Paradoxes of Subdiffusive Infiltration in Disordered Systems

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Infiltration of diffusing particles from one material to another is a widely investigated process in many fields of physics. In recent years much focus was diverted to the problem when the diffusion in one or in both materials is anomalous, namely \( \langle \chi^2 \rangle \sim t^\alpha \) with \( \alpha \neq 1 \) [1,2]. Among many examples where this behavior is important are infiltration of water into porous soil [3], contaminant diffusion [4], moisture ingress in zeolites [5] or in fired clay ceramics [6], diffusion of sugar through a membrane in a gel solvent [7], and polymer translocation through a membrane pore [8]. Infiltration is also important in biologically motivated experiments. For example, protein diffusion is anomalous [8]. Infiltration of diffusing particles from one material to another where the diffusion mechanism is either normal or anomalous is a widely observed phenomena. When the diffusion is anomalous we find interesting behavior: diffusion may lead to an averaged net drift \( \langle x \rangle \) from one material to another even if all particles eventually flow in the opposite direction. Furthermore, \( \langle x \rangle \) does not depend on the properties of the medium in which it is situated, indicating nonlocality of the process. Starting with an underlying continuous time random walk model we solve diffusion equations describing this problem. Similar drift against flow is found in the quenched trap model. We argue that such behavior is a general feature of diffusion in disordered systems.

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\[ \frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_1^{1-\alpha} K^- \frac{\partial^2}{\partial x^2} P(x,t) \right], \quad x < 0, \]
\[ \frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_1^{1-\alpha} K^+ \frac{\partial^2}{\partial x^2} P(x,t) \right], \quad x > 0, \]

where \( D_1^{1-\alpha} f(t) = \Gamma^{-1}(\alpha) \partial/\partial t \int_0^t dt' f(t') (t-t')^{\alpha-1} \) is the Riemann-Liouville fractional operator [13]. Without the boundary conditions soon to be derived Eq. (1) is nearly useless. The underlying random walk model we consider is the continuous time random walk model (CTRW) [1,2,14], which is now specified.

Model 2: CTRW.—Consider a jump process on a discrete lattice with lattice spacing \( a \). For lattice points \( x < 0 \), a particle has the probability \( 1/2 \) to jump to one of its nearest neighbors. Waiting times on each lattice point are independent, identically distributed random variables with a com-
mon PDF $\psi^-(\tau)$. For $x > 0$ a similar unbiased random walk takes place with a waiting time PDF $\psi^+(\tau)$. On the lattice point $x = 0$ (the boundary) a particle has the probability to jump right ($q^+$) or left ($q^- = 1 - q^+$) [15] and the waiting times are exponentially distributed with a rate $R_0$. Such biased interface is due, for example, to a difference of chemical potentials between the two samples [16]. Thus, a particle starting on the origin will jump, say to the right (with probability $q^+$) after waiting an average time $1/R_0$, then on the lattice point $x = a$, it will wait for time $\tau$ drawn from $\psi^-(\tau)$, and then with probability $1/2$ will jump to the left or right. For subdiffusion the waiting times have power law PDFs $\psi^-(\tau) \propto \tau^{-(1+\alpha^-)}$ or in Laplace space $\psi^-(s) \sim 1 - B^{-\alpha^-} e^{-s}$ when $s \to 0$ [2]. All along this work we denote the Laplace transform by the variable in the parentheses $f(s) = \int_0^\infty dte^{-st}f(t)$. The generalized diffusion constants are given by $K^\pm = \lim_{s \to 0} B^\pm s^{\alpha^-}/2B^\pm$ [17]. Large numbers of applications of the CTRW model are discussed in [1,2,14].

**Main results and the paradox.**—Consider the situation where $\alpha^- < \alpha^+$, so we call the domain $x < 0$ the “slow” medium. We will soon show that the probability to be in the slow medium is

$$P^-(t) \sim 1, \quad t \to \infty,$$

when initially the packet of particles is in the vicinity of the interface. We also prove that the mean drift is

$$\langle x(t) \rangle \sim \left( \frac{q^+ - q^-}{q^-} \right) \frac{\sqrt{K^-}}{\Gamma(1 + \alpha^-/2)} t^{\alpha^-/2}.$$

Thus, independent of the details of the model, all the particles flow into the slower medium which absorbs them in the long time limit. However, at the same time if $q^+ > q^-$ the drift $\langle x \rangle > 0$ is positive and increasing with time. Namely, $\langle x \rangle$ is located in the “fast” medium even though all the particles eventually accumulate in the slow one. A weaker paradox is found when $q_+ = q_-$, since then all the particles accumulate in the slower domain but still $\langle x \rangle = 0$. These behaviors are demonstrated in Figs. 1–3. Notice that while the dynamics in the faster domain $x > 0$ is clearly important (since $\langle x \rangle$ may be in that domain) the mean $\langle x \rangle$ does not depend on the diffusion constant $K^+$ of that medium, nor on the anomalous diffusion exponent $\alpha^+$. To understand better these strange behaviors we now turn to a detailed investigation of the infiltration problem.

