{\approx}{D}_{10} - \underset{\approx}{D}_{00} \quad , \tag{6.6g}$$

wherein the RHS's of each of the above expressions are either vectors or dyadics. In writing these relations we have introduced the simplified notation

$$\underset{\approx}{M}[\underset{\sim}{R}_A|\underset{\sim}{R}_B] = \underset{\approx}{M}_{AB} \quad , \quad \underset{\approx}{D}[\underset{\sim}{R}_A|\underset{\sim}{R}_B] = \underset{\approx}{D}_{AB} \quad , \tag{6.7}$$

since, in the absence of orientational variables, no confusion can result in the course of interpreting the RHS's of these expressions. Furthermore, in (6.6d,g) use was made of the identities

$$\underset{\approx}{D}_{01} = \underset{\approx}{D}_{10} \qquad (\underset{\approx}{M}_{01} = \underset{\approx}{M}_{10}) \ , \tag{6.8a}$$

$$\underset{\approx}{D}_{11} = \underset{\approx}{D}_{00} \qquad (\underset{\approx}{M}_{11} = \underset{\approx}{M}_{00}) \ . \tag{6.8b}$$

These low-Reynolds-number identities obtain when the two spheres composing the dumbbell 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 Section 5 to the present sedimenting flexible dumbbell problem.

Mean settling velocity vector

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

$$\underset{\sim}{\nabla}_{\underset{\sim}{r}_1} \cdot \left[(\underset{\approx}{M}_{10} - \underset{\approx}{M}_{00}) \cdot \underset{\sim}{F}\, P_0^\infty - 2e^{-E}(\underset{\approx}{D}_{00} - \underset{\approx}{D}_{10}) \cdot \underset{\sim}{\nabla}_{\underset{\sim}{r}_1}(e^E P_0^\infty)\right] = 0 \ , \qquad (6.9a)$$

$$\int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \, P_0^\infty = 1 \ , \qquad (6.9b)$$

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

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

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

$$W = \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \exp(-\hat{E}) \ . \qquad (6.10b)$$

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

$$E(\underset{\sim}{r}_1) = \begin{cases} \infty & |\underset{\sim}{r}_1| < 2a \ , \\ 0 & 2a \le |\underset{\sim}{r}_1| \le L \ , \\ \infty & L < |\underset{\sim}{r}_1| \ , \end{cases} \qquad (6.11)$$

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:

$$e^{-E}\, \underset{\sim}{\nabla}_{\underset{\sim}{r}_1}(e^E P_0^\infty) = - P_0^\infty \, \underset{\sim}{F}/2kT \ . \qquad (6.12)$$

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)]

$$\bar{\underset{\sim}{U}}^{*} = \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \left[P_0^{\infty} \underset{\approx}{M}_{00} \cdot \underset{\sim}{F} - e^{-E} \left(\underset{\approx}{D}_{10} - \underset{\approx}{D}_{00} \right) \cdot \underset{\sim}{\nabla}_{\underset{\sim}{r}_1} \left(e^{E} P_0^{\infty} \right) \right] \quad . \tag{6.13}$$

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

$$\bar{\underset{\sim}{U}}^{*} = \left[W^{-1} \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \exp(-\hat{E}) \, \underset{\approx}{M} \right] \cdot \underset{\sim}{F} \quad , \tag{6.14}$$

in which

$$\underset{\approx}{M} \overset{\text{def.}}{=} \tfrac{1}{2} \left(\underset{\approx}{M}_{00} + \underset{\approx}{M}_{10} \right) \quad . \tag{6.15}$$

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

$$\underset{\approx}{M} = M_{\parallel} \underset{\sim}{e}\underset{\sim}{e} + M_{\perp} \left(\underset{\approx}{I} - \underset{\sim}{e}\underset{\sim}{e} \right) \quad , \tag{6.16}$$

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

$$|\underset{\sim}{r}_1| = r \ , \qquad \underset{\sim}{r}_1 = r\underset{\sim}{e} \quad . \tag{6.17}$$

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

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

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

with the dimensionless functions x_{12}^{a}, x_{12}^{a}, y_{11}^{a} and y_{12}^{a} furnished by these

authors in their Sections 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 nondimensional sphere center separation parameter s here becomes $s = r/a$.) Numerical evaluation of (6.14) will subsequently be carried out for the tethered dumbbell 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 centers.

Pure molecular diffusion

Although this section is focused on dispersive effects accompanying sedimentation, it is instructive to consider first the simpler circumstance where sedimentation is absent ($\underset{\sim}{F}=\underset{\sim}{0}$), so that the only transport mechanism is molecular diffusion of the flexible dumbbell. The internal Boltzmann equilibrium probability density (6.10) obviously remains unchanged as $\underset{\sim}{F}\to\underset{\sim}{0}$, 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 dumbbell dispersivity adopts the form [cf. (5.13)]

$$\overline{\underset{\approx}{D}}^{M} = W^{-1}\int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \exp(-\hat{E})[\underset{\approx}{D}_{00} - \tfrac{1}{2}(\underset{\approx}{D}_{10} - \underset{\approx}{D}_{00}) \cdot (\underset{\approx}{D}_{00} - \underset{\approx}{D}_{10})^{-1} \cdot (\underset{\approx}{D}_{10} - \underset{\approx}{D}_{00})] ,$$

$$= W^{-1} \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \exp(-\hat{E})\ \underset{\approx}{D} \quad , \tag{6.19}$$

with

$$\underset{\approx}{D} \overset{def.}{=} \tfrac{1}{2}(\underset{\approx}{D}_{00} + \underset{\approx}{D}_{10}) \equiv kT\ \underset{\approx}{M} \quad . \tag{6.20}$$

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

Sedimentation-dispersion

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

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

$$\nabla_{\underset{\sim}{r}_1} \cdot [-2P_0^{\infty}(\underline{\underline{D}}_{00} - \underline{\underline{D}}_{10}) \cdot \nabla_{\underset{\sim}{r}_1}\underline{B} + P_0^{\infty}(\underline{\underline{D}}_{10} - \underline{\underline{D}}_{00})] = P_0^{\infty}(\underline{\underline{M}} - \bar{\underline{\underline{M}}}) \cdot \underline{F} \quad , \tag{6.21}$$

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

$$\bar{\underline{\underline{M}}} = W^{-1}\int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \exp(-\hat{E})\,\underline{\underline{M}} \quad . \tag{6.22}$$

The decomposition

$$\underline{B}(\underset{\sim}{r}_1) \overset{def.}{=} -\underset{\sim}{r}_1/2 + \underline{B}'(\underset{\sim}{r}_1) \tag{6.23}$$

together with the definition

$$\underline{\underline{d}} \overset{def.}{=} 2(\underline{\underline{D}}_{00} - \underline{\underline{D}}_{10}) \tag{6.24}$$

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

$$-\nabla_{\underset{\sim}{r}_1} \cdot (P_0^{\infty}\underline{\underline{d}} \cdot \nabla_{\underset{\sim}{r}_1}\underline{B}') = P_0^{\infty}(\underline{\underline{M}} - \bar{\underline{\underline{M}}}) \cdot \underline{F} \quad . \tag{6.25}$$

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

$$-P_0^{\infty}\underset{\sim}{n}\cdot\underset{\approx}{d}\cdot\underset{\sim}{\nabla}_{\underset{\sim}{r}_1}\underset{\sim}{B}' = \underset{\sim}{0} \quad \text{on } \partial\tau_{\underset{\sim}{r}_1} \quad , \tag{6.26}$$

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

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

$$\underset{\approx}{d} = d_{\parallel}\underset{\sim}{e}\underset{\sim}{e} + d_{\perp}(\underset{\approx}{I} - \underset{\sim}{e}\underset{\sim}{e}) \quad , \tag{6.27}$$

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

$$d_{\parallel} = \frac{kT}{3\pi\mu a}\,(x^a_{11} - x^a_{12}) \quad , \tag{6.28a}$$

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

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

$$\underset{\sim}{B}'(\underset{\sim}{r}_1) = \underset{\approx}{b}(\underset{\sim}{r}_1)\cdot\underset{\sim}{F} \quad , \tag{6.29}$$

(to which definition of $\underset{\approx}{b}$ 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 $\underset{\sim}{F}$ from both sides of the resulting equation, yields

$$\underset{\sim}{\nabla}_{\underset{\sim}{r}_1}\cdot(P_0^{\infty}\underset{\approx}{d}\cdot\underset{\sim}{\nabla}_{\underset{\sim}{r}_1}\underset{\approx}{b}) = P_0^{\infty}(\overline{\underset{\approx}{M}} - \underset{\approx}{M}) \quad . \tag{6.30}$$

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

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

$$d\underset{\sim}{r}_1 = r^2 dr\, d^2\underset{\sim}{e} \quad , \tag{6.31}$$

with $d^2\underset{\sim}{e}$ ($\equiv \sin\Theta d\Theta d\phi$) 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

$$W = \int_{r=0}^{\infty} r^2 dr \oint_{S_1} d^2\underset{\sim}{e}\, \exp[-\hat{E}(r)] = 4\pi\omega \quad , \tag{6.31a}$$

with

$$\omega \equiv \int_{r=0}^{\infty} dr\, r^2\, \exp(-\hat{E}) \quad , \tag{6.31b}$$

since

$$\oint_{S_1} d^2\underset{\sim}{e} = 4\pi \quad . \tag{6.32}$$

Furthermore, upon substitution of (6.31a) and (6.16) into (6.22), we find after performing the resulting S_1 integration that the dyadic $\underset{\approx}{\bar{M}}$ adopts the isotropic form

$$\underset{\approx}{\bar{M}} = \underset{\approx}{I}\, \bar{M} \quad , \tag{6.33a}$$

with

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

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

$$(4\pi)^{-1}\oint_{S_1} d^2\underset{\sim}{e}\ \underset{\sim}{e}\underset{\sim}{e} = \frac{1}{3}\ \underset{\approx}{I} \quad . \tag{6.34}$$

