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# Anomalous diffusion in elongated micelles and its Lévy flight interpretation

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Abstract. — We have observed anomalously enhanced self (tracer) diffusion in systems of polymer-like, 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 (« Lévy-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. We discuss in detail the fact that this anomalous régime only exists in a certain range of concentration and temperature. The theoretical dependence of the asymptotic diffusion constant on concentration is in quite good agreement with the experiment.

# 1. Introduction. Anomalous diffusion.

Brownian diffusion is a most widespread phenomenon, occurring in a variety of different physical situations and studied by many different experimental techniques. The two characteristic features of Brownian diffusion are well known: first, the position of the diffusing particle typically increases as the square root of the elapsed time t, and second, the diffusion front (or the probability distribution of the particles positions) is Gaussian. These two features are extremely general and robust, because the Central Limit Theorem (CLT) controlling the statistical properties of sums of random variables holds in an overwhelming majority of situations. In order to impede the application of CLT, strong statistical "preponderant role to rare events — or persistent correlations. These pathologies eventually lead to a departure from the usual laws (see [1] for a recent review): the position scales with an « anomalous » power of time ( $\neq 1/2$ ), and the diffusion front is no longer a Gaussian. Quite a few physical examples of non-Brownian diffusion exist (photoconductivity of amorphous materials [2], conductivity of disordered ionic chains [3], diffusion in convective rolls [4], random walk on fractal substrates [5]...). In most of them however one observes a

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« subdiffusive » behaviour, that is, the position of the particle increases more slowly than  $\sqrt{t}$ . The mechanism underlying this behaviour is either geometric (tortuous substrate) or due to the presence of « traps » (region of space where the particule is confined for a certain time  $\tau$ ) with a broad distribution of release time  $\Psi(\tau)$  — broad meaning in this case that the *mean* trapping time  $\tau = \int_0^\infty \tau \Psi(\tau) d\tau$  is infinite. *Enhanced diffusion* (i.e. when the particle position increases *faster* than  $\sqrt{t}$ ) is much rarer : classical examples are Richardson diffusion in turbulent velocity fields [6, 7], diffusion in layered porous media [8, 1, 9], or in shear or Poiseuille flows. In all these cases, the mechanism responsible for this enhanced diffusion is the long range (time) correlations present in the velocity of the tracer particle [1].

Another way to obtain enhanced diffusion is to imagine that the diffusing particle undergoes a series of *independent* steps of length  $\ell_1$ , with a « broad » distribution of step length,  $P(\ell)$ . If the variance of  $P(\ell)$  is infinite, it is easy to see that the usual derivation of the CLT fails; one must then, following Lévy [10], and others [11, 12], generalize the CLT to this case. A short review of the useful results is given in Appendix A and in [1a]; the important results are as follows. If the position of the particle is given by (we restrict to one dimensional motion for simplicity)

with 
$$P(\ell) = \ell^{-(1+\mu)}, \quad \mu < 2 \text{ and } \langle \ell_i \rangle = 0, \text{ then, } x \approx t^{-1/\mu}, \text{ and}$$
  
 $P(x, t) = t^{-1/\mu} L_{\mu} (xt^{-1/\mu})$ 

where  $L_{\mu}(u)$  is a Lévy (or stable) law — generalizing the Gaussian obtained if  $\mu = 2$  — defined in Appendix A. Such a generalisation of the Brownian motion has been called by Mandelbrot [13] a « Lévy flight ». A remarkable fact about these Lévy flights --- or Lévy sums such as (1) — is their hierarchical structure : if  $\ell_{max}$  is the largest number in the sequence  $\{\ell_i\}$ , one has  $x \approx \ell_{max}$ ; that is the full sum is dominated by its largest term (more precise statements can be found in Appendix A). However, despite the prophecy made by Gnedenko and Kolmogorov [12] in their remarkable book on the subject (All these laws, called stable, deserve the most serious attention. It is probable that the scope of applied problems in which they play an essential role will become in due course rather wide), no experiment for which the concept of Lévy flight was directly applicable was known, even if a few physical situations have been theoretically described as such (incoherent radiative transfer [33], conformation of a polymer just at adsorption threshold, diffusion in billiards, in chaotic maps — see e.g. [1a]). Turbulent diffusion was modeled as a Lévy flight by Shlesinger, West and Klafter [14] — but to the best of our knowledge, there is no experimental fact justifying this description. In particular, the Lévy diffusion front (Eq. (2)) has never been observed.

We want to present in this paper what we think to be the first experimental observation of a Lévy flight, where both the anomalously enhanced diffusion law and the Lévy diffusion front have been found. The system that we have studied (long cylindrical breakable micelles) is interesting in its own right and the initial motivation for the experiments we have performed was to understand the physical properties of these objects rather than to observe a Lévy flight. We shall however see that the interpretation of our results as a Lévy process is extremely natural when one is slightly acquainted with those micelles : this is why we shall spend the next paragraph reviewing the salient properties of these objects (for a recent comprehensive account, see [15]) before examining and interpreting in details our experimental results. A short version of this work has already appeared in [16].

## 2. Long breakable micelles : a short overview.

Amphiphilic molecules of CTAB (cetyl trimethyl ammonium bromide), when dissolved in salted water, aggregate to form long flexible cylindrical micelles. These objects may be grown very long and in this case they behave much as polymers — although at a different length scale : the basic unit is of the order of a few nanometers instead of a few Angstroems in the case of flexible polymers. In particular, light scattering experiments [17] on semidilute solutions of CTAB micelles are well accounted for by the standard « blob » picture [18] : a characteristic mesh size  $\xi$  (entanglement length) appears, below which the chains behave as if they were isolated, and above which the self interaction of the chain is screened. The dependence of  $\xi$  on  $\phi$  (the CTAB volume fraction) gives information on the conformation of the CTAB chains, since  $\xi$  is related to the number of monomers g needed to create an entanglement through  $\xi \approx \ell_p g^{\zeta}$  ( $\zeta$  is usually called  $\nu$  in polymer physics; however  $\nu$  will be used below with a different meaning;  $\ell_p$  is the «monomer» size, or more precisely the persistence length). Then, one finds [18] :

$$\xi \approx \phi^{\zeta/(1-3\zeta)} \tag{1}$$

Experimentally [15, 17], the law  $\xi \approx \phi^{-0.77}$  (corresponding to  $\zeta = 0.59$  — the value observed for three dimensional polymers in good solvents) seems compatible with both light scattering and elastic modulus data, although somewhat larger values of  $\zeta$  are not excluded. For scales >  $\xi$ , the chains are expected to be ideal [18]:  $\zeta = 0.5$ . This analogy is however restricted to static properties : the crucial difference between the two systems is the fact that, while for all practical purposes polymer systems are irreversibly tethered, micelles break and recombine constantly — they are « living polymers ». This polymerisation in equilibrium also occurs in other systems (see Ref. given in [15]), among which one may cite plastic sulphur [20] and liquid selenium [21]. The two main consequences of the « transient » (rather than permanent) nature of these objects are the following :