**The drift $\langle x \rangle$.**—We sketch the derivation of the drift using the CTRW approach. The position of a particle is $x = \sum_{i=0}^N \delta x_i$, where $\delta x_i$ is the $i$th displacement and $N$ is the random number of steps. Since the motion is unbiased in domains $x < 0$ and $x > 0$, we have

$$\langle x(t) \rangle = a(q^+ - q^-) \langle n_c(t) \rangle,$$

where $\langle n_c(t) \rangle$ is the average number of times the particle visits the origin. We define a three state process: $\xi(t) = 0$ if the particle is on the origin, $\xi(t) = +1$ if the particle is in $x > 0$, and $\xi(t) = -1$ if the particle is in $x < 0$. In the long time limit the number of visits to the origin is independent of $R_0$ since the average waiting times in state $+$ and $-$ are infinite. The waiting times in states $+$ and $-$ are the first passage times [18] from $x = a$ to $x = 0$ and from $-a$ to $0$, respectively. These first passage times in the continuum limit are one sided Lévy distributions whose long time (small $s$) Laplace transforms are [19] $\phi^-(s) \sim 1 - as^{\alpha^-}/\sqrt{K^-}$ for $x < 0$ and similarly $\phi^+(s) \sim 1 - as^{\alpha^+}/\sqrt{K^+}$ for $x > 0$. The Laplace transform of the probability to have $n_c$ transitions to state $\xi(t) = 0$ is found using the Laplace transform convolution theorem $P_{n_c}(s) = [1 - \phi(s)]^{n_c}(s)/s$, where $\phi(s) = q^- \phi^-(s) + q^+ \phi^+(s)$ and hence $\langle n_c(s) \rangle = \phi(s)/[s(1 - \phi(s))]$. Using the small $s$ expansion of $\langle n_c \rangle$ and Eq. (4) we obtain for $\alpha^- < \alpha^+$ our main result Eq. (3). The latter agrees well with simulation in Fig. 2. According to Eq. (3) the sign of the drift, i.e., its directionality, is determined by the sign of $q^+ - q^-$, and $\langle x \rangle = 0$ if $q^+ = q^-$. As mentioned, Eq. (3) exhibits a surprising behavior: $\langle x(t) \rangle$ can be very far from the interface, deep in the faster sample $x > 0$, but still is independent of the properties of that region $\alpha^+$ and $K^+$.

**Boundary conditions and solution of model 1.**—Using the initial condition given by $P(x,0) = \delta(x)$ the solution of Eq. (1) in Laplace space is given by

$$P(x,s) = C^+(s) \frac{s^{\alpha^+ - 1} \exp\left(-\frac{t\alpha^+ \xi}{\sqrt{K^+}}\right)}{2\sqrt{K^+}} \theta(x) + C^-(s) \frac{s^{\alpha^- - 1} \exp\left(-\frac{t\alpha^- \xi}{\sqrt{K^-}}\right)}{2\sqrt{K^-}} \left[1 - \theta(x)\right],$$

where $\theta(x)$ is the step function. To find $C^+(s)$ and $C^-(s)$ we need two boundary conditions. The conservation of probability $\int dx P(x,s) = 1/s$ gives $C^-(s) + C^+(s) = 2$. Hence using Eq. (5) we find the first boundary condition

$$J^+(x = 0^+, t) - J^-(x = 0^-, t) = \frac{1}{2} \delta(t),$$

where $J^+(x = 0^+, t)$ and $J^-(x = 0^-, t)$ are the density currents to $x = 0^+$ and $x = 0^-$, respectively.
where \( J_1(x, t) = -K_0 D_1^{0 - \alpha^-} \delta P(x, t)/\delta x \) is the probability current in \( x < 0 \) and similarly for \( x > 0 \) [20]. To derive the second boundary condition we calculate the first moment,

\[
\langle x(s) \rangle = \int_0^s \frac{dP(x, s)}{ds} dx,
\]

using Eq. (5)

\[
\langle x(s) \rangle = \frac{1}{2s} \left( \sqrt{K^+} C^+_s(s^{-(\alpha^-)/2}) - \sqrt{K^-} C^-_s(s^{-(\alpha^-)/2}) \right).
\]

(7)