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

$$\underset{\approx}{\bar{M}} - \underset{\approx}{M} = \left[\ \bar{M} - \frac{1}{3}\ (M_{\parallel} + 2M_{\perp})\right]\underset{\approx}{I} - \frac{2}{3}\ (M_{\parallel} - M_{\perp})\underset{\approx}{P}_2(\underset{\sim}{e}) \quad , \tag{6.35}$$

with the dyadic

$$\underset{\approx}{P}_2(\underset{\sim}{e}) = \frac{1}{2}(3\underset{\sim}{e}\underset{\sim}{e} - \underset{\approx}{I}) \tag{6.36a}$$

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

$$\nabla_e^2\ \underset{\approx}{P}_2(\underset{\sim}{e}) = -6\ \underset{\approx}{P}_2(\underset{\sim}{e}) \quad , \tag{6.36b}$$

in which $\underset{\sim}{\nabla}_e$ is the gradient operator on S_1 (Brenner & Condiff 1972, Brenner 1979), being related to $\underset{\sim}{\nabla}_{r_1}$ via the expression

$$\underset{\sim}{\nabla}_{r_1} = \frac{1}{r}\ \underset{\sim}{\nabla}_e + \underset{\sim}{e}\ \frac{\partial}{\partial r} \quad . \tag{6.37}$$

Introduction of (6.35) into (6.30) yields

$$\underset{\sim}{\nabla}_{r_1}\cdot(e^{-\hat{E}}\underset{\approx}{d} \cdot \underset{\sim}{\nabla}_{r_1}\underset{\approx}{b}) = e^{-\hat{E}}\left[\ \underset{\approx}{\bar{M}} - \frac{1}{3}\ (M_{\parallel} + 2M_{\perp})\right]\underset{\approx}{I} - \frac{2}{3}\ e^{-\hat{E}}(M_{\parallel} - M_{\perp})\underset{\approx}{P}_2(\underset{\sim}{e}) \quad . \tag{6.35}$$

The form of the forcing term on the RHS of the preceding equation suggests a trial solution of the form

$$\underset{\approx}{b}(\underset{\sim}{r}_1) = f(r)\ \underset{\approx}{I} + g(r)\ \underset{\approx}{P}_2(\underset{\sim}{e}) \quad . \tag{6.36}$$

Substitute (6.36) into governing equation (6.35) and employ the identities (Brenner & Condiff 1972)

$$\underset{\sim}{e} \cdot \underset{\sim}{\nabla}_e = 0 \quad , \tag{6.37a}$$

$$\underset{\sim}{\nabla}_e\underset{\sim}{e} = \underset{\approx}{I} - \underset{\sim}{e}\underset{\sim}{e} \quad , \tag{6.37b}$$

$$\underset{\sim}{\nabla}_e \cdot \underset{\sim}{e} = 2 \quad , \tag{6.37c}$$

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

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 e^{-\hat{E}} d_{\parallel}\frac{df}{dr}\right) = e^{-\hat{E}}\left[\bar{M} - \frac{1}{3}(M_{\parallel} + 2M_{\perp})\right] \quad , \tag{6.38a}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 e^{-\hat{E}} d_{\parallel}\frac{dg}{dr}\right) - \frac{6}{r^2} e^{-\hat{E}} d_{\perp} g = -\frac{2}{3} e^{-\hat{E}}(M_{\parallel} - M_{\perp}) \quad , \tag{6.39a}$$

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 $2a \le r \le L$ (outside of which P_0^{∞} vanishes) in the course of solving these equations. Boundary condition (6.26) can then be shown to require that

$$d_{\parallel} df/dr = 0 \qquad \text{at } r=2a,\ L \ , \tag{6.38b}$$

$$d_{\parallel} dg/dr = 0 \qquad \text{at } r=2a,\ L \ . \tag{6.39b}$$

Equations (6.38) and (6.39) are simple ODE's, 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 $\underset{\sim}{B}$-field will be fully known, adopting the form [cf. (6.23), (6.36)]

$$\underset{\sim}{B}(\underset{\sim}{r}_1) = -\underset{\sim}{r}_1/2 + [f(r)\ \underset{\approx}{I} + g(r)\ \underset{\approx}{P}_2(\underset{\sim}{e})] \cdot \underset{\approx}{F} \quad . \tag{6.40}$$

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

$$\overline{\underset{\approx}{D}}^{*} = W^{-1}\int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1\ e^{-\hat{E}}\{[\underset{\approx}{D}_{00} - (\underset{\approx}{D}_{10} - \underset{\approx}{D}_{00}) \cdot \nabla_{\underset{\sim}{r}_1}\underset{\sim}{B}] + (\underset{\approx}{M} - \bar{\underset{\approx}{M}}) \cdot \underset{\approx}{F}\underset{\sim}{B}\} \quad . \tag{6.41}$$

The contribution of the $-\underset{\sim}{r}_1/2$ term appearing in (6.40) to the value of (6.41) arises solely from the square-bracketed term in the integrand of the

latter, this contribution being identical to the so-called molecular portion (6.19) of the dispersivity. The contribution from the remaining part of the integrand in (6.41) vanishes in consequence of the polyadic integral identities

$$\frac{1}{(4\pi)} \oint_{S_1} d^2\underset{\sim}{e}\ \underset{\sim}{e}\ldots\underset{\sim}{e}\underset{\sim}{e} = \underset{\sim}{0} \quad , \tag{6.42}$$

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

On the other hand, the remaining term of (6.40) contributes to the dispersivity only as a consequence of the last term within the curly brackets in (6.41), this being the so-called 'convective' contribution $\overline{\underset{\approx}{D}}^{C}$ to the dispersivity. Thus, the total dispersivity of the sedimenting dumbbell becomes

$$\overline{\underset{\approx}{D}}^{*} = \overline{\underset{\approx}{D}}^{M} + \overline{\underset{\approx}{D}}^{C} \quad , \tag{6.43}$$

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

$$\overline{\underset{\approx}{D}}^{M} = \overline{D}^{M}\underset{\approx}{I} = kT\overline{M}\ \underset{\approx}{I} \quad , \tag{6.44}$$

while the convective contribution is given by

$$\overline{\underset{\approx}{D}}^{C} = \underset{\sim}{F} \cdot \Big[W^{-1}\int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1\ e^{-\hat{E}}(\underset{\approx}{M} - \overline{\underset{\approx}{M}})(f\underset{\approx}{I} + g\underset{\approx}{P}_2)\Big] \cdot \underset{\sim}{F} \quad . \tag{6.45}$$

Substitute (6.35) into (6.45) and use the dyadic spherical orthogonality condition

$$\frac{1}{4\pi} \oint_{S_1} d^2\underset{\sim}{e}\ \underset{\approx}{P}_2(\underset{\sim}{e}) = \underset{\approx}{0} \tag{6.46}$$

[since $P_0(\underset{\sim}{e}) = 1$], to obtain

$$\overline{\underset{\approx}{D}}^{C} = \alpha\underset{\sim}{F}\underset{\sim}{F} + \beta\underset{\sim}{F} \cdot \underset{\approx\approx}{T} \cdot \underset{\sim}{F} \quad . \tag{6.47}$$

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

$$\underset{\approx\approx\approx}{T} \equiv \frac{1}{4\pi} \oint_{S_1} d^2\underset{\sim}{e}\ \underset{\approx\approx}{P}_2(\underset{\sim}{e})\ \underset{\approx\approx}{P}_2(\underset{\sim}{e}) \quad , \tag{6.48}$$

whereas the dimensional scalar constants α and β are given by

$$\alpha = -\frac{1}{\omega}\int_0^\infty dr\ r^2\ e^{-\hat{E}}[\overline{M} - \frac{1}{3}(M_\parallel + 2M_\perp)]f(r) \quad , \tag{6.49}$$

$$\beta = \frac{2}{3\omega}\int_0^\infty dr\ r^2\ e^{-\hat{E}}(M_\parallel - M_\perp)g(r) \quad . \tag{6.50}$$

Expression (6.49) for α may be written in a more convenient form upon multiplying both sides of (6.38) by $r^2 f$ and integrating by parts; this eventually yields

$$\alpha = \frac{1}{\omega}\int_0^\infty dr\ r^2\ e^{-\hat{E}}\ d_\parallel (df/dr)^2 \quad . \tag{6.51}$$

The tetradic $\underset{\approx\approx\approx}{T}$ integral (6.48) can be evaluated explicitly (Brenner 1979, Haber & Brenner 1984), yielding the explicit Cartesian tensor form

$$T_{ijkl} = (1/20)[3(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 2\delta_{ij}\delta_{kl}] \quad . \tag{6.52}$$

