Purely global model for Taylor dispersion

J. Camacho*

Departament de Física, Grup de Física Estadística, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

(Received 11 January 1993)

We show a purely coarse-grained model for Taylor dispersion based on extended irreversible thermodynamics which captures the main features of Taylor dispersion along all the time span: asymptotic diffusive behavior, transient anisotropy, incorporation of transverse initial conditions, and transition to irreversibility. The macroscale model equation is recovered from an analysis in the detailed three-dimensional space, and its predictions for the lowest moments of the solute concentration are satisfactorily compared with numerical simulations at all times for initial distributions sufficiently spread along the tube section. Special attention is paid to the transition to irreversibility in Taylor dispersion.

PACS number(s): 47.60.+i, 05.70.Ln, 66.10.Cb, 05.60.+w

I. INTRODUCTION

Taylor dispersion originally arose in the study of the longitudinal dispersion of a solute dropped in a solvent which flows along a rectilinear tube [1–3]. In 1953, Taylor found the fundamental result that the combined action of a unidirectional velocity field and transverse molecular diffusion leads to a longitudinal diffusion for asymptotic long times. Since then much work has been done trying to generalize his results. These efforts have been addressed in different directions and from very different points of view; besides regarding Taylor dispersion as a hydrodynamic problem [4–9], some authors have stressed its relation to the elimination of fast modes [10, 11], or the theory of stochastic processes [12, 13].

From a different viewpoint, Brenner *et al.* have developed the so-called generalized Taylor dispersion (GTD) [14–19]; this theory provides a macroscale description of the corresponding microscale transport processes which confers a unified structure upon a wide variety of physical situations such as, for instance, sedimentation of nonspherical particles [20, 21], surface transport [22], or dispersion of polymers in solution [19], to name only a few. A special feature of GTD is that it can be applied to the study of flows under nonrectilinear ducts, in contrast to the original Taylor description, but like it, it is only valid in the long-time limit. Frankel and Brenner tried without success to extend the formalism of GTD in order to improve the asymptotic order of approximation [18].

The study of Taylor dispersion at intermediate times has been faced in the past by other authors [4–8, 10, 11]. All of them start from the tridimensional convection-diffusion equation

$$\frac{\partial c(x,t)}{\partial t} + u\frac{\partial c(x,t)}{\partial x} + \frac{\partial}{\partial x}\left[\overline{\Delta c \Delta v}\right] = D_m \frac{\partial^2 c(x,t)}{\partial x^2}, \quad (1)$$

where $\Delta v \equiv v(y,z) - u$ and $\Delta c \equiv c(x,y,z,t) - c(x,t)$ are the deviations from the mean (section-averaged) values of the velocity field, $v(y,z)$, and the concentration profile, $c(x,y,z,t)$, respectively (the overbar denotes section

averaging). On the other hand, they make some hypothesis on the dependence of the cross-sectional variation Δc in terms of the average concentration $c(x,t)$, following Taylor's ideas.

Thus, these authors try to find a closed equation for the one-dimensional quantity $c(x,t)$ from an analysis in three dimensions (3D). This standpoint is similar to the problem of finding the hydrodynamic equations starting from the more detailed description of kinetic theory. Hydrodynamic equations, however, can also be obtained from a formalism which corresponds to the *same* level of description: the thermodynamics of irreversible processes. The problem is that for the isothermal dispersion under study, the classical theory of irreversible processes [23] is only able to supply the diffusive behavior characterizing the asymptotic Taylor dispersion.

Using a different thermodynamic framework, the so-called extended irreversible thermodynamics (EIT) [24], we have demonstrated that the Taylor flux is an actual dissipative flux, with a related entropy, entropy flux, and entropy production, the latter being positive definite along time evolution as required by the second law of thermodynamics [25]; it contains Taylor's statement as a limit case, since in the long-time limit the dynamics of the fluxes is diffusive. Then, our basic aim is to use this fundamental result in order to obtain the simplest constitutive equation capturing the main features of the longitudinal dispersion of the solute along all the time span, paying special attention to the transition to irreversibility. This equation, by its own nature an approximation, is shown to be a renormalization over the whole spectrum of transverse modes, and its validity is tested through the comparison with numerical simulations. It is worth emphasizing that, in contrast to previous approaches, not only is the resulting equation we get one dimensional, but also it is the procedure we follow to obtain it.

The paper is organized as follows. In Sec. II, we obtain a constitutive equation for the Taylor dispersion flux from the formalism of extended thermodynamics. In Sec. III,

<u>48</u>   310

we recover the macroscale model equation starting from the detailed tridimensional space, thus getting the analog to the kinetic derivation of the hydrodynamic equations; this analysis provides us with specific values for the transport coefficients appearing in the coarse-grained equation. In Sec. IV, we perform numerical simulations for the study of the transition to irreversibility in Taylor dispersion and compare with the theoretical predictions of our model. In Sec. V, we contrast the results of numerical simulations under nonuniform initial distributions with the theoretical predictions for the lowest moments of the distribution. Section VI compares the global model with other theoretical approaches, and Sec. VII is devoted to conclusions.

II. A PURELY GLOBAL MODEL FOR TAYLOR DISPERSION BASED IN EIT

In Ref. [25], we saw that if we want to get an exact one-dimensional description of the solute dispersion in a tube, we have to deal with an infinite set of coupled constitutive equations — one for each mode — and, accordingly, an infinite number of transport coefficients. In this situation one can seriously wonder which are the advantages of working in the coarse-grained space instead of doing it in the complete three-dimensional space, where the dispersion follows a simple convection-diffusion equation. Therefore, our goal is obtaining an approximate equation by compacting the infinite number of modes constituting the Taylor dispersion flux into one single mode, the Taylor flux itself $\mathbf{J}_T$, considered as a single quantity. Since we have already proved that the Taylor flux is a dissipative flux of extended thermodynamics, we are qualified to use the machinery of EIT in order to find the constitutive equation for $\mathbf{J}_T$.

Extended thermodynamics differs from the classical theory of irreversible processes in that the local-equilibrium hypothesis is not assumed, and in that the variables used to describe a nonequilibrium state are not only the ones appearing in equilibrium, but also the dissipative fluxes (for a detailed study see Ref. [24]). It is thus proposed a generalized nonequilibrium entropy that depends on all these variables. In the simplest case, for Taylor dispersion under isothermal conditions one is lead to the following generalized Gibbs equation:

$$ds(x,t) = -\mu(x,t)T^{-1}\,dc(x,t) - \alpha\,\mathbf{J}_T{\cdot}d\mathbf{J}_T, \qquad (2)$$

$s(x,t)$ being the entropy per unit volume, $\mu(x,t)$ the chemical potential of the solute, T the absolute temperature, and α a scalar coefficient which does not depend on $\mathbf{J}_T$. The first term on the right-hand side corresponds to the local equilibrium contribution, and the second one is a flux–dependent purely nonlocal part of the generalized entropy.

