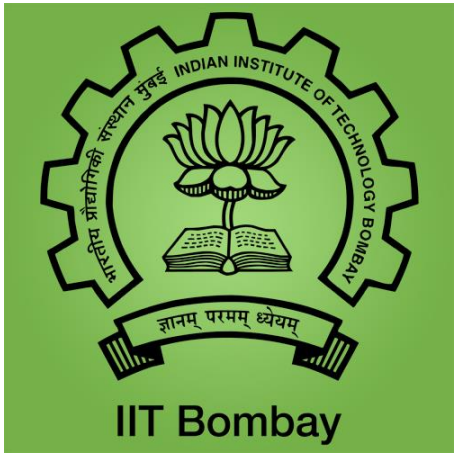
Tracer diffusion in a sea of polymers with binding zones: mobile vs frozen traps...



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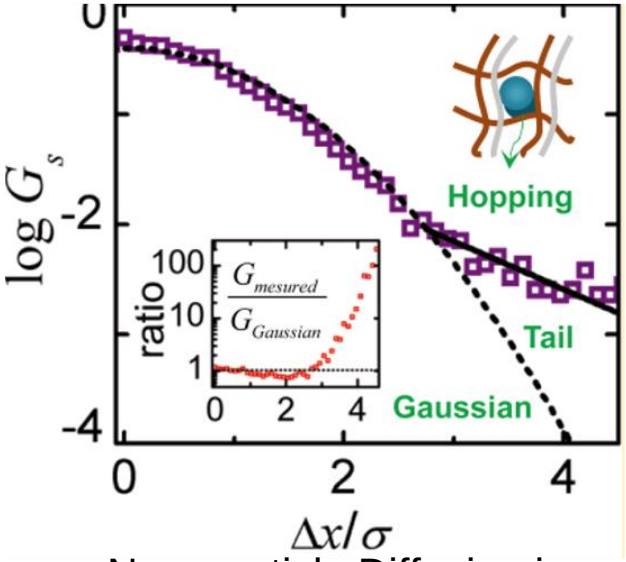
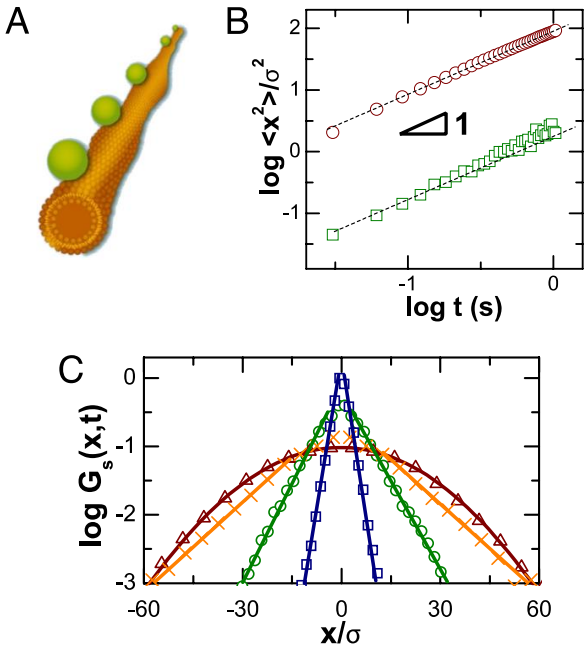
Tracer diffusion in polymeric environment……..



Nanoparticle Diffusion in Polymer Gel…..

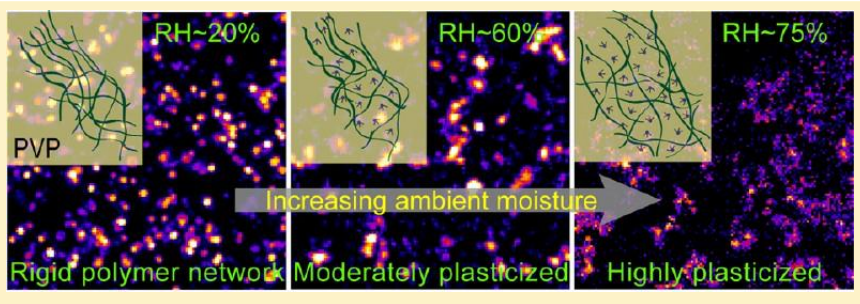
Xu et al. JPCLett (2016)



Colloids on lipid tubes

Wang et al. PNAS (2009)

