Anomalous Diffusion in "Living Polymers": A Genuine Levy Flight?

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We have observed anomalously enhanced self- (tracer) diffusion in systems of polymerlike breakable micelles. We argue that it provides the first experimental realization of a random walk for which the second moment of the jump-size distribution fails to exist ("Levy flight"). The basic mechanism is the following: Due to reptation, short micelles diffuse much more rapidly than long ones. As time goes on, shorter and shorter micelles are encountered by the tracer, and hence the effective diffusion constant increases with time.

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Much work has recently been focused on dynamical processes in disordered media. In particular, diffusion of test particles can be strongly affected by randomness: In certain instances, one may even lose the usual "square-root" dependence of the typical displacement with time.[1,2] In this case, one observes an anomalous diffusion law: $R(t) \approx t^{\nu}$, with $\nu \neq \frac{1}{2}$. As has been emphasized in Refs. 2 and 3, such behavior may arise either when events characterized by a broad probability distribution come into play, or when long-range (spatial or temporal) correlations are present in the system. Subdiffusive ($\nu < \frac{1}{2}$) behaviors are relatively common in physical systems where a broad distribution of local trapping times may build up. Examples are the photoconductivity of amorphous materials,[4] the conductivity of disordered ionic chains,[5] diffusion in convective rolls,[6] or the random walk on a percolation cluster (see, e.g., Ref. 1). Enhanced diffusion ($\nu > \frac{1}{2}$) is comparatively much rarer. The classical example is Richardson diffusion in turbulent fluids:[7] *Long-range correlations* in the velocity field lead to $\nu \approx \frac{3}{2}$ (see also Ref. 2). A different theoretical possibility is the "Levy flight": If the particle makes jumps of various sizes l, such that the probability distribution of those jump sizes, $P(l)$, decays as $l^{-(1+\mu)}$ for large l, the second moment of $P(l)$ fails to exist for $\mu \leq 2$, and formally the diffusion constant is infinite. This means that as time goes on, longer and longer steps are encountered in a self-similar manner, which eventually change the typical time dependence of the position from $t^{1/2}$ to $t^{1/\mu}$. However, to the best of our knowledge, there are no experimental results which may be naturally interpreted as a Levy-flight process (see, however, Ref. 8).

In this Letter we present an investigation of the diffusion of a fluorescent probe in a system of elongated micelles [aggregates of amphiphilic molecules—cethyl trimethyl ammonium bromide (CTAB)] by using fringe-pattern photobleaching. These micelles behave, for high enough concentration, as a semidilute solution of *transient* ("living") polymers: The chains are not chemically bonded and may hence break and recombine on a characteristic time τ_{break}.[9] The consequences of this finite breaking time on the viscosity and diffusion behavior of these systems have been investigated theoretically by Cates.[10] It is clear that the diffusion constant is enhanced if τ_{break} is shorter than the classical de Gennes reptation time τ_{rep}. In Ref. 10, it it argued that

$$D \approx D_{\text{rep}} \zeta^{-1/3}, \tag{1}$$

where $\zeta = \tau_{\text{break}}/\tau_{\text{rep}}$ and D_{rep} is the diffusion coefficient in the limit $\tau_{\text{break}} > \tau_{\text{rep}}$. From (1), a scaling law for the dependence of the diffusion constant versus concentration may be obtained. Our former experimental studies of CTAB micelles in salted water are compatible with this model in most cases.[11] We noticed, however, that for larger salinities the diffusion constant is not scale independent: The relaxation time τ varies with the fringe spacing i (which sets the diffusion length): $\tau \approx i^{\mu}$, with $\mu < 2$. This signals anomalously enhanced diffusion; see Fig. 1.