Consequently,

$$\underset{\sim}{F} \cdot \underset{\approx\approx\approx}{T} \cdot \underset{\sim}{F} = (F^2/20)\ [4\ \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}} + 3(\underset{\approx}{I} - \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}})] \quad , \tag{6.53}$$

in which $F = |\underset{\sim}{F}|$ and

$$\hat{\underset{\sim}{F}} = \underset{\sim}{F}/F \tag{6.54}$$

is a unit vector in the direction of $\underset{\sim}{F}$. Finally, substitute (6.53) into (6.47) and add the resulting expression to (6.44) to obtain the transversely isotropic dispersivity dyadic

$$\overline{\underset{\approx}{D}}^* = \overline{D}_\parallel^*\ \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}} + \overline{D}_\perp^*(\underset{\approx}{I} - \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}}) \quad , \tag{6.55a}$$

wherein

$$\overline{D}_\parallel^* = \overline{D}^M + (\alpha + \beta/5)F^2 \quad , \tag{6.55b}$$

$$\hat{\bar{M}}(\chi) = (3\hat{\omega})^{-1}\int_2^{\chi} ds\ s^2[\hat{M}_{\parallel} + 2\hat{M}_{\perp}] \quad , \tag{6.58a}$$

wherein

$$\hat{M}_{\parallel}(s) = M_{\parallel}/M_{\infty} = x_{I1}^{a} + x_{I2}^{a} \quad , \tag{6.58b}$$

$$\hat{M}_{\perp}(s) = M_{\perp}/M_{\infty} = y_{I1}^{a} + y_{I2}^{a} \quad , \tag{6.58c}$$

and

$$\hat{\omega}(\chi) = \int_2^{\chi} ds\ s^2 = \frac{1}{3}\ (\chi^3 - 8) \quad . \tag{6.59}$$

In the above,

$$\chi \equiv L/a \qquad (\chi \geq 2) \tag{6.60}$$

and

$$s = r/a \qquad (2 \leq s \leq \chi) \quad . \tag{6.61}$$

Define the additional nondimensional functions

$$\hat{d}_{\parallel}(s) = d_{\parallel}/D_{\infty} = 4(x_{I1}^{a} + x_{I2}^{a}) \quad , \tag{6.62a}$$

$$\hat{d}_{\perp}(s) = d_{\perp}/D_{\infty} = 4(y_{I1}^{a} + y_{I2}^{a}) \quad . \tag{6.62b}$$

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

$$\hat{f}(s) = kTf/a^2 \quad , \tag{6.63a}$$

$$\hat{g}(s) = kTg/a^2 \quad , \tag{6.63b}$$

eqs. (6.38a) and (6.39a) respectively become

$$\frac{1}{s^2}\frac{d}{ds}\left(s^2\hat{d}_{\parallel}\frac{d\hat{f}}{ds}\right) = \hat{\bar{M}} - \frac{1}{3}(\hat{M}_{\parallel} + 2\hat{M}_{\perp}) \quad , \tag{6.64a}$$

$$\frac{1}{s^2}\frac{d}{ds}\left(s^2\hat{d}_{\parallel}\frac{d\hat{g}}{ds}\right) - \frac{6}{s^2}\hat{d}_{\perp}\hat{g} = -\frac{2}{3}(\hat{M}_{\parallel} - \hat{M}_{\perp}) \quad . \tag{6.65a}$$

These are to be solved in the region $2<s<\chi$ subject to the no-flux conditions [cf. (6.38b), (6.39b)]

$$\hat{d}_{\parallel}d\hat{f}/ds = 0 \qquad \text{at} \qquad s=2,\chi, \tag{6.64b}$$

$$\hat{d}_{\parallel}d\hat{g}/ds = 0 \qquad \text{at} \qquad s=2,\chi. \tag{6.65b}$$

Equations (6.64a,b) possess the first integral

$$\frac{d\hat{f}(s)}{ds} = [s^2\hat{d}_{\parallel}(s)]^{-1} \int_2^s ds'\, s'^2 \{ \hat{\bar{M}} - \tfrac{1}{3}[\hat{M}_{\parallel}(s') + 2\hat{M}_{\perp}(s')]\} \quad . \tag{6.66}$$

Define the nondimensional Langevin parameter

$$\gamma = Fa/kT \quad , \tag{6.67}$$

embodying the ratio of gravitational to thermal energies of the dumbbell, to obtain

$$\alpha F^2/D_\infty = \gamma^2\hat{\alpha} \tag{6.68}$$

and

$$\beta F^2/D_\infty = \gamma^2\hat{\beta} \tag{6.69}$$

wherein

$$\hat{\alpha}(\chi) = \frac{1}{\hat{\omega}} \int_2^{\chi} ds\, s^2\, \hat{d}_{\parallel}(d\hat{f}/ds)^2 \quad , \tag{6.70}$$

and

$$\hat{\beta}(\chi) = \frac{2}{3\hat{\omega}} \int_2^{\chi} ds\, s^2(\hat{M}_{\parallel} - \hat{M}_{\perp})\hat{g} \quad . \tag{6.80}$$

Thus, the dimensionless total dumbbell dispersivity dyadic is given by [cf. (6.55a,b,c)]

$$\underset{\sim}{\bar{\bar{D}}}^*/D_\infty = (\bar{\bar{D}}_{\parallel}^*/D_\infty)\hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}} + (\bar{\bar{D}}_{\perp}^*/D_\infty)(\underset{\sim}{I} - \hat{\underset{\sim}{F}}\hat{\underset{\sim}{F}}) \quad , \tag{6.81a}$$

in which

$$\bar{\bar{D}}_{\parallel}^*/D_\infty = \hat{\bar{M}} + \gamma^2(\hat{\alpha} + \hat{\beta}/5) \tag{6.81b}$$

and

$$\bar{\bar{D}}_{\perp}^*/D_\infty = \hat{\bar{M}} + \gamma^2(3\hat{\beta}/20) \quad . \tag{6.81c}$$

Moreover, the dimensionless mean dumbbell velocity vector is

$$\underset{\sim}{\bar{U}}^*/(M_\infty F) = \hat{\bar{M}}\,\hat{\underset{\sim}{F}} \quad . \tag{6.82}$$

The three scalar constants $\hat{\bar{M}}$, $\hat{\alpha}$ 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 Figs. 2 to 4. The requisite input mobility data for the calculations were principally those of Jeffrey & Onishi (1984). For $s \leq 2.015$ and $s \geq 4.0$, 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 (Abramowitz & Stegun 1972). The ordinary differential equation (6.65) was solved via a finite difference scheme (Hornbeck 1975).

Figures 2a and 2b furnish $\hat{\bar{M}}$ vs χ. For touching spheres (χ=2), $\hat{\bar{M}}$ 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 χ=2, undergoes a rapid initial increase for increasing values of χ, and finally attains an asymptotic value of 1/160. Figures 4a and 4b show the dependence of $\hat{\beta}$ upon χ. For touching spheres, $\beta = 5.33 \times 10^{-3}$, decreasing rapidly to a minimum at $\chi \approx 2.09$, generally increasing thereafter to an eventual asymptotic limit of 1/96. (The pair of limiting χ=2,∞ results cited above were not part of the numerical calculations; rather, they were analytically calculated by appropriate asymptotic schemes.) The extreme χ-dependent behavior of $\hat{\bar{M}}$ and $\hat{\beta}$ near χ=2 is a manifestation of the singular behavior of the mobility functions (Jeffrey & Onishi 1984) for touching spheres. That $\hat{\alpha}$ and $\hat{\beta}$ attain constant nonzero limiting values as $\chi \to \infty$ indicates that, even with no potential interactions other than hard-sphere