Similarly, a generalized entropy flux is introduced as a general function of the dissipative fluxes. As in Ref. [25], we add to the classical expression for the entropy flux, $-\mu(x,t)T^{-1}\mathbf{J}_T$, a term aiming to describe the transient anisotropy in the solute dispersion induced by the velocity profile (this is a well-known feature of the Taylor

dispersion that the same Taylor had already observed in his early experiments [1, 2]), and a term accounting for spatial correlations (although no experimental observation of them has been mentioned in the literature, in Ref. [25] we saw that they stem from a theoretical analysis in three dimensions, so that we consider them here for the sake of completeness):

$$\mathbf{J}^s(x,t) = -\mu(x,t)T^{-1}\mathbf{J}_T - \frac{1}{2}\alpha_0 J_T^2\mathbf{u} - \delta\,\mathbf{P}_T\cdot\mathbf{J}_T, \qquad (3)$$

where α_0 and δ are phenomenological coefficients with no dependence on $\mathbf{J}_T$, $\mathbf{u}$ is a vector in the direction of the flow and with modulus u, the mean speed of the solvent as seen from the frame where the tube is fixed, and $\mathbf{P}_T$ is a second-order tensor designating the flux of $\mathbf{J}_T$; as we saw in Ref. [25], the inclusion of a term of this type in the entropy flux allows one to incorporate spatial correlations. The second term on the rhs accounts for the anisotropy induced by the flow, since the change $\mathbf{u} \to -\mathbf{u}$ modifies the sign of this contribution. Other terms, like $u^2\mathbf{J}_T$ or $\mathbf{P}_T\cdot\mathbf{u}$, although mathematically possible, are forbidden by thermodynamics because they lead to nonpositive values for the entropy production.

Combining Eqs. (2) and (3) with the entropy balance equation

$$\frac{ds(x,t)}{dt} + \frac{\partial J^s}{\partial x} = \sigma_s, \qquad (4)$$

one obtains for the entropy production (since we are working in one dimension, vectorial notation is omitted from now on)

$$\sigma_s = -\,J_T\left[T^{-1}\frac{\partial\mu}{\partial x} + \alpha\frac{dJ_T}{dt} + \alpha_0 u\frac{\partial J_T}{\partial x} + \delta\frac{\partial P_T}{\partial x}\right]$$
$$- P_T\left[\delta\frac{\partial J_T}{\partial x}\right]. \qquad (5)$$

The terms inside the square brackets are identified as the conjugate thermodynamic forces of the fluxes preceding them. The positiveness of entropy production stated by the second law of thermodynamics implies a relation between fluxes and forces which, in the simplest case, is assumed to be linear:

$$P_T = -K_2^{-1}\delta\frac{\partial J_T}{\partial x} \qquad (6)$$

and

$$J_T = -K_1^{-1}\left[T^{-1}\frac{\partial\mu}{\partial x} + \alpha\frac{dJ_T}{dt} + \alpha_0 u\frac{\partial J_T}{\partial x} + \delta\frac{\partial P_T}{\partial x}\right], \qquad (7)$$

K_1 and K_2 being positive coefficients. After introducing (6) into (7), some straightforward calculations yield

$$J_T + \tau_T\dot{J}_T + \tau_T\beta u\frac{\partial J_T}{\partial x} = -D_T\frac{\partial c}{\partial x} + l_T^2\frac{\partial^2 J_T}{\partial x^2} \qquad (8)$$

under the identifications

$$D_T = \frac{1}{K_1 T} \left.\frac{\partial \mu}{\partial c}\right|_T, \quad \tau_T = \frac{\alpha}{K_1}, \quad \beta = \frac{\alpha_0}{\alpha}, \quad l_T^2 = \frac{\delta^2}{K_1 K_2}.$$

$$(9)$$

The dot denotes substantial time differentiation, that is to say, the time derivative as seen from a framework moving with the barycentric velocity of the coarse-grained fluid particles. Note that in the Taylor dispersion, the solutions are usually considered to be diluted enough so as to identify the tridimensional barycentric speed with the solvent velocity, so that it turns out that the mass average speed of the one-dimensional fluid particles coincide with the mean solvent velocity, u. Since we set ourselves in the framework travelling with the mean solvent speed, this entitles us to substitute substantial derivatives by partial time derivatives throughout the paper.

Equation (8) is the central result of this work. Aside from the classical Fickian contribution for the Taylor dispersion flux, it contains a relaxational term characterized by the time parameter τ_T, a correlation length l_T, and an anisotropic term, the one in $\partial J/\partial x$, whose parity is obviously different from the one of the preceding terms, so that β is a numerical parameter characterizing the anisotropy.

This constitutive equation is obviously a simplification, since the Taylor dispersion flux is not a single quantity but the sum of an infinite number of partial fluxes. The rest of the paper is dedicated to analyze the validity of this equation for the study of the longitudinal dispersion of a solute suspended in a solvent flowing in a tube along all the time span; this is done both theoretically, Secs. III and VI, and through its comparison with numerical simulations, Secs. IV and VI. To this end, Eq. (8) for J_T must be combined with the mass balance equation

$$\frac{dc(x,t)}{dt} + \frac{\partial J(x,t)}{\partial x} = 0. \tag{10}$$

$J(x,t)$ is the total particle flux, which can be written as the sum of a molecular part, J_m, and a flow-dependent contribution, J_T, namely, $J = J_m + J_T$. The constitutive equation for J_m is assumed to be Fickian,

$$J_m = -D_m \frac{\partial c(x,t)}{\partial x}, \tag{11}$$

since molecular diffusion relaxes in a time of the order of the collision time, much smaller than the time scale under study.

With the help of (8), (10), and (11), one finds

$$\tau_T \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} + \tau_T \beta u \frac{\partial^2 c}{\partial x \partial t} - \left(\tau_T D_m + l_T^2\right) \frac{\partial^3 c}{\partial x^2 \partial t} = D\frac{\partial^2 c}{\partial x^2} + \tau_T \beta u D_m \frac{\partial^3 c}{\partial x^3} + l_T^2 D_m \frac{\partial^4 c}{\partial x^4} \tag{12}$$

with $D \equiv D_T + D_m$ the total diffusion coefficient. Let us comment on some features of this equation.

(a) It is of the telegrapher's type (a much more simplified version of it has been used in the study of solute dispersion in rivers by Thacker [26]), and the coefficients are constant, so that although solving may be extremely complicated, the analysis of its moments becomes quite simple.

(b) It allows for the incorporation of some details of the transverse initial distributions, since being a second-order differential equation in time its solution requires some initial conditions in $\partial c/\partial t$. This is a basic point in the description of the solute dispersion in the short-time limit, highly dependent on the initial solute distribution along the section of the tube.

(c) In the long-time limit it supplies the difusive behavior characterizing the Taylor-Aris result. This is like this because, in the Taylor limit, i.e., $L/u \gg \tau_T$ [1], with L the size of the solute distribution, the solute is so spread along the tube direction that the terms in the third and fourth spatial derivatives in (12) can be neglected as compared to the one in the second derivative, and all the terms on the left-hand side are negligible with respect to the one in $\partial c/\partial t$. (For a tube of section a, we will see in the next section that $l_T^2 \sim D_m \tau_T \sim a^2$.)

(d) It describes a transient anisotropic dispersion through the terms containing the parameter β: at intermediate times, the solute disperses differently in the sense of the flow and against it, but at long times these terms become negligible and the anisotropy disappears.

(e) It provides a transition from a partially reversible regime at short times to a purely irreversible regime at long times (a similar transition has been observed experimentally in tracer dispersion in porous media [27]). In effect, for $t \ll \tau_T$, the time reversal terms $\partial^2 c/\partial t^2$ and $u\partial^2 c/\partial x \partial t$ are relevant, so that some reversible behavior in the dispersion of the solute is predicted at these time scales, but in the long-time limit they become negligible and the behavior turns out completely irreversible. Section IV is devoted to the study of this transition with the aid of numerical simulations.