2.1 SOLUTIONS ARE INTRINSICALLY POLYDISPERSE. — If one assumes, following Cates [22], that scission can occur anywhere along the chain with equal probability, and that two chains may fuse in a way independent of their size, then the equilibrium size distribution  $\mathfrak{T}$  is found to be [22]:

$$\Im(L) = (1/L) \exp(-L/L)$$
<sup>(2)</sup>

with

$$\mathbf{L} \approx \phi^{1/2} \exp\left(E/2 \, kT\right) \tag{3}$$

and E is the energy needed to « cut » the chain into two pieces. Throughout this paper, we shall call L the total arc length of a chain, in units of the persistence length  $\ell_p$ . Equation (2) can be throught of as a mean field description of the size distribution of the aggregates. However, correlations of some sort could affect this simple law (for example, chains may rather break near their ends for purely energetic reasons; it is also conceivable that the probability that two « off springs » recombine very shortly after being « born » is greater when a large chain breaks than when a short chain breaks — because short chains diffuse away from each other faster, etc...). We propose that a semi-phenomenological way to take these correlations into account is to write :

$$\mathfrak{f}(L) \approx L^{-2\sigma} \mathbf{L}^{-1+2\sigma} \exp\left(-L/\mathbf{L}\right) \tag{2'}$$

where  $\sigma$  is a non trivial exponent (which is positive if short chains are favored). Such a law is very common in the physics of clusters : the best known example is the cluster size distribution in percolation (below threshold). In this case,  $\sigma \approx 1$  [23].

2.2 DIFFUSION IS ENHANCED. — Usually, diffusion is very slow in polymeric systems, because of strong steric constraints (usual polymers cannot « go through » each other) : the change of conformation can only be achieved through motion of the chain « along itself » (reptation). When the end part of the chain retracts and leaves a certain region of space, the environment is allowed to relax and « erases » the trace left behind. Hence the chain trying to creep back has to choose a new local conformation : the old configuration is « eaten up » by the two ends. Since the chain diffuses along its own « tube », the part of the chain which is still in the old configuration has a length given by  $L_{old} \approx L - 2\sqrt{Dt}$ , where D is the (curvilinear) diffusion constant of the whole chain, which is a factor L smaller than the diffusion constant of a single monomer  $D_0$ . The chain is completely desentangled when  $L_{old} = 0$ , i.e. after a time  $\tau_{rep}(L) \approx L^3/D_0$  (see [18, 24] for more details).

When scission occurs, polymers are in a sense allowed to «go through » each other every now and then. This accelerates diffusion and stress relaxation if the *typical* breaking time  $\tau_b$  is smaller than  $\tau_{rep}$ , since in this case only a fraction of the chain will have to disentangle through reptation. Two new characteristic times — governing stress relaxation and single monomer diffusion — appear.

\* Stress relaxation time : let C be the probability of scission per unit time and per unit length of the chain ( $\tau_b$  and C are then related by  $C\tau_b \mathbf{L} \approx 1$ ). For a mechanical constraint to be relaxed at a given point, a chain end must go through that point. The typical time  $\tau_r$  for this to happen is such that a « new end » must appear (through scission) and pass through the given point during its lifetime  $\tau_b$ . This takes a time  $\tau_r$  such that  $C\tau_r \sqrt{D(\mathbf{L})} \tau_b \approx 1$ , or  $\tau_r \approx \sqrt{\tau_b} \tau_{rep}(\mathbf{L})$  [15, 22].

\* Single monomer diffusion : The previous discussion was extended by Cates to predict the diffusion coefficient of a « marked » monomer. When  $\tau_b$  is infinite, a given monomer undergoes truly independent jumps only every  $\tau_{rep}$ . For  $t < \tau_{rep}$ , the back and forth motion of the chain in its tube means that the curvilinear coordinate s of a given monomer increases as  $\sqrt{t}$ ; its position in space hence scales as  $R \approx t^{\zeta/2}$ : motion of a single monomer is subdiffusive for  $t < \tau_{rep}(\zeta < 1)$ . For  $t \approx \tau_{rep}$ , the monomer will have spanned a distance of the order of the gyration radius of the whole chain  $R \approx L^{\zeta}$ . For  $t \gg \tau_{rep}$ , the particle will have undergone  $(t/\tau_{rep})$  independent steps of size  $L^{\zeta}$ , and hence  $R^2 \approx D_{rep}(L) t$  with  $D_{rep}(L) \approx L^{2\zeta}/\tau_{rep}$ . In the semi-dilute regime, one should take as the basic unit a blob of size  $\xi$ — this is important to get the concentration scalings right : this finally leads to (\*)  $D_{rep}(L) \approx L^{-2} \phi^{-7/4}$ , and hence, using  $L \approx \phi^{1/2} \exp(E/2 kT)$ ,

$$D_{\rm ren}(\mathbf{L}) \approx \phi^{-11/4} \tag{4}$$

When the scission time is smaller than the reptation time, the monomer, according to Cates, performs independent jumps of size  $(D(\mathbf{L}) \tau_{dis})^{\zeta/2}$  every  $\tau_{dis}$ , where  $\tau_{dis}$  denotes the time needed for a complete disengagement of the segment of the chain carrying the marked monomer. This occurs when the chain breaks on a segment which has created its new tube through reptation, i.e. when

$$C \tau_{\rm dis} \sqrt{D({\rm L}) \tau_{\rm dis}} \approx 1$$
 (5)

<sup>(\*)</sup> In particular, one has  $D_0(\xi) = T/(6 \pi \eta \xi)$  (Stokes law: see [18] p. 180).

or

$$\tau_{\rm dis} = \tau_{\rm b}^{2/3} \tau_{\rm rep} (\mathbf{L})^{1/3} \tag{6}$$

which is indeed smaller than  $\tau_{rep}$  when  $\tau_b < \tau_{rep}$ . Finally, one finds [22]:

$$D_{\text{Cates}} \approx (\tau_{\text{rep}}/\tau_b)^{1/3} D_{\text{rep}}(\mathbf{L})$$
 (7)

(in the semi-dilute régime). Inserting all the concentration dependences (in particular  $\tau_b \approx \phi^{-1/2}$ ), one obtains

$$D_{\text{Cates}} \approx \phi^{-1.57}$$
 (8)

which is markedly different from (4) (\*\*). Note however that, implicit in the reasoning is the assumption that only the motion of the *typical* chain (of size L) needs to be considered to obtain the asymptotic diffusion constant. This will be discussed at length below.