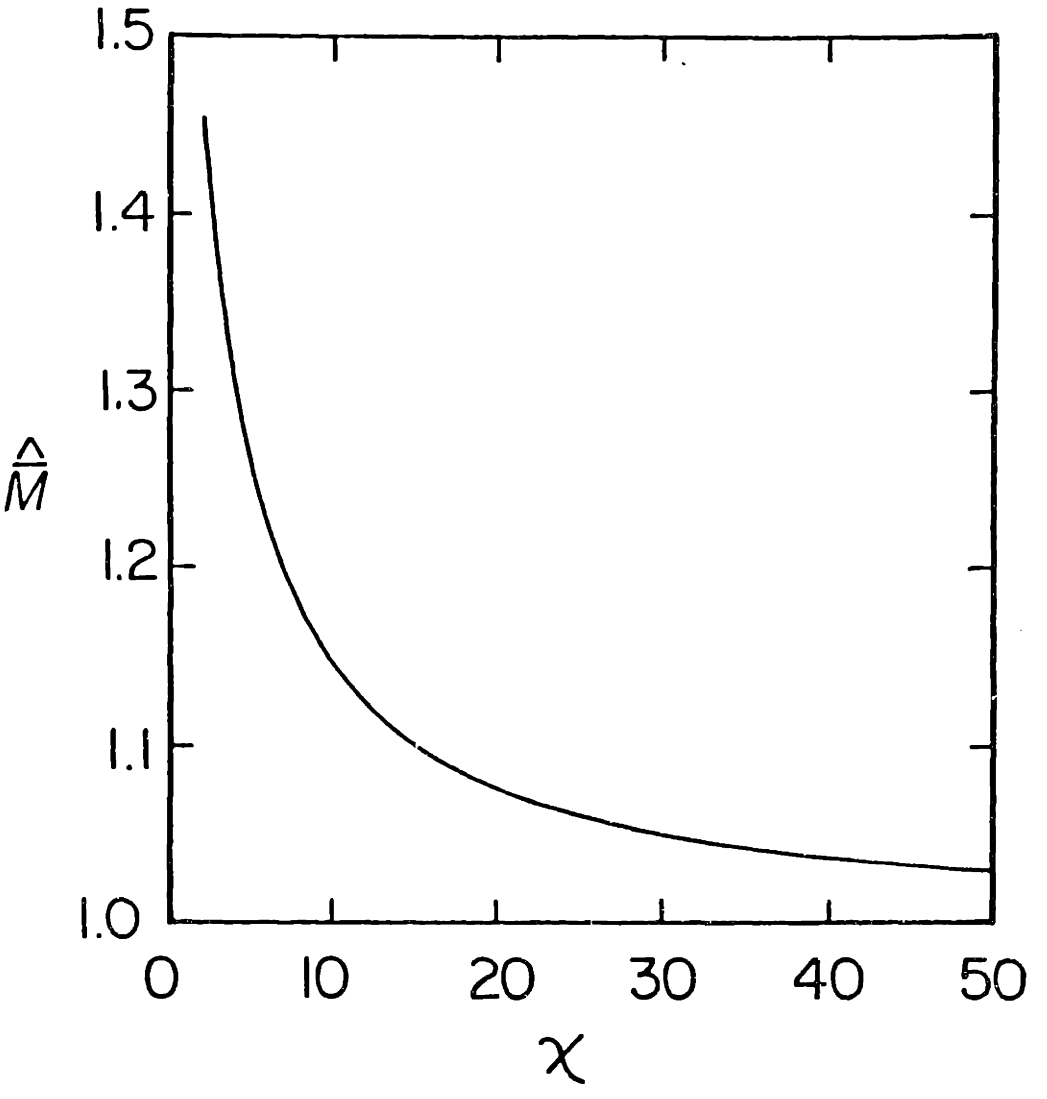

Fig. 2. (a) Mean nondimensional mobility $\hat{\bar{M}}$ vs nondimensional tether length χ.

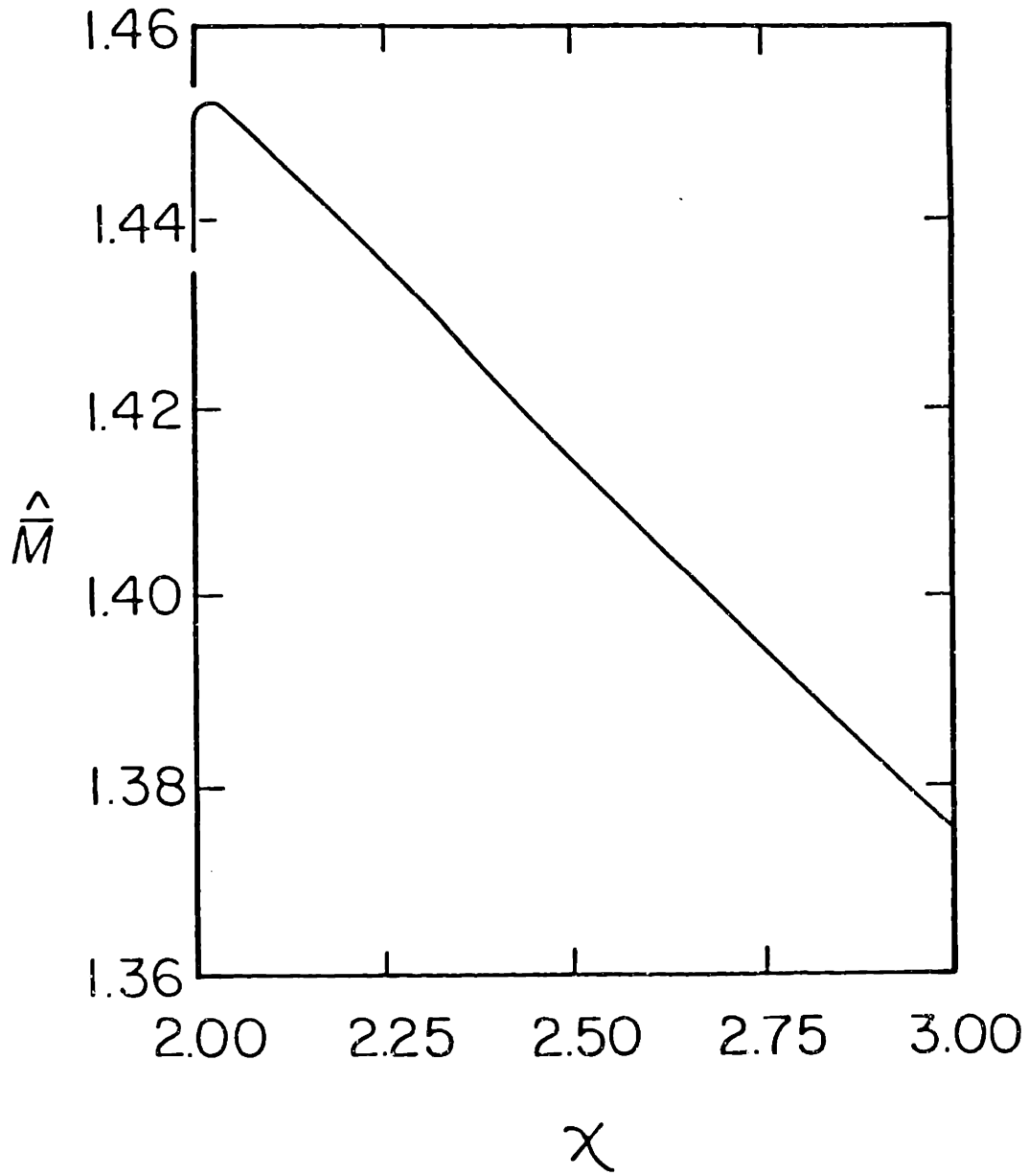

Fig. 2. (b) Enlargement of the near-touching range $2 \leq \chi \leq 3$.

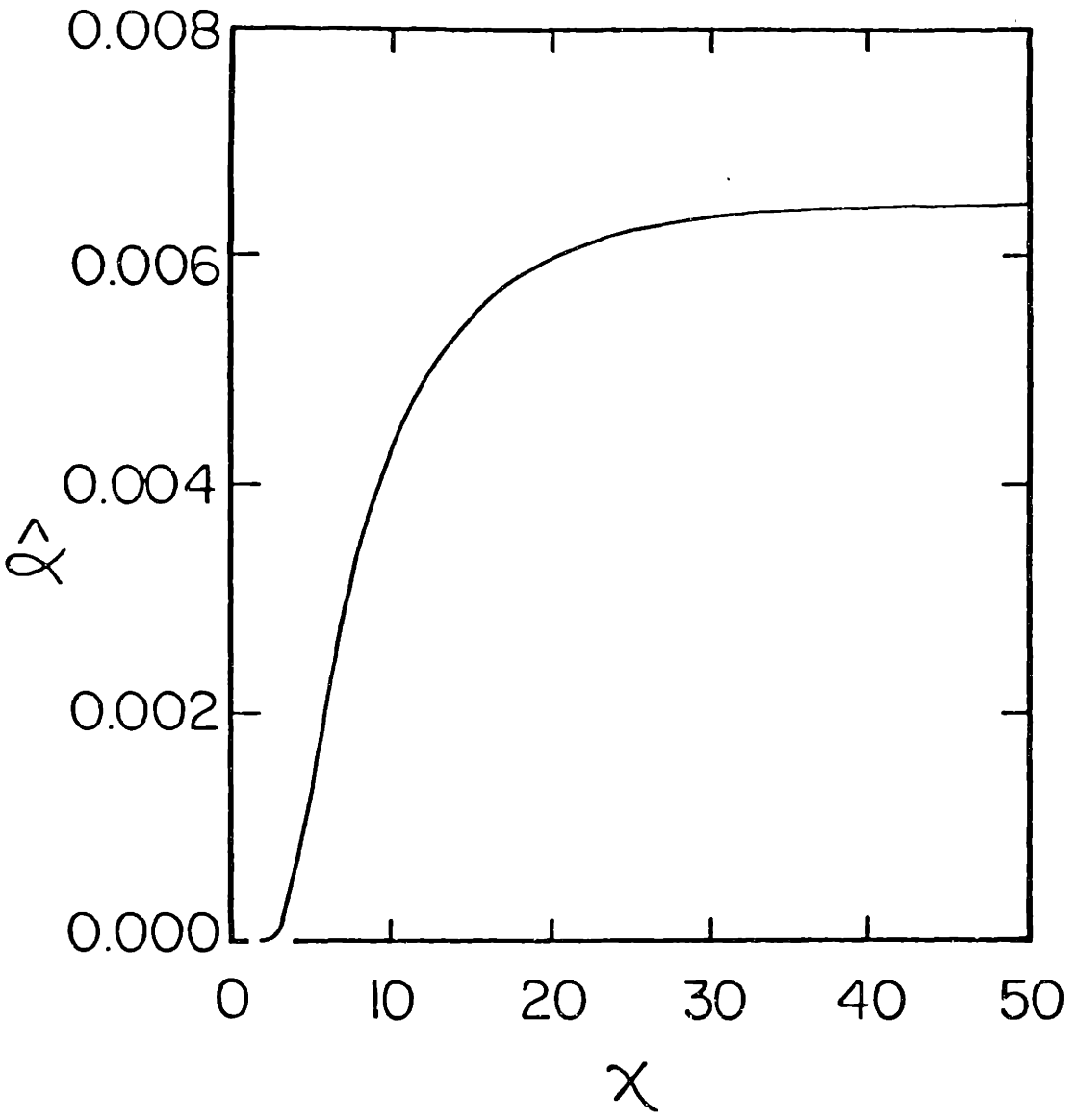

Fig. 3 Taylor dispersivity coefficient $\hat{\alpha}$ vs nondimensional tether length χ.