Experimental aspects.—The present study is made with CTAB in 0.5, 1, and 2 M KBr at 40 °C using the technique of fluorescence recovery after fringe-pattern photobleaching (FRAP[11,12]). This technique allows us to measure the self-diffusion coefficient D of fluorescent probes incorporated to the micelles. The probe molecules are similar to the CTAB molecules: a polar head (fluorescein group) and an aliphatic tail. When strongly illuminated by a laser flash, these probes irreversibly lose their fluorescent properties. The fluoresence recovery, in the "bleached" region, is controlled by the diffusion of new, unbleached probes, and monitored by a low-intensity laser beam; the diffusion constant D can be deduced from this signal.

In order to improve the signal-to-noise ratio, we use fringe patterns with a modulation of the fringe position at a frequency ω. The signal is detected at two different frequencies, ω and 2ω, using a lock-in amplifier. It may be shown[12] that the signal at ω is nonzero only if there is a convective motion with a velocity v in the medium: This signal is proportional to $I_0 \sin(qvt)$, where $q = 2\pi/i$ and I_0 is the intensity of the recovery beam. We sys-

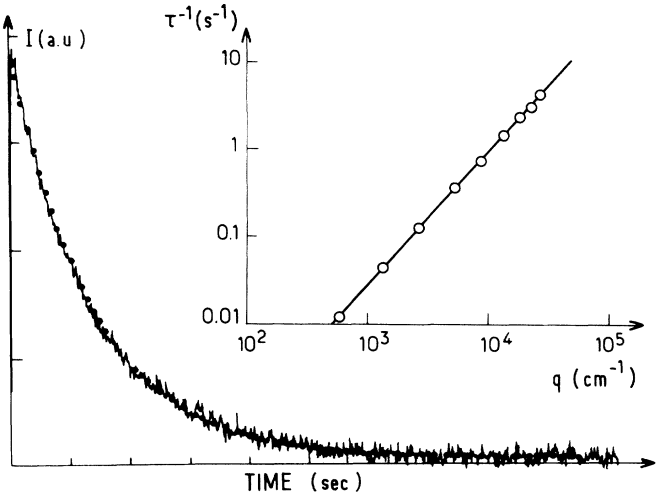

FIG. 1. 10 mM CTAB, 2 M KBr: Exponential fit to the recovery curve. Inset: The inverse relaxation time $\tau(q)$ vs $q=2\pi/i$ on a log-log scale. Experimental errors are smaller than the point size.

tematically checked that no signal was detected at ω. In the case of monodisperse diffusing objects, the signal at 2ω is then proportional to $I_0\exp(-t/\tau)$. The self-diffusion constant is obtained as

$$D=[q^2\tau(q)]^{-1}. \quad (2)$$

Normal diffusion is associated with the fact that D is q independent. Experiments were made at at least six fringe spacings with $2\leq i\leq 100$ μm.[13]

Results.—A typical result is presented in Fig. 1. Each recovery signal was fitted by a single exponential (Fig. 1, inset). An example of a plot of the recovery rate $1/\tau(q)$ vs q is given in Fig. 1 on a log-log scale. The striking result is that $\tau(q)\approx q^{-\mu}$, with $\mu\neq 2$ on more than two (time) decades. This behavior was observed for many samples (see Table I). In other words, we observe an anomalously enhanced diffusion: $r\approx t^{\nu}$, with $\nu=1/\mu > \frac{1}{2}$. We can, however, still define a (distance-dependent) diffusion constant using Eq. (2). The values of $D(q)$ for several q values are plotted versus micelle concentration in Fig. 2.

Since there is no flow in our samples, a mechanism based on a convective regime allowing rapid motion on the fringe length scale is *a priori* excluded. As will be argued in next section, anomalous diffusion arises from a *purely statistical mechanism.*

Discussion.—In a "mean-field" approach, each chain of length L has a constant probability per unit time to recombine, and also a constant probability per unit length and unit time to break. This leads to an equilibrium concentration of chains of (arc) length L of the form[10] $\mathcal{N}(L)\approx L\exp(-L/L^*)$, where L^* is the average length. It is related to the micellar concentration through $\Phi=\int L\exp(-L/L^*)dL\approx L^{*2}$. In the following, L will always denote a reduced length, in units of the micellar radius a (≈ 25 Å).

