

Superdiffusion in
micelle growth
A case of Genuine Levy
Flight?

[from Ott, Bouchard, Langevin, Urbach.
PRL **65**, 2201 (1990)]

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Phys 510

1. DIFFUSION

Normal Gaussian diffusion:

Under Fick's law

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \rightarrow \quad t \sim x^\mu, \text{ with } \mu=2$$

when D is constant

Sub-diffusion ($\mu > 2$)

Contains rare “local trapping” events

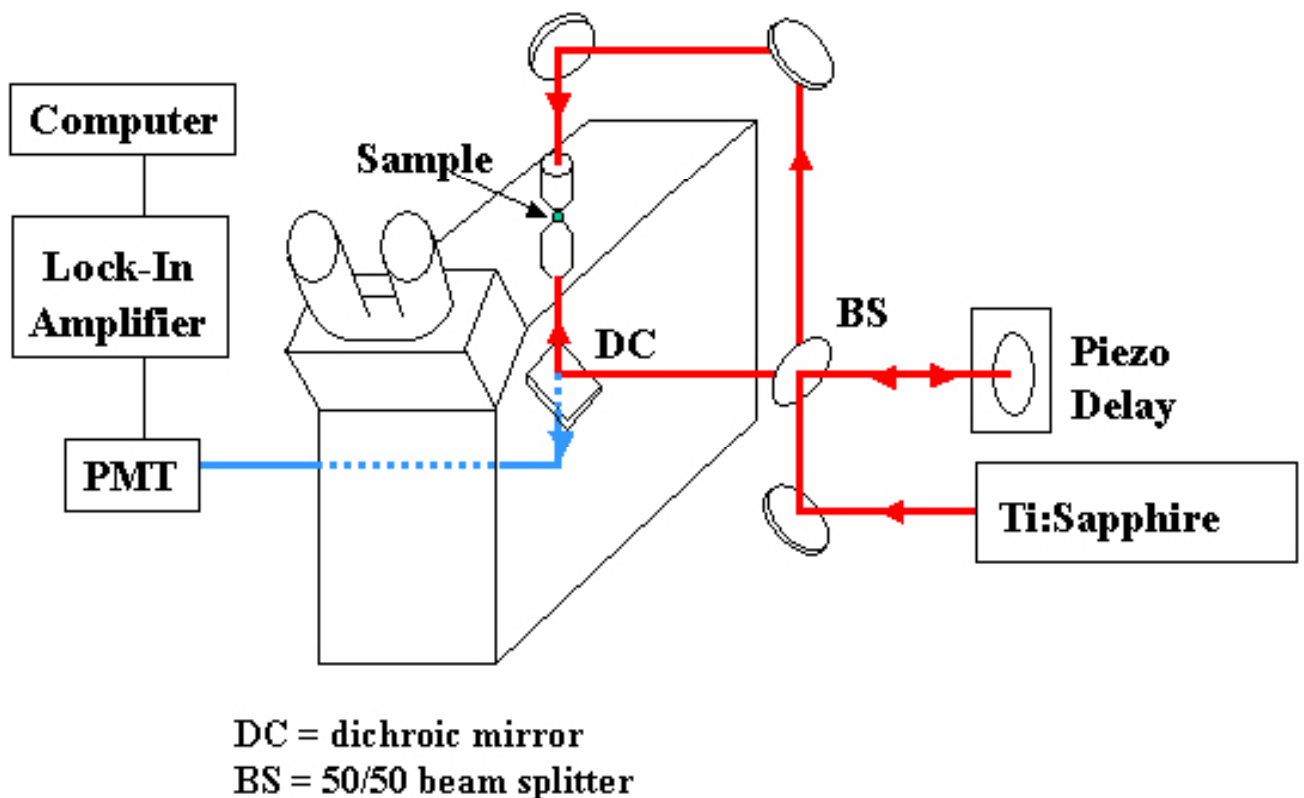
- photoconductivity of amorphous materials
- conductivity of disordered ionic chains
- diffusion in convective rolls (in weather systems)

Super-diffusion / enhanced diffusion ($\mu < 2$)

