# Subdiffusion and Long-Time Anticorrelations in a Stochastic Single File

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The subdiffusion of a stochastic single file is interpreted as a jumping process. Contrary to the current continuous time random walk models, its statistics is characterized by finite averages of the jumping times and square displacements. Subdiffusion is then related to a persistent anticorrelation of the jump sequences. In continuous time representation, this corresponds to negative power-law velocity autocorrelations, attributable to the restricted geometry of the file diffusion.

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Anomalous diffusion [1,2] is by now a well established law in nonequilibrium statistical mechanics, where the long-time mean square displacement $\delta x^2(t)$ of a random variable, for simplicity in one dimension (1D), grows like

$$\delta x^2(t) \equiv \langle [x(t) - x(0)]^2 \rangle = 2D_\alpha t^\alpha \quad (t \to \infty) \tag{1}$$

with either $\alpha < 1$ (subdiffusion) or $\alpha > 1$ (superdiffusion); by contrast, the more popular Einstein relation with $\alpha = 1$ is termed the normal diffusion law. The evidence for natural phenomena exhibiting anomalous diffusion with $\alpha \neq 1$ has grown so compelling as to prompt punchlines such as "anomalous is normal" [3].

The key ingredients responsible for anomalous diffusion are best identified in terms of a random walk description, where the diffusive process $x(t)$ evolves in time stepwise, by taking jumps of random length $|\sigma|$ in either direction, at random times. Anomalous diffusion is characterized by vastly sparse waiting times $\tau$ between consecutive jumps (subdiffusion) or abnormally long jumps (superdiffusion) [1]; moreover, the predominance of such exceedingly large jumps induces strong "memory effects" in the diffusive dynamics [4,5].

These conditions have been rigorously expressed in the context of the continuous time random walk (CTRW) theory [6]. Here a jumping process is defined through two probability densities $P(|\sigma|)$ and $P(\tau)$, which determine the length and time of the jump, respectively: The $n$th jump is defined by picking at random a waiting time $\tau_n$ and a displacement $\sigma_n$. The anomalous diffusion of a CTRW requires that these distributions decay like power laws, say, $P(\tau) \propto \tau^{-1-g}$ and $P(|\sigma|) \propto |\sigma|^{-1-f}$. If the jump lengths and times are *uncorrelated*, we have the following rule [7]: $g < 1$, $f > 2$ subdiffusion; $f < 2$, $g > 1$ superdiffusion; if both $g < 1$ and $f < 2$, then $f < 2g$, subdiffusion and $f > 2g$, superdiffusion. In other words, anomalous diffusion implies diverging waiting times for $\alpha < 1$ and diverging mean square displacements for $\alpha > 1$; if both quantities diverge, exceedingly large waiting times (displacements) are the prevalent feature of a subdiffusive (superdiffusive) process. Finally, in the case $f = 2g$ with $g < 1$, $f < 2$, *marginal* normal diffusion is restored. Most remarkably, normal diffusion with $f = 2g$ always occurs also when $\tau$ and $\sigma$ are *correlated* through a subordinated Brownian motion [8].

Jumping processes in a variety of natural systems are claimed to combine anomalous diffusion and power-law jump distributions [5,9]. However, establishing such power laws is a difficult experimental task and the outcome can often be disputed. For this reason, we turned our attention to a 1D subdiffusive system with $\alpha = \frac{1}{2}$, the stochastic single file (SF), which is relatively easy to handle both mathematically and numerically. Our conclusion is that SF diffusion does not fit the CTRW criterion for anomalous diffusion but, rather, points to a different class of subdiffusive systems.