Experimentally, fluorescence recovery after fringe pattern photobleaching (FRAP) is a technique particularly well suited to study monomer (self-) diffusion in these systems [25, 26]. Some details concerning the experimental set up are given in Appendix B. In a previous work [27] we tried to test equation (8) by studying solutions of CTAB at different CTAB concentrations and different salinities. While for high salinities, Cates law (8) is approximatively obeyed, we found that the exponent depends much on salt concentration at lower salinities [27]. Growth laws such as  $L \approx \phi^{1/2} \exp(E/2kT)$  are however throught to be inadequate when strong polyelectrolyte effects are present [28]. Two ways have thus been explored : the first one was to get rid of the ions altogether by working with inverted micelles in oil. FRAP experiments on lecithin inverse micelles were therefore performed [29] and the results are compatible with Cates' model — although the exponent obtained experimentally (-1.35) is slightly smaller than predicted by Cates (but see below). The second possibility was to hope that the charge effects would saturate at very high salinities (of the order of the micellar concentration): this however led to the unexpected superdiffusive behaviour [16] that we are going to describe and interpret in the next two sections. (Superdiffusive effects were in fact also observed in lecithin micelles, but they are much weaker because the chains are shorter — see section 4.3).

## 3. The experimental observation of superdiffusive behaviour.

3.1 EXPERIMENTAL DATA. — Fluorescence recovery after fringe pattern photobleaching allows to follow the evolution of a *tracer fluorescence* modulation of wave vector  $q = 2 \pi/i$ , where *i* is the fringe spacing, which ranges, in the present experiment, from 2  $\mu$ m to 100  $\mu$ m. In the case of usual Brownian motion of *monodisperse objects*, the equation governing the tracer probability distribution  $P(\mathbf{r}, t)$  reads:

$$\partial P/\partial t = D \,\Delta P \,. \tag{9}$$

The technique directly measures the amplitude of the modulation of  $P(\mathbf{r}, t)$  for a wave vector  $\mathbf{q}$ , which thus evolves as :

$$\partial P_{\mathbf{q}}/\partial t = -Dq^2 P_{\mathbf{q}} \tag{10}$$

or :

$$P_{q}(t) = P_{q}(0) \exp(-Dq^{2}t).$$
(11)

(\*\*) These concentration dependences are in fact very sensitive to the value of  $\zeta$  (the conformation of the chains for scales  $\langle \xi \rangle$ ). For  $\zeta = 0.5$  (ideal blobs/mean field), one finds  $D_{\text{Cates}} \approx \phi^{-2.33}$  and  $D_{\text{rep}}(\mathbf{L}) \approx \phi^{-4}$ , while for  $\zeta = 1$  (« stretched » blobs — for example if the chains are charged),  $D_{\text{Cates}} \approx \phi^{-0.83}$  and  $D_{\text{rep}}(\mathbf{L}) \approx \phi^{-3/2}$ 

One thus usually determine the inverse relaxation time  $\tau_q^{-1}$  at a given wave vector by analysing the decay of  $P_q(t)$ ; the slope of  $\tau_q^{-1}$  versus  $q^2$  then directly yields D (cf. Appendix B for more details). We have studied aqueous solutions of CTAB in the presence of potassium bromide (KBr). The micelles entangle above a certain surfactant concentration  $c^* \simeq 10^{-3}$ (Mole/litres). c = 1 M/l corresponds to a volume fraction equal to 0.3. In previous experiments [27], we had found that above  $c^*$ , the relaxation of  $P_q(t)$  is exponential, not because the micelles are monodisperse (the relaxation is in fact non exponential below  $c^*$ ), but rather because, due to breakage and recombination on a time scale much shorter than the experimental time, one observes the average diffusion constant (given by Eq. (8) or (21) below). The diffusion constant was found to follow a power law dependence on c, but with a salinity dependent exponent, varying between  $\approx -4.5$  for 0.05 M KBr solutions to -1.5 for 0.25 M KBr. In the last case, the salt concentration is larger than the surfactant concentration for most samples, and one can expect that the ionic strength does not change much as c is varied : the micellar growth is in that case expected to be well described by equation (3). It was in order to clarify this point that we have studied micellar solutions of very high salinities (0.5, 1 and 2 M).



Fig. 1. — Fluorescence recovery showing a single exponential relaxation, but with a relaxation time scaling with an anomalous power of the wave vector:  $\tau \approx q^{-\mu}$  (insert). Sample is 10 mM CTAB, 2 M KBr.

Surprisingly, in CTAB samples at high salt concentration, while  $P_q(t)$  is still relaxing exponentially (see Fig. 1),  $\tau_q^{-1}$  is not linear in  $q^2$ . One rather has (Fig. 1, insert):

$$\tau_q^{-1} \approx q^{\mu} \tag{12}$$

with  $\mu < 2$  (see Fig. 2). In other words, if one tries to define an effective diffusion constant by forming  $D_q = (q^2 \tau_q)^{-1}$ , one finds that this diffusion constant *increases* steadily with the fringe separation  $i = 2 \pi/q$ . This is not a small effect since one finds a factor  $\approx 10$  between the diffusion constant measured with  $i = 90 \,\mu\text{m}$  and the one measured with  $i = 3 \,\mu\text{m}$  (see Fig. 3). The power law (12) typically holds for  $5 \times 10^2 \,\text{cm}^{-1} \le q \le 5 \times 10^4 \,\text{cm}^{-1}$  (corresponding to three time decades : 0.01-10 s). Equation (12) essentially means that the distance spanned by the tracer during a time t scales as  $t^{1/\mu}$ , i.e., since  $\mu < 2$ , that the tracer motion is superdiffusive.



Fig. 2. — The value of the effective exponent  $\mu$  (determined through  $\tau \approx q^{-\mu}$ ), as a function of the CTAB concentration, for different salinities.



Fig. 3. — Effective diffusion constant, measured for various fringe separations (3  $\mu$ m-diamonds; 10  $\mu$ m-squares, 89  $\mu$ m-circles) versus CTAB concentration. Note that this effective diffusion constant increases with distance.

3.2 LENGTH AND TIME SCALES. — We now want to specify somewhat the experimental length and time scales which set the scenery for the theoretical interpretation of this rather unusual behaviour.

The diameter of the cylindrical micelle is of the order of 50 A. The mesh size of the « coils » network just after entering the semi-dilute régime ( $\phi = \phi^*$ , corresponding to  $\approx 1 \text{ mM/l}$ ) is

estimated — through light scattering experiments [17, 34] on similar systems — to be  $\approx 600$  A. Low salinity experiments on these systems have determined the persistence length  $l_p$  to be  $\approx 150$  A [22]; high concentrations of salt are expected to make the chains more flexible — this may reduce  $l_p$  to say  $\approx 100$  A. The number L of « monomers » — independent subparts of the chain of size  $l_p$  — on the typical chain is thus estimated as:  $600 \approx 100 \text{ L}^{\zeta}$ , and hence L  $\approx 30$ . For  $\phi \approx 10 \phi^*$ , L is multiplied by  $\sqrt{10}$  (see Eq. (3)), i.e. takes the value L  $\approx 100$ .