Neglecting molecular diffusivity, i.e., making $D_m = 0$, Eq. (8) yields

$$\tau_T \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} + \tau_T \beta u \frac{\partial^2 c}{\partial x \partial t} - l_T^2 \frac{\partial^3 c}{\partial x^2 \partial t} = D_T \frac{\partial^2 c}{\partial x^2}, \tag{13}$$

which aside from the term in l_T coincides with the equation found by Smith as an approximation to his delay-diffusion equation [8], obtained through a completely different method based in a three-dimensional analysis. Smith showed that the concentration profiles predicted by Eq. (13) — with $l_T = 0$ — are inadequate at short times. Despite this, from the comparison with numerical simulations we are seeing in Sec. IV that the predictions of (12) for the second moments of the distribution under uniform initial conditions are very satisfactory at all times, including the short-time limit.

Contrary to Smith, our main interest is not to find an excellent curve-fitting equation, but to point out that

our Eq. (12), obtained in a purely macroscale way from the second law of thermodynamics, contains the essence of the longitudinal dispersion in a tube, namely, incorporation of molecular diffusion, transition to irreversibility, transient anisotropy, dependence on transverse initial conditions at short times, and asymptotic diffusion at long times. Also notice that the transport coefficients appearing in it are general, as corresponds to a thermodynamic framework; Eq. (8) could be the constitutive equation for a general flux, not necessarily related to Taylor dispersion; in the case of tracer dispersion in porous media, for instance, it may describe the mass flux associated to mechanical dispersion.

III. KINETIC FOUNDATIONS OF THE GLOBAL MODEL

In the latter section, we have obtained a purely macroscale equation for Taylor dispersion by means of a completely unidimensional framework. The aim of the present section is to derive the one-dimensional equation for the Taylor dispersion flux starting from a detailed tridimensional analysis, similarly as hydrodynamic equations can be deduced from kinetic theory. This will enable us to get specific expressions for the coefficients τ, β, and l_T for the case of the Taylor dispersion.

The procedure followed by Smith [8] to obtain a telegrapher equation similar to our Eq. (12) from the three-

dimensional convection-diffusion equation is not adequate for our purposes for several reasons. Aside from the fact that Smith did not pay any attention to the Taylor flux: (a) the corresponding quantity in his paper is affected from the beginning by the main ansatz of the article, Eq. (1.5); (b) a truncation is required to obtain his delay-diffusion equation whose approximation yields the telegrapher equation; and (c) Smith's development is limited to uniform discharges. We develop here a more general analysis, not based on an ansatz and without a priori restrictions on specific initial conditions.

In Ref. [25], we showed that the Taylor flux, J_T, is the sum of an infinite number of contributions, $J_n(x, t)$, satisfying the following constitutive equations for a steady flow:

$$\dot{J}_n + \frac{J_n}{\tau_n} + \frac{\partial}{\partial x} \sum_{m=1}^{\infty} \gamma_{mn} J_m = -\frac{D_n}{\tau_n} \frac{\partial c(x,t)}{\partial x} + D_m \frac{\partial^2 J_n}{\partial x^2},$$

(14)

where the coefficients are related to the Fourier components of the velocity field through

$$D_n = \frac{1}{2} v_n^2 \tau_n, \quad \gamma_{mn} = \frac{1}{2} \left(v_{m-n} + v_{m+n} \right) \frac{v_n}{v_m}. \quad (15)$$

The time spectrum τ_n depends on the section geometry; for flows between two parallel plates separated by a distance d, it takes the form $\tau_n = d^2 / D_m \pi^2 n^2$.

In order to obtain a constitutive equation for J_T we have to add all the contributions,

$$\frac{\partial J_T}{\partial t} + \sum_{n=1}^{\infty} \frac{J_n}{\tau_n} + \frac{\partial}{\partial x} \sum_{m,n=1}^{\infty} \gamma_{mn} J_m = -\left(\sum_{n=1}^{\infty} \frac{D_n}{\tau_n} \right) \frac{\partial c(x,t)}{\partial x} + D_m \frac{\partial^2 J_T}{\partial x^2}, \quad (16)$$

and approximate the summations so that they only contain the variables J_T and $c(x, t)$. This is done by considering each sum separately.

(i) Since the last term on the rhs of (16) has exactly the same form as the last term of Eq. (8), we may connect the correlation length l_T and the relaxation time τ_T through the relation $l_T^2 = \tau_T D_m$.

(ii) In the short-time limit, the term in $\tau_n \dot{J}_n$ of (14) is much more important than the one in J_n. For this reason, the summation $\sum_{n=1}^{\infty} (J_n/\tau_n)$ is negligible in front of $\dot{J}_T$ in this limit. Similarly, the term in J_T of Eq. (8) can be neglected as compared to $\tau_T \dot{J}_T$ at short times, and we can identify (to simplify notation from now on we write τ instead of τ_T)

$$\tau = \frac{\sum_{n=1}^{\infty} D_n}{\sum_{n=1}^{\infty} (D_n/\tau_n)}. \quad (17)$$

Analogous expressions for effective relaxation times in the short-time limit have been found for every dissipative phenomenon in systems described by a spectrum of fluxes, each with its own relaxation time [28, 29].

In contrast, at long times the term in $\sum_{n=1}^{\infty} J_n/\tau_n$ is

the most important one; in this limit we may approximate $J_n \simeq -D_n \partial c(x,t)/\partial x$ so that $D_T = \sum_{n=1}^{\infty} D_n$ and, from (17),

$$\sum_{n=1}^{\infty} \frac{J_n}{\tau_n} \simeq -\frac{D_T}{\tau} \frac{\partial c}{\partial x} \simeq \frac{J_T}{\tau}. \quad (18)$$

The substitution of (18) into (16) is exact both in the short- and long-time limits, but only an approximation at intermediate times.

By using (15), (17) yields

$$\tau = \frac{\sum_{n=1}^{\infty} v_n^2 \tau_n}{\sum_{n=1}^{\infty} v_n^2} = \frac{D_T}{\overline{v^2}}. \quad (19)$$

This expression differs from Smith's parameter [8]:

$$\tau_{\text{Smith}} = \frac{\sum_{n=1}^{\infty} v_n^2 \tau_n^2}{\sum_{n=1}^{\infty} v_n^2 \tau_n}. \quad (20)$$

The origin of the discrepancy is that Smith obtained his time constant to get the correct value of the variance at long times for a uniform initial discharge. In contrast,

our analysis is placed in the opposite limit, it does not restrict to the variance, but is referred to the whole Taylor flux, and it is not limited to specific initial conditions. Expression (17) is thus set in a very general basis.

(iii) Finally, we approximate the double summation by a term of the same form but exclusively written in terms of J_T:

$$\sum_{m,n=1}^{\infty} \gamma_{mn} J_m \simeq v\, J_T, \qquad (21)$$

where the coefficient v has been introduced to be compared with Smith's expression. After substituting (17), (18), and (21) into Eq. (16) one obtains the average equation

$$J_T + \tau \dot{J}_T + v\tau \frac{\partial J_T}{\partial x} = -D_T \frac{\partial c(x,t)}{\partial x} + D_m \tau \frac{\partial^2 J_T}{\partial x^2}, \qquad (22)$$

which has the same form as (8), as we wanted to show; this allows one to identify the parameter β as $\beta \equiv v/u$. In the Appendix we find two expressions for this parameter, one from a study at short times and the other from a long-time analysis.

In the following sections we deepen in the dynamical consequences of our model equation, Eq. (12). Since this is approximate, it is interesting to evaluate its validity through the comparison of its theoretical predictions with numerical simulations. We start with the study of the transition to irreversibility.