TABLE I. Values of μ versus concentration for different KBr concentrations, and for different temperatures. Note that, as expected, μ increases towards 2 as the temperature is raised. This is because the experimental time scale becomes too long, and usual Brownian motion takes over. Experimental reproductibility is better than ± 0.05.

CTAB (mM)	T (°C)	μ 2 M KBr	1 M KBr	0.5 M KBr
400	40	1.93	2.02	1.91
200	40	1.92	1.98	1.93
100	40	1.89	1.92	1.93
50	40	1.66	1.67	1.95
20	40	1.52	1.55	1.95
10	40	1.51	1.68	1.82
5	40	1.54	1.76	2.04
2.5	40	...	1.89	...
2	40	1.51	...	1.79
1	40	1.84	1.85	1.80
0.5	40	1.92	1.90	1.86
20	40	1.52		
20	45	1.57		
20	50	1.81		
20	55	1.79		
20	65	1.90		

We shall slightly generalize this usual description and assume that the probability to break and recombine depends on L: Wormlike micelles have indeed a larger probability to lose their ends then to be cut in the middle. We will assume that the equilibrium distribution is changed into $P(L)\approx\Phi^{-1}L^{1-2\sigma}\exp(-L/L^*)$.[14] The algebraic prefactor is frequently present in "cluster"-size distributions (e.g., percolation clusters).

The distance spanned by the chain before recombining is typically

$$l(L)\approx[D_{\rm rep}(L)\tau_{\rm break}]^{1/2}, \quad (3)$$

where $D_{\rm rep}(L)$ is the diffusion constant of a chain of length L. Assuming that the chains are ideal for L much larger than the entanglement length L_e, $D_{\rm rep}(L)\approx D_0\times(L_e/L)^2$;[15] we shall again be slightly more general and write $D_{\rm rep}(L)\approx D_0(L_e/L)^{2\beta}$, allowing for deviations from the classical reptation model (for example, the chains may not be ideal at large scales). Thus, $l(L)\approx l_0L^{-\beta}$, with $l_0^2=D_0\tau_{\rm beak}(L_e)^{2\beta}$. The probability to undergo a jump of length l is then simply obtained as[16]

$$P(l)=P(L)dL/dl\approx\Phi^{-1}l_0^{\mu}l^{-(1+\mu)}, \quad (4)$$

with $\mu=2(1-\sigma)/\beta$. In a given long time interval $T=N\tau_{\rm break}$, a given fluorescent particle will have encountered N different "vehicles" and spanned the distance R:

$$R^2(N)=\sum_{i}^{N}l^2(L_i). \quad (5)$$

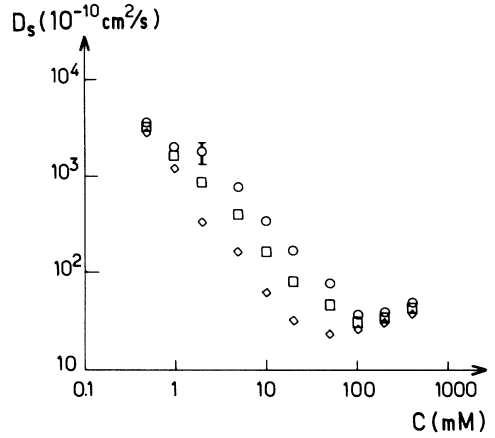

FIG. 2. Effective diffusion constant determined at different length scales vs CTAB concentration in 2 M KBr brine. Circles, $i=89$ μm; squares, $i=20$ μm; diamonds, $i=3$ μm. Experimental errors are smaller than the point size except for the 2-mM sample at large i.