We require Eq. (7) to be equal to \( \langle x(s) \rangle \) Eq. (3) calculated from the CTRW model. For \( \alpha^- < \alpha^+ \), Eqs. (3) and (7) yield when \( s \to 0 \),

\[
C^+_s(s) \sim \frac{2q^+}{q} \sqrt{K^-} s^{(\alpha^- - \alpha^-)/2}, \quad C^-_s(s) = 2 - C^+_s(s).
\]

(8)

Using Eqs. (5) and (8) we derive the second boundary condition

\[
q^+ K^- s^\alpha^- P(x = 0^-, s) = q^- K^+ s^\alpha^+ P(x = 0^+, s).
\]

(9)

which shows that generally the PDF at the boundary is not continuous, similar to the normal diffusion case [15]. Such a jump in the PDF on the origin is shown in Fig. 3.

**Occupation fraction.**—From Eqs. (5) and (8) the probability \( P^-(t) \) to be in the slow medium \( x < 0 \) is easily obtained. In Laplace space \( P^-(s) = \int_0^\infty dx P(x, s) = C^-(s)/(2s) \). In the long time limit equivalent to \( s \to 0 \) we get \( P^-(s) \sim 1/[s(1 + \mathcal{R}(s))] \) with \( \mathcal{R}(s) = (q^+ \sqrt{K^+})/(q^+ \sqrt{K^-}) s^{(\alpha^- - \alpha^-)/2} \). When \( \alpha^- < \alpha^+ \) we get \( P^-(s) \sim 1/s \) when \( s \to 0 \); hence the probability to be in \( x < 0 \) is \( P^-(t) \sim 1 \) when \( t \to \infty \) as stated in our main result Eq. (2). Namely in the long time limit all the particles flow to the region \( x < 0 \), where the diffusion is slower (see Fig. 2). A similar result can be obtained from the CTRW model including the correction term [16].
Model 3: Quenched trap model.—We proceed to show that effects discussed for the CTRW model and fractional diffusion equation are found also for systems with quenched disorder. Consider the quenched trap model where a particle is undergoing a one-dimensional random walk on a quenched random energy landscape on a lattice [1,21]. On each lattice point a random energy \( E_x > 0 \) is assigned, which is the depth of a trap on site \( x \) and the escape time from a trap is \( \tau_x = \exp(E_x/T_g) \). The energies are random variables distributed with a common PDF \( \rho(E) = (1/T_g) \exp(-E/T_g) \). In the composite quenched trap we have \( T^*_g \) for \( x < 0 \) and \( T^+_g \) for \( x > 0 \). Once \( T/T_g < 1 \) one finds a subdiffusive phase [1,21]. If \( T^-_g > T^+_g \) medium \( x < 0 \) is the slower medium in the sense that statistically the traps in that medium are deeper. In this model we have jumps to nearest neighbors with equal probability, with waiting times \( \tau_x \), and the interface is defined in a way similar to the CTRW model. Numerical simulations reveal behaviors which are similar to those we found for the annealed models considered so far. Namely, for \( T^+_g < T^-_g \) we find the drift (\( C \) is a constant)

\[
\langle x \rangle \sim C(q^+ - q^-)h^{T/(T^+ + T^-)}, \tag{11}
\]

which is positive for \( q^+ > q^- \), while particles are accumulating in \( x < 0 \), \( P^- \rightarrow 1 \) as shown in Fig. 2. We anticipate that similar behaviors will take place in other models of transport with composite quenched disorder.

Suggested experiment.—It is interesting to verify experimentally our theoretical predictions. While systems mentioned in the introduction are candidates, we suggest to investigate anomalous infiltration of magnetic beads in the actin network (where anomalous diffusion takes place) into water (where diffusion is normal). The beads in the actin network (where anomalous diffusion operates) are random variables distributed with a common PDF \( \rho(x) \). We anticipate that similar behaviors will take place in other models of transport with composite quenched disorder.

To summarize, we investigated infiltration in subdiffusive systems. Both for the annealed CTRW model and for the quenched trap model all the particles will be accumulated in the slow medium reflecting the longer trapping times there. The direction of the averaged drift is determined by breaking of the symmetry \( q_L \neq q_R \) in our model. This leads to interesting and we believe general phenomena unique to anomalous diffusion. The drift \( \langle x \rangle \) may be located deep in the fast domain even if eventually all the particles flow in the opposite direction. The drift does not depend on the properties of the fast domain; i.e. \( \langle x \rangle \) is independent of \( \alpha^+ \) and \( \alpha^- \) even though \( \langle x \rangle \) might be located deep in that medium. This surprising result, that drift does not depend on the properties of the medium in which it is located, was explained by analyzing the first passage time to the origin, which are statistically dominated by the slow medium.

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