Effective Medium Approximation of Taylor Transport in Systems with Static Disorder†

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The article presents studies on the Taylor transport in disordered systems. We assume that a moving particle can exist in different states and that for each state its transport properties are described by a different linear evolution operator. The transition from one state to another is described by a Markov process in continuous time. The transition rates of the Markov process depend on a set of variable parameters that are randomly selected from a known probability density. This type of transport model is of interest in connection with the study of multiphasic transport, for example, in the case of chromatographic separation, neutron migration in nuclear reactions, or neutrino flow in astrophysical problems. We consider two different types of effective medium approximations: (1) a global approach, which consists of solving the Taylor problem for a given set of values of the of the random parameters, followed by averaging the result, and (2) a local approach, for which the averaging is done for small macroscopic regions of the system, which leads to a system of age-dependent master equations. We show that the averaging in the global approach induces an artificial collective behavior that results in ballistic diffusion. The local approach may lead either to normal or dispersive transport. We apply our theory to the experiment of Drazer and Zanette (*Phys. Rev. E.* **1999**, *60*, 5858) and show that that the local approach is in agreement with experimental data.

1. Introduction

Five decades ago, Taylor[1] introduced a simple model for turbulent diffusion based on the assumption that a moving particle can exist in different states and that for each state the transport properties of the particle are different. This type of model was used for describing the process of chromatographic separation.[2] In 1979, van Kampen published an important theoretical paper[3] in which he investigated the stochastic properties of the total sojourn times of the different states of a Markov process in continuous time and showed that the Taylor transport is intimately connected to the distribution of sojourn times. Van Den Broek[4] introduced a systematic approach for solving various generalizations of the Taylor problem. An alternative approach to generalized Taylor transport was suggested by Vlad, Ross, and Mackey.[5] An approach similar to the theory of Taylor transport has been developed by mechanical engineers for the study of particle transport in stochastic mixtures, with application in nuclear engineering.[6]

A recent experimental study published by Drazer and Zanette[7] has led us to the conclusion that the development of a theoretical approach for Taylor transport in systems with static disorder may be useful. Such an approach would make a connection between the classical Taylor models and the theory of dispersive transport suggested by Montroll.[8] Drazer and Zanette[7] have shown that the solute transport in desorption experiments in porous media, made of packings of activated carbon grains, follows the dispersive mechanism suggested by Montroll,[8] which corresponds to power law trapping time distributions. They have used nonconsolidated packings of relatively uniform, spherical, activated carbon grains obtained from apricot pits, with an average radius of $d = (0.13 \pm 0.01)$ cm. The carbon grains were packed in a 30 cm high, 2.54 cm inner diameter cylinder. In the experiments, the porous medium is initially filled up with aqueous 0.1 M NaI solution tagged with I^{131}. The authors have performed measurements of tracer adsorption and dispersion, in which a stepwise variation of the concentration of I^{131} is induced at time $t = 0$ and kept constant thereafter. Two different types of experiments with a total constant flow rate were carried out, by using different displacing fluids. In the first set of experiments, the system was flushed with an untagged NaI solution having the same concentration as the initial, labeled, solution (exchange experiments), whereas in the second set of experiments the untagged NaI solution was replaced by distilled water (desorption experiments). The results of the exchange experiments show that the replacement of the radioactive isotope I^{131} obeys a classical adsorption−desorption and dispersion mechanism commonly encountered in chemical engineering. In this case, the observed concentration profiles can be reproduced theoretically by using a classical reaction-convection-diffusion equation. The time dependence of the concentration of I^{131} is described by kinetic curves, which decay very fast to zero. For desorption experiments the concentration profiles I^{131} also decrease to zero for large times but this decrease is much slower than for exchange experiments. In the case of desorption for large times, the concentration profiles in the liquid converge toward a long time tail of the negative power law type, $C_{\text{liquid}}(t) \sim t^{-\mu}$, $t \gg 0$, characterized by a fractal exponent $\mu = 0.63$. Such long tails cannot be explained by assuming a classical reaction−diffusion mechanism. The experimental results of the authors suggest that the displacement of the radioactive isotope I^{131} involves a very slow, dispersive[8] (Montroll) diffusion

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processs. The authors suggested a simplified transport model, based on the following qualitative physical picture. The motion of an atom of the radioactive isotope along the column can be represented by a hopping mechanism involving a succession of desorption and readsoption processes, which is basically a random walk in continuous time (CTRW[8,9]). According to Montroll's theory of dispersive diffusion,[8−9] such a continuous time random walk may lead to concentration profiles with long time tails of the negative power law type, if the probability density of the trapping time of the radioactive isotope in the adsorbed state on the surface has a long time tail. This simplified model can be improved by developing a Taylor approach for disordered systems. Such an approach can be useful not only for the interpretation of the experimental data of Drazer and Zanette but also for the study of other problems involving multiphasic flow, such as mass transport in catalytic columns, chromatographic separation, or neutron diffusion in nuclear reactors.

In this paper we generalize the theory of Taylor transport to systems with static disorder and apply our results to the experiment of Drazer and Zanette. The structure of the paper is the following. In section 2 we give a general formulation of our problem. In sections 3 and 4 we introduce an effective medium approximation based on local averaging which leads to a system of age-dependent master equations. Finally, in section 5 we show that our local theory is consistent with the experimental results of Drazer and Zanette.

2. Global versus Local Averaging

We consider the linear stochastic transport of a particle, which can exist in M different states, $j = 1, ..., M$. For a given state j of a particle, we introduce the probability $g_j(\mathbf{r};\ t)d\mathbf{r}$ that the position of the particle at time t is between $d\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ provided that at time $t = 0$ its position was $\mathbf{r} = 0$. This probability is the solution of a partial differential or integral transport equation of the type

$$\partial_t g_j(\mathbf{r};\ t) = \mathbb{L}_j g_j(\mathbf{r};\ t) \text{ with } g_j(\mathbf{r};\ t = 0) = \delta(\mathbf{r}) \tag{1}$$

where $\mathbb{L}_j$ is a translationally invariant linear differential or integral operator. For example, $\mathbb{L}_j$ can have the form of a master or of a Fokker−Planck operator

$$\mathbb{L}_j g_j(\mathbf{r};\ t) = \int \mathscr{W}_i(\mathbf{r} - \mathbf{r}')g_j(\mathbf{r}';\ t)\ \mathrm{d}\mathbf{r}' - g_j(\mathbf{r};\ t)\int \mathscr{W}_i(\mathbf{r}' - \mathbf{r})\ \mathrm{d}\mathbf{r}' \tag{2}$$

$$\mathbb{L}_j g_j(\mathbf{r};\ t) = -\nabla[\mathbf{v}_j g_j(\mathbf{r};\ t)] + \sum_u \sum_{u'} D^{(j)}_{uu'}[\partial^2 g_j(\mathbf{r};\ t)/\partial r_u \partial r_{u'}] \tag{3}$$

where $\mathscr{W}_i(\mathbf{r} - \mathbf{r}')$ are translationally invariant jump rates, $\mathbf{v}_j$ are drift velocities and $D^{(j)}_{uu'}$ are diffusion coefficients. The transition from one state of the particle to other states is described by a Markov process in continuous time. The probability P_j that at time t the particle is in the state j is described by a Markovian master equation:

$$\mathrm{d}P_j(t)/\mathrm{d}t = \sum_{j'\neq j}[P_{j'}(t)W_{j'j} - P_j(t)W_{jj'}] \tag{4}$$

where $W_{j'j}$ is the rate of transition from the state j' to the state j. The static disorder is implemented into the model by assuming that the transition rates $W_{j'j} = W_{j'j}(\mathbf{x})$ depend on a set of random variables $\mathbf{x} = (x_1, x_2, ...)$ that are selected from a known probability density

$$p(\mathbf{x})\ \mathrm{d}\mathbf{x} \text{ with } \int p(\mathbf{x})\ \mathrm{d}\mathbf{x} = 1 \tag{5}$$

Our purpose is to evaluate the overall stochastic properties of the moving particle, expressed by the probability density

$$\xi(\mathbf{r};\ t)\ \mathrm{d}\mathbf{r} \text{ with } \int \xi(\mathbf{r};\ t)\ \mathrm{d}\mathbf{r} = 1 \tag{6}$$

that at time t the position of the particle is between d$\mathbf{r}$ and $\mathbf{r}$ + d$\mathbf{r}$.