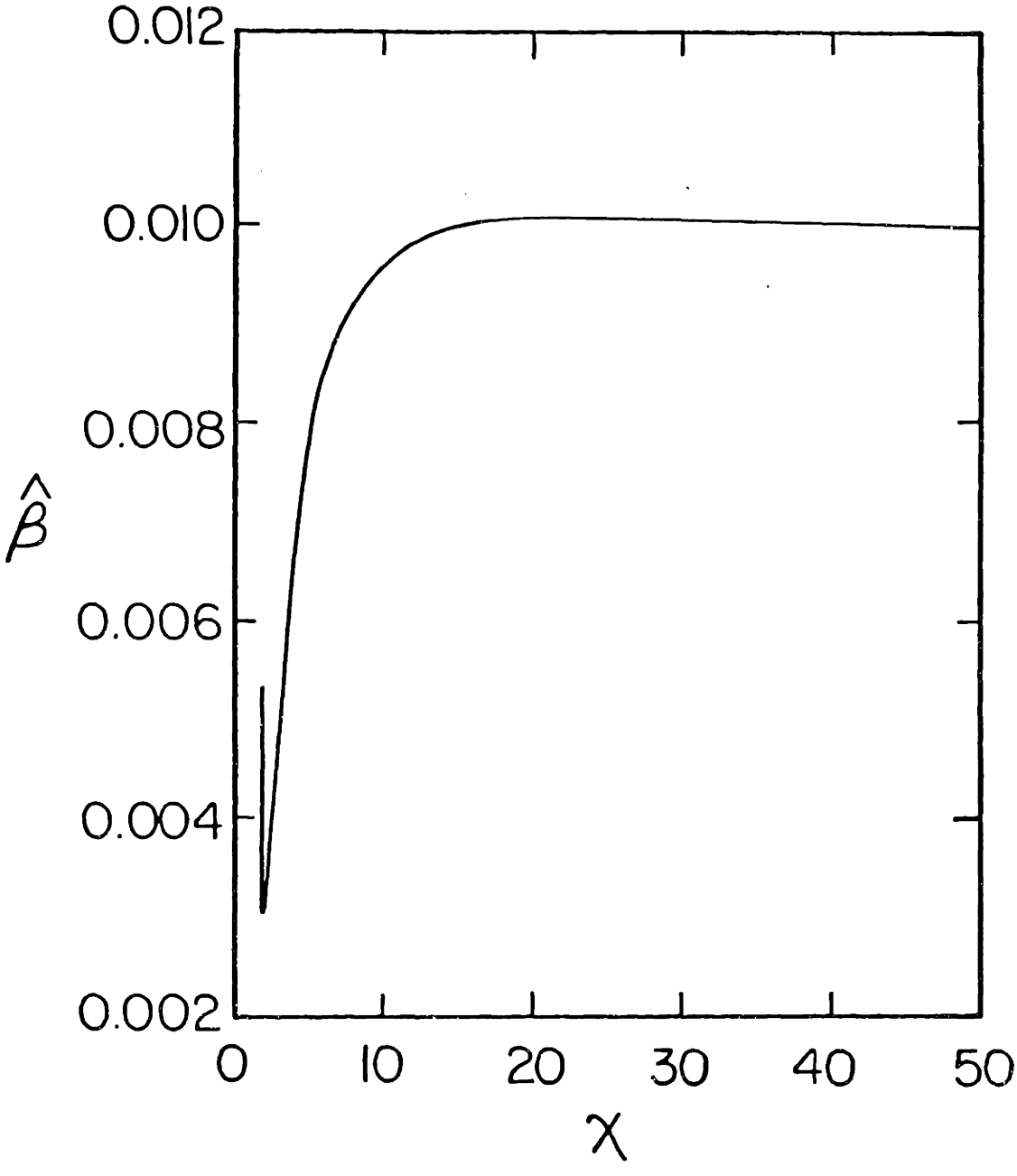

Fig. 4. (a) Taylor dispersivity coefficient $\hat{\beta}$ vs nondimensional tether length χ.

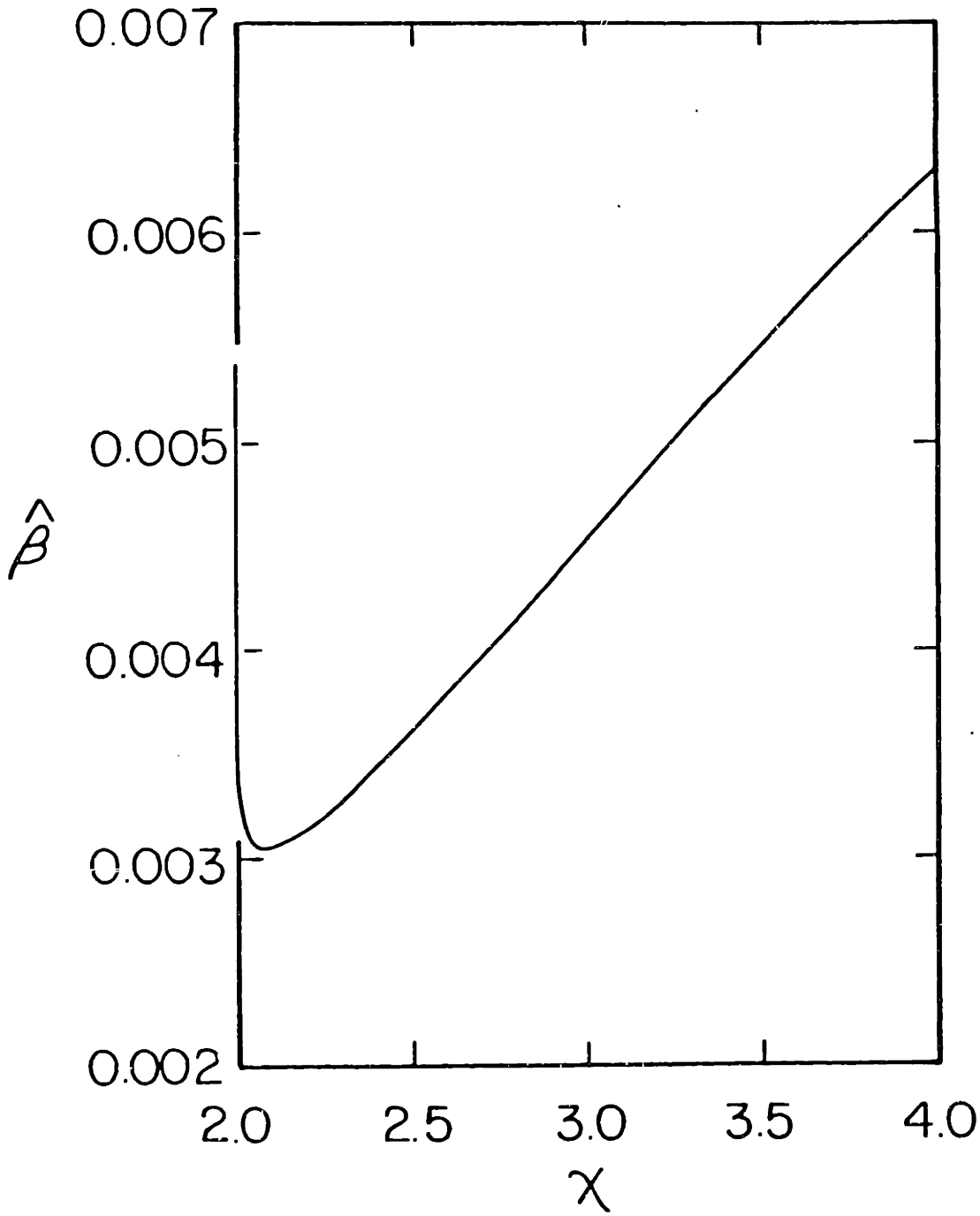

Fig. 4. (b) Enlargement of the near-touching range $2 \leq \chi \leq 4$.

repulsion (e.g., no tether or spring), the effect of the second sphere upon the dispersivity of a sedimenting dumbbell 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 DUMBBELL IN A GRAVITY FIELD

As a second application we consider the tethered dumbbell discussed in the previous section for circumstances wherein the dumbbell is neutrally buoyant as a whole, while -- of the two individually homogeneous spheres comprising the dumbbell -- 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 $\underset{\sim}{F} = \underset{\sim}{0}$, the dumbbell 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 center 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' dumbbell.

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

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

whence the total dumbbell potential here takes the form

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

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

$$\bar{\underset{\sim}{U}}^{*} = \underset{\sim}{0} \quad , \tag{7.3}$$

confirming the absence of sedimentation of the dumbbell as a whole.