The entanglement length  $\xi$  in the semi-dilute regime behaves as  $\xi \approx 600 (\phi/\phi^*)^{-0.77}$ .

Hence for a concentration of 10 mM, corresponding to  $\phi \approx 10 \phi^*$ , one finds :  $\xi \approx 100$  A. This shows that persistence length effects (shifting the exponent  $\zeta$  to higher effective values) certainly come into play.

The breaking time has been measured by Candau *et al.* to be of order 1-1 000 ms; the ratio between the breaking time and a microscopic time is thus of the order of  $10^7$ - $10^{10}$ , which one may identify with  $\exp(E/kT)$ . Hence, for a concentration of 10 mM ( $\phi \approx 3 \times 10^{-3}$ ), one estimates L as  $\sqrt{\phi} \exp(E/2kT) \approx 100$  which is thus compatible with the above figure.

The experimental length scale (fixed by the fringe spacing) varies between 1  $\mu$ m and 100  $\mu$ m (the chains thus move on scales much larger than their own size) and the corresponding time scales are (see Fig. 1)  $t_{exp} \approx 0.1$  to 10 s. Hence we are in a régime where the chains have indeed time to break and recombine quite a number of times *but not a very large number of times*: taking — say  $\tau_b = 100$  ms, one has  $t_{exp}/\tau_b \approx 1-100$ . It is obvious that if one observes a tracer initially standing on a typical chain, this tracer will visit, as time goes on and due to scission and recombination, shorter and shorter chains. More precisely, the typical size  $L_{min}$  of the shortest chain visited by the probe is determined by the condition (see Appendix A):

$$[t_{\exp}/\tau_{\rm b}] \int_{1}^{L_{\rm mun}} dLP(L) \approx 1$$
(13)

where P(L) is the *(a priori)* probability to find this tracer on a chain of length L: (cf. Eq. (3)):

$$P(L) = L \mathfrak{I}(L) = L^{2\sigma - 2} L^{1 - 2\sigma} \exp(-L/L).$$
(14)

Using equation (13) and (14), one finds (in the regime  $1 \ll L_{\min} \ll L$ )

$$L_{\min} \approx \mathbf{L} \left( \tau_{\rm b} / t_{\rm exp} \right)^{1/(2 - 2\sigma)} \tag{15}$$

Hence, for the values of  $t_{exp}/\tau_b$  quoted above and for example for  $\sigma = 1/4$  (see below), one finds  $L_{min} \approx (1 - 0.01) \mathbf{L} \approx 100 - 1$ : only after the longest experimental time scale  $(t_{exp}/\tau_b \approx 1000)$  is the ergodic exploration of P(L) completed. As we shall detail in next section, this feature turns out to be crucial to understand the observed superdiffusion. Finally, the reptation time (for the typical chain)  $\tau_{rep}$  may be deemed as:  $\tau_{rep} = (6 \pi \eta \xi^3)/T (\mathbf{L}/g)^3$  (g is the number of independent segments « per blob » [18] — in our case  $g \approx 1$ ), or  $\tau_{rep} \approx 1$  s, which is a little larger than the breaking time for the system we consider. However, since  $\tau_{rep}(L) = \tau_{rep}(\mathbf{L})$ .  $(L/\mathbf{L})^3$ , chains only slightly shorter than  $\mathbf{L}$  will be such that  $\tau_{rep}(L) < \tau_b$ .

# 4. Superdiffusion : basic mechanism and Lévy flight description.

4.1 SHORT CHAIN DOMINATED DIFFUSION. — We are now in position to understand why superdiffusion occurs in this system. Take a given tracer particle and follow its fate : due to the «living» nature of the chains, the tracer rides chains of different sizes  $L_1$ ,  $L_2$ , ...,  $L_N$  where  $N = t/\tau_h$  is the total number of scission/fusion events after time t (we neglect

unimportant fluctuations of N from tracer to tracer). Each chain will contribute to the square displacement of the tracer from its initial position proportionally to  $D(L_i) \tau_b$ , where

$$D(L_i) = D_0(\xi) (g/L_i)^{2\beta}$$
 if  $\tau_{\rm rep}(L_i) < \tau_{\rm b}$  (16a)

$$= \xi^{2} / \tau_{0} (g/L_{i})^{\zeta} (\tau_{b} / \tau_{\xi})^{\zeta} \quad \text{if} \quad \tau_{\text{rep}}(L_{i}) > \tau_{b}$$
(16b)

(see Fig. 4).  $D_0(\xi)$  is the diffusion constant of a sphere of size  $\xi$ , and  $\beta$  is an exponent which is equal to 1 if the classical reptation theory holds and  $\xi = 1/2$  if the chains may be considered as ideal for  $R > \xi$ . (More generally,  $\zeta = 3/2 - \beta$ ). The crossover length  $L_c$  such that  $\tau_{\rm rep}(L_c) = \tau_b$  is given (for  $\beta = 1$ ) by:  $L_c = L(\tau_b/\tau_{\rm rep})^{1/3}$  [22]. The strong dependence of D(L) for  $L < L_c$  is responsible for anomalous diffusion : equation (16) makes quantitative the obvious fact that short chains diffuse much more rapidly than long ones and thus contribute a lot to the total displacement of the tracer — but of course, the tracer has fewer occasions to find itself on a short chain than on a long one. Since successive hops are uncorrelated, the total displacement of the tracer will be given by (<sup>1</sup>):

$$R^{2}(t) = \sum_{t=1,N} D(L_{t}) \tau_{b}.$$
(17)

One may now try to apply the usual law of large numbers to this sum. This yields :

 $\ell = \sqrt{D(L)} \tau_h$ 

$$R^{2}(t) = t \int_{0}^{\infty} \mathrm{d}LP\left(L\right) D\left(L\right) = \mathfrak{D}t .$$
(18)



Fig. 4. — a) Typical displacement of the fluorescent probe during a time  $\tau_{break}$  as a function of the size of the chain on which it resides. The dependence is strong for  $g < L < L_c$  and it is this regime which is responsible of the anomalous diffusion exponent. b) Ordering of time scales which make possible the observation of Lévy flights: the chains must have travelled a distance much greater than their size before breaking, the fluorescent probe must have encountered many different chains on the experimental time scale, and finally the time needed to explore the full distribution P(L) must be greater than the experimental time scale.

<sup>(&</sup>lt;sup>1</sup>) In the following discussion, we assume that the recombination time  $\tau_b$  does not depend on L for short chains. Calculation for the case  $\tau_b(L) = \tau_0 \cdot L^{-\alpha}$  are presented in Appendix C.