A naïve approach to this problem is the evaluation of the probability $\xi(\mathbf{r}|\mathbf{x};\ t)\ \mathrm{d}\mathbf{r}$ for a given realization of the random vector $\mathbf{x}$ by solving the Taylor problem for an ordered system and then take the average of the result over $\mathbf{x}$, resulting in

$$\xi(\mathbf{r};\ t)\ \mathrm{d}\mathbf{r} = \int \xi(\mathbf{r}|\mathbf{x};\ t)p(\mathbf{x})\ \mathrm{d}\mathbf{x} \tag{7}$$

It is easy to show that this overall averaging approach induces an artificial collective effect, which leads to ballistic transport. By using the asymptotic analysis developed by Vlad, Ross, and Mackey[5] it is easy to show that for an ordered system with a finite number of states the moments of first and second order of the position of the moving particle obey the following asymptotic laws

$$\langle r_u(t)\rangle|_{\mathbf{x}} = \int r_u \xi(\mathbf{r}|\mathbf{x};\ t)\ \mathrm{d}\mathbf{r} \sim A_u(\mathbf{x})t \text{ as } t \to \infty \tag{8}$$

$$\langle r_u(t) r_{u'}(t)\rangle|_{\mathbf{x}} = \int r_u r_{u'} \xi(\mathbf{r}|\mathbf{x};\ t)\ \mathrm{d}\mathbf{r} \sim A_u(\mathbf{x})A_{u'}(\mathbf{x})t^2 + B_{uu'}(\mathbf{x})t \text{ as } t \to \infty \tag{9}$$

where $A_u(\mathbf{x})$ and $B_{uu'}(\mathbf{x})$ are proportionality factors which depend on the disorder vector $\mathbf{x}$. By using eqs 7−9 it is easy to evaluate the covariance matrix of the position vector at time t:

$$\langle \Delta r_u(t)\Delta r_{u'}(t)\rangle = \int (r_u - \langle r_u(t)\rangle)(r_{u'} - \langle r_{u'}(t)\rangle)\xi(\mathbf{r};\ t)\ \mathrm{d}\mathbf{r} \sim \langle \Delta A_u(\mathbf{x})\Delta A_{u'}(\mathbf{x})\rangle t^2 + \langle B_{uu'}(\mathbf{x})\rangle t, \text{ as } t \to \infty \tag{10}$$

where

$$\langle \Delta A_u(\mathbf{x})\Delta A_{u'}(\mathbf{x})\rangle = \int (A_u(\mathbf{x}) - \langle A_u(\mathbf{x})\rangle)(A_u(\mathbf{x}) - \langle A_u(\mathbf{x})\rangle)p(\mathbf{x})\ \mathrm{d}\mathbf{x} \tag{11}$$

$$\langle A_u(\mathbf{x})\rangle = \int A_u(\mathbf{x})p(\mathbf{x})\ \mathrm{d}\mathbf{x} \tag{12}$$

$$\langle B_{uu'}(\mathbf{x})\rangle = \int B_{uu'}(\mathbf{x})p(\mathbf{x})\ \mathrm{d}\mathbf{x} \tag{13}$$

We notice that in a global model the averaging over the disorder parameters leads to enhanced diffusion characterized by a covariance matrix increasing proportionally with the square of time as $t \to \infty$. This ballistic behavior is an artificial feature generated by the overall averaging. The global averaging is based on the assumption of a strong collective behavior, that is, the fluctuation of the transition rates $W_{jj'}(\mathbf{x})$ in the whole system is controlled by a single realization of the random vector $\mathbf{x}$. Although the possible existence of such a strong collective behavior cannot be completely ruled out, it is rather uncommon. For this reason in this paper we focus on developing a method of local averaging.

As pointed out by a referee, the $\sim t^2$ collective behavior corresponding to eq 10 is different from the $\sim t^3$ behavior characteristic for Richardson diffusion in turbullent flows.[8] Richardson diffusion is actually local but corresponds to a random walk in the velocity space rather than in real space. If a global averaging procedure similar to the one considered in this section is applied to Richardson diffusion, then the corresponding dispersion law displays a ballistic effect characterized by a $\sim t^4$ behavior.

Local averaging leads to an effective medium approximation for which the transitions among the different states of the moving particle are non-Markovian. Such a non-Markovian behavior can be described in terms of a continuous random walk[9] (CTRW) or of a generalized master equation[10] (GME). Unfortunately, both the CTRW and GME approaches are nonlocal in time and for this reason it is difficult to describe the Taylor transport. To avoid these difficulties, we are going to use the method of age-dependent master equations[11] (ADME).

3. Effective Medium Approximation for Taylor Transport in Disordered Systems

In the following we introduce an effective medium approximation by constructing a local CTRW propagator that describes the transitions among the different states of the moving particles for a given prescribed value of the disorder vector **x**. An effective CTRW propagator can be derived by performing an average of the local CTRW propagator over all possible values of the disorder vector **x**. In terms of this effective CTRW propagator we define a set of age-dependent transition rates. Finally, these age-dependent transition rates are used for deriving a system of local evolution equations for the description the Taylor transport in disordered systems.

We denote by $\ell_j(a|\mathbf{x})$ the probability that, for a given realization of the disorder vector **x**, the moving particle stays in the state j for a time interval between a and $a + \mathrm{d}a$. The symbol a denotes the age of the state j of the particle, and $\ell_j(a|\mathbf{x})$ is the survival function of the state j of the particle for a given realization of the disorder vector **x**. We have

$$\frac{\partial}{\partial a}\ell_j(a|\mathbf{x}) = -\ell_j(a|\mathbf{x})\sum_{j'\neq j} W_{jj'}(\mathbf{x}) \text{ with } \ell_j(a=0|\mathbf{x}) = 1 \tag{14}$$

The solution of eq 14 is

$$\ell_j(a|\mathbf{x}) = \exp[-a\sum_{j'\neq j} W_{jj'}(\mathbf{x})] \tag{15}$$

In terms of $\ell_j(a|\mathbf{x})$ we can compute the local CTRW propagator

$$\varphi_{jj''}(a|\mathbf{x})\,\mathrm{d}a = \ell_j(a|\mathbf{x})W_{jj''}(\mathbf{x})\,\mathrm{d}a = W_{jj''}(\mathbf{x})\exp[-a\sum_{j'\neq j} W_{jj'}(\mathbf{x})]\,\mathrm{d}a \tag{16}$$

Here, $\varphi_{jj''}(a|\mathbf{x})\,\mathrm{d}a$ is the probability that, for a given realization of the disorder vector **x**, a moving particle spends a time interval between a and $a + \mathrm{d}a$ in the state j and then it jumps to the state j''. The CTRW propagator $\psi_{jj''}(a)\,\mathrm{d}a$ of our effective medium theory is the average of the local propagator $\varphi_{jj''}(a|\mathbf{x})\,\mathrm{d}a$ over all possible values of the disorder vector **x**

$$\psi_{jj''}(a)\,\mathrm{d}a = \int_{\mathbf{x}} \varphi_{jj''}(a|\mathbf{x})p(\mathbf{x})\,\mathrm{d}\mathbf{x}\,\mathrm{d}a = \int_{\mathbf{x}} W_{jj''}(\mathbf{x})\exp[-a\sum_{j'\neq j} W_{jj'}(\mathbf{x})]p(\mathbf{x})\,\mathrm{d}\mathbf{x}\,\mathrm{d}a \tag{17}$$

In a similar way we can also introduce the average survival function

$$\ell_j(a) = \int_{\mathbf{x}} \ell_j(a|\mathbf{x})p(\mathbf{x})\,\mathrm{d}\mathbf{x} = \int_{\mathbf{x}} \exp[-a\sum_{j'\neq j} W_{jj'}(\mathbf{x})]p(\mathbf{x})\,\mathrm{d}\mathbf{x}\,\mathrm{d}a = \sum_{j''\neq j}\int_a^\infty \psi_{jj''}(a'')\,\mathrm{d}a'' \tag{18}$$

The ratio between $\psi_{jj''}(a)\,\mathrm{d}a$ and $\ell_j(a)$

$$\mathscr{M}_{jj''}(a)\,\mathrm{d}a = \psi_{jj''}(a)\,\mathrm{d}a/\ell_j(a) \tag{19}$$

is the rate of occurrence of a transition between the state j, with an age between a and $a + \mathrm{d}a$, to the state j'. The dynamics of transition among the different possible states of a moving particle can be fully characterized in terms of the age-dependent transition rates $\mathscr{M}_{jj''}(a)$, j, $j'' = 1, ..., M$, $j \neq j''$. We introduce the age-state joint probability

$$\mathscr{P}_j(a, t)\,\mathrm{d}a \text{ with } \sum_{j=1}^{M}\int_0^\infty \mathscr{P}_j(a, t)\,\mathrm{d}a = 1 \tag{20}$$

For this joint probability we can derive a system of age-dependent master equations (ADME)

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\mathscr{P}_j(a, t) = -\mathscr{P}_j(a, t)\sum_{j'\neq j}\mathscr{M}_{jj'}(a) \tag{21}$$

$$\mathscr{P}_j(a = 0, t) = \sum_{j'\neq j}\int_0^\infty \mathscr{P}_{j'}(a', t)\mathscr{M}_{j'j}(a') \tag{22}$$

which describe completely the time evolution of the age-state joint probability density $\mathscr{P}_j(a, t)$. Equations 21 and 22 were derived in the literature in a different physical context.[11] It was shown[11] that the ADME approach based on eqs 21 and 22 is equivalent to the GME or CTRW approach. Compared to the CTRW or GME theory, the ADME approach has the advantage that it leads to evolution equations that are local in time. The time locality is achieved at the expense of introducing an additional state variable, the age a of a state.