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

$$P_0^{\infty}(\underset{\sim}{r}_1) = e^{-E(\underset{\sim}{r}_1)/W} \quad , \tag{7.4a}$$

$$W = \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \; e^{-E(\underset{\sim}{r}_1)} \quad , \tag{7.4b}$$

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

$$\bar{\underset{\approx}{D}}^{M} = W^{-1} \int_{\tau_{\underset{\sim}{r}_1}} d\underset{\sim}{r}_1 \; \exp(-E) \; \underset{\approx}{D} \tag{7.5}$$

of the loaded dumbbell, in which the configuration-specific molecular diffusivity $\underset{\approx}{D}$ is identical to that defined in (6.20). Explicit evaluation of (7.5) requires use of the identities

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

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

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

Upon noting that [cf. (6.16), (6.18), (6.20), (6.58b,c)]

$$\underset{\approx}{D}/D_{\infty} = \underset{\sim}{e}\underset{\sim}{e} \; \hat{M}_{\parallel} + (\underset{\approx}{I} - \underset{\sim}{e}\underset{\sim}{e}) \; \hat{M}_{\perp} \quad , \tag{7.7}$$

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

$$\lambda \equiv |\Delta m| g a / kT \quad , \tag{7.8}$$

the identities (7.6a,b) may be used to obtain the dimensionless form of (7.5) [with D_∞ given by (6.56b)] as

$$\begin{aligned} \overline{\overline{\mathcal{D}}}^{M}/D_\infty &= \underline{\underline{I}}\, A + \hat{g}\hat{g}\, B \\ &\equiv (\underline{\underline{I}} - \hat{g}\hat{g})\, A + \hat{g}\hat{g}\, (A + B) \quad , \end{aligned} \tag{7.9}$$

with components A and B respectively given by

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

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

wherein

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

Dimensionless scalars A and B depend functionally only upon the nondimensional parameters χ and λ, the latter being the Langevin parameter (7.8) measuring the ratio of the orienting gravitational potential energy $|\Delta m| g a$ to the disorienting thermal energy kT, while the former is defined in (6.60). Analogously to the calculations of the preceding section, the evaluation of (7.10a,b,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 dumbbell dipole parallel to the gravitational field) the quadratures can be performed analytically, leading to the following asymptotic limiting values:

$$A \simeq \hat{M}_\perp(\chi) + O(\chi\lambda)^{-2} \quad , \tag{7.11a}$$

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

valid when $\chi\lambda >> 1$. 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

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

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

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 to the function $\hat{\bar{M}}$ 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).

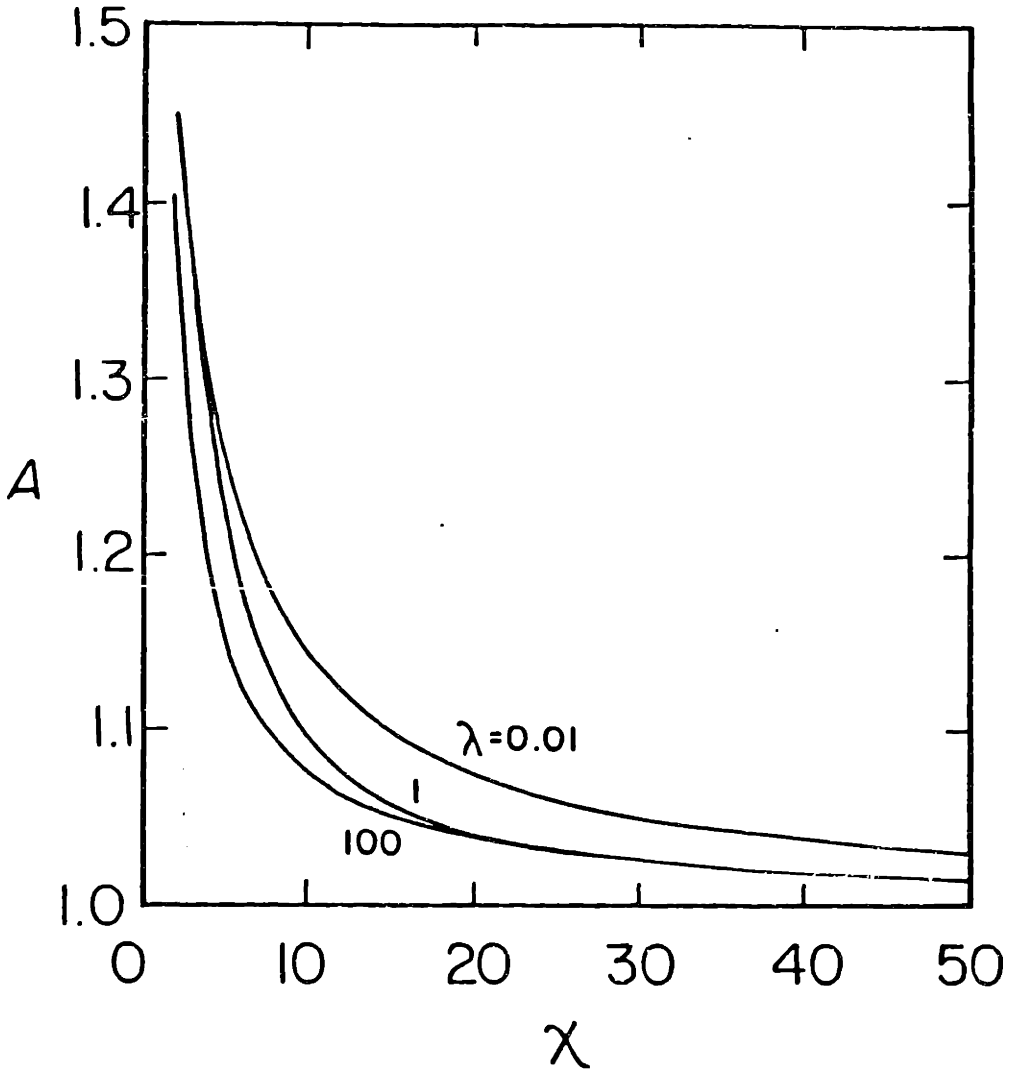

Fig. 5. Isotropic Taylor dispersion coefficient A vs nondimensional tether length χ at various Langevin parameters λ for the loaded dumbbell.

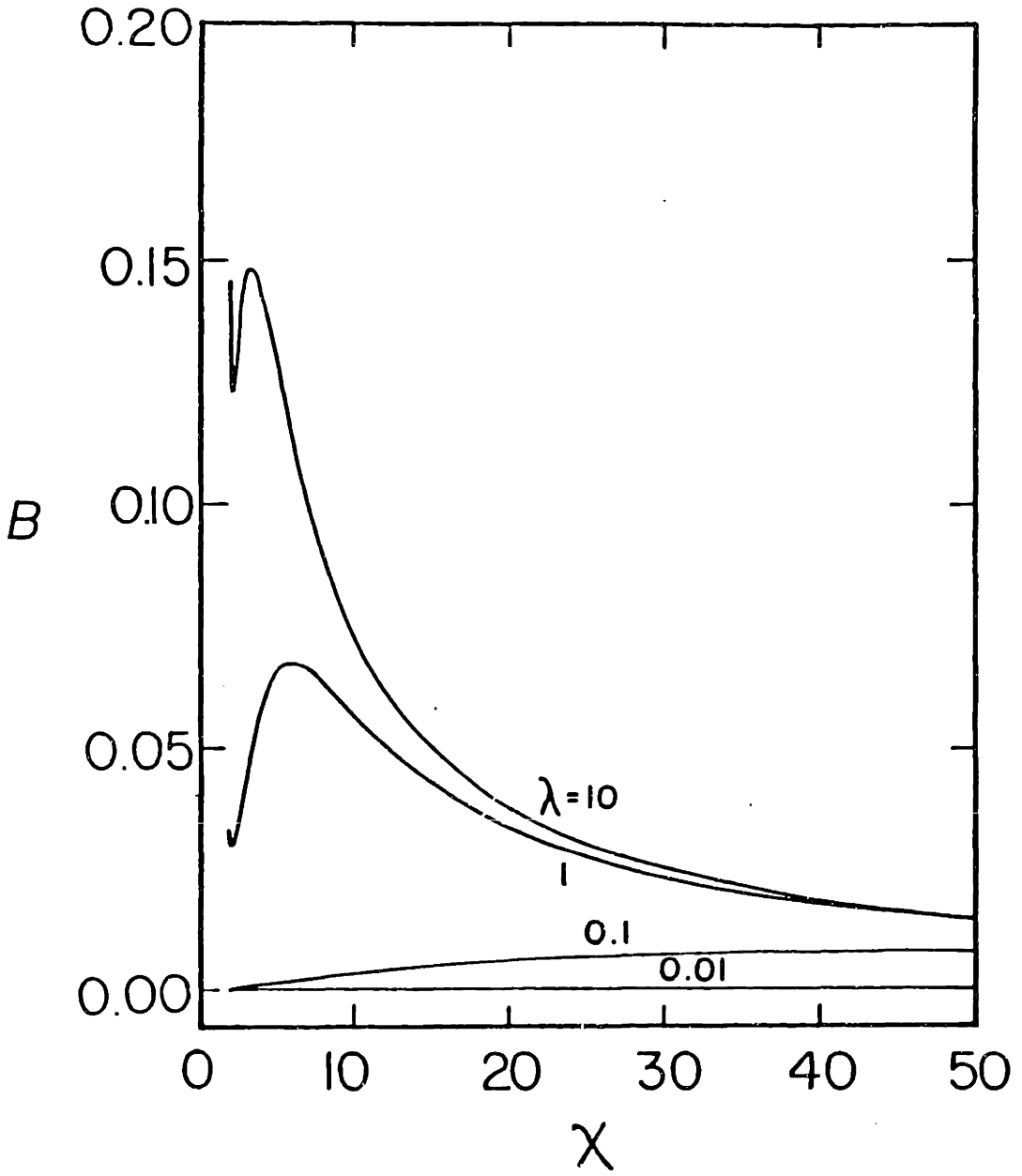

Fig. 6 Anisotropic Taylor dispersion coefficient B vs nondimensional tether length χ at various Langevin parameters λ for the loaded dumbbell.