We considered a file of $N$ indistinguishable, unit-mass Brownian particles moving on a circle of length $L$; if the particle interaction is hard-core (zero radius), the file constituents can be labeled according to a given ordered sequence and the long-time diffusion of an individual particle gets strongly suppressed [10]. In the thermodynamic limit ($L, N \to \infty$ with constant density $\rho \equiv N/L$), the mean square displacement of each file particle can be calculated analytically [10–12]. The subdiffusion law of a SF of Brownian particles with damping constant $\gamma$ at temperature $T$ can be expressed in terms of the free-particle diffusion constant $D_0 = kT/\gamma$, that is [13],

$$\delta x^2(t) = 2\sqrt{D_0 t/\pi}/\rho \quad (t \to \infty). \tag{2}$$

The SF regime (2), $D_{1/2} = \sqrt{D_0/\pi}/\rho$, has been observed both numerically [12,14] and experimentally [15,16].

To break up the continuous SF dynamics into discrete jumps, we introduced an *ad hoc* impact representation. We set the time origin $t = 0$ after an adequate thermalization transient and traced the diffusing trajectory of, say, the $i$th particle until it underwent its $n$th collision at point $x_n^{(i)} = x_i(t_n^{(i)})$ and time $t_n^{(i)}$; the time interval $\tau_n^{(i)} = t_n^{(i)} - t_{n-1}^{(i)}$, with $t_0^{(i)} = 0$, denotes the duration of the $n$th jump of the $i$th particle; analogously, $\sigma_n^{(i)} = x_n^{(i)} - x_{n-1}^{(i)}$ defines the displacement associated with the jump and $|\sigma_n^{(i)}|$ is its length.

 

Finally, we ensemble (or file) averaged over the jumps of impact order $n$, $\tau_n \equiv \langle \tau_n^{(i)} \rangle$ and $\sigma_n^2 \equiv \langle \sigma_n^{2(i)} \rangle$, irrespective of their duration (*asynchronous* averaging) [17].

We anticipate here three conclusions of our simulation work: (a) The jump size distributions $P(\tau)$ and $P(|\sigma|)$ decay according to CTRW power laws with $g = \frac{1}{2}$ and $f = 1$, only up to a certain value of $\tau$ or $|\sigma|$, above which they sharply drop to zero. Such tail truncations occur when the file particles diffuse from one neighbor to the other, namely, for times $\tau_d$ and mean square displacements $\sigma_d$ such that $\sigma_d^2 = 2D_0\tau_d = 2/\rho^2$. (b) The limits $\lim_{n\to\infty}\tau_n = \langle\tau\rangle$ and $\lim_{n\to\infty}\sigma_n^2 = \langle\sigma^2\rangle$ are finite, with $\langle\sigma^2\rangle = 2D_0\langle\tau\rangle$, and set the characteristic time and length scales of the SF collisional dynamics. (c) The stationary autocorrelation functions $C_{\tau\tau}(n) = \langle \tau_{n_0}^{(i)}\tau_{n_0+n}^{(i)}\rangle - \tau_{n_0}^2$ and $C_{\sigma\sigma}(n) = \langle \sigma_{n_0}^{(i)}\sigma_{n_0+n}^{(i)}\rangle$, with $n_0 \to \infty$, develop persistent tails, respectively, $C_{\tau\tau}(n) \propto n^{-1/2}$ and $C_{\sigma\sigma}(n) \propto -n^{-3/2}$. The $\tau$-$\sigma$ cross correlations in the stationary regime are compatible with the subordinated Brownian dynamics [8].

Properties (a) and (b) seem at odds with a CTRW interpretation of SF diffusion. Regarding property (a), even on assuming ideal power-law decays for the jump densities (e.g., as $\tau_d$, $\sigma_d^2 \to \infty$ for $\rho \to 0$), the relevant exponents $g$ and $f$ would obey the normal diffusion condition $f = 2g$. On the other hand, the finiteness of the jump parameters $\langle\tau\rangle$ and $\langle\sigma^2\rangle$ [property (b)] seems to indicate a *bona fide* normal diffusion. The solution to this apparent paradox is in property (c): At variance with the CTRW models, here the jump sequence is characterized by strong memory effects; in particular, the jump displacements $\sigma_n$ are anticorrelated. The connection between persistent jump autocorrelation and SF diffusion hinges on the generalization of Kubo's theorem presented below; as a consequence, SF diffusion seems to tell us more about subdiffusion than initially expected.