This of course only makes sense if the integral  $\mathfrak{D}$  converges — in which case this integral defines the *asymptotic* diffusion constant of the tracer. However, in the case that we consider, this integral *diverges* at small L id  $\sigma + \beta \ge 1$ ; in other words this integral is *dominated* by the lower bound :  $\mathfrak{D} \approx (L_{\min})^{2(1-\sigma-\beta)}$ . But, as we have explained at the end of the previous paragraph, the smallest chain visited by a typical tracer after a time t has a non zero, time dependent size (see Eq. (15)) :  $L_{\min} \approx L(\tau_b/t)^{1/(2-2\sigma)}$  The effective diffusion constant  $\mathfrak{D}$  thus evolves with time :

$$\mathfrak{D}(t) \approx t^{(\sigma + \beta - 1/1 - \sigma)} \tag{19}$$

leading to a superdiffusive behaviour for  $R: R^2(t) = \mathfrak{D}(t) t \approx t^{2/\mu}$  with  $\mu = 2(1-\sigma)/\beta \leq 2$ : the tracer visits, as time goes on, shorter and shorter chains; and since the shortest chain met gives the dominant contribution to the total displacement of the tracer, the effective diffusion constant increases with time. This effect ceases when the shortest available chain is visitedthat is, when (<sup>2</sup>)  $L_{\min} = g$ . This takes a time given by equation (15):  $t_{\text{erg}} \approx (g/L)^{2\sigma-2} \tau_b$ above which the ergodic exploration of the full distribution of sizes P(L) can be assumed. The conditions under which the non stationary, superdiffusive behaviour may be observed are summarized in figure 4. In particular,

$$t_{\rm erg} > t_{\rm exp} \ . \tag{20}$$

For  $t > t_{erg}$ , the system does not « learn » anything new as time increases and the asymptotic diffusion constant is reached (for simplicity, we set  $\beta = 1$  in the remaining of this section : see § 4.3) :

$$\mathfrak{D}(t > t_{\rm erg}) = \mathfrak{D}_{\rm asym} = \int_{g}^{L_{\rm C}} \mathrm{d}LP(L) D(L) \approx D_{\rm rep}(\mathbf{L}) [\mathbf{L}/g]^{2\sigma}$$
(21)

This value should be compared with equation (7), which gives the contribution of the *typical* chains (of length  $\approx$  L):

$$D_{\text{Cates}} = D_{\text{rep}}(\mathbf{L})[\mathbf{L}/L_{\text{C}}]$$
(22)

where  $L_{\rm C} = L(\tau_{\rm b}/\tau_{\rm rep})^{1/3}$  is the length of the chains which break and disentangle within about the same time (cf. Eq. (16)). The inequality  $\mathfrak{D}_{\rm asym} > D_{\rm Cates}$  (which is a necessary condition for anomalous diffusion to be observed) is thus equivalent to :

$$g < L_{\rm C} [{\rm L}/L_{\rm C}]^{\rm y} \tag{23}$$

with  $y = 1 - (1/2 \sigma)$ . Condition (23) will turn out to be more stringent that the condition  $g < L_{\rm C}$  underwhich the region of strong dependence of the diffusion constant D(L) exists. Let us finally indicate the concentration dependence of  $\mathfrak{D}_{\rm asym} \approx \phi^{-\gamma}$  As was the case for  $D_{\rm Cates}$  (see footnote after Eq. (8)),  $\gamma$  is very sensitive to the conformation of the chains at scales  $< \xi$ . From equation (21), one finds, assuming  $L \sim \sqrt{\phi}$ ,

$$\gamma = [\zeta (2 - 3 \sigma) + (1 - \sigma)]/(3 \zeta - 1).$$
(24)

In the particular case  $\sigma = 1/4$ ,  $\gamma = 1.0$ , 1.87 or 2.75 for  $\zeta = 1$ , 3/5 or 1/2 respectively. These values are somewhat larger than those found by Cates (0.83, 1.57, 2.33 resp.).

<sup>(2)</sup> For L < g, the chains evolve quasi freely through the polymeric net, and their diffusion constant depends much less on  $L(D(L) \approx L^{-2\zeta})$ . It is easy to show that these extremely short chains are not responsible for anomalous diffusion.

4.2 LÉVY FLIGHT DESCRIPTION : THE FULL DIFFUSION FRONT. — The above arguments can be restated slightly differently : suppose that one follows with time a given tracer particle, taking snapshots of its position every  $\tau_b$ . We thus describe the motion of this tracer as a succession of independent jumps of size  $\ell_i$ . The probability distribution of the  $\ell_i$ 's is obtained as :

$$P(\ell) = 4 \pi \ell^2 \int_0^\infty dL P(L) [4 \pi D(L) \tau_b]^{-3/2} \exp(-\ell^2/(4 D(L) \tau_b))$$
(25)

which simply follows from the fact that the probability distribution of the distance spanned by the tracer on a chain of length L during  $\tau_b$  is Gaussian with a variance given by  $2 D(L) \tau_b$ . Now, using the asymptotic dependences of P(L) and D(L) for  $L \to 0$  given by (3, 16), one finds, for  $D(L_C) \tau_b \ll \ell^2 \ll D(\xi) \tau_b$ .

$$P(\ell) \approx \ell_0^{\mu} \, \ell^{-(1+\mu)} \tag{26}$$

with  $\mu = 2(1 - \sigma)/\beta$  and  $\ell_0^2 = D_0(\xi) \tau_b g^{2\beta}$  Hence, the jump size distribution decays as a power law, and for certain values of the parameters, that is if  $\mu \leq 2$ , the second moment of  $P(\ell)$  diverges. The position of the tracer particle  $R = \sum_{\substack{i=1,N\\ i=1,N}} \ell_i$  then follows a Lévy process, the

asymptotic probability distribution of R being given by (see Appendix A):

$$P(R,t) = N^{-1/\mu} L_{\mu} [(R/\ell_0) N^{-1/\mu}]$$
(27)

where  $L_{\mu}$  is the (symmetric) stable law of order  $\mu$  and  $N = t/\tau_b$ . By definition,  $L_{\mu}$  is the Fourier transform of exp  $-q^{\mu}$  Thus the experimental signal — proportional to the modulation of P(R, t) at wave vector q, is predicted to be a simple time exponential:

$$P_{\mathbf{q}}(t) = \exp\left(-\Omega q^{\mu} t\right) \tag{28}$$

 $(\Omega \approx \ell_0^{\mu}/\tau_b)$  with an anomalous relaxation time  $\approx q^{-\mu}$  This is precisely what we observe experimentally (see § 3). While superdiffusion has already been observed in a few other systems, it is to our knowledge the first time that a Lévy flight — and in particular its anomalous « diffusion front » — has been characterized in full detail.