- harder to find examples of this
- Richardson diffusion in turbulent fluids

2. MEASURING DIFFUSION CONSTANTS

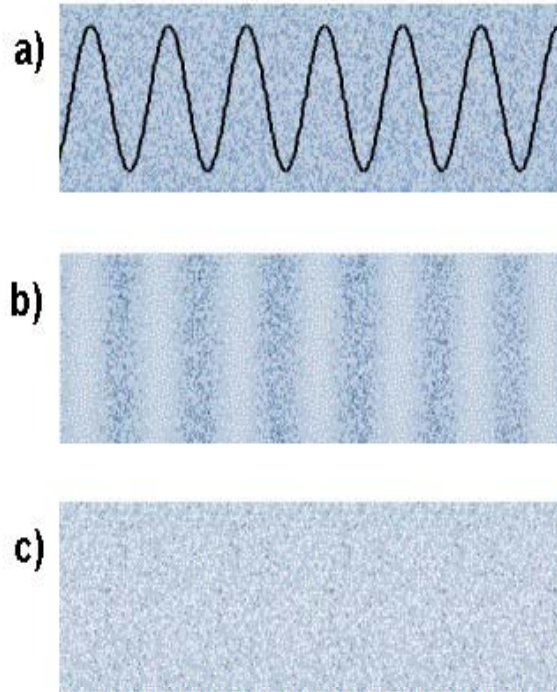
FRAP – fluorescence recovery after photobleaching



Laser is split and reformed at sample to form standing wave interference patterns at the sample.

3. FRAP FRINGES – Lock-in Techniques

Fringe spacing d (which sets the measured length of diffusion)



- (a) Probes fluoresce normally under low-level power
- (b) Photobleached with a high-power pulse
- (c) Wait for probes to diffuse.

Wait for the local fluorescence level to equilibrate due to diffusion, then measure τ .

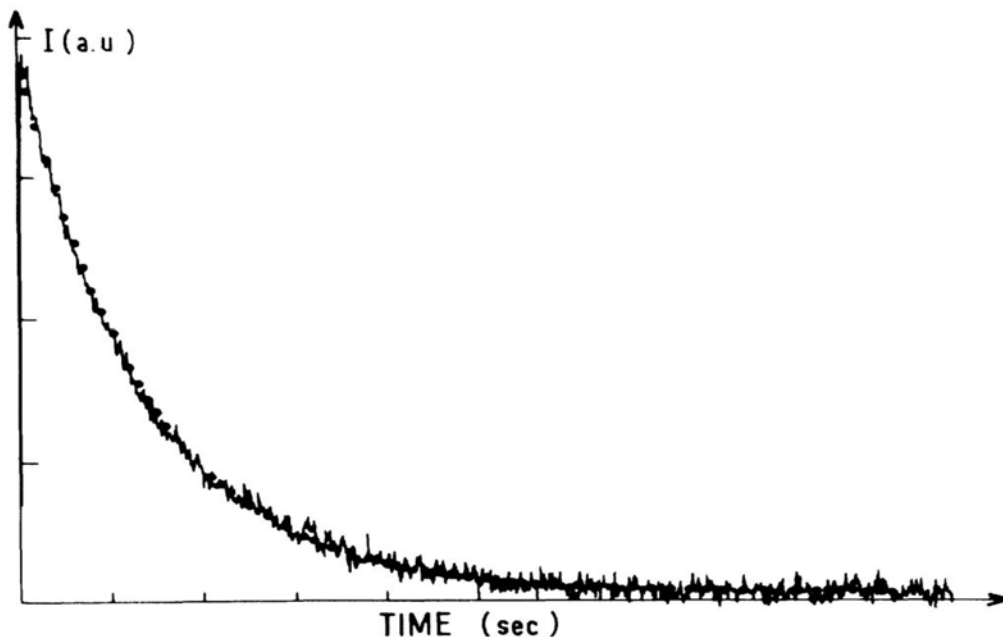
FRAP FRINGES – Lock-in Techniques

The signal measured at 2ω decays as the probes diffuse:

$$I = I_0 e^{-t/\tau}$$

$\tau = Dq^2$ in the case of monodisperse diffusion molecules ($q = 2\pi/d$)

Can find D empirically for various fringe spaces, concentrations, etc.