We introduce the age-state-position joint probability

$$\Xi_j(a, \mathbf{r}; t)\,\mathrm{d}a\,\mathrm{d}\mathbf{r} \text{ with } \sum_{j=1}^{M}\int_{\mathbf{r}}\int_0^\infty \Xi_j(a, \mathbf{r}; t)\,\mathrm{d}a\,\mathrm{d}\mathbf{r} = 1 \tag{23}$$

and derive a system of age-dependent master equations for it

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\Xi_j(a, \mathbf{r}; t) = \mathbb{L}_j\Xi_j(a, \mathbf{r}; t) - \Xi_j(a, \mathbf{r}; t)\sum_{j'\neq j}\mathscr{M}_{j'j}(a) \tag{24}$$

$$\Xi_j(a = 0, \mathbf{r}; t) = \sum_{j'\neq j}\int_0^\infty \Xi_{j'}(a', \mathbf{r}; t)\mathscr{M}_{j'j}(a')\,\mathrm{d}a' \tag{25}$$

Since we are interested in the large time behavior we assume that initially the system is in a state of age zero:

$$\Xi_j(a, \mathbf{r}; 0) = P_j(0)\delta(a)\delta(\mathbf{r}) \tag{26}$$

To solve the problem for Taylor transport, we integrate the linear evolution equations (24 and 25) with suitable initial and boundary conditions and then compute the probability density of the position of a particle:

$$\rho(\mathbf{r}; t) = \sum_{j=1}^{M}\int_{\mathbf{0}}^\infty \Xi_j(a, \mathbf{r}; t)\,\mathrm{d}a\,\mathrm{d}\mathbf{r} \tag{27}$$

By analogy with the theory of Taylor diffusion in ordered systems, we are going to show that $\Xi_j(a, \mathbf{r}; t)$ is related to the joint probability density $\mathcal{R}_j(a,\boldsymbol{\theta};t)$ of state, j age a, and sojourn times $\theta = (\theta_1, ..., \theta_M)$ at time t:

$$\mathcal{R}_j(a, \boldsymbol{\theta}; t)\mathrm{d}a\, \mathrm{d}\boldsymbol{\theta} \text{ with } \sum_{j=1}^{M}\int_0^\infty \int_{\boldsymbol{\theta}} \mathcal{R}_j(a, \boldsymbol{\theta}; t)\, \mathrm{d}a\, \mathrm{d}\boldsymbol{\theta} = 1 \quad (28)$$

Here, by the sojourn time θ_j of a state j we mean the total time spent by the particle in the state j, from the initial moment $t = 0$, to the current time t. The sojourn time θ_j is made up of the additive contributions of the durations of the different stays of the particle in the state j. Although the sojourn times of the different states are random variables, their sum is constant and equal to the total time t

$$\sum_{j=1}^{M} \theta_j(t) = t \quad (29)$$

The joint probability density $\mathcal{R}_j(a, \boldsymbol{\theta}; t)$ obeys a system of evolution equations similar to eqs 24 and 25

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial \theta_j} + \frac{\partial}{\partial a}\right)\mathcal{R}_j(a, \boldsymbol{\theta}; t) = -\mathcal{R}_j(a,\boldsymbol{\theta}; t) \sum_{j'\neq j}\mathcal{M}_{j'j}(a) \quad (30)$$

$$\mathcal{R}_j(a = 0, \boldsymbol{\theta}; t) = \sum_{j'=j} \int_0^\infty \mathcal{R}_{j'}(a'\boldsymbol{\theta}; t)\mathcal{M}_{j'j}(a')\, \mathrm{d}a' \quad (31)$$

For consistency we choose a set of initial conditions similar to eq 26

$$\mathcal{R}_j(a, \boldsymbol{\theta}; t = 0) = P_j(0)\delta(a)\delta(\boldsymbol{\theta}) \quad (32)$$

It is easy to show that the solution of evolution equations 24 and 25 can be represented as

$$\Xi_j(a, \mathbf{r}; t) = \frac{1}{(2\pi)^{d_s}} \int_{-\infty}^{\infty} \exp(-i\mathbf{kr})\tilde{\mathcal{R}}_j(a, \boldsymbol{\omega} = -i[\tilde{\mathbb{L}}_j(\mathbf{k})]; t)\, \mathrm{d}\mathbf{k} \quad (33)$$

where

$$\tilde{\mathcal{R}}_j(a, \boldsymbol{\omega}; t) = \int_{-\infty}^{\infty} \exp(i\boldsymbol{\omega\theta})\mathcal{R}_j(a, \boldsymbol{\theta}; t)\, \mathrm{d}\boldsymbol{\theta} \text{ with } \mathcal{R}_j(a, \forall\theta_j < 0; t) = 0 \quad (34)$$

is the Fourier transform of the joint probability density $\mathcal{R}_j(a, \boldsymbol{\theta}; t)$ with respect to the sojourn times,

$$\tilde{\mathbb{L}}_j(\mathbf{k}) = \int_{-\infty}^{\infty} \mathrm{d}\mathbf{k} \exp(i\mathbf{kr})\mathbb{L}_j \quad (35)$$

are the Fourier transforms of the transport operators $\mathbb{L}_j$, $\mathbf{k}$ and $\boldsymbol{\omega}$ are the Fourier variables conjugate to $\mathbf{r}$ and θ, respectively, and d_s is the space dimension. The derivation of eq 33 is straightforward. By applying the Fourier transformation to eqs 24−26 and eqs 30−32, we come to

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\tilde{\Xi}_j(a, \mathbf{k}; t) = \tilde{\mathbb{L}}_j(\mathbf{k})\tilde{\Xi}_j(a, \mathbf{k}; t) - \tilde{\Xi}_j(a, \mathbf{k}; t)\sum_{j'\neq j}\mathcal{M}_{j'j}(a) \quad (36)$$

$$\tilde{\Xi}_j(a = 0, \mathbf{k}; t) = \sum_{j'=j} \int_0^\infty \tilde{\Xi}_{j'}(a', \mathbf{k}; t)\mathcal{M}_{j'j}(a')\, \mathrm{d}a' \quad (37)$$

$$\tilde{\Xi}_j(a, \mathbf{k}; 0) = P_j(0)\delta(a) \quad (38)$$

and

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\tilde{\mathcal{R}}_j(a, \boldsymbol{\omega}; t) = i\omega_j\tilde{\mathcal{R}}_j(a, \boldsymbol{\omega}; t) - \mathcal{R}_j(a, \boldsymbol{\omega}; t)\sum_{j'\neq j}\mathcal{M}_{j'j}(a) \quad (39)$$

$$\tilde{\mathcal{R}}_j(a = 0, \boldsymbol{\omega}; t)\mathcal{R}_j(a = 0, \boldsymbol{\theta}; t) = \sum_{j'=j} \int_0^\infty \tilde{\mathcal{R}}_{j'}(a', \boldsymbol{\omega}; t)\mathcal{M}_{j'j}(a')\, \mathrm{d}a' \quad (40)$$

$$\tilde{\mathcal{R}}_j(a, \boldsymbol{\omega}; t = 0) = P_j(0)\delta(a) \quad (41)$$

By comparing eqs 36−38 with eqs 39−41, we notice that they have nearly the same structure with the difference that in eqs 39−41 $\tilde{\Xi}_j(a, \mathbf{k}; t)$ is replaced by $\mathcal{R}_j(a, \boldsymbol{\omega}; t)$ and $\tilde{\mathbb{L}}_j(\mathbf{k})$ is replaced by $i\omega_j$. It follows that

$$\tilde{\Xi}_j(a, \mathbf{k}; t) = \tilde{\mathcal{R}}_j(a, \boldsymbol{\omega} = -i[\tilde{\mathbb{L}}_j(\mathbf{k})]; t) \quad (42)$$

from which, by means of inverse Fourier transformation, we come to eq 33.