IV. COMPARISON WITH NUMERICAL SIMULATIONS: TRANSITION TO IRREVERSIBILITY

The aim of Secs. IV and V is the comparison of the theoretical predictions of the global model and the results of numerical simulations. For the sake of simplicity, the simulations have been performed for a flow between parallel plates. In all of them, we have considered a plane Poiseuille flow.

A. Description of the simulations and their results

The basis of the simulations is quite simple (this type of simulation has been previously performed by Rigord [30]). We start by considering two parallel lines separated by a distance $d = 2a$ and a big amount of points (N) uniformly distributed between them in $x = 0$ (see Fig. 1); these points represent the solute particles. At every time step τ_s each particle develops two motions: it travels a length $l_c(y) = v(y)\tau_s$, as corresponds to the convection under the solvent flow $v(y) = (3/2)u(1 - y^2/a^2)$, and a length l_d—independent of y—in a random direction, aiming to simulate the two-dimensional Brownian motion of the solute particles. When the random motion takes the points out of the lines, a specular reflexion of total distance l_d is assumed. One lets the system evolve, computes the value of $\langle \Delta x^2 \rangle$ at different points in time, t ($\langle \rangle$ denotes the average over the simulation distribution), and represents the ratio $(\Delta x)^2(t)/2t \equiv \overline{D}(t)$ versus the penetration length of the solute as a whole, $L = \langle x(t) \rangle$.
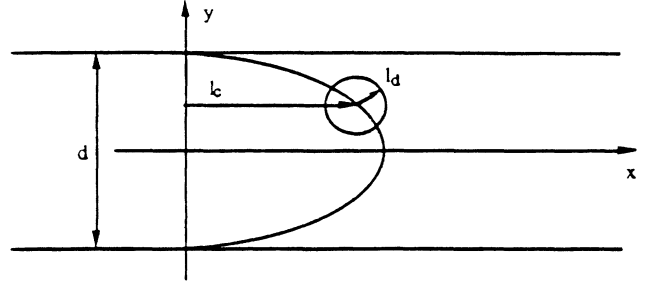

FIG. 1. Description of the simulations: every time step τ_s a solute particle located at a point (x, y) displays a convective motion $l_c = v(y)\tau_s$, modeling the solvent velocity field, and a diffusive one of constant length l_d with random orientation (in two dimensions), trying to modelize the Brownian motion of the solute due to collisions with the solvent.

We have introduced the function $\overline{D}(t)$ that may be called the "effective dispersion coefficient" since it has the dimensions of a diffusion coefficient and it tends asymptotically to D in the long-time limit. This simulation is referred to as a *transmission* dispersion simulation. The results for some specific values of the parameters are displayed in Fig. 2 (squares).

Other simulations consist of letting the system evolve during a time span t_i, suddenly reverse the velocity field, $v(y) \rightarrow -v(y)$, and represent again $\overline{D}(t)$ as a function of $\langle x(t) \rangle$. These are called *echo* dispersion simulations. In Fig. 2 some inversion curves are displayed (diamonds) for different inversion lengths.

We may give a rough interpretation of the results shown in Fig. 2. In the transmission simulation curve one can distinguish three regions: two constant ones, one at short times (short penetration lengths), and the other at long times, and a transition region between them. The constant behavior in the short-time limit obviously corresponds to the domain of molecular diffusion, and the flat regime in the long-time limit to the completely developed Taylor dispersion.

Referring to the echo simulation curves, there are some points to comment on.

(i) For very short inversion times the effective dispersion coefficient approaches the value D_m at a time twice the inversion time ($t = 2t_i$). This is understood in a very simple way: the fluid particles initially start moving with the velocity profile, inside each of them the diffusion process takes place but because of the short time of the "experiment," the fraction of solute particles that escape from their original fluid particles is negligible so that when one reverses the velocity field and analyzes the dispersion at $t = 2t_i$ every fluid particle is found at the same place that in $t = 0$ but with a diffusion process that has been occurring along all the time. The behavior is thus partially reversible.

(ii) In the long-time limit, in the regions where the transmission curve is flat, the echo curves are straight lines. It means that the reversion of the velocity field does not affect the dispersion process; this is like this because at those long times the mixing process is so intricate, the

coupling between the solute and the velocity field has been so strong, that the reversion of the velocities does not contribute to recover the initial distribution, but the mixing process is similar to the case when one keeps the velocity field unchanged. In this limit, the dispersion is thus completely irreversible.

(iii) At intermediate times, in the transient region between the two pure diffusive regimes, the effect of reversing the velocity field is, essentially, a fast decrease of $\overline{D}(t)$ just after it, followed by an increase, reaching at $t = 2t_i$ values between D_m and D which are smaller than the corresponding ones at $t = t_i$. Then the reversion of the velocities leads to a stronger dispersion than the simple molecular diffusion, but smaller than in developed Taylor dispersion.

In summary, echo simulations evidence the existence of a transition from a partially reversible regime at short times and a completely irreversible regime at long times, in agreement with the qualitative prediction of our model equation (12). In the following section we analyze its consequences quantitatively.
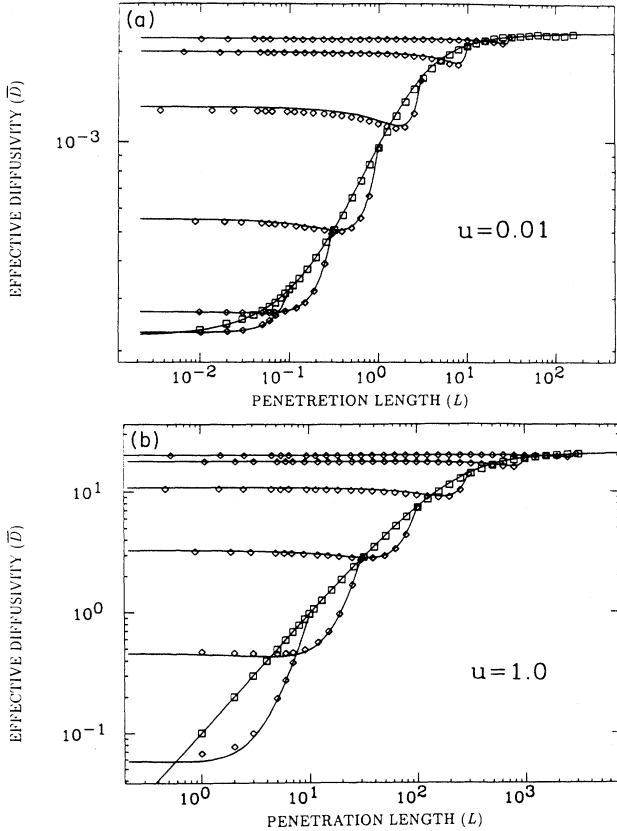

FIG. 2. Comparison between theoretical predictions and simulations. Squares and diamonds correspond to transmission and echo simulations, respectively; the theoretical curves are denoted by solid lines. We show the results for two different Péclet numbers (Pe= ud/D_m). In all the cases we have chosen $l_d = 0.03$ and $d = \tau_s = 1$; the inversion times are given in time step units: $t_i = 10, 30, 100, 300, 1000, 3000$. (a) $u = 0.01$ (Pe= 44), $N = 5 \times 10^4$; (b) $u = 1.0$ (Pe= 4400), $N = 10^5$.

B. Theoretical analysis of the simulations

In order to compare with the preceding numerical simulations we must calculate an expression for the effective dispersivity $\overline{D}(t)$. To do this, we use the method of moments in Eq. (12), keeping in mind that the amount of solute in the system is constant in time:

$$\tau \frac{d^2\overline{x^2}}{dt^2} + \frac{d\overline{x^2}}{dt} = 2D. \qquad (23)$$

It is noticed that for a uniform initial distribution the parameter β does not affect the evolution of the second moments; this is not like this for nonuniform initial distributions, as we will see in the next section.