Let us consider a continuous differentiable stochastic process $x(t)$ with $\langle\dot{x}(t)\rangle = 0$. Kubo's relation [18] between the mean square displacement $\delta x^2(t)$ [Eq. (1)] and the corresponding stationary autocorrelation function $C(t) = \langle\dot{x}(t)\dot{x}(0)\rangle$ can be written for $t \to \infty$ as

$$\frac{1}{2}\frac{d}{dt}\delta x^2(t) = \alpha D_\alpha t^{\alpha-1} = I(t) \equiv \int_0^t C(\tau)d\tau. \quad (3)$$

If the integral $I(t)$ converges to a positive value $I(\infty)$, then the identity (3) is satisfied for $\alpha = 1$ and $D_1 = I(\infty)$: $x(t)$ diffuses according to Einstein's law.

Suppose, however, that the $\dot{x}$ autocorrelation $C(t)$ tends to zero like $C(t) \sim c_\beta t^{-\beta}$; we are presented with two additional possibilities: (i) $I(t)$ diverges for $t \to \infty$, i.e., $0 \le \beta < 1$; (ii) $I(\infty) = 0$, i.e., $1 < \beta < 2$. In both cases, diffusion is anomalous, since in view of Eq. (3)

$$\alpha = 2 - \beta, \qquad c_\beta = \alpha(\alpha - 1)D_\alpha. \quad (4)$$

Case (i): *Superdiffusive*, $1 < \alpha < 2$.—The process $\dot{x}(t)$ is characterized by a persistent positive autocorrelation with $c_\beta > 0$; $x(t)$ tends to retain its velocity, thus executing exceedingly long jumps.

Case (ii): *Subdiffusive*, $0 < \alpha < 1$.—The tail of $C(t)$ is always negative, $c_\beta < 0$; it denotes a persistent $\dot{x}$ anticorrelation typical of constrained geometries: An initial velocity $\dot{x}(0)$ is likely to be countered by a backflow velocity of opposite sign.

The argument above can be specialized to handle also the limit of weakly anomalous diffusion, $\beta \to 1 \mp$, that is, $\alpha \to 1 \pm$. For $t \to \infty$, we can assume $\delta x^2(t) \propto t\ln^\gamma t$, with $\gamma > 0$ for case (i) and $\gamma < 0$ for case (ii). The identity (3) is satisfied for $C(t) \propto \gamma\ln^{\gamma-1}t/t$ (see Ref. [4] for an example). Another special limit occurs for $\beta \to 2$, that is, for $\alpha \to 0$; the logarithmic subdiffusion law $\delta x^2(t) \propto \ln^\gamma t$, $\gamma > 0$ (Sinai's diffusion), corresponds to the strong anticorrelation tail $C(t) \propto -\ln^{\gamma-1}t/t^2$.

For a stochastic SF, $\alpha = \frac{1}{2}$, this generalization of Kubo's theorem predicts a negative power-law tail of the velocity autocorrelation function $C(t)$ with $\beta = \frac{3}{2}$ and $\int_0^\infty C(\tau)d\tau = 0$ (see also [19]). Our numerical simulations support this conclusion. In Fig. 1, we display the curves $\delta x^2(t)$ and $C(t)$ for different $\rho$ and $\gamma$. In Fig. 1(a), the crossover of $\delta x^2(t)$ from normal diffusion at short times [$\delta x^2(t) = 2D_0 t$, free diffusing particles] to subdiffusion with $\alpha = \frac{1}{2}$ at large times [Eq. (2), SF diffusion] occurs for $t \sim \tau_d$, where $\tau_d$ is the average time a single colliding