8. DISCUSSION

Invariance of $\overset{*}{\underset{\sim}{U}}$ and $\overset{*}{\underset{\approx}{D}}$ with respect to choice of chain-fixed locator point

The foregoing analysis implicitly assumed that any point rigidly affixed to any one of the constituent particles could serve equally well to localize the flexible chain in physical space, and that the physical results thereby obtained are necessarily independent of the explicit choice made. Thus, the locator point O_0 rigidly attached to the zeroth particle was arbitrarily selected as the point externally locating the chain in space, while the relative position vectors of the remaining particles -- as well as each of their orientational-coordinate triplets -- were considered to be local variables, describing the internal conformation of this chain. Here, we shall formally prove the validity of this invariance conjecture by showing that the choice of another locator point -- attached to any of the other constituent particles (or indeed a more mobile general point, such as the center of mass or volume of the chain) -- leads to results identical to those derived previously. The quintessential substance of the proof lies in the fact that, being an absolute (true) scalar (cf. Section 2), the conditional probability density P is necessarily independent of the particular coordinate parameterization chosen for the global/local subspace decomposition.

Suppose, therefore, that rather than choosing the position vector $\underset{\sim}{R}_0$ of the locator point O_0 in (4.1) at which to localize the cluster or chain in physical space, the position vector $\underset{\sim}{R}_G$ of an arbitrary point G had instead been chosen. Point G may be rigidly affixed to one of the other

constituent particles, or indeed may be a more general point, such as the center of mass or volume of all or any portion of the chain, or its center of reaction or diffusion, etc. Let such an alternative parameterization of the global space be designated by the operational symbol $\underset{\sim}{X}$, as in

$$\underset{\sim}{X} \equiv \underset{\sim}{R}_G \quad , \tag{8.1}$$

in order to distinguish it from $\underset{\sim}{Q}$ in (4.1). Suppose further that the corresponding new (symbolic, i.e., nonoperational) parameterization $\underset{\sim}{x}$ of the local space is chosen to be identical with (4.3), so that

$$\underset{\sim}{x} = \underset{\sim}{q} \quad . \tag{8.2}$$

Define new global- and local-space gradient operators as usual via the respective relations

$$\underset{\sim}{\nabla}_X \equiv (\partial/\partial \underset{\sim}{X})_{\underset{\sim}{x}} \quad , \tag{8.3a}$$

$$\underset{\sim}{\nabla}_x \equiv (\partial/\partial \underset{\sim}{x})_{\underset{\sim}{X}} \quad . \tag{8.3b}$$

Observe that the symbolic notation of Section 2 is being employed here for notational simplicity; conversion to either of the functional (tensorial or hybrid partitioned matrix) forms is trivial.

Our invariance proof hinges upon the fact that the position vectors $\underset{\sim}{R}_0$ and $\underset{\sim}{R}_G$ are related by the expression

$$\underset{\sim}{R}_G - \underset{\sim}{R}_0 = {}^0\underset{\sim}{r}_G(\underset{\sim}{q}) \quad , \tag{8.4}$$

in which the displacement vector ${}^0\underset{\sim}{r}_G$ of G relative to O_0 is functionally dependent only upon the internal coordinates $\underset{\sim}{q}$; that is, in order to relate two arbitrary points, either of which may serve equally as chain locator points, only the internal configuration of the chain need be specified, not

its external physical-space location. As such, $\underset{\sim}{X}$ and $\underset{\sim}{Q}$ are related quite generally by

$$\underset{\sim}{X} = \underset{\sim}{Q} + \underset{\sim}{H}(\underset{\sim}{q}) \quad , \tag{8.5}$$

with $\underset{\sim}{H}$ a global-space vector, functionally dependent only upon the local coordinates $\underset{\sim}{q}$. Equation (8.5) allows derivation of the operator relations[6]

$$\underset{\sim}{\nabla}_Q = \underset{\sim}{\nabla}_X \quad , \tag{8.6a}$$

$$\underset{\sim}{\nabla}_q = \underset{\sim}{\nabla}_x + \underset{\approx}{\Delta}^{qQ} \cdot \underset{\sim}{\nabla}_X = \underset{\sim}{\nabla}_x + \underset{\sim}{\nabla}_X \cdot \underset{\approx}{\Delta}^{Qq} \quad , \tag{8.6b}$$

in which

$$\underset{\approx}{\Delta}^{qQ}(\underset{\sim}{q}) = \underset{\approx}{\Delta}^{Qq\dagger}(\underset{\sim}{q}) \overset{\text{def.}}{=} \underset{\sim}{\nabla}_{\underset{\sim}{q}} \underset{\sim}{H}(\underset{\sim}{q}) \quad . \tag{8.7}$$

The governing transport equation expressing conservation of the conditional probability density P -- now considered to have a functional dependence of the form $P(\underset{\sim}{X},\underset{\sim}{x},t|\underset{\sim}{X}',\underset{\sim}{x}')$ -- is obtained by effecting the transformation (8.6) in (2.17') [or (4.16)], yielding

$$\partial P/\partial t + \underset{\sim}{\nabla}_X \cdot \underset{\sim}{J}_G + \underset{\sim}{\nabla}_x \cdot \underset{\sim}{j}_G = \delta(t)\delta(\underset{\sim}{X} - \underset{\sim}{X}')\delta(\underset{\sim}{x} - \underset{\sim}{x}') \quad . \tag{8.8}$$

Here, and in subsequent equations, the subscript G is affixed to dependent variables so as to explicitly differentiate the transformed quantities from their previous affix-free counterparts. The $\underset{\sim}{X}$- and $\underset{\sim}{x}$-space flux density vectors appearing above are respectively related to their $\underset{\sim}{Q}$- and $\underset{\sim}{q}$-space counterparts via the transformations

$$\underset{\sim}{J}_G = \underset{\sim}{J} + \underset{\approx}{\Delta}^{Qq} \cdot \underset{\sim}{j} \quad , \tag{8.9a}$$

$$\underset{\sim}{j}_G = \underset{\sim}{j} \quad . \tag{8.9b}$$

Use of the constitutive relations (2.19') [or (4.18)] and (2.20') [or (4.17)] in (8.9), in conjunction with (8.6), ultimately yields the following explicit constitutive flux expressions:

$$\underset{\sim}{J}_G = \underset{\sim}{U}_G P - \underset{\approx}{D}^{XX} \cdot \underset{\sim}{\nabla}_X P - e^{-E}\, \underset{\approx}{D}^{Xx} \cdot \underset{\sim}{\nabla}_x (e^E P) \quad , \tag{8.10}$$

$$\underset{\sim}{j}_G = \underset{\sim}{u}_G P - \underset{\approx}{D}^{xX} \cdot \underset{\sim}{\nabla}_X P - e^{-E}\, \underset{\approx}{D}^{xx} \cdot \underset{\sim}{\nabla}_x (e^E P) \quad . \tag{8.11}$$

The internal potential $E(\underset{\sim}{x})$ appearing above is identical to its earlier counterpart $E(\underset{\sim}{q})$, whereas the remaining transformed phenomenological coefficients are respectively given by the relations

$$\underset{\sim}{U}_G = \underset{\sim}{U} + \underset{\approx}{A}^{Qq} \cdot \underset{\sim}{u} \quad , \tag{8.12a}$$

$$\underset{\approx}{D}^{XX} = \underset{\approx}{D}^{QQ} + \underset{\approx}{D}^{Qq} \cdot \underset{\approx}{A}^{qQ} + \underset{\approx}{A}^{Qq} \cdot \underset{\approx}{D}^{qQ} + \underset{\approx}{A}^{Qq} \cdot \underset{\approx}{D}^{qq} \cdot \underset{\approx}{A}^{qQ} \quad , \tag{8.12b}$$

$$\underset{\approx}{D}^{Xx} = \underset{\approx}{D}^{xX\dagger} = \underset{\approx}{D}^{Qq} + \underset{\approx}{A}^{Qq} \cdot \underset{\approx}{D}^{qq} \quad , \tag{8.12c,d}$$

$$\underset{\sim}{u}_G = \underset{\sim}{u} \quad , \tag{8.12e}$$

$$\underset{\approx}{D}^{xx} = \underset{\approx}{D}^{qq} \quad . \tag{8.12f}$$

Equation (8.8), together with (8.10) and (8.11), possesses the requisite canonical form of coupled generalized Taylor dispersion theory [albeit the notational change from $(\underset{\sim}{Q}, \underset{\sim}{q})$ to $(\underset{\sim}{X}, \underset{\sim}{x})$]. Hence, subject to appropriate initial and boundary conditions, these equations may themselves be subjected to the entire Taylor dispersion analysis of Section 2, eventually yielding

$$\overline{\underset{\sim}{U}}^{*}_G = \int_{\underset{\sim}{x}_0} d\underset{\sim}{x} [P_0^{\infty}\, \underset{\sim}{U}_G - e^{-E}\, \underset{\approx}{D}^{Xx} \cdot \underset{\sim}{\nabla}_x (e^E P_0^{\infty})] \quad , \tag{8.13}$$

in accordance with (2.38'). A corresponding expression obtains for $\overline{\underset{\approx}{D}}^{*}_G$, analogous to (2.43').

To demonstrate invariance of the mean chain velocity $\overline{\underset{\sim}{U}}^{*}$ under a change in the choice of chain locator point, it must be demonstrated that eq.