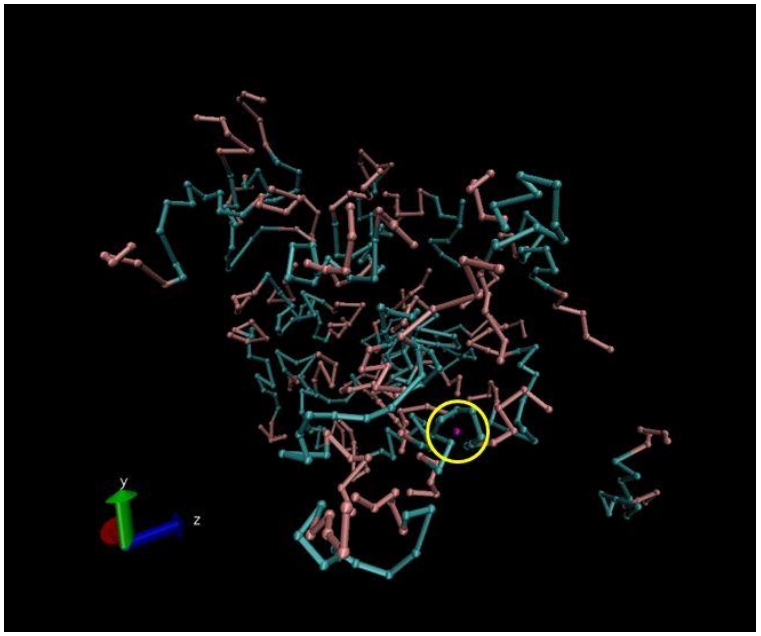
- Gaussian or Non-Gaussian
- Normal or Subdiffusive
- Size of the tracer !!



Single molecule dynamics in polymer thin films

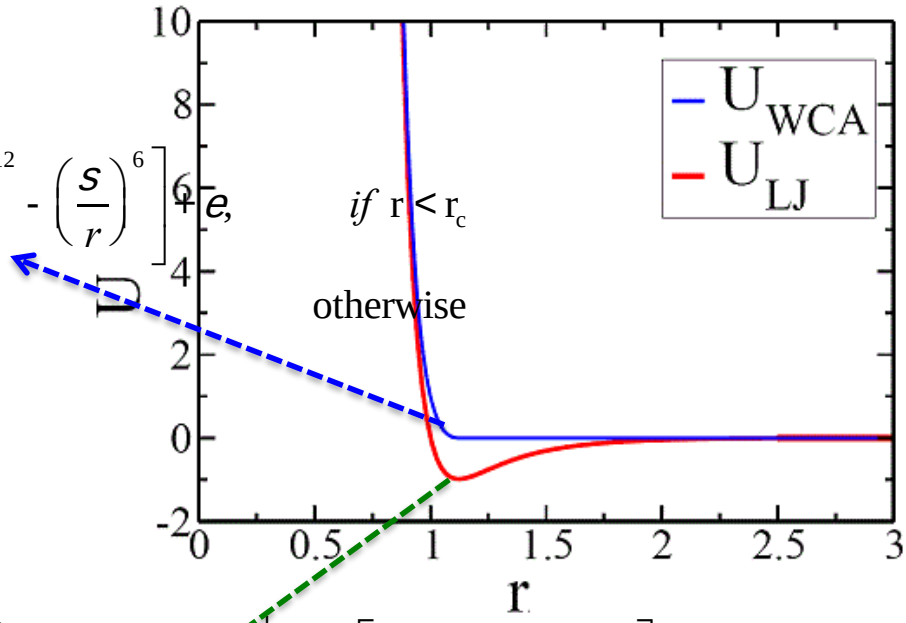
Bhattacharya et al. JPCB (2013)

A Generic model: Tracers in polymeric environment with binding zones…….

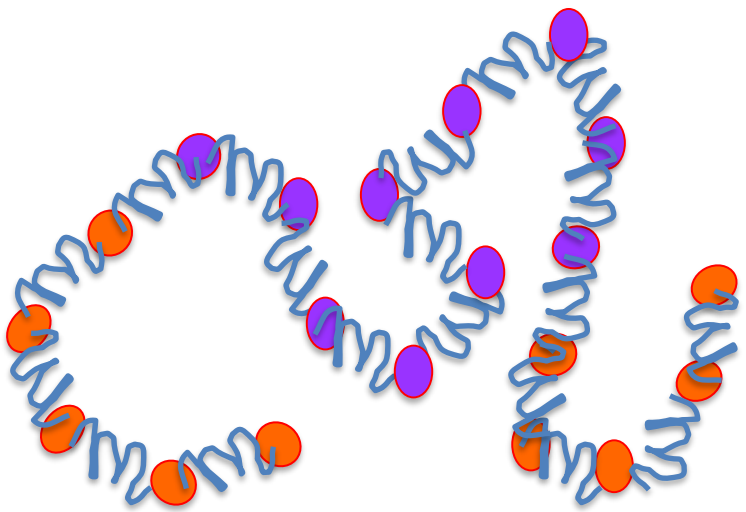


Samanta & Chakrabarti, Soft Matter, 12, 8554 (2016)