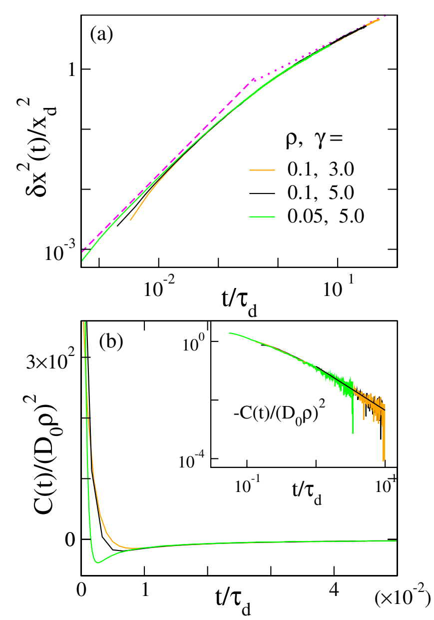


FIG. 1 (color online). Single file diffusion: (a) $\delta x^2(t)$; (b) $C(t)$ for different $\rho$ and $\gamma$, both vs $t$ and rescaled like in Eqs. (8) and (9). SF diffusion law (2) (dotted line) and free-particle normal diffusion $\delta x^2(t) = 2D_0 t$ (dashed line) are displayed for a comparison in (a). Inset: log-log plot of the negative $C(t)$ tails; the solid line is the predicted tail $-C(t)/(D_0\rho)^2 \simeq (t/\tau_d)^{-3/2}/(4\sqrt{\pi})$. We simulated the SF dynamics by integrating $N = 5 \times 10^3$ standard Langevin equations for "nonpassing" particles driven by independent zero-mean, delta-correlated Gaussian noises with $kT = 1$.

pair takes to diffuse against its neighbors. In Fig. 1(b), the negative tails of the corresponding $C(t)$ are apparent and compare well with the estimate of Eq. (4) for $D_{1/2} = \sqrt{D_0/\pi}/\rho$ (see inset).

We now discuss the SF dynamics in impact representation. In Fig. 2, we summarize the jump statistics by looking at the jump length $|\sigma|$ [Fig. 2(a)] and duration $\tau$ [Fig. 2(b)]. The distributions $P(\tau)$ and $P(|\sigma|)$ decay, respectively, like $\tau^{-3/2}$ for $\tau < \tau_d$ and $\sigma^{-2}$ for $|\sigma|^2 < \sigma_d^2$. Such power laws have been predicted in the earlier literature [20]. Indeed, one can map the collisions of a particle pair of coordinates $x_i(t)$ and $x_{i+1}(t)$ into the zero crossings of the Brownian process $x_{i+1}(t) - x_i(t)$; in CTRW notation, $\tau_n$ and $\sigma_n$ are thus correlated through a subordinated Brownian motion [8]. However, deviations from these ideal power laws occur at both the short and the large scales (see insets in Fig. 2). In particular, the $\tau^{-3/2}$ law for $P(\tau)$ is not tenable for times shorter than $\tau_b = \gamma^{-1}$, when the particle motion is ballistic [20], and for times longer than $\tau_d = (D_0\rho^2)^{-1}$, when the collisions of the selected pair with its neighbors cannot be neglected. This geometric constraint is responsible for the sharp truncation of the $\tau$ and $\sigma$ distribution tails and, consequently, for the finite values of $\langle\tau\rangle$ and $\langle\sigma^2\rangle$. For $\tau_d \gg \tau_b$, one obtains the working approximation

$$\langle\tau\rangle = \int_{\tau_b}^{\tau_d} \tau P(\tau)d\tau \Big/ \int_{\tau_b}^{\tau_d} P(\tau)d\tau = (\rho\sqrt{kT})^{-1}. \qquad (5)$$