4.3 QUANTITATIVE ANALYSIS OF THE EXPERIMENTS. VALUE OF  $\mu$ . ROLE OF THE CONCEN-TRATION AND TEMPERATURE. — As apparent from figures 2, 3, the exponent  $\mu$  extracted from the  $\tau(q)$  dependence is markedly different from 2 only in a certain region of CTAB concentration — roughly between 1 and 100 mM (corresponding to  $\phi^* < \phi < 100 \phi^*$ ). In this « Lévy flight » régime, the measured value of  $\mu$  is about 1.5, although values between 1.5 and 2 are encountered near the « boundaries » of the anomalous region (see below). As we have explained in § 4.1, 4.2, the value of  $\mu$  is related, in our model, to the two exponents  $\sigma$ ,  $\beta$ which describe, respectively, to the chain size distribution (Eq. (3)), and to the dependence of the diffusion constant on the chain size. Another independent experiment would be needed to determine those two exponents (see Conclusion for a suggestion); we thus make here the assumption that the chain size distribution is more complicated than a (mean field) exponential. We thus propose that  $\sigma > 0$  but  $\beta = 1$  and hence (<sup>3</sup>):

$$\mu = 2 - 2 \sigma \approx 1.5 \tag{29}$$

<sup>(3)</sup> Note however that the mean field value  $\sigma = 0$  already corresponds to marginal anomalous diffusion  $R^2(t) \approx t \ln t$ .

leading to  $2\sigma \approx 1/2$ . It could however be that the reptation model underestimates the diffusion exponent  $\beta$  in this system, and thus that one has — say —  $\sigma = 0$  and  $\beta \approx 4/3$ .

It is easy to understand why superdiffusion ceases both for high and low CTAB concentrations:

For low concentrations ( $\phi < \phi^*$ ), the chains do not overlap. Reptation in this case looses its meaning, and the diffusion constant of the chains does not depend sufficiently strongly on their length to induce a «long tail » in  $P(\ell)$ . Diffusion is thus normal in this case.

For high concentrations ( $\phi \approx 100 \phi^* \approx 0.1 \text{ M}$ ) L becomes larger ( $\approx 300$ ), while  $\tau_b$  decreases (see [15], Fig. 10) and  $\tau_{rep} (\approx L^3 \phi^{3/2})$  becomes very large. In this case, one of the two observability criteria (Eqs. (20) and (23)) may be violated.

a) Equation (23) (which compares the contribution of the short chains to that of the «typical » ones) can be written, with y = -1:

$$g < L(\tau_{\rm b}/\tau_{\rm rep})^{2/3}$$

Taking e.g. (4)  $\tau_{\rm b} = 200 \,\mathrm{ms}$  [30, 16],  $\tau_{\rm rep} \approx 900 \,\mathrm{s}$ ,  $\mathbf{L} = 300$ , one indeed finds  $\mathbf{L}(\tau_{\rm b}/\tau_{\rm rep})^{2/3} \approx 1 \approx g$ : the superdiffusion due to short chains is completely masked by the background of typical chains. For a comparison, one has, for  $\phi \approx 10 \,\phi^*$ ,  $\tau_{\rm b} = 700 \,\mathrm{ms}$  [16, 30],  $\tau_{\rm rep} \approx 1 \,\mathrm{s}$ ,  $\mathbf{L} = 100$ , one finds  $\mathbf{L}(\tau_{\rm b}/\tau_{\rm rep})^{2/3} \approx 80 \geq g$ .

b) Equation (20) ceases to be satisfied for a fringe spacing equal to  $\approx 20 \,\mu\text{m}$  since in that case  $t_{\text{exp}} \approx (\mathfrak{D}q^2)^{-1} \approx 1\,000 \,\text{s}$  (with  $\mathfrak{D} \approx 2 \times 10^{-9} \,\text{cm}^2/\text{s}$ ) while  $t_{\text{erg}} \approx (g/\text{L})^{2\,\sigma-2} \,\tau_b \approx 1\,000 \,\text{s}$ .

From the above estimates, it is clear that near the « boundaries » of the anomalous régime, the time interval where superdiffusion can be observed becomes very small : strong crossover effects are expected, leading to an effective value of  $\mu$  intermediate between  $\mu = 1.5$  and  $\mu = 2$  (normal diffusion).

A curious feature must be noted: at high CTAB concentration (>100 mM), while diffusion seems to be normal ( $\mu = 2$ ), the diffusion constant *increases* with concentration. In our opinion, the reason is the following: for these concentrations, the CTAB network is nearly a melt — and thus the true *monomer* diffusion constant should saturate. The tracer particle, however, should hop more easily from chain to chain for these concentrations through transient cross links. The diffusion of the tracer on the network may thus start contributing in this régime.

Rôle of temperature and salinity: The measured value of  $\mu$  versus temperature (for c = 20 mM) is shown in figure 5. One can see that  $\mu$  rapidly approaches 2 as temperature increases. This is easy to interpret since  $\tau_b$  varies extremely quickly (through an Arrhenius exponential) with temperature [15]: a rise of 20° may well reduce the breaking time by a factor 1 000 (see Fig. 13 of Ref. [15]). The length of the chain will thus decrease by a factor  $\approx 30$  and thus  $L(\tau_b/\tau_{rep})^{2/3}$  is only reduced by a factor  $\approx 3$ . However,  $t_{erg} \approx (g/L)^{2\sigma-2} \tau_b$  is divided by 10<sup>5</sup>, while the experimental time scale is only a factor  $\approx 200$  shorter (see Eq. (21)): the ergodic exploration of the size distribution is much more rapid. Hence, condition (20) is very quickly violated, and normal diffusion recovered quite abruptly (see Fig. 4). For these high temperatures where diffusion constant should scale as  $\phi^{-\gamma}$  with  $\gamma = 1.0$  (since it appears that for the concentrations used, the correlation length  $\xi$  is of the

<sup>(&</sup>lt;sup>4</sup>) No measurement was performed at 40 °C and high salinities (1 M KBr). However, 200 ms seems a reasonable extrapolation of the data given in [30].

same order as the persistent length  $\ell_p$ , we took  $\zeta \approx 1$ ). This is in good agreement with our data at 55 °C : see figure 6, where it is seen that  $\gamma \approx 1.0 \pm 0.05$ . This probably shows that the assumption that  $\sigma = 1/4$  is not unreasonable. Note that  $\gamma$  was found equal to  $\approx 1.35$  in lecithin in oil systems [29], which can be interpreted as a decrease of the (effective) exponent  $\zeta$  in this system.

The role of salinity can be understood similarly: adding salt allows us to increase significantly both the length of the chains L and the breaking time  $\tau_b$ . The inequality  $t_{erg} > t_{exp}$  is thus easier to reach at high salinities.



Fig. 5. — The value of the effective exponent  $\mu$  as a function of temperature, for CTAB concentration equal to 20 mM and 1 MKBr. Note that  $\mu$  quickly recovers its normal value ( $\mu = 2$ ) as the temperature is increased.

Fig. 6. — Dependence of the asymptotic diffusion constant on concentration, for T = 55 °C. Between c = 5 mM and 50 mM, one observes  $D \approx \phi^{-\gamma}$  with  $\gamma = 1.0 \pm 0.05$ , in good agreement with our prediction (assuming that the chains are locally stretched, i.e.  $\zeta = 1$ , and that the exponent  $\sigma$  is equal to 1/4). Experimental errors are represented by the point sizes, except for 2 mM where a  $q^{-2}$  dependence was hard to obtain.