Analogously, it is straight to prove that for the initial distribution under study the mass center of the solute moves with the mean velocity of the flow all over the time: $\overline{x}(t) = 0$. Therefore, Eq. (23) describes the evolution of the width Δx. Its integration under initial conditions, $\overline{x^2}(0) = 0$ and $\frac{d\overline{x^2}}{dt}(0) = 2D_m$ — since at very short times molecular diffusion is the only one that does exist — gives

$$(\Delta x)^2(t) = \overline{x^2}(t) = 2Dt + 2D_T\tau[\exp(-t/\tau) - 1] \qquad (24)$$

and defining $L = ut$ we may write

$$\overline{D}(t) = \frac{(\Delta x)^2(t)}{2t} = D + D_T\tau u L^{-1}\left[\exp(-L/u\tau) - 1\right]. \qquad (25)$$

In Fig. 2, Eq. (25) is displayed for two different values of the mean velocity (solid lines), from values of D_T similar to D_m [Fig. 2(a)] to $D_T \gg D_m$ [Fig. 2(b)]. In both cases is shown a good agreement. We thus see that including only one new parameter, the relaxation time ($\tau = d^2/42D_m$ for a plane Poiseuille flow), we are able to predict the results of the transmission simulations with high accuracy.

In the description of an echo experiment, one must consider separately the going interval and the returning one; we denote them by $\overline{x_+^2}(t)$ and $\overline{x_-^2}(t)$, respectively. The first function is described by Eq. (24) and the second one can be found by integrating (23) under the proper initial conditions; one is obvious: $\overline{x_+^2}(t_i) = \overline{x_-^2}(t_i)$, the other one is more subtle. Notice that Eq. (23) can be considered as the composition of two equations that neatly split Taylor and molecular effects

$$\tau \frac{d^2\overline{x_T^2}}{dt^2} + \frac{d\overline{x_T^2}}{dt} = 2D_T \qquad (26)$$

and

$$\frac{d\overline{x_m^2}}{dt} = 2D_m \qquad (27)$$

with $\overline{x^2}(t) = \overline{x_T^2}(t) + \overline{x_m^2}(t)$. Since the molecular part is flow independent by definition, the reversion of the flow tends to decrease only the Taylor contribution. Therefore, the suitable initial condition is

$$\frac{d(\overline{x_T^2})_+}{dt}(t_i) = -\frac{d(\overline{x_T^2})_-}{dt}(t_i). \qquad (28)$$

This condition not only has a clear physical meaning but it is also mathematically consistent with the fact that only Eq. (26) is of second order in time. A straightforward calculation yields the expressions

$$\overline{x_-^2}(t) = -\tau A \exp(-t/\tau) + 2Dt + C \qquad (29)$$

with

$$A = 2D_T[1 - 2\exp(t_i/\tau)], \qquad (30)$$

$$C = 2D_T\tau[2\exp(-t_i/\tau) - 3]. \qquad (31)$$

In order to draw the echo curves one must substitute the parameter t by $(2L_i - L)/u$, L being the position of the mass center of the solute at time t. The curves are thus

$$\overline{D}(L) = -\frac{\tau A u}{2}\frac{1}{2L_i - L}\exp\left(\frac{L - 2L_i}{u\tau}\right) + D + \frac{Cu}{2}\frac{1}{2L_i - L}. \qquad (32)$$

In Fig. 2 a good agreement is shown between the theoretical curves (solid lines between diamonds) and echo dispersion simulations (diamonds). We notice again that it is quite surprising that such a good fit is obtained by only introducing one new parameter.

From the viewpoint of extended thermodynamics, the excellent agreement between theoretical predictions and numerical simulations emulating Taylor dispersion constitutes a new support for the theory that, up to the moment, had essentially limited the comparison with experimental systems to wave speed measurements.[31]

V. COMPARISON WITH NUMERICAL SIMULATIONS: NONUNIFORM INITIAL DISTRIBUTIONS

In the latter section, we did not have to use any value of the parameter β characterizing the anisotropic dispersion in the study of the theoretical predictions for the second moments under the uniform initial distribution considered. The question we address now is to test the different values of β and the terms themselves that are affected by this parameter. It is evident that the third moments in the simulations developed there should necessarily involve the parameter β, since it is the lowest-order moment which accounts for the asymmetry in the solute concentration which this parameter intends to describe. Nevertheless, this average turns out to be extremely sensitive to the number of points used in the simulations so that an enormous calculation power is required. For this reason, we have chosen a different option and studied the time evolution of the mean square deviation for initial distributions in which the solute is not uniformly distributed along the section. This will let us study the

validity of our model equation for different initial conditions.

A. Theoretical analysis

For the second moments, Eq. (12) supplies the equation

$$\tau\frac{d^2\overline{x^2}}{dt^2} + \frac{d\overline{x^2}}{dt} = 2D + 2\beta\tau u\frac{d\overline{x}}{dt} \qquad (33)$$

($D = D_m + D_T$) which depends on β through a term that contains the time derivative of the mean position of the solute. For an initially uniform distribution $\overline{x}(t) = 0$ all over the time, but for nonuniform discharges things are different. Thus, we consider an initial distribution in which the solute occupies a fraction A of the distance which separates the plates and it is centered between them (for $A = 1$ we recover uniform initial conditions).

In terms of the dimensionless parameter A, the initial velocity of the solute under a Poiseuille flow can be written as

$$v_0 = \frac{1}{d}\int_{-Ad/2}^{Ad/2} v(y) = \frac{u}{2}\left(1 - A^2\right), \qquad (34)$$

and solving the evolution equation for $\overline{x}(t)$ one finds

$$\overline{x}(t) = v_0\tau\left[1 - \exp(-t/\tau)\right]. \qquad (35)$$

This expression — which does not contain β — will also be compared with the simulations. It must be stressed that Eq. (35) predicts that at asymptotic long times the solute moves with the mean flow velocity, as Aris proved [3].

After introducing (35) in (33) and integrating under initial conditions $\dot{\overline{x^2}}(0) = 2D_m$ and $\overline{x^2}(0) = 0$, one arrives at

$$\overline{x^2}(t) = 2Dt + 2D_T\tau\left[\exp(-t/\tau) - 1\right] - 2\beta u v_0\tau^2\left[\left(1 + \frac{t}{\tau}\right)\exp(-t/\tau) - 1\right]. \qquad (36)$$

The effective diffusivity, $\overline{D}(t) = (\overline{x^2}(t) - \overline{x}(t)^2)/2t$, is obtained by direct substitution of (35) and (36).