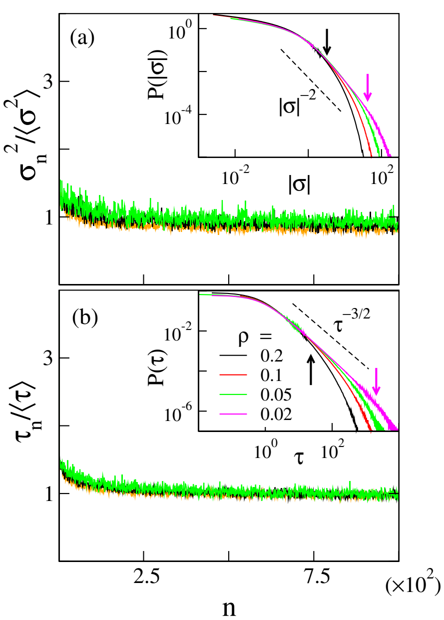


FIG. 2 (color online). Jump statistics: (a) $\sigma_n^2$ vs $n$; (b) $\tau_n$ vs $n$, for $\rho$ and $\gamma$ like in Fig. 1, both rescaled with rescaling parameters $\langle\sigma^2\rangle$ [Eq. (6)] and $\langle\tau\rangle$ [Eq. (5)]. Insets: (a) $P(\tau)$; and (b) $P(|\sigma|)$ for $\gamma = 3$ and different $\rho$; the power laws $\tau^{-3/2}$ and $|\sigma|^{-2}$ are also shown (dashed lines); the vertical arrows are, respectively, $\tau_d$ and $\sqrt{\sigma_d^2}$ for the smallest and largest density (same color as for the relevant curves). Other simulation parameters are $kT = 1$ and $N = 5 \times 10^3$.

Moreover, recalling the definition of $|\sigma|$, as the absolute displacement of an individual particle between two successive collisions, we conclude that

$$\langle\sigma^2\rangle = 2\sqrt{kT}/(\rho\gamma). \qquad (6)$$

Our estimate for $\langle\tau\rangle$ coincides with the time a ballistic particle with thermal speed $\sqrt{kT}$ takes to cross the mean interparticle distance $\rho^{-1}$. When comparing estimates (5) and (6) with the data in Fig. 2, one notes that $\tau_n$ and $\sigma_n^2$ approach their asymptotic values only after a time transient of the order of $\tau_d$, that is, a jump sequence of length $n_d = \tau_d/\langle\tau\rangle = \gamma/(\rho\sqrt{kT})$.

The finite distribution moments $\langle\tau\rangle$ and $\langle\sigma^2\rangle$ allow us to rederive the SF diffusion law (2). In Fig. 3, we added up $n$ consecutive jumps of the same particle after a transient of $n_0$ jumps and computed the file averages

$$t(n) = \left\langle \sum_{k=1}^{n} t_{n_0+k}^{(i)} \right\rangle, \qquad x^2(n) = \left\langle \left( \sum_{k=1}^{n} \sigma_{n_0+k}^{(i)} \right)^2 \right\rangle. \qquad (7)$$

The phenomenological relation

$$t(n) = \langle\tau\rangle n = \tau_d(n/n_d) \qquad (8)$$

fits well the curves of the inset in Fig. 3 for $n > n_d$, regardless of the transient cutoff $n_0$. An analytical estimate for $x^2(n)$ can be obtained from de Gennes' theory of reptation of a polymer chain [21], namely,

$$x^2(n) = x_d^2(n/n_d)^{1/2}, \qquad (9)$$

with $x_d^2 = \sigma_d^2/\sqrt{\pi}$. This formula fits well the asymptotic $n$ dependence of the $x^2(n)$ curves in Fig. 3. For $n_0 \gg n_d$, the diffusion crossover of Fig. 1 becomes also apparent: $x^2(n)$ increases first linear in $n$ for $n \ll n_d$, $x^2(n) = \langle\sigma^2\rangle n$ and then proportional to $n^{1/2}$ for $n \gg n_d$ [Eq. (9)]. On combining Eqs. (8) and (9), we eventually recover the SF law (2) in the impact representation.

Finally, we present our results for the jump autocorrelations. The tails of both $C_{\sigma\sigma}(n)$ and $C_{\tau\tau}(n)$ in Fig. 4 clearly