$$U_{WCA}(r) = \begin{cases} 4e\left[\left(\frac{s}{r}\right)^{12} - \left(\frac{s}{r}\right)^{6}\right] + e, & if\ r < r_c \\ 0, & otherwise \end{cases}$$



$$U_{LJ}(r) = \begin{cases} 4e\left[\left(\frac{s}{r}\right)^{12} - \left(\frac{s}{r}\right)^{6}\right], & \text{if } r < r_c \\ 0, & \text{otherwise} \end{cases}$$



Each polymer is made of monomers connected with FENE springs…

$$U_{FENE}(r) = -\frac{k_f r_{max}^{\ 2}}{2} \log\left[1 - (r/r_{max})^2\right]$$

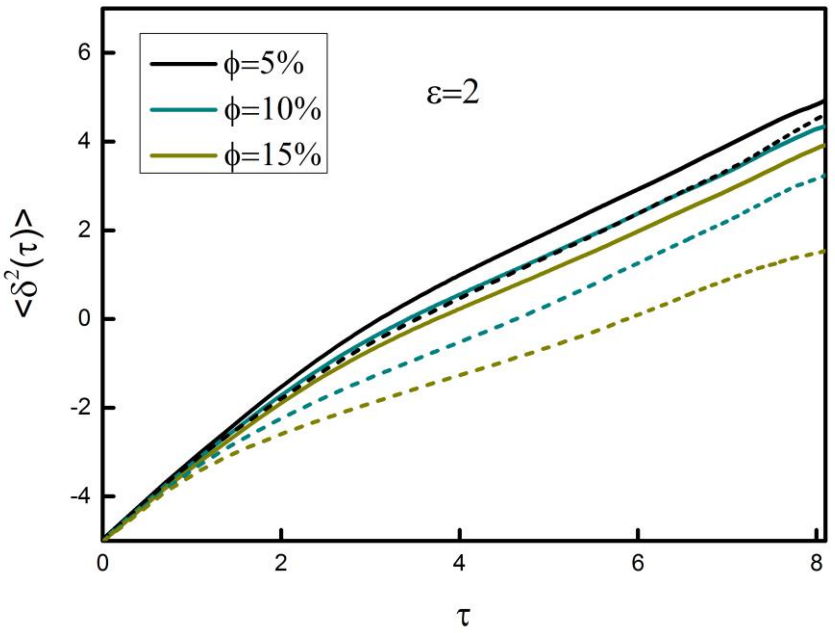
Simulation details…

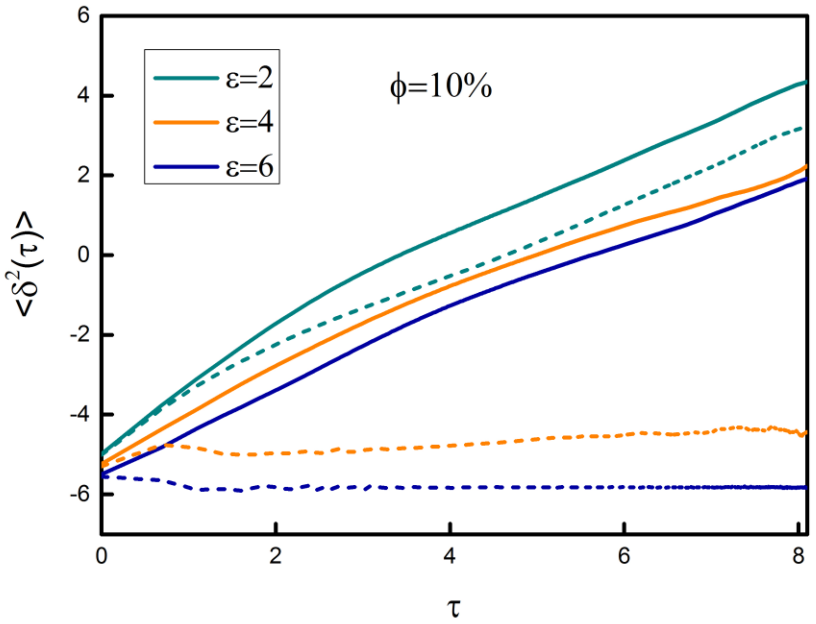
$$m\frac{d^2 r_i}{dt^2} = -\chi\frac{dr_i}{dt} + f_i(t) - \nabla\sum_j V(|r_i - r_j|)$$