B. Numerical simulations

In the present section only transmission simulations have been carried out. Three cases are considered: (a)
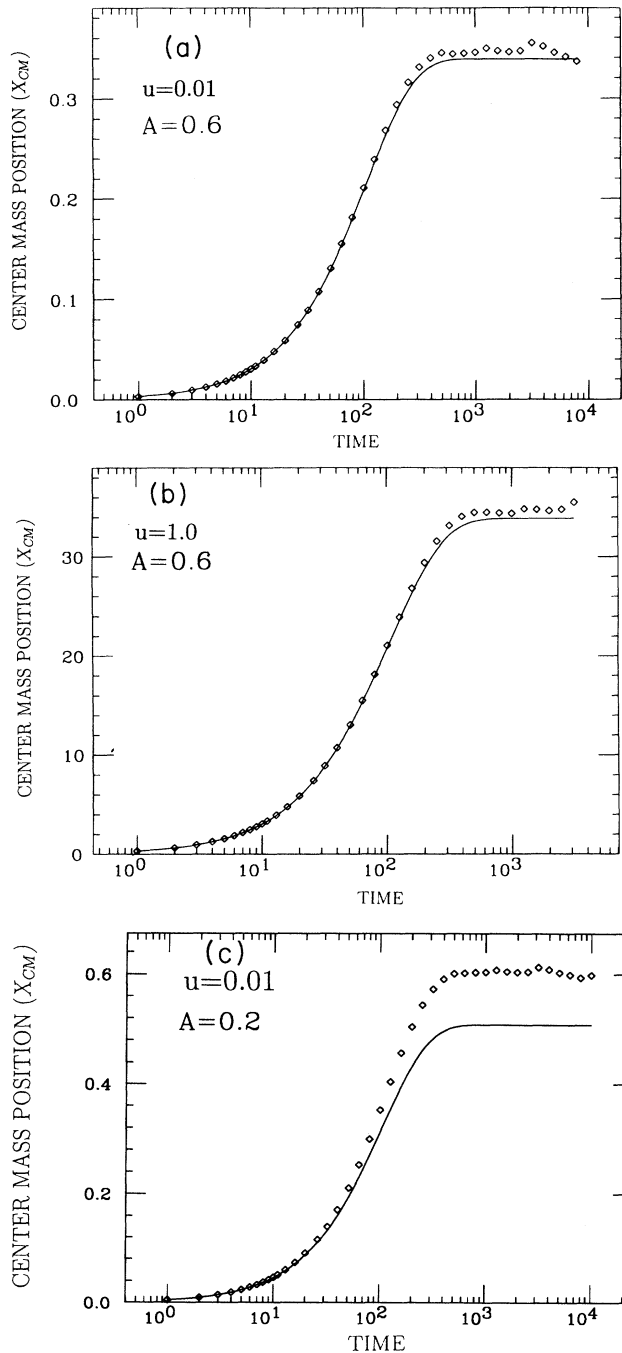
$A = 0.6$, $u = 0.01$; (b) $A = 0.6$, $u = 1.0$; and (c) $A = 0.2$, $u = 0.01$. In this way the effects of the occupation factor A and the mean velocity u are pointed out.

In Fig. 3 the simulation results for the evolution of the center mass of the solute, $X_{\text{c.m.}}$, as seen in a framework

FIG. 3.   Comparison between theoretical curves (—) and numerical simulations (◊) for the mass center position of the solute as a function of time. The influence of the mean flow velocity (u) and the occupation factor (A) are shown.

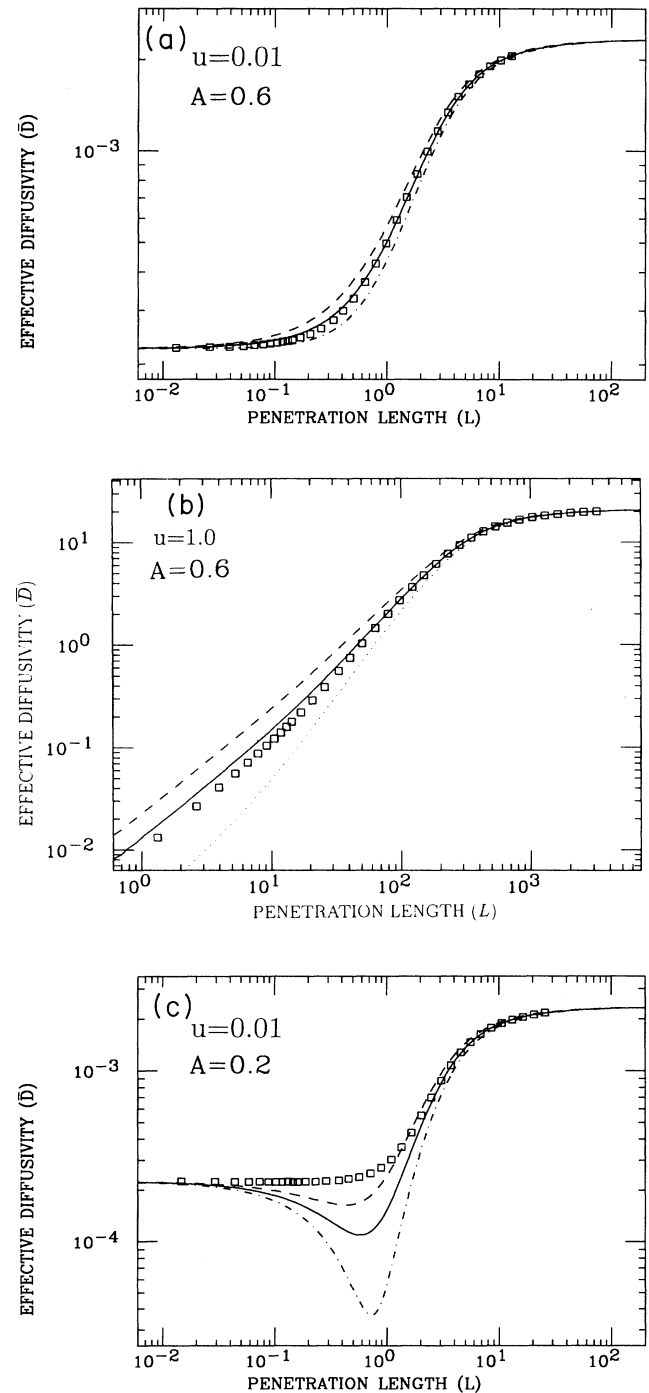FIG. 4.   Comparison of the theoretical effective diffusivity with numerical simulations (□) for three values of the parameter β: $-1/5$ (—); $-4/33$ (Smith, - -); $-2/7$ ($\cdots$). The influence of the mean flow speed and initial conditions are shown.

which travels with the mean flow speed, are represented with diamonds. This quantity is obviously more adequate for our purposes than the penetration length $L = \langle x(t) \rangle$, which at long times tends to mask the displacement described by (35); solid lines correspond to this expression.

The fits are shown to be good along all the time interval for simulations in which $A = 0.6$. For them, the maximum disagreement is reached for asymptotic long times, being of the order of 3%. For $A = 0.2$, however, the error is small at times shorter than τ ($\simeq 100$), but reaches 15% at long times. We thus prove that, though the dynamics predicted by (35) is qualitatively correct, it is not quantitatively for small values of A. For values greater than, let us say 0.5, the agreement is excellent independent of the velocity of the flow.

Figure 4 displays the results of the simulation for the effective diffusivity $\overline{D}(t) \equiv (\langle x^2 \rangle - \langle x \rangle^2)/2t$ as a function of the penetration length L (squares). The shape of these curves is obviously similar to the corresponding ones in Sec. III. With solid lines we draw the theoretical diffusivity for the value $\beta_\infty = -1/5$; broken lines refer to Smith's parameter $\beta_{\mathrm{Smith}} = -4/33$, and dotted lines to $\beta_0 = -2/7$.

In all the cases an excellent agreement is observed between numerical simulations and theoretical predictions with $\beta = -1/5$ for times greater than τ; for the other values of β the fit is clearly worse.

For $u = 0.01$ and $A = 0.6$, the predictions using β_∞ are excellent over all the time interval. For $u = 1.0$ and $A = 0.6$, theoretical curves are qualitatively good at all times but there exist quantitative discrepancies at short times for the β parameters considered; again, β_∞ provides the best fit; the choice of a slightly smaller value of β would supply a good fit at all times. For $u = 0.01$ and $A = 0.2$, however, the curves exhibit a wrong behavior at times smaller than τ.