Rôle of the tracer concentration: Let us finally comment on the influence of the concentration of fluorescent molecules used in the experiments. In the above discussion, we have assumed the motion of two different tracers were independent. Each one performs an independent Lévy flight because the micelles carrying no tracers act as an infinite « bath » from which the tracer randomly picks its next vehicle. This is justified if the tracer concentration is very small, but is no longer the case if every chain carries many tracers (proportionally to their length), since then breaking/recombination events merely swap the tracers among chains of different lengths, without affecting the global distribution. The equation governing the evolution of small perturbations of tracer concentration  $\delta C_{\rm T}$  is thus the usual diffusion equation, with a diffusion constant  $\mathfrak{D}$  given by equation (21):  $\mathfrak{D} = \int_0^\infty dLP(L) D(L)$ . In other words, since all chains, long or short, are visited by the tracers from the start, all non stationary effects, and thus anomalous diffusion, disappear. Diffusion is thus expected to by normal, with a diffusion constant given by the asymptotic expression, equation (21).

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We have checked experimentally this curious feature. We have indeed found that the effective exponent  $\mu$  rises from  $\mu \approx 1.5$  to  $\mu \approx 1.8$  when the concentration of tracers changes from 1/200 to 1/45. Accordingly, the recovery time for small fringe separation is smaller in the latter case, since short chains already fully contribute.

# 5. Conclusion.

We have thus seen that the essential ingredients which made possible the first experimental observation of a Lévy flight process in these CTAB systems are :

a) the polydispersity of the solution and the possibility for the tracer particle to probe the full size distribution of the chains and

b) a strong dependence — induced by reptation — of the diffusion constant of the chains on their length.

It is interesting to note that our experimental results in fact fully *confirm* that CTAB micelles really behave as one might think — that is, as a semi-dilute, polydisperse solution of breakable polymers.

A priori, those ingredients should be also present in other systems : examples of « living polymers » are not only provided by worm like surfactant micelles. One may think for example of liquid sulphur around 160 °C; the time scale for observing anomalous diffusion is however much shorter in this case and other experimental techniques should be used.

This superdiffusive behaviour could also be seen in *usual* polydisperse polymer solutions : if the tracer particles are not too strongly bound to the chains — more precisely if these tracer particles may hop from chain to chain at a rate  $\Gamma$  such that  $\Gamma \tau_{rep} \ll 1$ , the above mechanism will again operate.

Very recently, M. Cates [31] has suggested that the same effect could be seen in the angular relaxation of entangled rigid rods : indeed, the angular diffusion constant of such objects varies widly with their size  $(D_{ang}(L) \approx L^{-7})$ . Unfortunately, anomalous diffusion on a *sphere* is much more difficult to detect since all the relaxation functions of this process remain pure exponentials in the anomalous regime — only the relaxation time is affected [32, 31].

Let us finally emphasize that non trivial values of the exponents  $\sigma$ ,  $\beta$  are needed to explain anomalous diffusion. An independent confirmation could be reached by studying the spreading of a drop of living polymers : if one could monitor the local concentration of living polymers in the speading drop (using e.g. interferometry) to obtain the time dependent (singular) concentration profile, one could try to deduce the non linear diffusion equation governing the problem, which reads, for  $\phi \ll 1$ 

$$\partial_t \phi = D \partial_x (\phi^{-\theta} \partial_x \phi)$$

where  $\theta$  is an exponent related to  $\beta$  and  $\zeta$  ( $\theta = 3/2$  if  $\beta = 1$ ,  $\zeta = 1$ ). Work in that direction is underway.

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# Appendix A. Sums of broadly distributed variables and Lévy's stable laws.

Let us consider the following sum :

$$Z = \sum_{i=1,N} x_i \tag{A.1}$$

where the  $x_i$  are random variables distributed according to a symmetric probability distribution p(x) = p(-x), decaying for large x as  $p(x) \approx Ax^{-1-\mu}$ . For large N, the generalised central limit theorem states that the rescaled variable  $z = Z/(AN)^{\nu}$  is distributed according to a stable law  $L_{\mu}(z)$  with:

\* For  $\mu > 2$ :  $\nu = 1/2$  and  $L_{\mu}(z)$  is the Gaussian  $G(z) = (\sqrt{2 \pi \sigma})^{-1} \exp(-(z^2/2 \sigma))$ .

\* For  $\mu < 2$ :  $\nu = 1/\mu$  and  $L_{\mu}(z)$  is the Lévy (symmetric) law of order  $\mu$ , defined through its Fourier transform (which we observe directly experimentally):

$$L_{\mu}(z) = 1/2 \pi \int_{-\infty}^{+\infty} dk \exp(ikz - |k|^{\mu})$$
 (A.2)

which takes a finite value at z = 0:

$$L_{\mu}(0) = (\pi \mu)^{-1} \Gamma(1/\mu)$$
 (A.3)

and decays asymptotically with the same power law as p(x):

$$L_{\mu}(z) \approx \sin (\pi \mu/2) \Gamma (1+\mu)/z^{1+\mu}$$
 (A.4)

The case  $\mu = 1$  corresponds to the Cauchy distribution :

$$L_1(z) = (1/\pi) 1/(1+x^2).$$
 (A.5)

For more details on these laws, and for asymmetric Lévy Laws, see [12] and [1, Appendix 2].

The scaling  $Z \approx N^{1/\mu}$  can be interpreted as follows: the largest value taken by one of the N variables  $x_i$  is itself of order  $N^{1/\mu}$  and this value completely dominates the sum Z. One may express more precisely: the probability  $P_{\max}(u, N)$  that the *largest term* in the set  $\{x_i\}$  is equal to u is given by  $P_{\max}(u, N) = Np(u) \left[ \int_{-\infty}^{u} p(y) \, dy \right]^{N-1}$  The most probable value of u (which maximizes  $P_{\max}(u, N)$ ) may be computed and is found to be:

$$(x_{\rm M})^{\mu} = AN/(1+\mu)$$
 (A.6)

which shows that indeed  $x_M \approx N^{1/\mu}$  In order to see that this extreme event dominates the whole sum, one may ask how the quantity

$$Z_2 = \sum_{i=1,N} x_i^2$$
 (A.7)

reflects the value of the  $x_i^2$ . In particular, the weight  $W_i$  of a given term, defined as  $W_i = x_i^2/Z_2 = x_i^2/(B + x_i^2)$  is a random variable distributed according to :

$$\rho(W) = \mathcal{N}W^{-1 - (\mu/2)}(1 - W)^{(\mu/2) - 1}$$
(A.8)

This distribution diverges both for W = 1 (if  $\mu < 2$ ) and for W = 0. One may characterize this distribution by the quantity  $Y = \langle W^2 \rangle / \langle W \rangle = \sum W_i^2$  which is of order 1 if a few W share the whole weight, and of order  $1/N(\rightarrow 0)$  if all W get an equal share. From (A.8), one obtains :

$$Y = 1 - (\mu/2)$$
 ( $\mu < 2$ )  
 $Y = 0$  ( $\mu \ge 2$ )

which gives a precise meaning to the fact that, for  $\mu < 2$ , only a finite number of terms (the largest ones, which are of order  $N^{1/\mu}$ ) contribute significantly to the sum. One should note [35] the deep analogy between the above discussion and the problem of spin glasses [36], in particular the random energy model [36] where the partition function is also distributed, in the low temperature phase, according to a Lévy stable law [37, 35].