Equation 33 can be derived by means of a more intuitive approach that clarifies its physical meaning. Since the transport equations are linear, the superposition principle applies and the probability density $g_j(\delta\mathbf{r}_j; \theta_j)$ of the total $\delta\mathbf{r}_j(\theta_j)$ displacement of a particle during the sojourn time θ_j can be computed from eq 1, which can be rewritten as

$$\partial_{\theta_j}g_j(\delta\mathbf{r}_j; \theta_j) = \mathbb{L}_j g_j(\delta\mathbf{r}_j; \theta_j) \text{ with } g_j(\delta\mathbf{r}_j; \theta_j = 0) = \delta(\delta\mathbf{r}_j) \quad (43)$$

For solving eq 43, we apply the Fourier transformation with respect to the space variables, integrate the resulting ordinary differential equation, and come back to the space variables by means of an inverse transformation. We obtain

$$g_j(\delta\mathbf{r}_j; \theta_j) = \frac{1}{(2\pi)^{d_s}} \int_{-\infty}^{\infty} \exp(-i\mathbf{k}\cdot\delta\mathbf{r}_j + \theta_j\tilde{\mathbb{L}}_j(\mathbf{k}))\, \mathrm{d}\mathbf{k} \quad (44)$$

The total displacement $\mathbf{r}(t)$ corresponding to a time interval of duration t can be expressed as the sum of the different displacements $\delta\mathbf{r}_j(\theta_j)$ corresponding to the sojourn times θ_j of the different states

$$\mathbf{r}(t) = \textstyle\sum_{j=1}^{M} \delta\mathbf{r}_j(\theta_j) \quad (45)$$

It follows that the joint probability density $\Xi_j(a, \mathbf{r}; t)$ of the age, state, and position of the moving particle at time t can be obtained by averaging a delta-shaped probability density corresponding to eq 45,

$$\delta[\mathbf{r} - \textstyle\sum_{j=1}^{M} \delta\mathbf{r}_j(\theta_j)]\, \mathrm{d}\mathbf{r} \quad (46)$$

over all possible values of the displacements $\delta\mathbf{r}_j(\theta_j)$ and of the sojourn times θ_j. We have

$$\Xi_j(a, \mathbf{r}; t) = \int_{\delta\mathbf{r}_1} \mathrm{d}\delta\mathbf{r}_1 ... \int_{\delta\mathbf{r}_M} \mathrm{d}\delta\mathbf{r}_M \int_{\theta_1} \mathrm{d}\theta_1 ... \int_{\theta_M} \mathrm{d}\theta_M \delta[\mathbf{r} - \textstyle\sum_{j=1}^{M} \delta\mathbf{r}_j(\theta_j)]\displaystyle\prod_{j=1}^{M}[g_j(\delta\mathbf{r}_j; \theta_j)]\mathcal{R}_j(a, \boldsymbol{\theta}; t) \quad (47)$$

Now we take the Fourier transform with respect to the space variable and use eq 44. We obtain

$$\tilde{\Xi}_j(a, \mathbf{k}; t) = \int_{\theta_1} d\theta_1 ... \int_{\theta_M} d\theta_M \prod_{j=1}^{M} [\exp[i\theta_j[-i\tilde{\mathbb{L}}_j(\mathbf{k})]]]\mathcal{R}_j(a, \boldsymbol{\theta}; t) = \tilde{\mathcal{R}}_j(a, \boldsymbol{\omega} = -i[\tilde{\mathbb{L}}_j(\mathbf{k})]; t) \quad (48)$$

from which, by means of an inverse Fourier transformation, we come to eq 33. From this derivation it follows that the physical interpretation of eq 33 is straightforward: This equation expresses the contributions of the of individual displacements corresponding to the sojourn times attached to the different states of the moving particle to the probability density $\Xi_j(a, \mathbf{r}; t)$ of the state, age, and position of the moving particle at time t.

We have shown that the problem of Taylor transport in disordered systems can be reduced to the integration of the evolution equations 30−32 for the joint probability density $\mathcal{R}_j(a, \boldsymbol{\theta}; t)$. At least in principle, these equations can be solved by means of Fourier and Laplace transformations. We denote by

$$\hat{\mathcal{R}}_j(a, \boldsymbol{\omega}; s) = \int_{-\infty}^{\infty} \int_0^{\infty} \exp(i\boldsymbol{\omega\theta} - st)\mathcal{R}_j(a, \boldsymbol{\theta}; t)\, d\boldsymbol{\theta}\, dt \quad (49)$$

the Fourier and Laplace transform of $\mathcal{R}_j(a, \boldsymbol{\theta}; t)$ with respect to the sojourn times and the real time, and by

$$\mathcal{G}_j(x, \boldsymbol{\omega}; s) = \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} \exp(i\boldsymbol{\omega\theta} - st - ax)\mathcal{R}_j(a, \boldsymbol{\theta}; t)\, d\boldsymbol{\theta}\, dt\, da \quad (50)$$

the Fourier and Laplace transform of $\mathcal{R}_j(a, \boldsymbol{\theta}; t)$ with respect to the sojourn times, age, and the real time. Here x and s are the Laplace and Fourier variables conjugated to the age a and the time t, respectively, and the other symbols have the same meaning as before. The solution of eqs 30−32 proceeds in two steps. We first apply the Fourier and Laplace transformation with respect to the sojourn times and the real time and integrate the resulting differential equation in the age domain. We have

$$\left(s - i\omega_j + \sum_{j' \neq j} \mathcal{M}_{j'j}(a) + \frac{\partial}{\partial a}\right)\hat{\mathcal{R}}_j(a, \boldsymbol{\omega}; s) = P_j(0)\delta(a) \quad (51)$$

$$\hat{\mathcal{R}}_j(a = 0, \boldsymbol{\omega}; s) = \sum_{j'=j} \int_0^{\infty} \hat{\mathcal{R}}_{j'}(a', \boldsymbol{\omega}; s)\mathcal{M}_{j'j}(a')\, da' \quad (52)$$

The solution of eq 51 with the initial condition (eq 52) is

$$\hat{\mathcal{R}}_j(a, \boldsymbol{\omega}; s) = [Z_j(\boldsymbol{\omega}; s) + P_j(0)]\mathcal{J}_j(a) \exp[-a(s - i\boldsymbol{\omega}_j)] \quad (53)$$

where the functions $Z_j(\boldsymbol{\omega}; s)$ are given by

$$Z_j(\boldsymbol{\omega}; s) = \hat{\mathcal{R}}_j(a = 0, \boldsymbol{\omega}; s) = \sum_{j'=j} \int_0^{\infty} \hat{\mathcal{R}}_{j'}(a', \boldsymbol{\omega}; s)\mathcal{M}_{j'j}(a')\, da' \quad (54)$$

Now we apply the Laplace transformation with respect to the age a to eqs 53 and 54. We come to

$$\mathcal{G}_j(x, \boldsymbol{\omega}; s) = [Z_j(\boldsymbol{\omega}; s) + P_j(0)]\bar{\mathcal{J}}_j(x + s - i\omega_j) \quad (55)$$

$$Z_j(\boldsymbol{\omega}; s) = \sum_{j' \neq j} [Z_{j'}(\boldsymbol{\omega}; s) + P_{j'}(0)]\bar{\psi}_{j'j}(s - i\omega_{j'}) \quad (56)$$

where

$$\bar{\mathcal{J}}_j(x) = \int_0^{\infty} \mathcal{J}_j(a) \exp(-sa)\, da \quad (57)$$

$$\bar{\psi}_{j'j}(x) = \int_0^{\infty} \psi_{j'j}(a) \exp(-sa)\, da \quad (58)$$

are the Laplace transforms of the average survival functions $\mathcal{J}_j(a)$ and of the average CTRW propagators $\psi_{j'j}(a)$, respectively.

Equation 56 is a linear algebraic equation in $Z_j(\boldsymbol{\omega}; s)$, which can be solved analytically. We have

$$\mathbf{Z}(\boldsymbol{\omega}; s) = \mathbf{P}(0)[\mathbf{I} - \bar{\boldsymbol{\psi}}]^{-1} \quad (59)$$

By inserting eq 57 into eq 55 we can compute the Fourier and Laplace transforms $\mathcal{G}_j(x, \boldsymbol{\omega}; s)$. From eqs 27, 33, 50, and 55 we can show that the Laplace and Fourier transform of the probability density of the position of the particle at time, t, $\rho(\mathbf{r}; t)$

$$G(\mathbf{k}; s) = \int_{-\infty}^{\infty} \int_0^{\infty} \exp(i\mathbf{kr} - st)\rho(\mathbf{r}; t)\, d\mathbf{r}\, dt \quad (60)$$

can be expressed as

$$G(\mathbf{k}; s) = \sum_j \mathcal{G}_j(x = 0, \boldsymbol{\omega} = -i[\tilde{\mathbb{L}}_j(\mathbf{k})]; s) = \sum_j [Z_j(-i[\tilde{\mathbb{L}}_j(\mathbf{k})]; s) + P_j(0)]\bar{\mathcal{J}}_j(s - \tilde{\mathbb{L}}_j(\mathbf{k})) \quad (61)$$

from which we can obtain the probability density $\rho(\mathbf{r}; t)$ by means of inverse Fourier and Laplace transformation. Even if the evaluation of the inverse Fourier and Laplace transformations is too complicated to be of practical use, eq 61 may serve as a basis for deriving expressions for the moments and cumulants of the position of the moving particle. Since eq 61 does not involve global averaging, the transport processes described by this equation do not have the ballistic behavior predicted by eq 7. Depending on the structure of the probability $p(\mathbf{x})$ of the disorder vector, eq 61 leads either to normal or dispersive transport.