(8.13) -- obtained with the arbitrary point G serving as locator point -- yields a result identical to that of its predecessor, (2.38'). Towards that end, note that $P_0^\infty(\underset{\sim}{x})$ appearing in (8.13) satisfies [cf. (2.36')]

$$\underset{\sim}{\nabla}_x \cdot \underset{\sim}{j}_0^\infty = 0 \quad , \tag{8.14a}$$

$$\underset{\sim}{j}_0^\infty = \underset{\sim}{u}_G P_0^\infty - e^{-E} \underset{\approx}{D}^{xx} \cdot \underset{\sim}{\nabla}_x (e^E P_0^\infty) \quad , \tag{8.14b}$$

along with appropriate normalization and zero normal-flux boundary conditions. Therefore, in consequence of identities (8.2), (8.12e) and (8.12f), it is readily proved that

$$P_0^\infty(\underset{\sim}{x}) = P_0^\infty(\underset{\sim}{q}) \quad . \tag{8.15}$$

Substitute (8.12a), (8.12c) and (8.15) into (8.13) and effect the variable change (8.2) to obtain

$$\overrightarrow{\underset{\sim}{U}}_G^* - \overrightarrow{\underset{\sim}{U}}^* = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \underset{\approx}{\Delta}^{Qq} \cdot [\underset{\sim}{u} P_0^\infty - e^{-E} \underset{\approx}{D}^{qq} \cdot \underset{\sim}{\nabla}_q (e^E P_0^\infty)] \quad , \tag{8.16}$$

with $\overrightarrow{\underset{\sim}{U}}^*$ given by (2.38'). The RHS of (8.16) may be rewritten as [cf. (8.14), (8.7)]

$$\int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \underset{\sim}{j}_0^\infty \cdot \underset{\sim}{\nabla}_q \underset{\approx}{H} = \int_{\underset{\sim}{q}_0} d\underset{\sim}{q}\ \underset{\sim}{\nabla}_q \cdot (\underset{\sim}{j}_0^\infty \underset{\approx}{H}) = \int_{\partial \underset{\sim}{q}_0} ds\ \underset{\sim}{n} \cdot \underset{\sim}{j}_0^\infty \underset{\approx}{H} = \underset{\sim}{0} \quad , \tag{8.17}$$

whose vanishing is a consequence of the boundary condition (2.36b'). As a result, (8.16) yields

$$\overrightarrow{\underset{\sim}{U}}_G^* = \overrightarrow{\underset{\sim}{U}}^* \quad , \tag{8.18}$$

thereby demonstrating the required invariance of the mean velocity vector. A comparable invariance proof for the dispersivity dyadic $\overrightarrow{\underset{\approx}{D}}^*$ may be

effected in much the same manner.

Alternative methods exist for establishing these invariance properties. In particular, it is possible to begin from the fundamental Lagrangian asymptotic definitions of $\overline{\underset{\sim}{U}}^{*}$ and $\overline{\underset{\approx}{D}}^{*}$ (Brenner 1982b), namely

$$\overline{\underset{\sim}{U}}^{*}_{G} = \lim_{t\to\infty} \; d\langle \underset{\sim}{R}_G \rangle / dt \quad , \tag{8.19a}$$

$$2\overline{\underset{\approx}{D}}^{*}_{G} = \lim_{t\to\infty} \; d(\langle \underset{\sim}{R}_G \underset{\sim}{R}_G \rangle - \langle \underset{\sim}{R}_G \rangle \langle \underset{\sim}{R}_G \rangle)/dt \quad , \tag{8.19b}$$

wherein

$$\langle \Psi \rangle \overset{\text{def.}}{=} \int_{\underset{\sim}{Q}_\infty} d\underset{\sim}{Q} \int_{\underset{\sim}{q}_0} d\underset{\sim}{q} \; P \; \Psi \tag{8.20}$$

denotes an 'expected' value. This type of origin invariance proof possesses the added advantage of being independent of the specific forms chosen for the constitutive equations obeyed by $\underset{\sim}{J}$ and $\underset{\sim}{j}$.

Size-fluctuation dispersion and pre-averaging 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 pre-averaging 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 nonexistence of any simple rigorous relation which would a priori allow a 'pre-averaged' 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 exami-

ning the merits of pre-averaging approximations. For example, in the case of a rigid homogeneous dumbbell undergoing sedimentation, the term corresponding to f(r) in (6.36) can be shown to be completely absent (cf. Brenner 1979), whence no contribution comparable to $\hat{\alpha}$ in the dispersivity [cf. (6.81b), (6.70)] would be surmised by any pre-averaging scheme. Figures 3 and 4 indicate that the latter coefficient can be comparable in magnitude to the contribution $\hat{\beta}$, which continues to exist (albeit with some modifications) even for rigid nonspherical 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 1987).

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 nonzero sizes and of the hydrodynamic interactions among the individual rigid particles comprising the flexible chain.

Our formulas are free of any pre-averaging approximations. Explicit examples are given only for dumbbells, since these are currently the only multiparticle objects for which complete configuration-specific hydrodynamic interaction data are available over the entire range of geometrically accessible conformations.

APPENDIX A: TRANSFORMATION JACOBIAN

Subsequent paragraphs formally demonstrate that the transformation

$$(\underset{\sim}{R}_0, \underset{\sim}{R}_1, \ldots, \underset{\sim}{R}_n) \longleftrightarrow (Q, \underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_n) \tag{A.1}$$

of the independent variables defined via (4.1) and (4.2) leaves the respective volume elements invariant. Explicitly,

$$d\underset{\sim}{R}_0 \, d\underset{\sim}{R}_1 \ldots d\underset{\sim}{R}_n = dQ \, d\underset{\sim}{r}^n \quad . \tag{A.2}$$

The proof entails showing that the Jacobian determinant (Jeans 1940, Chapman & Cowling 1961) of the transformation (A.1) satisfies the equality

$$|J| \equiv \left| \frac{\partial(Q, \underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_n)}{\partial(\underset{\sim}{R}_0, \underset{\sim}{R}_1, \ldots, \underset{\sim}{R}_n)} \right| = 1 \quad . \tag{A.3}$$

Transformation laws (4.1) and (4.2) readily provide the explicit expansion of the Jacobian as

$$J = \det \begin{Vmatrix} \underset{\approx}{I} & \cdot & \cdot & \cdot & \cdot \\ -\underset{\approx}{I} & \underset{\approx}{I} & \cdot & \cdot & \cdot \\ -\underset{\approx}{I} & \cdot & \underset{\approx}{I} & \cdot & \cdot \\ -\underset{\approx}{I} & \cdot & \cdot & \underset{\approx}{I} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ -\underset{\approx}{I} & \cdot & \cdot & \cdot & \underset{\approx}{I} \end{Vmatrix} \quad , \tag{A.4}$$

wherein the partitioned matrix appearing therein contains n+1 dyadic idemfactors

$$\underset{\approx}{I} \equiv \begin{bmatrix} 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \end{bmatrix}$$

along its pricipal diagonal, n factors $-\underset{\approx}{I}$ as the remaining entries of its

first column, and zeros for all its other entries. Evaluation of the determinant (A.4) immediately yields (4.3). Thus, in present circumstances, the standard vector calculus identities

$$d\underset{\sim}{Q}\, d\underset{\sim}{r}_1 \ldots d\underset{\sim}{r}_n = |J|\, d\underset{\sim}{R}_0\, d\underset{\sim}{R}_1 \ldots d\underset{\sim}{R}_n \quad , \tag{A.5}$$

$$\delta(\underset{\sim}{Q} - \underset{\sim}{Q}') \prod_{a=1}^{n} \delta(\underset{\sim}{r}_a - \underset{\sim}{r}'_a) = |J|^{-1} \prod_{A=0}^{n} \delta(\underset{\sim}{R}_A - \underset{\sim}{R}'_A) \quad , \tag{A.6}$$

with $|J|$ defined in (4.3), reduce to their simplified counterparts (A.2) together with the delta function product relations

$$\prod_{A=0}^{n} \delta(\underset{\sim}{R}_A - \underset{\sim}{R}'_A) = \delta(\underset{\sim}{Q} - \underset{\sim}{Q}') \prod_{a=1}^{n} \delta(\underset{\sim}{r}_a - \underset{\sim}{r}'_a) \quad . \tag{A.7}$$

Relations (A.2) and (A.7) were employed in Section 4 to derive the local/global form of the configurational transport equation [cf. (4.7)] from its predecessor in Section 3.

FOOTNOTES

[1] Note that $(ds)^2$ appearing in (2.5) and (2.6) is of dimensionality ML^2T^{-1}. However, it can be made to have the units of length squared (L^2 dimensionality) by dividing the RHS's by the product of the fluid viscosity and a characteristic chain length. This feature will not, however, prove necessary.

[2] More properly, that experiment would furnish the comparable intrinsic hydrodynamic resistance dyadics $\underset{\sim}{K}[A|B]$, 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.

[3] 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 $\underset{\sim}{R}_0$ 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 $\underset{\sim}{R}_0$, 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.

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

[5] This is possible since the phenomenological coefficients appearing in each of the constitutive flux expressions are presently independent of $\underset{\sim}{\phi}_A$.

[6] By way of example, for the case of a single <u>rigid</u> body, to which two distinct body-fixed locator points G an 0 have been rigidly affixed,

$$\underset{\sim}{R}_G - \underset{\sim}{R}_0 = {}^0\underset{\sim}{r}_G(\underset{\sim}{\phi})$$

and

$$\underset{\approx}{\Delta}^{\phi R} = \partial {}^0\underset{\sim}{r}_G / \partial \underset{\sim}{\phi} = - \underset{\approx}{\varepsilon} \cdot {}^0\underset{\sim}{r}_G = - \underset{\approx}{I} \times {}^0\underset{\sim}{r}_G$$

(cf. Brenner & Condiff 1972).

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