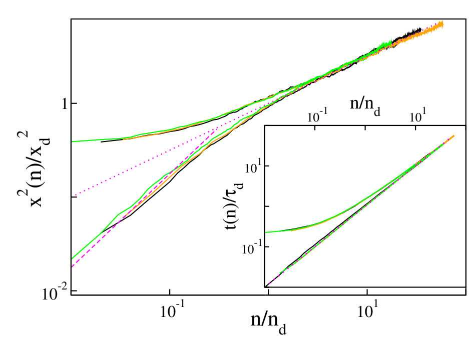


FIG. 3 (color online). Anomalous diffusion: main panel: $x^2(n)$ vs $n$; inset: $t(n)$ vs $n$, for $n_0 = 0$ (upper curve sets) and $n_0 = 250$ (lower curve sets); $\rho$ and $\gamma$ are chosen as in Figs. 1 and 2. Both quantities have been rescaled for a comparison with Eqs. (8) and (9) (dotted lines). The dashed line in the main panel is the normal diffusion law $x^2(n) = \langle\sigma^2\rangle n$ (see text). Other simulation parameters are $kT = 1$ and $N = 5 \times 10^3$.

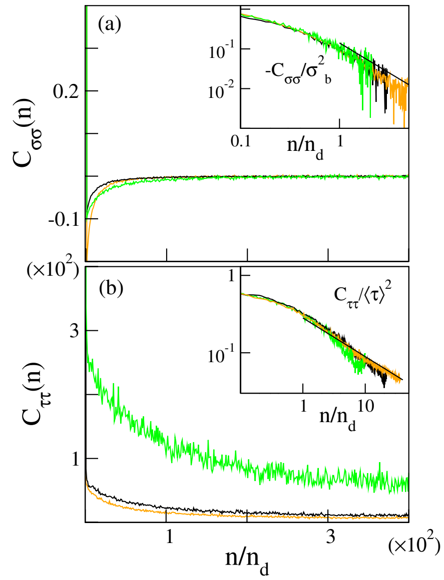


FIG. 4 (color online). Jump correlations: (a) $C_{\sigma\sigma}(n)$; (b) $C_{\tau\tau}(n)$, for $\rho$ and $\gamma$ like in Figs. 1–3. (a), inset: log-log plot of the negative $C_{\sigma\sigma}(n)$ tails after appropriate rescaling; the solid line represents the power-law decay (1). The sum $\sum_{k=0}^{n} \tilde{C}_{\sigma\sigma}(k)$ vanishes proportionally to $n^{-1/2}$ (not shown). (b): log-log plot of $C_{\tau\tau}(n)/\langle\tau\rangle^2$ vs $n/n_d$ against the asymptotic tail (12) (solid line). Other simulation parameters are $kT = 1$ and $N = 5 \times 10^3$.

cross over from an exponential to a power-law decay at around $n \sim n_d$. This mechanism is closely connected with the onset of the SF diffusion. On introducing the "symmetrized" autocorrelation function $\tilde{C}_{\sigma\sigma}(n) \equiv C_{\sigma\sigma}(n) - \frac{1}{2}\delta_{0,n}\langle\sigma^2\rangle$, definition (7) of $x^2(n)$ in the stationary regime is equivalent to

$$x^2(n) = 2\sum_{k=0}^{n-1}(n-k)\tilde{C}_{\sigma\sigma}(k). \tag{10}$$

The asymptotic result (9) can thus be recovered only under the two simultaneous conditions

$$\sum_{k=0}^{\infty}\tilde{C}_{\sigma\sigma}(k) = 0, \qquad C_{\sigma\sigma}(n) \simeq -\frac{\sigma_b^2}{4\sqrt{\pi}}\left(\frac{n_d}{n}\right)^{3/2}, \tag{11}$$

with $\sigma_b^2 = 2D_0\tau_b = 2kT/\gamma^2$, both verified in Fig. 4(a). Analogously, for the slow $C_{\tau\tau}(n)$ tail one comes up with

$$C_{\tau\tau}(n) \simeq \frac{\langle\tau\rangle^2}{2\sqrt{\pi}}\left(\frac{n_d}{n}\right)^{1/2}, \tag{12}$$

also plotted in Fig. 4(b). Negative power-law tails of the velocity and/or the jump autocorrelation functions have been predicted, indeed, for other 1D systems, such as Jepsen's gas [11,22] and files of interacting particles [23], and, much earlier, also for the diffusive dynamics of a concentrated lattice gas in 3D [24]. Note, however, that *both conditions* in Eq. (11)—equivalent to Eqs. (3) and (4) in continuous time representation—are required to predict SF diffusion.