In the particular case where the moving particle can exist only in two states, the $G(\mathbf{k}; s)$ is given by

$$G(\mathbf{k}; s) = \left[\frac{\bar{\psi}_{21}(s - \tilde{\mathbb{L}}_2(\mathbf{k}))P_2(0) + P_1(0)}{1 - \bar{\psi}_{12}(s - \tilde{\mathbb{L}}_1(\mathbf{k}))\bar{\psi}_{21}(s - \tilde{\mathbb{L}}_2(\mathbf{k}))}\right]\frac{(1 - \bar{\psi}_{12}(s - \tilde{\mathbb{L}}_1(\mathbf{k})))}{(s - \tilde{\mathbb{L}}_1(\mathbf{k}))} + \left[\frac{\bar{\psi}_{12}(s - \tilde{\mathbb{L}}_1(\mathbf{k}))P_1(0) + P_2(0)}{1 - \bar{\psi}_{12}(s - \tilde{\mathbb{L}}_1(\mathbf{k}))\bar{\psi}_{21}(s - \tilde{\mathbb{L}}_2(\mathbf{k}))}\right]\frac{(1 - \bar{\psi}_{21}(s - \tilde{\mathbb{L}}_2(\mathbf{k})))}{(s - \tilde{\mathbb{L}}_2(\mathbf{k}))} \quad (62)$$

In conclusion, in this section we have introduced an effective medium approximation for the Taylor transport in disordered systems. We have defined a CTRW propagator as the local average value of the exponential, Markovian, CTRW propagator corresponding to a given value of the disorder vector. In terms of the CTRW propagator, we have introduced a set of age-dependent transition rates that make it possible to describe the Taylor transport in terms of a set of age-dependent evolution equations that are local in time. We have shown that the integration of the age-dependent evolution equations can be reduced to the determination of the stochastic properties of the sojourn times attached to the different states of the moving particle.

4. Numbers of Transition Events and Taylor Transport in Disordered Systems

In some cases it is more appropriate to describe the transport in a given state of a moving particle in terms of a single jump probability rather than in terms of an evolution equation in continuous time. The evolution eq 1 is replaced by a probability density of the jump vector $\delta\mathbf{r}_j$ attached to one stay of the moving particle in the state j

$$\phi_j(\delta\mathbf{r}_j)\,\mathrm{d}\delta\mathbf{r}_j \text{ with } \int_{\delta\mathbf{r}_j}\phi_j(\delta\mathbf{r}_j)\,\mathrm{d}\delta\mathbf{r}_j = 1 \tag{63}$$

and the evolution equations 24 and 25 for the probability density $\Xi_j(a, \mathbf{r}; t)$ of the state, age, and position of the moving particle are replaced by

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\Xi_j(a, \mathbf{r}; t) = \Xi_j(a, \mathbf{r}; t)\sum_{j'\neq j}\mathscr{M}_{j'j}(a) \tag{64}$$

$$\Xi_j(a = 0, \mathbf{r}; t) = \sum_{j'=j}\int_{\mathbf{r}'}\int_0^\infty \Xi_{j'}(a', \mathbf{r} - \mathbf{r}'; t)\phi_j(\mathbf{r}')\mathscr{M}_{j'j}(a')\,\mathrm{d}a'\,\mathrm{d}\mathbf{r}' \tag{65}$$

with the initial condition (eq 26). In this case it makes sense to introduce a set of discrete state variables, the different total numbers q_j, $j = 1, ..., M$ of stays of the moving particle in the different possible states, $j = 1, ..., M$, in a time interval of duration t. We introduce a joint probability $\mathscr{B}_j(a, \mathbf{q}; t)$ for the state, the age and the vector $\mathbf{q} = [q_j]$ of the number of transition events of the moving particle at time t. The joint probability density $\mathscr{B}_j(a, \mathbf{q}; t)$ obeys a system of evolution equations similar to eqs 30−32 for the joint probability density $\mathscr{R}_j(a, \boldsymbol{\theta}; t)$

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\right)\mathscr{B}_j(a, \mathbf{q}; t) = -\mathscr{B}_j(a, \mathbf{q}; t)\sum_{j'\neq j}\mathscr{M}_{j'j}(a) \tag{66}$$

$$\mathscr{B}_j(a = 0, \mathbf{q}; t) = \sum_{j'=j}\int_0^\infty \mathscr{B}_{j'}(a, \mathbf{q} - [\delta_{j'u}]; t)\mathscr{M}_{j'j}(a')\,\mathrm{d}a' \tag{67}$$

with the initial condition

$$\mathscr{B}_j(a, \mathbf{q}; t = 0) = P_j(0)\delta(a)\delta_{\mathbf{q0}} \tag{68}$$

By following the same steps as in the preceding section it is easy to show that the solutions of the transport equations (eqs 64 and 65) can be represented in terms of the solution $\mathscr{B}_j(a, \mathbf{q}; t)$ of the evolution equations (eqs 67−68). We obtain a relation similar to eq 33 from section 3:

$$\Xi_j(a, \mathbf{r}; t) = \frac{1}{(2\pi)^{d_s}}\int_{-\infty}^{\infty}\exp(-i\mathbf{k}\mathbf{r})\tilde{\mathscr{B}}_j(a, \mathbf{z} = [\tilde{\Phi}_j^{-1}(\mathbf{k})]; t)\,\mathrm{d}\mathbf{k} \tag{69}$$

where

$$\tilde{\mathscr{B}}_j(a, \mathbf{z}; t) = \sum_{q_1=0}^{\infty} .... \sum_{q_M=0}^{\infty}\prod_{u=1}^{M}(z_u)^{-q_u}\mathscr{B}_j(a, \mathbf{q}; t) \text{ with } \mathrm{Re}(z_u) \geq 1 \tag{70}$$

is the z transform of the joint probability density $\mathscr{B}_j(a, \mathbf{q}; t)$ with respect to the numbers q_j, $j = 1, ..., M$ of transition events, z_u; $j = 1, ..., M$ are the z variable conjugated to the numbers q_j, $j = 1, ..., M$; and

$$\tilde{\Phi}_j(\mathbf{k}) = \int_{-\infty}^{\infty}\Phi_j(\mathbf{r})\exp(i\mathbf{k}\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{71}$$

are the Fourier transforms of the jump probability densities $\Phi_j(\mathbf{r})$. The mathematical proof of eq 70 is similar to the proof of eq 33. We apply the Fourier and z transforms to eqs 26, 64, 65, and 66−68, respectively, and compare the resulting equations, which leads to an identity similar to eq 42:

$$\tilde{\tilde{\Xi}}_j(a, \mathbf{k}; t) = \tilde{\mathscr{B}}_j(a, \mathbf{z} = [\tilde{\Phi}_j^{-1}(\mathbf{k})]; t) \tag{72}$$

from which, by means of inverse Fourier transformation, we come to eq 69.

There is also a more intuitive derivation of eq 69 that clarifies its physical meaning. The probability density $\Phi_j(\delta\mathbf{r}_j; q_j)$ of the jump vector $\delta\mathbf{r}_j$ corresponding to q_j stays in the state j can be expressed as the q_j-fold convolution product of the jump probability density $\Phi_j(\delta\mathbf{r}_j)$

$$\Phi_j(\delta\mathbf{r}_j; q_j) = [\Phi_j(\delta\mathbf{r}_j)\otimes]^{q_j} \tag{73}$$

where $\otimes$ denotes the spatial convolution product. By using a pair of Fourier transforms, eq 73 can be rewritten in a form similar to eq 44

$$\Phi_j(\delta\mathbf{r}_j; q_j) = \frac{1}{(2\pi)^{d_s}}\int_{-\infty}^{\infty}\exp(-i\mathbf{k}\delta\mathbf{r}_j)[\tilde{\Phi}_j(\mathbf{k})]^{q_j}\,\mathrm{d}\mathbf{k} \tag{74}$$