- NVT simulations in Langevin thermostat
- Friction=1, $k_B T$=1, sigma=0.5, dt=0.001 (time step)
- Each simulation is averaged over 30 trajectories (each trajectory 5000 data points)
- All the parameters are dimensionless and normalized accordingly, e.g. $D_0 = k_B T$/friction=1.

Diffusive ($b=1$) or Subdiffusive ($b<1$)

Mean Square Displacement = $\left\langle \overline{\delta^2(\tau)} \right\rangle = \left\langle \overline{[r(t+\tau) - r(t)]^2} \right\rangle \sim t^{b}$



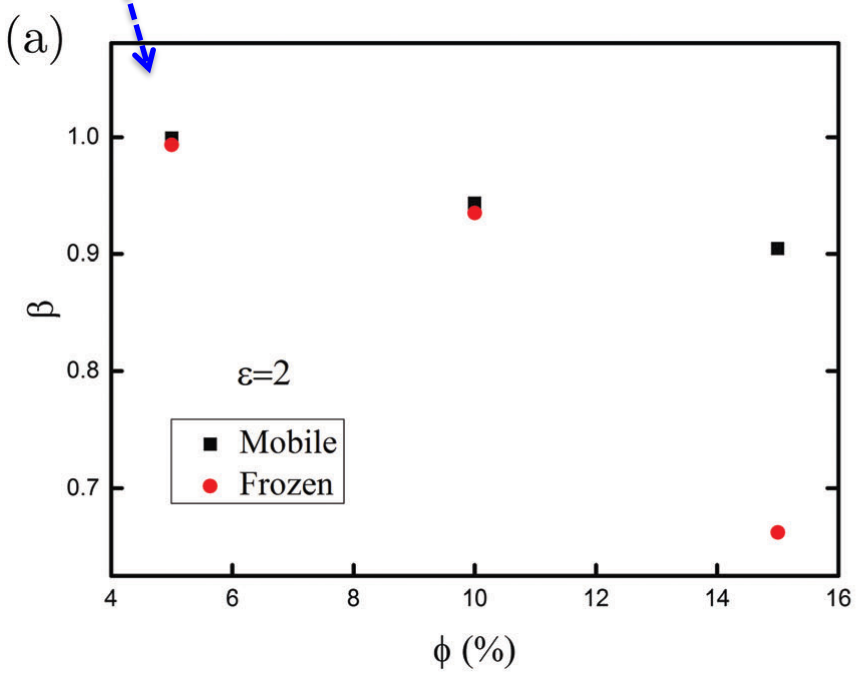


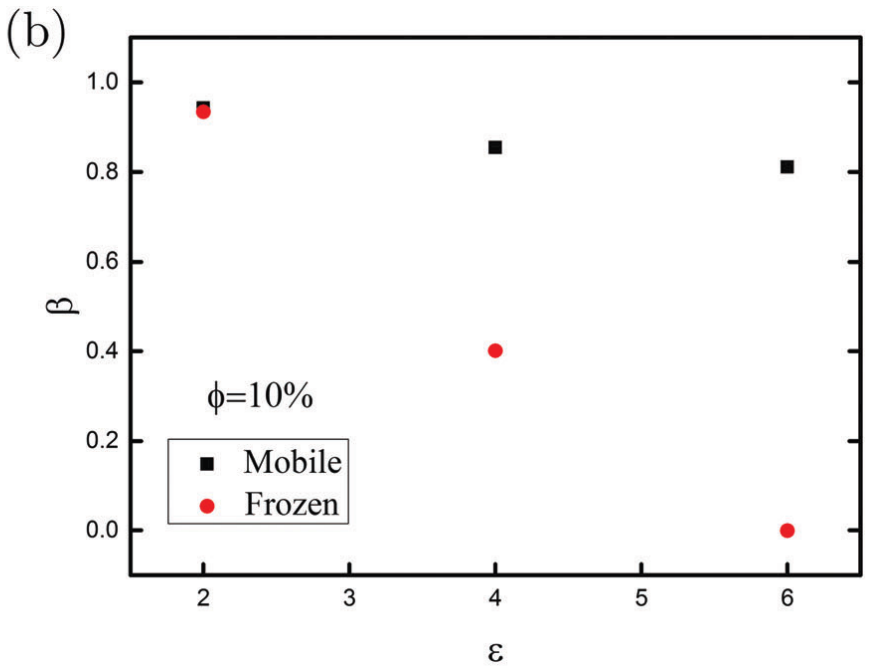
- As the stickiness or the crowding increases dynamics becomes increasingly subdiffusive…....