It can be shown[17] that the longest jump undergone in N steps is $l_m \approx N^{1/\mu}$: As time goes on, *shorter and shorter chains will be visited by the probe.* It is thus important to keep the modulation of the tracer concentration low, otherwise *all* chains are visited from the start and nonstationary effects cannot be observed because, in this case, breaking and recombination only swaps the tracers. Gaussian behavior should hence reapear if a high concentration of probes is used. Preliminary observations show that this is indeed the case,[18] confirming the purely statistical nature of the phenomenon.

Hence, $R^2(N)$ is given by $N\int^{l_m} l^2 P(l)dl \approx N^{2/\mu}$ if $\mu<2$ (and N if $\mu>2$). The diffusion exponent is thus $\nu=\beta/2(1-\sigma)$. More precisely, since R is a sum of (broadly distributed) random variables, the probability distribution $P(R,t=N\tau_{\text{break}})$ converges[19] towards a Levy stable law of order μ, solution of a "generalized" diffusion equation which reads, in Fourier space,

$$\partial P(q,t)/\partial t = -q^{\mu}P(q,t)\,. \tag{6}$$

As in the experiment, a single mode q is excited, the signal is indeed expected to be a *pure exponential,* with a decay rate proportional to q^{μ} (see Fig. 1). Note that the "classical" values ($\beta=1,\sigma=0$) already correspond to the marginal case $\mu=2$, for which $R^2(t)$ evolves as $t\ln t$. A very small departure from those values, say, $\beta=1,\sigma=\frac{1}{4}$, leads to the observed value $\mu\sim 1.5$ (see Table I).

Equation (4) for $P(l)$ with $\mu=2(1-\sigma)/\beta$ of course only applies in a limited interval. *For large l,* or small L: $L<L_e$ reptation loses its meaning and[15] $D(L)\approx 1/\xi(L)$ [$\xi(L)$ is the gyration radius for a chain of length L]. This corresponds to $\mu>2$, and hence very short chains will not be responsible for anomalous diffusion. *For small l,* or large L: If $L>L_c=L^*\zeta^{1/3}$, the chain recombines in a time shorter than its disentanglement time. One may show that $D(L)$ [defined in Eq. (3)] behaves as $D(L)\approx D_{\text{rep}}\zeta^{-1/2}(L^*/L)^{1/2}$, which again corresponds to $\mu>2$. If for some reason the solution only contains chains of length $L>L_c$, the average diffusion constant is given by Cates' expression, Eq. (1) [but see also after Eq. (8)].

The reason why anomalous diffusion is only found in a certain range of concentrations and salinities is because, for some reason, either the crossovers L_e and L_c or the exponents β and σ depend on those parameters. A first condition for the existence of anomalous diffusion is $L_c \gg L_e$: The region where the diffusion constant strongly depends on L must exist. One role of salt is to reduce the entanglement length because the chains are then more flexible. Another important condition for the observation of anomalous diffusion is that the experimental time scale must be sufficiently short: The crossover time t_c above which Gaussian diffusion is recovered is given by the condition $L[l_m(N)]\approx L_e$ with $t_c=N\tau_{\text{break}}$. Hence,

$$t_c \approx \Phi\tau_{\text{break}}L_e^{-2(1-\sigma)} \approx \Phi^{3-5\sigma/2} \tag{7}$$

[with $L_e\approx\Phi^{-5/4}$ and $\tau_{\text{break}}\approx L^{*-1}\approx\Phi^{-1/2}$ (Ref. 10)]. For $t_{\text{expt}}\gg t_c$, the contribution of the short chains to the average diffusion constant is given by

$$D\approx\tau_{\text{break}}^{-1}\int_{L_e}^{L_c} l^2(L)P(L)dL \approx D_{\text{rep}}\left(\frac{L^*}{L_e}\right)^{2(\beta+\sigma-1)} \tag{8}$$

Comparing with Eq. (1), one finds that the short-chains contribution indeed dominates the diffusion constant when $L_e \ll L_c(L^*/L_c)^{y}$, with $y=1-1/2(\sigma+\beta-1)$.[20] Taking[15] $D_0\approx 1/\xi(L_e)$ and $\sigma=\frac{1}{4}$, the concentration dependence of the diffusion constant given by (8) reads $D\approx\Phi^{-\gamma}$, with $\gamma=3$ for ideal blobs, 2.12 for "swollen" blobs, and 1.25 for "stretched" blobs. γ is thus very sensitive to the chain conformation inside one blob. The values of γ obtained using Eq. (1) are, respectively, 2.33, 1.57, and 0.83.