In summary, the macroscale equation provides a good description of the time evolution of the mass center of the solute and the effective diffusivity for initial conditions where the solute is spread enough over the section. For the effective diffusivity the fit is excellent at times greater than τ for all initial distributions.

VI. COMPARISON TO OTHER APPROACHES

The problem of the Taylor dispersion has been faced from very different points of view. Using stochastic theory, Van Den Broeck obtained an expansion at short times of the exact expression for the second moments of the concentration under uniform initial conditions [12]:

$$\langle \delta x^2(t) \rangle = 2D_m t + \frac{1}{d} \left(\int_0^d dy \, [v_x(y) - u]^2 \right) t^2 - \cdots . \tag{37}$$

Therefore, the first-order correction to pure molecular diffusion turns out to be simply the mean square deviation of the flow velocity. This is in agreement with the short-time expansion of Eq. (24), namely,

$$(\Delta x)^2(t) = 2D_m t + \frac{D_T}{\tau} t^2 + \cdots \tag{38}$$

since our relaxation time, Eq. (19), provides $D_T/\tau = \overline{v^2}$. The asymptotic result (37) has the inconvenience that the coefficient of the term in t^4 and the following ones diverge for common stream patterns, as linear shear or Poiseuille flow, that make the exact expression heavily intractable. Then Eq. (24) seems to supply a simple way of describing Δx^2 avoiding the mathematical problems of the detailed development.

Gill and Sankarasubramanian [5, 6] and Smith [8] proposed different one-dimensional equations for contaminant distribution including time-dependent coefficients. Smith's delay-diffusion model presents two main advantages with respect to the first one: (a) there is no restriction to sudden discharges of solute at a single point in time, and (b) its coefficients have a clearer physical interpretation. The problem of this equation is that it generally does not provide analytical solutions, but Smith showed that his delay-diffusion equation could be approximated by a telegrapherlike equation, with the advantage of known analytical solutions, but it leads to bad results for the solute concentration at short times when compared with exact numerical solutions. Nevertheless, in view of the preceding sections we may conclude that, although the telegrapher equation may not supply a suitable solute distribution as a whole in the short-time limit, its second moments are described with great accuracy at all times for spread enough initial distributions. A quantitative analysis between the results of the simulations and the theoretical transmission curves for uniform initial concentrations shows excellent agreement along all the time scale but with a systematic error for times of the order of τ always smaller than 2%, independent of the mean velocity (outside this region there is no systematic error). This is the cause of the (small) disagreement between the theoretical echo curves and the simulation results at intermediate times shown in Fig. 2. The similarity between the time parameter obtained by Smith for asymptotic long times [8], $d^2/40D_m$, and our relaxation time, $d^2/42D_m$, evaluated at short times, explains why the same parameter works very well all over the time.

One may take benefit of this fact by using the study of the second moments at short times to measure molecular diffusion coefficients without the inconvenience of long observation times and long tubes that characterize their measurement through asymptotic Taylor dispersion in the case of Brownian particles [13].

Young and Johns [10], on the other hand, find an equation including only constant coefficients which allows one to evaluate exactly the time-independent corrections for the asymptotic moments of the solute distribution, but omits the exponential transients. The present approach, however, in spite of providing only approximate values for these corrections, is able to describe properly the second moments at all times.

Finally, we emphasize that the philosophy of the present approach is closer to the generalized Taylor dispersion than to the previous models. While Frankel and Brenner's attempt to improve the asymptotic long-time

character of GTD by introducing an expansion in gradients, $J = -D\nabla c + D_3 \cdot \nabla\nabla c$, did not succeed, our approach, with only a few new parameters (τ and β) seems to work very well for the second moments along all times. Like them, we propose a constitutive equation for a global (y-averaged) flux in terms of constant phenomenological coefficients but, in contrast, we have set this equation in the framework of extended irreversible thermodynamics instead of classical thermodynamics.

Third moments

Although we have not been able to compare the predictions of (12) for the third moments with numerical simulations because of computational limitations, instead we can contrast to other theoretical models. Referred to third moments, the theoretical studies performed up to now basically restrict their analysis to the asymptotic regime [3, 4, 18, 10].

Chatwin [4] demonstrated that the mean cubic deviation of the solute distribution, $\nu_3(t)$, in the limit of long times verifies the following properties: (i) linearity in t, and (ii) independence on initial conditions.

A simple analysis of Eq. (12) for the first three moments in the long-time limit under nonuniform initial discharges yields, for the leading term,

$$\overline{x^3} = (6D_T\tau\beta u + 6Dx_\infty)\,t, \tag{39}$$

where x_∞ denotes the asymptotic center mass position which, as we have seen, depends on initial conditions. In this limit

$$\nu_3(t) = \overline{(x - \overline{x})^3} \simeq \overline{x^3} - 3\overline{x^2}x_\infty, \quad t \to \infty \tag{40}$$

and $\overline{x^2}(t) = 2Dt$; therefore we get

$$\nu_3(t) = 6D_T\tau\beta u\,t, \tag{41}$$

which fulfills Chatwin's conclusions: linearity in time and independence on initial conditions.

On the other hand, Frankel and Brenner [18], also by means of an analysis in the complete coordinate space, find some expressions for the moments of the distribution in the asymptotic limit. For odd moments — $\overline{x^{2k+1}}(t|y_0)$ in our notation, where y_0 indicates its dependence on initial conditions — their Eq. (3.15) writes

$$\overline{x^{2k+1}}(t|y_0) \simeq \frac{(2k+1)!}{k!}\left[(Dt)^k A(y_0)\right] + \frac{(2k+1)!}{(k-1)!}\left[(Dt)^{k-1}D_3 t\right] + O(t^{k-1}) \tag{42}$$

with D_3 a coefficient (in general a tensor) independent of position, time, and initial conditions, and $A(y_0)$ a function of the latter.

For $k = 1$, it yields

$$\overline{x^3}(t|y_0) = 6DA(y_0)\,t + 6D_3\,t, \tag{43}$$

which shows two contributions: one independent of the initial distribution — which can be used to define $\beta \equiv D_3/D_T\tau u$ — and another which depends on them. For $k = 0$, (43) gives $\overline{x}(t|y_0) = A(y_0)$, so that $6DA(y_0) = 6Dx_\infty$, which coincides identically with the corresponding term in (39).

Therefore, our purely global model provides good agreement with the other theoretical models for the leading terms of the third moments. It can be seen that it also supplies qualitatively suitable contributions for the correction to these terms from the viewpoint of the functional dependence on the Péclet number (P) as well as the incorporation of initial conditions. For instance, under uniform initial conditions in a circular tube of radius a the asymptotic second moments are [10]

$$\overline{x^2}(t) = 2Dt - \frac{P^2a^2}{360} \tag{44}$$

meanwhile our model yields $-2D_T\tau = -P^2a^2/384$ (and similarly for third moments).

As Frankel and Brenner proved, the inclusion of transverse initial conditions in these corrections is completely forbidden for a global model in which the flux is written as a gradient expansion of the average concentration.

Young and Jones [10], on the other hand, find exactly the second-order corrections but their model does not allow one to obtain the transient terms, in contrast to our model, which at short times also provides qualitative good behavior.

VII. CONCLUSIONS

Starting from the formalism of extended irreversible thermodynamics we have shown a purely global model for the Taylor dispersion. Contrary to previous approaches, where the coarse-grained equations are found from a study in the three-dimensional space, ours is completely one dimensional. The macroscale equation thus obtained is not intended to be exact but the simplest equation capturing the main features of Taylor dispersion along all the time span. From an analysis in three dimensions we have recovered the macroscale equation, thus getting a microscale confirmation, and obtained some explicit expressions for the general transport coefficients appearing in it.