- On freezing the polymers (gel like), tracer dynamics becomes more subdiffusive.....

Subdiffusivity

Normal

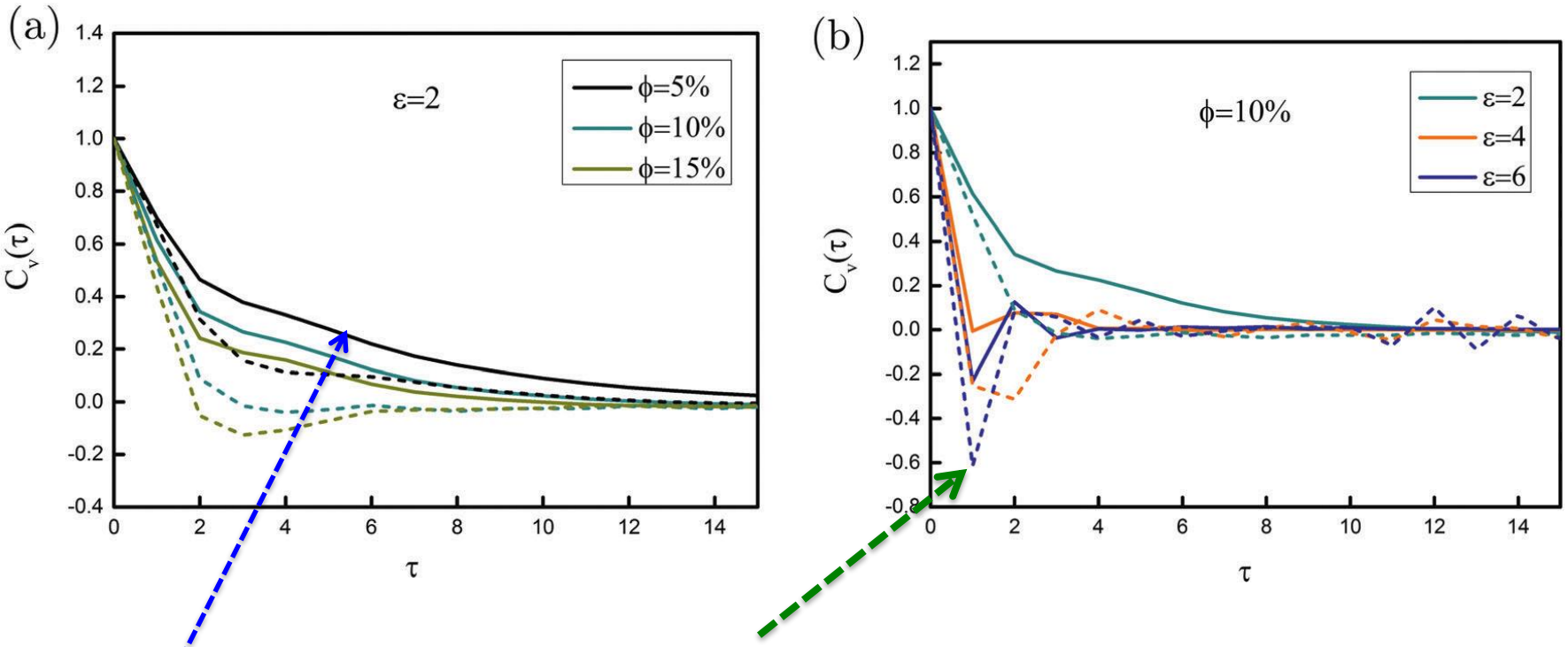




Crowding and stickiness makes it subdiffusive

Velocity auto correlation

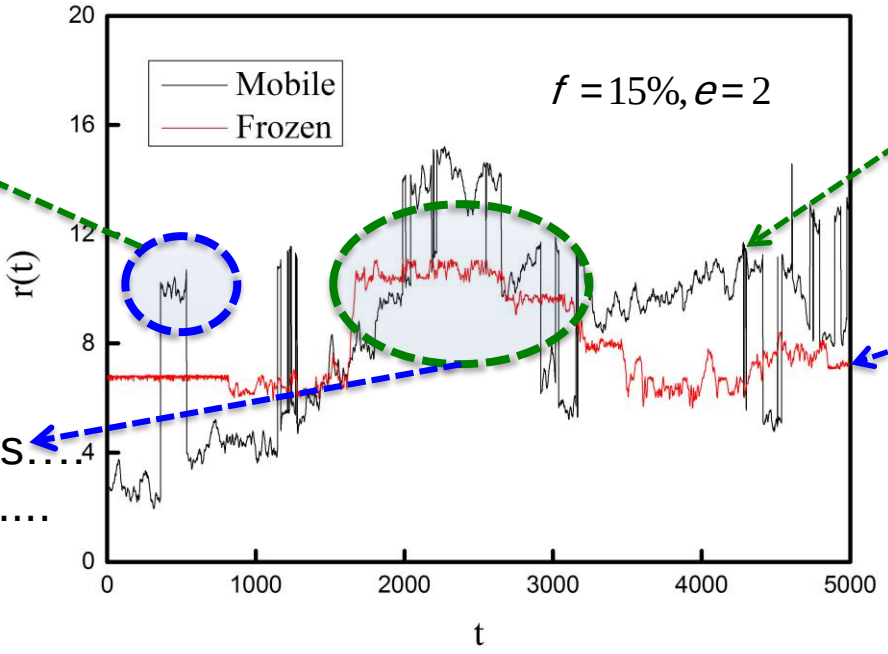
$$C_{\mathrm{v}}(\tau) = \left\langle \overline{\vec{v}(t+\tau).\vec{v}(t)} \right\rangle \Big/ \left\langle \overline{v^2(t)} \right\rangle$$



Normal but non-Gaussian

Negative values of velocity autocorrelation …confined motion, tracer changing direction of motion frequently.. (Caging)

Caging followed by jumps….



Cages are transient..

Weakly subdiffusive and Gaussian

Subdiffusive and non-Gaussian

Heterogeneous environment..