Experimentally, the anomalous exponent disappears for low concentrations, which is reasonable to interpret as $L_e>L_c(L^*/L_c)^{y}$. For high concentrations, the experimental time scale $t_{\text{expt}}\approx i^2/D(i)$ becomes large (see Fig. 2). The anomalous behavior is lost when $t_{\text{expt}}>t_c$. This is experimentally seen to occur when the mesh size of the network is of the order of the diameter of the micelles a ($L_e\approx 1$) where (7) becomes $t_c\approx\Phi\tau_{\text{break}}$. We thus think σ,β take definite values, and that the apparent variation of the anomalous exponent μ_{eff} in fact results in situations where $t_c\approx t_{\text{expt}}$, from a mixture between Brownian diffusion ($\mu=1$) and a *unique* anomalous diffusion exponent ($\mu\approx\frac{3}{2}$).

The fact that the anomalous behavior is only observable if the experimental time is shorter than the crossover time t_c and if $L_e \ll L_c$ suggests that a temperature

increase suppresses the effect, since in that case the breaking time τ_{break} diminishes rapidly[21] (τ_{break} has an activated form). The experiment fully confirms this prediction: We show in Table I the evolution of the apparent exponent μ_{eff} with temperature. Thus our Levy flight model indeed qualitatively accounts for all our experimental results.

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[13]We have checked that our results are the same for fluorescent probes with different aliphatic tails (which changes the residence time in the micelle by 1 order of magnitude). This shows that we indeed observe the motion of the micelles, and not that of the fluorescent probes. We have also checked that the results do not depend on the intensity of the recovery laser beam, i.e., that this beam does not induce spurious bleaching.

[14]If the survival time for a chain of length L depends on L through $\tau(L) \approx \tau_{break}(L^*/L)^{2\sigma}$, it would also lead to an equilibrium distribution $P(L) \sim L^{1-2\sigma}\exp(-L/L^*)$. The Levy flight analysis should, however, be slightly modified. In particular, μ would become $\mu' = 2(1-\sigma)/(\beta+\sigma)$.

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[16]A more correct formula should read

$$P(l) = 4\pi l^2 \int dL\, P(L)[4\pi l'^2(L)]^{-3/2}\exp\{-[l/2l'(L)]^2\}$$

but this does not change the asymptotic shape given by (4).

[17]See, e.g., Refs. 2, 3, and 20, and also A. Blumen, G. Zumofen, and J. Klafter, Phys. Rev. A **40**, 3964 (1989); J. P. Bouchaud and A. Georges, Phys. Rev. A **41**, 1156 (1990).

[18]Changing the probes concentration from $\frac{1}{200}$ to $\frac{1}{45}$ (per micellar unit) indeed shifts the apparent exponent μ from 1.5 to 1.8.

[19]See, e.g., B. Gnedenko and A. Kolmogorov, *Limit Distributions for Sums of Independent Random Variables* (Addison-Wesley, Reading, MA, 1954); E. W. Montroll and M. F. Schlesinger, in *Studies in Statistical Mechanics,* edited by J. Lebowitz and E. W. Montroll (North-Holland, Amsterdam, 1984). For a simple introduction, see Appendix B in Ref. 2.

[20]It is easy to see that the contribution of the very short chains (such that $L < L_e$) to the average D is of the same order of magnitude as (8).

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