4. MATERIALS

Cethyl trimethyl ammonium bromide (CTAB),

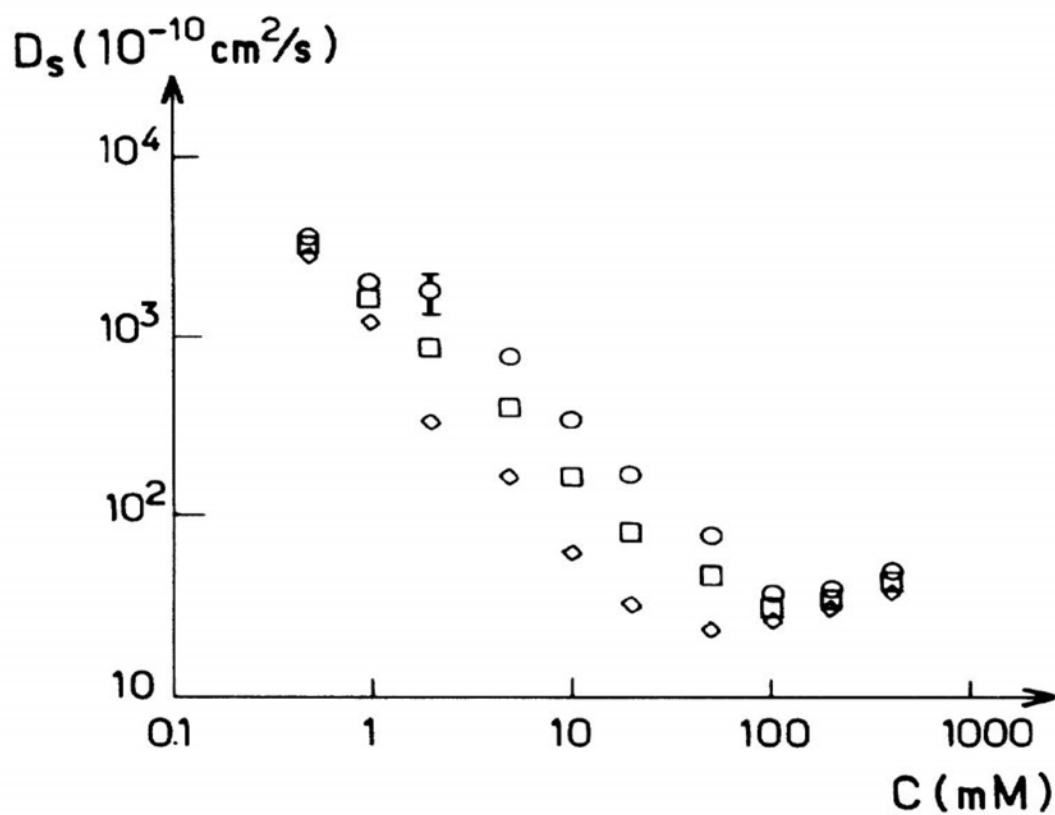
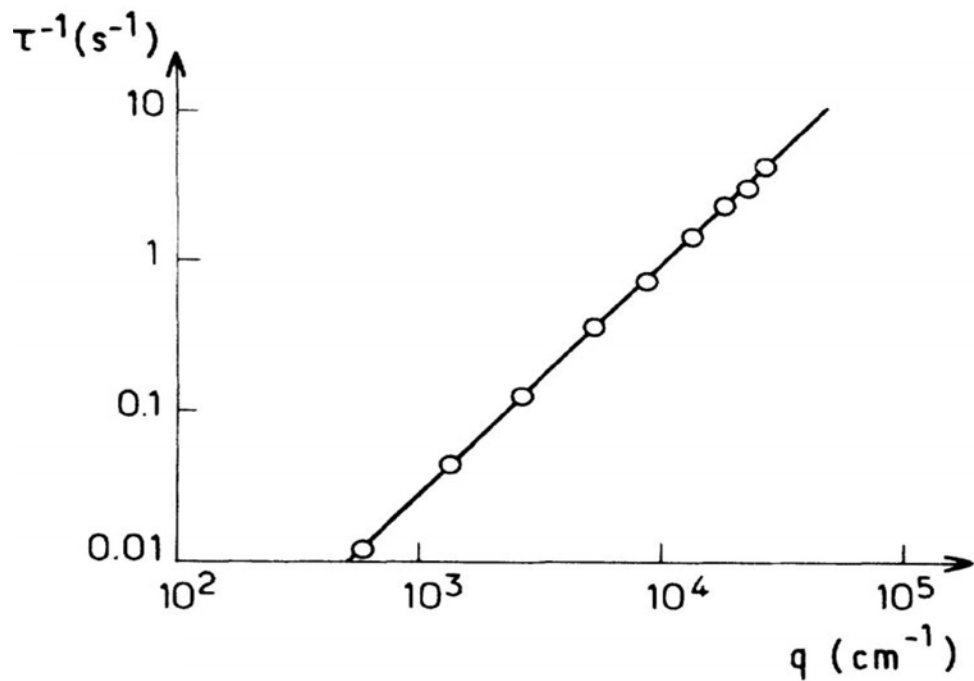
- $\sim 2.5\text{nm}$ per unit
- Forms long chains of molecules in electrolyte solution (0.5-2M KBr)
- Chains break and recombine with a characteristic time $\sim 1\text{ ms}$, much shorter than diffusion times
=>Therefore, solution is *not* monodisperse – have chains of all lengths co-existing.
- Can add fluorescent probes which have similar structure to incorporate into the CTAB chains