Frozen: Motion inside stable cages…. followed by jumps.... non-Gaussian

For moderate crowding/stickiness: Anomalous yet Brownian

Biophysical Journal
Article

Biophysical Society

Cytoplasmic RNA-Protein Particles Exhibit Non-Gaussian Subdiffusive Behavior

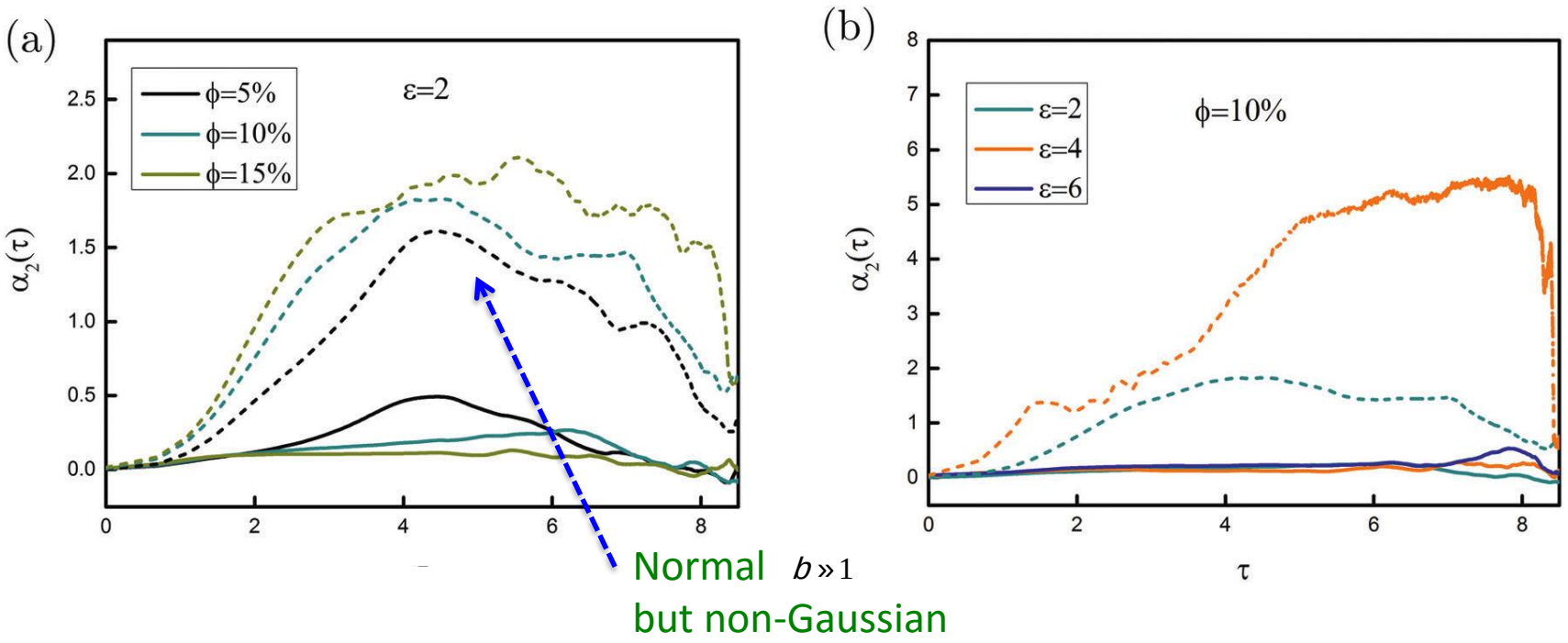
2017

Thomas J. Lampo,[1] Stella Stylianidou,[6] Mikael P. Backlund,[2] Paul A. Wiggins,[6,7,8] and Andrew J. Spakowitz[1,3,4,5,*]
[1]Department of Chemical Engineering, [2]Department of Chemistry, [3]Department of Applied Physics, [4]Department of Materials Science, and [5]Biophysics Program, Stanford University, Stanford, California; and [6]Department of Physics, [7]Department of Bioengineering, and [8]Department of Microbiology, Washington University, Seattle, Washington

What about the nature of the distribution of tracer displacement?

Non-Gaussian Parameter

$$\alpha_2(\tau) = \frac{3\left\langle \overline{\delta r^4(\tau)} \right\rangle}{5\left\langle \overline{\delta r^2(\tau)} \right\rangle^2} - 1$$



Freezing the environment makes the dynamics non-Gaussian, so as the stickiness

For moderate crowding/stickiness: Anomalous yet Brownian

Gaussian vs Non-Gaussian

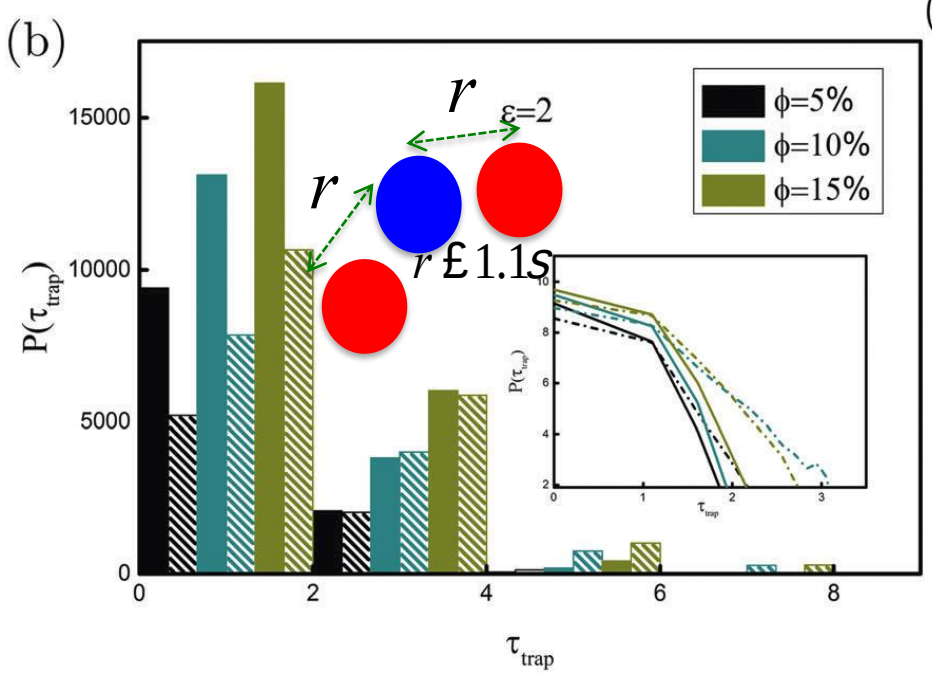
Heterogeneous environment around the tracer