### Appendix B. Self diffusion measurements by FRAP.

FRAP [25] (Fluorescence Recovery After fringe pattern Photobleaching) experiments use fluorescent molecules incorporated to the objects one wants to study. These molecules have aliphatic tails, the length of which can be varied to change the residence time of the tracers within a micelle. This has been used to check that tracers are always bound to the micelles and that free diffusion does not affect the observations.

When illuminated by a high intensity laser flash, these molecules *irreversibly* lose their fluorescent properties — they are « bleached ». A non uniform concentration of active tracers is created by bleaching and its relaxation is monitored by a second low intensity beam. The diffusion constant of the objects under study can usually be extracted from the recovery time. In order to improve the signal to noise ratio and to simplify the theoretical interpretation, one uses sinusoidal fringe pattern bleaching, produced by two crossed laser beams:  $\ell(x) = \ell_B[1 + \cos(q_0 x)]$ , where x is the axis perpendicular to the fringes. The relaxation of the concentration profile is then monitored with the same fringe pattern, but of reduced intensity:  $\ell_M(x) = \varepsilon \ell_B[1 + \cos(q_0 x)]$ , with  $\varepsilon \ll 1$ . The total fluorescence intensity during recovery is given by:

$$F(t) = \int d^3r \ell_{\rm M}(r) C_{\rm T}(r,t)$$
(B.1)

where  $C_{\rm T}(r, t)$  is the local concentration of *active* (unbleached) tracers: (B.1) simply means that the fluorescence intensity is proportional to the number of active tracers and to the exciting intensity.

In general,  $C_{\rm T}(r, t)$  evolves according to the diffusion equation:  $\partial C_{\rm T}(r, t)/\partial t = D \Delta C_{\rm T}(r, t)$ , where D is the asymptotic diffusion constant of the objects carrying the tracers. More generally, in the case of Lévy flights, the Fourier transform of  $C_{\rm T}(r, t)$  satisfies equation (28):  $\partial C_{\rm T}(q, t)/\partial t = -\Omega q^{\mu} C_{\rm T}(q, t)$ .  $\mu = 2$  corresponds to the usual case and  $\Omega$  is a generalized diffusion constant. Using Fourier transforms, equation (B.1) thus reads:

$$F(t) = \int d^3q \ell_{\rm M}(-q) C_{\rm T}(q, t=0) \exp(-\Omega q^{\mu} t)$$
(B.2)

Using  $\ell_{\rm M}(-q) = \varepsilon \ell_{\rm B} \left\{ \delta(q) + (1/2) \left[ \delta(q-q_0) + \delta(q+q_0) \right] \right\}$ , one finds:

 $F(t) = \varepsilon \ell_{\rm B} [C_{\rm T}(q=0,0) + C_{\rm T}(q_0,0) \exp(-\Omega q_0^{\mu} t)].$ (B.3)

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Our experimental setup is slightly more complicated since the monitoring intensity is modulated, and the modulated fluorescence signal is detected by a lock-in amplifier. This is both to improve the signal to noise, and to check for the presence of convection during the experiments. We have :

$$\ell_{M}(x,t) = \varepsilon \ell_{B}[1 + \cos(q_{0}x + u\cos\omega t)]$$
(B.4)

and hence:

$$F(t) = \varepsilon \ell_{\rm B} [C_{\rm T}(q=0,0) + C_{\rm T}(q_0,0) \cos(u\cos\omega t) \exp(-\Omega q_0^{\mu} t)]$$
(B.5)

which can be decomposed into an harmonic series of the modulation frequency :

$$F(t) = \sum_{n=0,\infty} f_n(t) \cos n\omega t .$$
 (B.6)

In the absence of convection, only even harmonics are generated.

Furthermore, the constant term  $C_T(q = 0, 0)$  appearing in (B.3) is only present in  $f_0$ . We thus measure  $f_2(t) = 2 \varepsilon \ell_B C_T(q_0, 0) J_2(u) \exp(-\Omega q_0^{\mu} t)$ , for which there is no baseline problem.  $J_2(u)$  is the Bessel function of order 2, and the value of u is chosen to maximize  $J_2$ . From the decay time of  $f_2(t)$  we measure  $\Omega q_0^{\mu}$ , and thus a (scale dependent) diffusion constant  $D(q_0) = \Omega q_0^{\mu-2}$ 

The fringe spacing is typically between 2 and 100  $\mu$ m, which allows to measure — within reasonable observation times — diffusion constants in the range  $10^{-10}$  to  $10^{-5}$  cm<sup>2</sup>/s.

# Appendix C. Role of a size dependent lifetime.

Let us rapidly explore the consequence of a strongly size dependent life time for short micelles. Suppose for example that a short, mobile chain of size L does not break or recombine before a time  $\tau(L) \approx \tau_0 L^{-2\alpha}$  We now define P(L) as the probability for the tracer to choose a chain of size L. Using an ergodicity hypothesis, the *a priori* probability for a given monomer to belong to a chain of size L, is  $L\mathcal{F}(L)$  (cf. (14)), and is also proportional to  $\tau(L) P(L)$ . Hence  $P(L) \approx L^{1+2\alpha-2\sigma}$  Now, let us define N as the number of different breakage/recombination events experienced by the tracer. The elapsed time is given by:

$$t = \sum_{i=1,N} \tau(L_i) = N \int_0^\infty dL P(L) \tau(L).$$
 (C.1)

The travelled distance is given by :

$$R^{2}(N) = \sum_{i=1,N} D(L_{i}) \tau(L_{i}) \approx N \int_{L_{\min}}^{\infty} dL P(L) D(L) \tau(L)$$
(C.2)

where  $L_{\min}(N)$  is determined as usual as  $N \int_{L_{\min}}^{\infty} dLP(L) = 1$ . Assuming that  $\int_{0}^{\infty} dLP(L) \tau(L) = \langle \tau \rangle$  is finite (i.e. that  $\sigma < 1$ ), one finds instead of equation (27):

$$R(t) \approx t^{1/\mu'} \tag{C.3}$$

with  $\mu' = 2(1 + \alpha - \sigma)/(\beta + \alpha)$ . Note that  $\mu' = \mu$  when  $\alpha = 0$ .

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