The total displacement $\mathbf{r}(t)$ corresponding to a time interval of duration t can be expressed as the sum of the different displacements $\delta\mathbf{r}_j(q_j)$ corresponding to the total numbers of stays q_j of the different states:

$$\mathbf{r}(t) = \sum_{j=1}^{M}\delta\mathbf{r}_j(q_j) \tag{75}$$

It follows that the joint probability density $\Xi_j(a, \mathbf{r}; t)$ of the age, state and position of the moving particle at time t can be obtained by averaging a delta-shaped probability density corresponding to eq 75

$$\delta[\mathbf{r} - \sum_{j=1}^{M}\delta\mathbf{r}_j(q_j)]\,\mathrm{d}\mathbf{r} \tag{76}$$

over all possible values of the displacements $\delta\mathbf{r}_j(q_j)$ and of the total numbers of stays q_j. We have

$$\Xi_j(a, \mathbf{r}; t) = \int_{\delta\mathbf{r}_1}\mathrm{d}\delta\mathbf{r}_1 ... \int_{\delta\mathbf{r}_M}\mathrm{d}\delta\mathbf{r}_M\sum_{q_1=1}^{\infty} ... \sum_{q_M=1}^{\infty}\delta[\mathbf{r} - \sum_{j=1}^{M}\delta\mathbf{r}_j(q_j)]\prod_{j=1}^{M}[g_j(\delta\mathbf{r}_j; q_j)]\mathscr{B}_j(a, \mathbf{q}; t) \tag{77}$$

We take the Fourier transform of eq 77 with respect to the position vector and use the definition (eq 70) of the z transform $\tilde{\mathscr{B}}_j(a, \mathbf{z}; t)$. After some calculations we come to eq 72, which is equivalent to eq 69.

To solve eqs 66−68, we use the z and Laplace transformations; we introduce the notation

$$\mathscr{H}_j(x, \mathbf{z}; s) = \sum_{q_1=1}^{\infty} ... \sum_{q_M=1}^{\infty}\prod_{u=1}^{M}(z_u)^{-q_u}\int_0^\infty\int_0^\infty \exp(-st - ax)\mathscr{B}_j(a, \mathbf{q}; t)\,\mathrm{d}t\,\mathrm{d}a \tag{78}$$

After a number of calculations, eqs 66−68 lead to the following expression for $\mathscr{H}_j(x, \mathbf{z}; s)$:

$$\mathscr{H}_j(x, \mathbf{z}; s) = [Z_j(\mathbf{z}; s) + P_j(0)]\bar{\mathscr{I}}_j(x + s) \tag{79}$$

where the functions $Z_j(\mathbf{z}; s)$ are the solutions of the linear algebraic equations

$$Z_j(\mathbf{z}; s) = \sum_{j' \neq j} [Z_{j'}(\mathbf{z}; s) + P_{j'}(0)] z_{j'} \bar{\psi}_{j'j}(s) \tag{80}$$

The Laplace and Fourier transform $G(\mathbf{k}; s)$ of the probability density of the position of the particle at time, t, $\rho(\mathbf{r}; t)$, can be expressed by a relation similar to eq 61

$$G(\mathbf{k}; s) = \sum_j \mathscr{H}_j(x, \mathbf{z}; s)(x = 0, \mathbf{z} = [\tilde{\Phi}_j^{-1}(\mathbf{k})]; s) = \sum_j [Z_j([\tilde{\Phi}_j^{-1}(\mathbf{k})]; s) + P_j(0)] \bar{\mathscr{T}}_j(s) \tag{81}$$

In conclusion, in this section we have extended the theory of Taylor transport in disordered systems to the case where it is more appropriate to describe the transport in a given state of a moving particle in terms of a single jump probability.

5. Application to the Experiment of Drazer and Zanette

The Taylor transport approach suggested in this paper can be applied to the study of various problems of multiphasic transport in disordered systems. For illustrating our method in this section, we discuss the experiments of Drazer and Zanette.[7] For simplicity, we focus only on the case of flushing experiments that leads to dispersive transport. The moving particle can basically exist in two different states, a free, moving state, in the fluid, denoted with the label $j = 1$, and an adsorbed, immobile, state, on the surface, denoted with the label $j = 2$. Strictly speaking, there is also a third state, a chemical-hydrodynamic boundary layer, which makes the transition from the immediate neighborhood of the surface to the bulk of fluid, but the contribution of this boundary layer can be neglected. A local region of the surface is in a state of local equilibrium; thus, according to the experiments of Drazer and Zanette, it can be described by an adsorption isotherm of the Freundlich type, which suggest that the surface is heterogeneous and characterized by an exponential distribution of adsorption energies of the Zeldovich−Roginskii[12,13] type. The chemical aspects of the surface heterogeneity and its connections with the distribution of the residence times of the adsorbed particles on the surface have been discussed by Drazer and Zanette[7] and by Vlad, Cerofolini, and Ross.[14] In this article we focus mainly on the transport theory, not on the chemistry of the problem. The experimental data suggest that only the desorption rates from the surface are randomly distributed and that the adsorption rate constants are not variable. The transition rates between the surface and the fluid can be represented as

$$W_{12} = \nu_{12} c_b \tag{82}$$

$$W_{21} = \nu_{21} \{\exp[\epsilon/k_B T]\}^{-1} \tag{83}$$

where ν_{12} and ν_{21} are rate coefficients, c_b is the local equilibrium concentration of the solute at the boundary between the solid and the chemical-hydrodynamic boundary layer, ϵ is the adsorption energy, k_B is Boltzmann's constant, and T is the absolute temperature of the medium. The adsorption energy is a random quantity that is selected from an exponential distribution of the Zeldovich type

$$p(\epsilon) = (k_B T^*)^{-1} \exp[-\epsilon/(k_B T^*)] \text{ with } \int_0^\infty p(\epsilon)\, d\epsilon = 1,\ T^* > T \tag{84}$$

By using our effective medium approximation we can evaluate the CTRW propagators $\psi_{12}(a)$ and $\psi_{21}(a)$ from eq 17 by computing local averages with respect to the values of the absorption energy. We obtain

$$\psi_{12}(a) = \nu_{12} c_b \exp(-a \nu_{12} c_b) \tag{85}$$

$$\psi_{21}(a) = \alpha a^{-(1+\alpha)} (\nu_{21})^{-\alpha} \gamma(1 + \alpha, \nu_{21} a) \tag{86}$$

where

$$\alpha = T/T^* \tag{87}$$

is a fractal exponent between zero and one and $\gamma(a, x) = \int_0^x x^{a-1} \exp(-x)\, dx$, $a > 0$, $x \geq 0$ is the incomplete gamma function. The CTRW propagator $\psi_{12}(a)$, which expresses the distribution spent by the moving particle in the fluid, has an exponential shape and is characterized by a finite average lifetime

$$\langle a \rangle_{\text{fluid}} = \int_0^\infty a \psi_{12}(a)\, da = 1/(\nu_{12} c_b) \tag{88}$$

The CTRW propagator $\psi_{21}(a)$, which expresses the distribution spent by the particle on the surface, has a long tail of the negative power law type and is characterized by an infinite average lifetime

$$\psi_{21}(a) \sim \alpha a^{-(1+\alpha)} (\nu_{21})^{-\alpha} \Gamma(1 + \alpha) \text{ as } a \to \infty \tag{89}$$

$$\langle a \rangle_{\text{surface}} = \int_0^\infty a \psi_{21}(a)\, da = \infty \tag{90}$$

It follows that a particle spends extremely large time periods trapped on the surface, alternating with very short periods of time in the fluid. Under these circumstances it seems reasonable to use the approach developed in section 4, based on the number of stays of the particle in the fluid. Such an approach is justified by the fact that a particle spends most of the time on the surface and that, compared to the time spent on the surface, the time spent in the fluid can be neglected.

We assume that the transport in the fluid phase is given by an evolution equation of the master equation type:

$$\frac{\partial}{\partial \theta_1} g(\delta\mathbf{r}; \theta_1) = \int \mathscr{W}(\delta\mathbf{r} - \delta\mathbf{r}') g(\delta\mathbf{r}'; \theta_1)\, d\delta\mathbf{r}' - g(\delta\mathbf{r}; \theta_1) \int \mathscr{W}(\delta\mathbf{r}' - \delta\mathbf{r})\, d\delta\mathbf{r}' \tag{91}$$

with

$$g(\delta\mathbf{r}; \theta_1 = 0) = \delta(\delta\mathbf{r}) \tag{92}$$

where the transition rate $\mathscr{W}_j(\mathbf{r} - \mathbf{r}')$ can be expressed as

$$\mathscr{W}(\delta\mathbf{r} - \delta\mathbf{r}') = \Omega p(\delta\mathbf{r} - \delta\mathbf{r}') \tag{93}$$

Ω is a characteristic frequency and $p(\delta\mathbf{r} - \delta\mathbf{r}')$ is the probability density of the displacement vector corresponding to a jump event. By considering the Kramers−Moyal expansion, eq 91 can include the convection-dispersion equations as particular cases. We take the Fourier transform of eq 91, solve the resulting differential equation in the sojourn time θ_1, and come back to the space variable by means of an inverse Fourier transformation. We come to

$$g(\delta\mathbf{r}; \theta_1) = \frac{1}{(2\pi)^{d_s}} \int_{-\infty}^{\infty} \exp((\tilde{p}(\mathbf{k}) - 1)\Omega\theta_1 - i\mathbf{k}\delta\mathbf{r}_j)\, d\mathbf{k} \tag{94}$$

where

$$\tilde{p}(\mathbf{k}) = \frac{1}{(2\pi)^{d_s}} \int_{-\infty}^{\infty} \exp(i\mathbf{k}\Delta\delta\mathbf{r}) p(\Delta\delta\mathbf{r})\, \mathrm{d}\Delta\delta\mathbf{r} \qquad (95)$$

is the Fourier transform of the probability density $p(\delta\mathbf{r} - \delta\mathbf{r}')$.