Tested using FRAP on spacings of $2\mu\text{m}$ - $100\mu\text{m}$

5. EXPERIMENTAL RESULTS

$\tau \sim d^\mu$, with $\mu < 2$ over two decades in time and for several concentrations of CTAB and salt (0.5, 1, and 2M KBr)

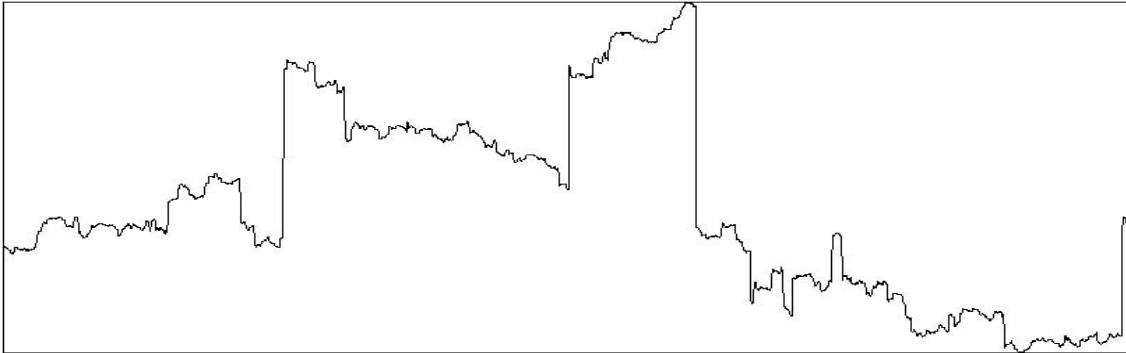
- ⇒ Over longer distances (smaller q), τ does not rise as d^2 , but as d^μ , with $\mu < 2$.
- ⇒ The probes actually diffuse FASTER over longer distances than they do shorter ones (i.e. super-diffusion)



[circles = 89 μm , squares = 20 μm , diamonds = 3 μm]

6. THEORY

Is this effect a case of Levy-flight?



Levy-flight is a possibility if:

(1) Probes make jumps of different sizes r
AND

(2) $P(r)$ decays as power law, $r^{-(1+\mu)}$ for large r

If $\mu < 2$, $P(r)$ has no variance and the diffusion constant becomes “infinite” over infinite time.