The comparison with numerical simulations has shown that our macroscale scheme works well over all times for the evolution of the mass center and the effective diffusivity for spread enough initial distributions; the fit is also good from intermediate times for any initial distribution. We have seen as well that the coarse-grained model is in agreement with theoretical analysis carried out in the tridimensional space for the third moments, both at long and short times. These points, added to

the incorporation of transverse initial conditions (as seen from the fact that our model equation is of second order in time), of the anisotropy induced by the velocity profile, the description of the transition to irreversibility, and the asymptotic diffusive behavior, allow one to conclude that our — conceptually and operatively — simple macroscale model captures the essential features of Taylor dispersion along all the time interval.

From the viewpoint of levels of description, we have presented here a macroscale framework (which works in a reduced coordinate space) that leads to a macroscale equation with general phenomenological coefficients (D, τ, and β). The explicit form of these coefficients in terms of more fundamental quantities depends on the specific system under study (tube geometry, porous media, etc.), which implies an analysis in the complete coordinate space. This is analogous to the relation between thermodynamics and kinetic theory, where the restricted coordinate space coincides with the spatial coordinates, and the complete space besides includes some internal ones, such as angles or velocities, for instance. It is nice to see that in both coarse-graining processes the resulting equations have essentially the same form: relaxational equations for the fluxes with Fickian behavior at long times, and telegrapherlike equations for the specific magnitude under study, with asymptotic diffusive behavior.

ACKNOWLEDGMENTS

APPENDIX: EXPRESSIONS FOR THE PARAMETER β

In order to obtain some expressions for the parameter $\beta \equiv v/u$, which incorporates the anisotropy in the macroscale equation, we must properly work approximation (21); this can be carried out in the long- or the short-time limits.

1. Long times

For asymptotic long times we may approximate $J_n \simeq -D_n \partial c(x,t)/\partial x$, so that

$$\sum_{m,n=1}^{\infty} \gamma_{mn} J_m \simeq \left(\sum_{m,n=1}^{\infty} \gamma_{mn} \frac{D_m}{D_T} \right) J_T \qquad (A1)$$

and using (15) v can be expressed as

$$v = \frac{1}{4D_T} \sum_{m,n=1}^{\infty} (v_{m-n} + v_{m+n}) v_n v_m \tau_m. \qquad (A2)$$

This formula can be written in terms of the shape factor $g(y,z)$ introduced by Chatwin [4,8] in the following way:

$$D_m \nabla^2 g = u - v(y,z)$$

with $\overline{g} = 0$, and $\mathbf{n} \cdot \nabla g = 0$ at the boundaries. After some calculations, one finds

$$v = \frac{\overline{gv^2}}{\overline{gv}} \qquad (A3)$$

(again, overbars denote section averaging). For a plane Poiseuille flow, Eq. (A3) yields $v = -u/5$, or what is the same, $\beta \equiv \beta_\infty = -1/5$.

Notice that our expression for v is different from Smith's [8], $v = \overline{vg^2}/\overline{g^2}$, obtained from the analysis of the third moments under uniform initial conditions; for a Poiseuille flow, $\beta_{\text{Smith}} = -4/33$.

2. Short times

In this limit, Eq. (14) can be approximated by $\dot{J}_n \simeq -(D_n/\tau_n)\partial c(x,t)/\partial x$. Working in the space of frequencies it is immediate to arrive to

$$\sum_{m,n=1}^{\infty} \gamma_{mn} J_m \simeq \left(\sum_{m,n=1}^{\infty} \gamma_{mn} \frac{D_m}{\tau_m} \frac{\tau}{D_T} \right) J_T. \qquad (A4)$$

With the help of (15) and (19) it can be rewritten as $v = \overline{v^3}/\overline{v^2}$, which is the same value that one would have found from an analysis at short times of the mean cubic deviation under uniform initial conditions. From (12), for these conditions, we have

$$\frac{d^2 \overline{x^3}}{dt^2} \simeq 6v\overline{v^2}t \Rightarrow \overline{x^3}(t) = v\overline{v^2}t^3 = \overline{v^3}t^3 \qquad (A5)$$

and $v = \overline{v^3}/\overline{v^2}$. For a plane Poiseuille flow, $\beta \equiv \beta_0 = -2/7$.

* Electronic address: iftg1@cc.uab.es

[1] G.I. Taylor, Proc. R. Soc. London, Ser. A **219**, 186 (1953).

[2] G.I. Taylor, Proc. R. Soc. London, Ser. A **223**, 446 (1954).

[3] R. Aris, Proc. R. Soc. London, Ser. A **235**, 67 (1956).

[4] P.C. Chatwin, J. Fluid Mech. **43**, 321 (1970).

[5] W.N. Gill and R. Sankarasubramanian, Proc. R. Soc. London, Ser. A **316**, 341 (1970).

[6] W.N. Gill and R. Sankarasubramanian, Proc. R. Soc. London, Ser. A **322**, 101 (1971).

[7] V.I. Maron, Int. J. Multiphase Flow **4**, 339 (1977).

[8] R. Smith, J. Fluid Mech. **105**, 469 (1981).

[9] R. Smith, J. Fluid Mech. **182**, 447 (1987).

[10] W.R. Young and S. Jones, Phys. Fluids A **3**, 1087 (1991).

[11] R. Smith, J. Fluid Mech. **175**, 201 (1987).

[12] C. Van Den Broeck, Physica A **112**, 343 (1982).

[13] C. Van Den Broeck, Physica A **168**, 677 (1990).

[14] H. Brenner, PhysicoChem. Hydrodyn. **1**, 91 (1980).

[15] H. Brenner, PhysicoChem. Hydrodyn. **3**, 139 (1982).

[16] A. Nadim, R.G. Cox, and H. Brenner, J. Fluid Mech. **164**, 185 (1986).

[17] M. Shapiro and H. Brenner, Chem. Eng. Sci. **43**, 551 (1988).

[18] I. Frankel and H. Brenner, J. Fluid Mech. **204**, 97 (1989).

[19] I. Frankel, F. Mancini, and H. Brenner, J. Chem. Phys. **95**, 8636 (1991).

[20] H. Brenner, J. Colloid Interface Sci. **71**, 189 (1979).

[21] H. Brenner, J. Colloid Interface Sci. **80**, 548 (1981).

[22] L.H. Dill and H. Brenner, J. Colloid Interface Sci. **85**, 101 (1982).

[23] S.R. de Groot and P. Mazur, *Nonequilibrium Thermody-* *namics* (Dover, New York, 1984).

[24] D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105 (1988).

[25] J. Camacho, Phys. Rev. E **47**, 1049 (1993).

[26] W.C. Thacker, J. Phys. Oceanog. **6**, 66 (1976).

[27] J.C. Bacri, J.P. Bouchaud, A. Georges, E. Guyon, J.P. Hulin, N. Rakotomalala, and D. Salin, in *Hydrodynamics* *of Dispersed Media*, edited by J.P. Hulin *et al.* (North-Holland, Amsterdam, 1990), p. 249.

[28] J. Camacho and D. Jou, Phys. Lett. A **144**, 71 (1990).

[29] J. Camacho, Phys. Lett. A **151**, 114 (1990).

[30] P. Rigord, Ph.D. thesis, Université de Paris 6, 1990.

[31] M. Carrasi and A. Morro, Nuovo Cimento B **9**, 321 (1972).