Since the CTRW propagator $\psi_{12}(a)$ corresponding to the fluid phase is exponential, the probability density

$$P(\theta_1; q_1) \text{ with } \int P(\theta_1; q_1)\, \mathrm{d}\theta_1 = 1 \qquad (96)$$

of the total sojourn time corresponding to the occurrence of q_1 stay events is between θ_1 and $\theta_1 + \mathrm{d}\theta_1$ is given by a gamma distribution

$$P(\theta_1; q_1) = \prod_{u=1}^{q_1} [\psi_{12}(\theta_1)\odot] = \frac{(\nu_{12}c_b\theta_1)^{q_1-1}}{(q_1-1)!} \nu_{12}c_b \exp(-\nu_{12}c_b\theta_1) \qquad (97)$$

where $\odot$ denotes the temporal convolution product.

The probability density $\Phi_1(\mathbf{r}; q_1)$ of the jump vector corresponding to q_1 stays in the fluid can be evaluated by averaging eq 91 over all possible values of the sojourn time θ_1

$$\Phi_1(\mathbf{r}; q_1) = \int_0^t P(\theta_1; q_1) g(\mathbf{r}; \theta_1)\, \mathrm{d}\theta_1 \approx \int_0^{\infty} P(\theta_1; q_1) g(\mathbf{r}; \theta_1)\, \mathrm{d}\theta_1 = \\ = \frac{1}{(2\pi)^{d_s}} \int_{-\infty}^{\infty} \left[\frac{\nu_{12}c_b}{\nu_{12}c_b + (1 - \tilde{p}(\mathbf{k}))\Omega}\right]^{q_1} \exp(-i\mathbf{k}\mathbf{r})\, \mathrm{d}\mathbf{k} \qquad (98)$$

We take into account that a stay on the surface alternates with a stay in the fluid and thus $q_1 = q_2 + 1$. Since a moving particle spends most of the time trapped on the surface, we can assume that $\theta_2 \cong t$. By using these approximations we find the distribution of the number of stays in the fluid, $P(q_1; t)$, during a total time interval of length t, to be

$$P(q_1; t) \cong P(q_2; \theta_2) \qquad (99)$$

The probability $P(q_2; \theta_2)$ can be expressed as a multiple convolution product of the CTRW propagator $\psi_{21}(a)$. We have

$$P(q_2; \theta_2) = \prod_{u=1}^{q_2} [\psi_{21}(\theta_2)\odot] \odot \int_{\theta_2}^{\infty} \psi_{21}(\theta')\, \mathrm{d}\theta' = \mathscr{L}_{\theta 2}^{-1}\left\{\frac{1}{s}[\bar{\psi}_{21}(s)]^{q_2}[1 - \bar{\psi}_{21}(s)]\right\} \qquad (100)$$

where $\mathscr{L}_{\theta 2}^{-1}$ denotes the inverse Laplace transformation. By applying the approximation eq 99 to eq 100 we obtain

$$P(q_1; t) \cong \mathscr{L}_t^{-1}\left\{\frac{1}{s}[\bar{\psi}_{21}(s)]^{q_1-1}[1 - \bar{\psi}_{21}(s)]\right\} \qquad (101)$$

The probability density $\xi(\mathbf{r}; t)$ of the position of the moving particle at time t can be evaluated by averaging the probability density $\Phi_1(\mathbf{r}; q_1)$ of the position corresponding to q_1 stays in the fluid over all possible values q_1 corresponding to a time interval of length t

$$\xi(\mathbf{r}; t) = \sum_{q_1=1}^{\infty} \Phi_1(\mathbf{r}; q_1) P(q_1; t) \cong \mathscr{L}_t^{-1}\left\{\frac{1}{(2\pi)^{d_s} s} \int_{-\infty}^{\infty} \frac{\nu_{12}c_b[1 - \bar{\psi}_{21}(s)] \exp(-i\mathbf{k}\mathbf{r})}{\nu_{12}c_b[1 - \bar{\psi}_{21}(s)] + (1 - \tilde{p}(\mathbf{k}))\Omega}\, \mathrm{d}\mathbf{k}\right\} \qquad (102)$$

Since we are interested in the large time behavior, $t \to \infty$, we evaluate the Laplace transform in the limit $s \to 0$. From eq 86 it follows that

$$\bar{\psi}_{21}(s) = 1 - \left(\frac{s}{\nu_{21}}\right)^{\alpha} \alpha B\left(\alpha, 1 - \alpha, \frac{\nu_{21}}{\nu_{21} + s}\right) \sim 1 - \left(\frac{s}{\nu_{21}}\right)^{\alpha} \frac{\pi\alpha}{\sin(\pi\alpha)} \text{ as } s \to 0 \qquad (103)$$

where $B(p, q, x) = \int_0^x x^{p-1}(1 - x)^{q-1}\, \mathrm{d}x$, $x \le 1$, $p, q > 0$ is the incomplete beta function.

It follows that the large time behavior of the probability $\xi(\mathbf{r}; t)$ for large times is given by a negative power law of the type

$$\xi(\mathbf{r}; t) \sim A(\mathbf{r})/t^{\alpha} \text{ as } t \to \infty \qquad (104)$$

where

$$A(\mathbf{r}) = -\frac{\alpha\Gamma(1 + \alpha)}{(2\pi)^{d_s}(\nu_{21})^{\alpha}} \int_{-\infty}^{\infty} \frac{\nu_{12}c_b \exp(-i\mathbf{k}\mathbf{r})}{\nu_{12}c_b + (1 - \tilde{p}(\mathbf{k}))\Omega}\, \mathrm{d}\mathbf{k} \qquad (105)$$

Since the concentration in the fluid, $C(r,t)$ is proportional to the probability $\xi(\mathbf{r}; t)$, eq 104 is consistent with the experimental result[7] $C_{\text{liquid}}(t) \sim t^{-\mu}$, $t \gg 0$, with $\mu = 0.63$. Drazer and Zanette[7] suggested a simplified model, which essentially uses the number of stays q_1 in the fluid as a measure of the position $\mathbf{r}$ of the moving particle. Within the framework of our approach, their approximation consists of assuming that the probability density $\Phi_1(\mathbf{r}; q_1)$ can be approximated by the convolution of a uniform distribution. Their approximation is also compatible with the temporal scaling behavior predicted by eq 104. However, eq 104 is not appropriate for the effective computation of the transport properties of the system, such as the fractional diffusion coefficients of the process.

We finish this article with a computation of effective transport coefficients for our model of the Drazer–Zanette experiment. We denote by

$$\tilde{\xi}(\mathbf{k}; t) = \int_{-\infty}^{+\infty} \exp(i\mathbf{k}\mathbf{r}) \xi(\mathbf{r}; t)\, \mathrm{d}\mathbf{r} = \mathscr{L}_t^{-1} G(\mathbf{k}; s) \qquad (106)$$

the Fourier transform overall probability density for the position of a particle at time t. The various cumulants $\langle\langle r_{u1}(t) ... r_{um}(t)\rangle\rangle$ of the position $\mathbf{r}$ can be evaluated by expanding $\ln \tilde{\xi}(\mathbf{k}; t)$ in a Taylor series. We have

$$\ln \tilde{\xi}(\mathbf{k}; t) = \sum_{m=1}^{\infty} \frac{i^m}{m!} \sum_{u_1} ... \sum_{u_m} k_{u1} ... k_{um} \langle\langle r_{u1}(t) ... r_{um}(t)\rangle\rangle \qquad (107)$$

from which we obtain

$$\langle\langle r_{u1}(t) ... r_{um}(t)\rangle\rangle = -i^m \frac{\partial^m}{\partial k_{u1} ... \partial k_{um}} \ln \tilde{\xi}(\mathbf{k}; t)\Big|_{\mathbf{k}=\mathbf{0}} = -i^m \frac{\partial^m}{\partial k_{u1} ... \partial k_{um}} \ln[\mathscr{L}_t^{-1} G(\mathbf{k}; s)]\Big|_{\mathbf{k}=\mathbf{0}} \qquad (108)$$