This eventually changes the time dependence of x from $t^{1/2}$ to $t^{1/\mu}$

7. EQUILIBRIUM CHAIN CONCENTRATIONS

Breaking:

All strands break with identical rate per unit length per unit time of rate c_1

Reforming:

Rate is proportional to the product of the concentrations of the two smaller chains, independent of their length, with rate c_2

$dP(L)/dt =$

- (decrease from breakage into two short chains)
- (decrease from joining another chain and forming one longer chain)
- + (increase from breaking long chains into two shorter ones)
- + (increase from joining two shorter chains)

Taking $dP/dt = 0$ and solving integrals leads to a steady-state distribution of:

$$P(L) = (2c_1 / c_2) \exp(-L/L_0)$$

where L_0 is the average chain length

Mass concentration at each length L is:

$$\begin{aligned} N(L) &= L P(L) \\ &\sim L \exp(-L/L_0) \end{aligned}$$

Total mass concentration

$$\Phi = \int N(L) dL = \int L P(L) dL = (2c_1 / c_2) L_0^2$$

Small correction to the probability distribution to compensate for fact that chains are more likely to lose single units at ends than have cuts in middle of strand, which should skew slightly towards *shorter* strands:

$$P(L) \sim L^{(1-2\sigma)} \exp(-L/L_0)$$

Where σ *appears* to be a measure of the deviation from the ideal case.

8. PROBE JUMPING

During the characteristic break/reform time τ_{break}

The probe joins a chain of length L and diffuses under Brownian motion with a diffusion constant $D(L)$ over a distance r , where:

$$r(L) \sim [D(L) * \tau_{\text{break}}]^{1/2}$$

After τ_{break}

The probe joins a new chain, which is either longer and slower, or shorter and faster, since the diffusion constant scales with length as:

$$D(L) \sim D_0 * L^{-2\beta}$$

with $\beta \sim 1$ for reptation of linear chain (from de Gennes).

This means that:

$$r(L) \sim r_0 L^{-\beta} \Rightarrow L = (r/r_0)^{-1/\beta}$$

Probability to undergo a jump of length r is obtained as:

$$\begin{aligned}
 P(r) &= P(L) dL / dr \\
 &= P(L(r)) * dL / dr \\
 &\sim [(r/r_0)^{-1/\beta}]^{(1-2\sigma)} \exp(-(r/r_0)^{-1/\beta}/L_0) \\
 &\quad * (-1/\beta)(r/r_0)^{-1/\beta - 1} \\
 &\sim \exp[-(r^{-1/\beta})] r^{-(1-2\sigma)/\beta} r^{-1/\beta - 1} \\
 &\sim \exp[-(r^{-1/\beta})] r^{-1 - 2(1-\sigma)/\beta - 1} \\
 &\sim \mathbf{\exp[-(r^{-1/\beta})] r^{-(1 + \mu)}}
 \end{aligned}$$

$$\text{where } \mu = 2(1-\sigma)/\beta$$

For large r , the probability goes as $r^{-(1 + \mu)}$, which looks like a Levy stable power law.

For $\sigma=0 \rightarrow \mu = 2$, normal diffusion

$\sigma>0 \rightarrow \mu < 2$, super-diffusion effect

Over time $T = N \tau_{\text{break}}$, the probe jumps on N different molecules and spanned a total distance R , with:

$$R(N) = \sum_{i=1}^N r(L_i),$$

where L_i is the length of the i th chain that the probe joins.

In a Levy stable law, the longest jump undergone in N steps is $r_{\text{max}} \sim N^{1/\mu} \Rightarrow R(N)$ depends almost entirely on r_{max} .

The Fourier transform of a symmetric Levy distribution is $\exp[-Dq^\mu t]$

In this experiment, a single mode q is excited, and the resulting signal is a pure exponential with a decay rate proportional to q^μ - this recovers the μ -value for the system.

9. REGIME OF VALIDITY

D is a function of L

Requires a region where the diffusion constant is chain strongly dependent on the length of the.

Fluorescent particle concentration must be LOW

Otherwise ALL CHAINS (short and long) will be visited from the start.

(note that only the PROBES have measurable super-diffusion, and not the bulk micelles themselves)

Finite Size Limit

All calculations assume that L is a continuous down to 0, but in reality the size of the micelle units sets a lower bound to the maximum diffusion value

10. CONCLUSIONS

Power-law distributions resulting in a Levy stable law can be found experimentally.

Empirical measurement of super-diffusion is possible for low concentration fluorescent probes in a higher-concentration sample.

Ott, Bouchard, Langevin, Urbach. PRL **65**, 2201 (1990)

Cates. Macromolecules, **20**, 2289 (1987)