In conclusion, SF diffusion is tied to the restricted file geometry that confines the diffusion of individual particles rather than to the effect of long trapping (waiting) times. Such a mechanism, different but not necessarily in conflict with the CTRW scheme, is likely to play a key role, e.g., in the particle transport through narrow channels in biology and nanodevices [25]; it can also be generalized to describe the spatial dispersion of (assemblies of) elastic (polymer) chains on a disordered substrate [21].

[1] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).
[2] J.-P. Bouchaud and A. Georges, Phys. Rep. **195**, 127 (1990).
[3] J. Klafter and I. M. Sokolov, Phys. World **18**, 29 (2005); I. M. Sokolov *et al.*, Phys. Today **55**, No. 11, 48 (2002).
[4] T. Srokowski and A. Kaminska, Phys. Rev. E **70**, 051102 (2004).
[5] W. Min *et al.*, Phys. Rev. Lett. **94**, 198302 (2005).
[6] E. W. Montroll and G. H. Weiss, J. Math. Phys. (N.Y.) **6**, 167 (1965).
[7] H. C. Fogedby, Phys. Rev. E **50**, 1657 (1994).
[8] M. F. Shlesinger *et al.*, J. Stat. Phys. **27**, 499 (1982).
[9] J. M. Sancho *et al.*, Phys. Rev. Lett. **92**, 250601 (2004); M. Dentz *et al.*, Adv. Water Resour. **27**, 155 (2004); K. Ritchie *et al.*, Biophys. J. **88**, 2266 (2005); D. Boyer *et al.*, Physica (Amsterdam) **342A**, 329 (2004).
[10] T. E. Harris, J. Appl. Probab. **2**, 323 (1965); D. G. Levitt, Phys. Rev. A **8**, 3050 (1973).
[11] D. W. Jepsen, J. Math. Phys. (N.Y.) **6**, 405 (1965); J. L. Lebowitz and J. K. Percus, Phys. Rev. **155**, 122 (1967).
[12] K. Hahn and J. Kärger, J. Phys. A **28**, 3061 (1995); K. Hahn *et al.*, Phys. Rev. Lett. **76**, 2762 (1996); M. Kollmann, Phys. Rev. Lett. **90**, 180602 (2003).
[13] K. Hahn and J. Kärger, J. Chem. Phys. **100**, 316 (1996); A. Taloni and F. Marchesoni, Phys. Rev. Lett. **96**, 020601 (2006).
[14] H. van Beijeren *et al.*, Phys. Rev. B **28**, 5711 (1983); D. S. Sholl and K. A. Fichthorn, Phys. Rev. E **55**, 7753 (1997).
[15] P. Demontis *et al.*, J. Chem. Phys. **120**, 9233 (2004); R. L. June *et al.*, J. Chem. Phys. **94**, 8232 (1990); U. Hong *et al.*, Zeolites **11**, 816 (1991).
[16] Q. H. Wei *et al.*, Science **287**, 625 (2000); C. Lutz *et al.*, Phys. Rev. Lett. **93**, 026001 (2004).
[17] S. Giuseppone and F. Marchesoni, Europhys. Lett. **64**, 36 (2003).
[18] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).
[19] J. K. Percus, Phys. Rev. A **9**, 557 (1974).
[20] A. Papoulis, *Probability, Random Variables, and Stochastic Processes* (McGraw-Hill, New York, 1991).
[21] J. P. de Gennes, J. Chem. Phys. **55**, 572 (1971).
[22] V. Balakrishnan *et al.*, Phys. Rev. E **65**, 031102 (2002).
[23] S. Pal *et al.*, J. Chem. Phys. **116**, 5941 (2002).
[24] K. W. Kehr *et al.*, Phys. Rev. B **23**, 4931 (1981).
[25] B. Alberts *et al.*, *Molecular Biology of the Cell* (Garland, New York, 1994); J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).