In particular, for $m = 1, 2$

$$\langle r_u(t)\rangle = \langle\langle r_u(t)\rangle\rangle = \mathscr{L}_t^{-1}\left\{\frac{\Omega\langle\delta r_u\rangle}{\nu_{12}c_b s[1-\bar{\psi}_{21}(s)]}\right\} \quad (109)$$

$$\langle\langle r_u(t)r_{u'}(t)\rangle\rangle = \langle\Delta r_u(t)\Delta r_{u'}(t)\rangle = \mathscr{L}_t^{-1}\left\{\frac{\Omega\langle\delta r_u\delta r_{u'}\rangle}{\nu_{12}c_b s[1-\bar{\psi}_{21}(s)]} + 2\frac{\Omega^2\langle\delta r_u\rangle\langle\delta r_{u'}\rangle}{(\nu_{12}c_b)^2 s[1-\bar{\psi}_{21}(s)]^2}\right\} - \mathscr{L}_t^{-1}\left\{\frac{\Omega\langle\delta r_u\rangle}{\nu_{12}c_b s[1-\bar{\psi}_{21}(s)]}\right\}\mathscr{L}_t^{-1}\left\{\frac{\Omega\langle\delta r_{u'}\rangle}{\nu_{12}c_b s[1-\bar{\psi}_{21}(s)]}\right\} \quad (110)$$

where

$$\langle\delta r_u\rangle = \int \delta r_u p(\mathbf{r})d\mathbf{r},\ \langle\delta r_u\delta r_{u'}\rangle = \int \delta r_u\delta r_{u'}p(\mathbf{r})\,\mathrm{d}\mathbf{r} \quad (111)$$

We express the position vectors $\mathbf{r}$ and $\delta\mathbf{r}$ in cylindrical coordinates $\mathbf{r} = (l, r, \varphi)$, $\delta\mathbf{r} = (\delta l, \delta r, \delta\varphi)$ and consider only the component of motion along the longitudinal position l of the pipe. From eqs 103 and 109−110, we evaluate the asymptotic behavior for large time of the cumulants of order one and two of the longitudinal position l of a moving particle. We obtain

$$\langle l(t)\rangle = \langle\langle l(t)\rangle\rangle \sim \frac{(\nu_{21})^{\alpha}\Omega\langle\delta l\rangle}{\nu_{12}c_b\Gamma(1-\alpha)}t^{\alpha} = \mathscr{U}t^{\alpha}, \text{ as } t\to\infty \quad (112)$$

$$\langle\langle[l(t)]^2\rangle\rangle = \langle[\Delta l(t)]^2\rangle \sim t^{2\alpha}\left[\frac{(\nu_{21})^{\alpha}\Omega\langle\delta l\rangle}{\nu_{12}c_b\Gamma(1-\alpha)}\right]^2\left[\frac{\Gamma(1+2\alpha)\Gamma(1-\alpha)}{\alpha^2\Gamma(\alpha)} - 1\right] = \mathscr{D}t^{2\alpha}, \text{ as } t\to\infty \quad (113)$$

where

$$\mathscr{U} = \frac{(\nu_{21})^{\alpha}\Omega\langle\delta l\rangle}{\nu_{12}c_b\Gamma(1-\alpha)} \quad (114)$$

$$\mathscr{D} = \left[\frac{(\nu_{21})^{\alpha}\Omega\langle\delta l\rangle}{\nu_{12}c_b\Gamma(1-\alpha)}\right]^2\left[\frac{\Gamma(1+2\alpha)\Gamma(1-\alpha)}{\alpha^2\Gamma(\alpha)} - 1\right] \quad (115)$$

are fractional transport coefficients: $\mathscr{U}$ is a dispersive drift factor and $\mathscr{D}$ is a dispersive diffusion coefficient. From eqs 112 and 113 we can compute the asymptotic value of the relative fluctuation of order two of the position l as $t\to\infty$. We have

$$\zeta_2 = \frac{\langle\langle[l(t)]^2\rangle\rangle}{\langle[l(t)]\rangle^2} \sim \frac{\Gamma(1+2\alpha)\Gamma(1-\alpha)}{\alpha^2\Gamma(\alpha)} - 1 \neq 0, \text{ as } t\to\infty,\ 1 > \alpha > 0 \quad (116)$$

Since $\zeta_2 \neq 0$ as $t\to\infty$, it follows that the fluctuations of the longitudinal position of the moving particle are intermittent.

In conclusion, in this section we have shown that our effective medium approach to Taylor diffusion is consistent with the experimental results of Drazer and Zanette.

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References and Notes

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

(2) Giddings, J. C.; Eyring, H. *J. Phys Chem.* **1955**, *59*, 416. Giddings, J. C. *J. Chem. Phys.* **1957**, *26*, 169. Iordache, O. *Polystochastic Models in Chemical Engineering*, VNU Science Press: Utrecht, 1987, and references therein.

(3) Van Kampen, N. G. *Physica A* **1979**, *A96*, 435. Van Kampen, *Stochastic Processes in Physics and Chemistry*, 2nd ed.; North-Holland: Amsterdam 1992; chapter V.

(4) Van den Broeck, C.; Mazo, R. M. *Phys. Rev. Lett.* **1983**, *51*, 1309. Van den Broeck, C.; Mazo, R. M. *J. Chem. Phys.* **1984**, *81*, 3624. Van den Broeck, C. *Drunks, Drift and Dispersion*, Vrije Universiteit Brussels: Brussels, 1988. Van den Broeck, C. *Physica A* **1990**, *A168*, 677.

(5) Vlad, M. O.; Ross, J.; Mackey, M. C. *Physica A* **1997**, *A243*, 340.

(6) Pomraning, G. C. *Linear Kinetic Theory and Particle Transport in Stochastic Mixtures*, World Scientific: Singapore, 1991.

(7) Drazer, G.; Zanette, D. Z. *Phys. Rev. E.* **1999**, *60*, 5858.

(8) Montroll, E. W.; Scher, H. *J. Stat. Phys.* **1973**, *9*, 101. Scher, H.; Montroll, E. W. *Phys. Rev.* **1975**, *B12*, 2455. Berkowitz, B.; Scher, H. *Transport in Porous Media* **2001**, *42*(*1*−*2*), 241. Berkowitz, B.; Scher, H.; Silliman, S. E. *Water Resour. Res.* **2000**, *36*(*1*), 149.

(9) Montroll, E. W.; Bendler, J. T. *J. Stat. Phys.* **1984**, *34*, 129. Montroll, E. W.; West, B. J. In *Fluctuation Phenomena, Studies in Statistical Mechanics v. VII*, North-Holland: Amsterdam, 1979, pp 61−175. Shlesinger, M. F.; Montroll, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1280. Haus, J. W.; Kehr, K. W. *Phys. Rep.* **1987**, *150*, 263. Shlesinger, M. F. *Annu. Rev. Phys. Chem.* **1988**, *39*, 269.

(10) Kenkre V. M.; Knox, R. S. *Phys. Rev. B* **1974**, *B9*, 5279. Landmann, U.; Montroll, E. W.; Shlesinger, M. F. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 430. Kenkre, V. M.; Montroll, E. W.; Shlesinger, M. F. *J. Stat. Phys.* **1073**, *9*, 45; Shugard, W. J.; Reiss, H. *J. Chem. Phys.* **1976**, *65*, 2877.

(11) Vlad, M. O.; Popa, V. T.; Segal, E. *Phys. Lett. A* **1984**, *100*, 387. Vlad, M. O. *J. Phys. AMath. Gen.* **1987**, *20*, 3367. Vlad, M. O. *Phys. Rev. A* **1992**, *45*, 3600. Vlad, M. O.; Pop, A. *J. Phys. A: Math. Gen.* **1989**, *22*, 3945; *Zeit. f. Physik B* **1989**, *75*, 413; *Physica A* **1989**, *155*, 276; Vlad, M. O.; Ross, J. *J. Phys. Lett. A* **1994**, *184*, 403.

(12) Roginskii, S. Z. *Adsorption and Catalysis on Heterogeneous Surfaces*, N.A.: Moscow, 1948. S. L. Kiperman, *Introduction to the Kinetics of Heterogeneous Surfaces*, N. A., Moscow, 1964.

(13) Temkin, M. I. *Kinet. Katal.* **1967**, *8*, 1005. Boudart, M. In *Physical Chemistry. An Advanced Treatise, Vol. VII/Reactions in Condensed Phases*, Academic Press: New York, 1975, pp 349−411.

(14) Vlad, M. O.; Cerofolini, G.; Ross, J. *Phys. Rev. E* **2000**, *E 62*, 837.