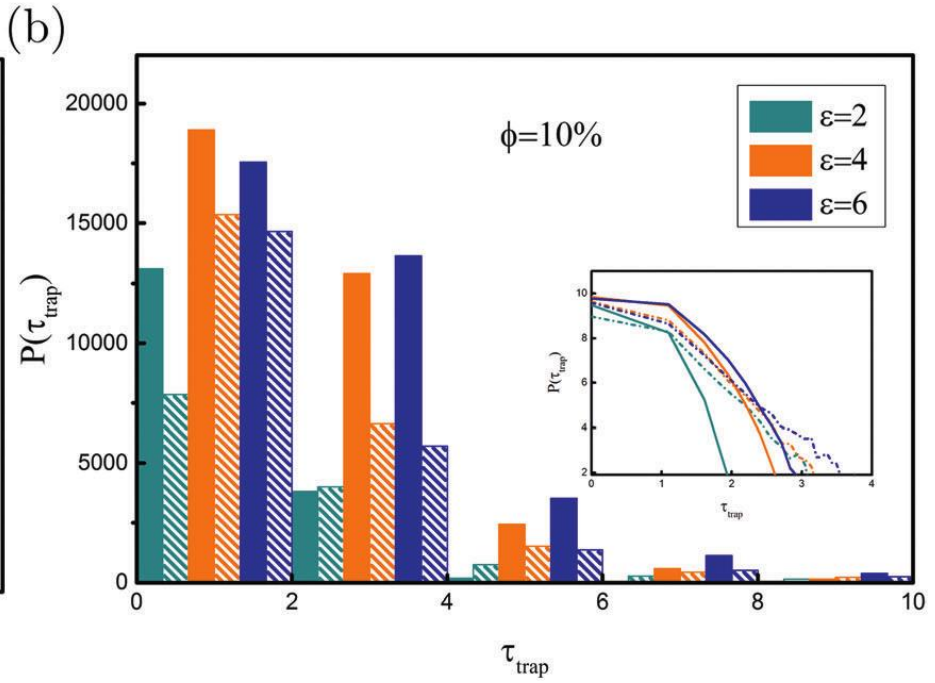
- Diffusivity has a distribution (Slater, PRL 2014)
- Diffusivity is fluctuating (the tracer is experiencing different environment while moving) (Sebastian JPCB 2016, Metzler PCCP 2016, CondMat 2016)

$$D(t) = \boldsymbol{\xi}^2(t)$$

- On a longer time scale heterogeneity averages out leading to Gaussian distribution. But you may not see this in the experimental time scale.

Trapping of the tracer (Distribution of trapping time)

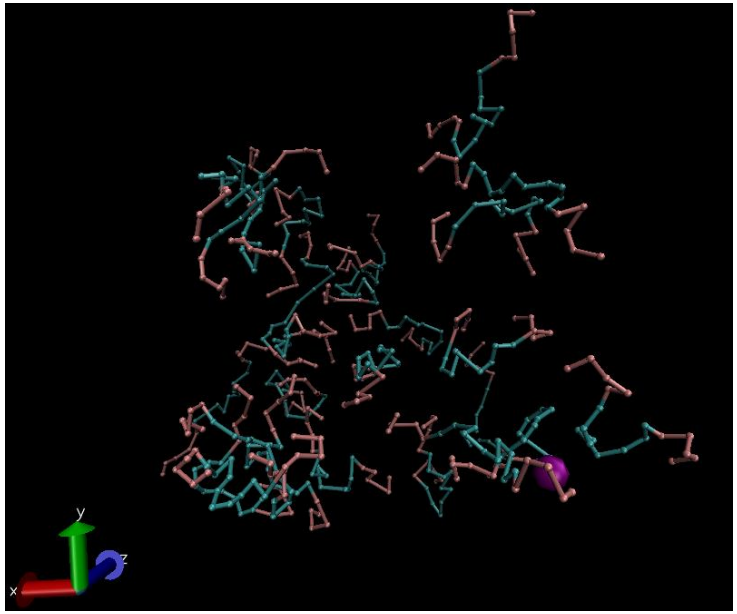




Volume Fraction, $f=5\%$	$\langle t_{trap} \rangle$	$\langle t_{trap} \rangle$
Binding Affinity, e	Mobile	Frozen
2	1.3	1.84
4	1.84	55.27

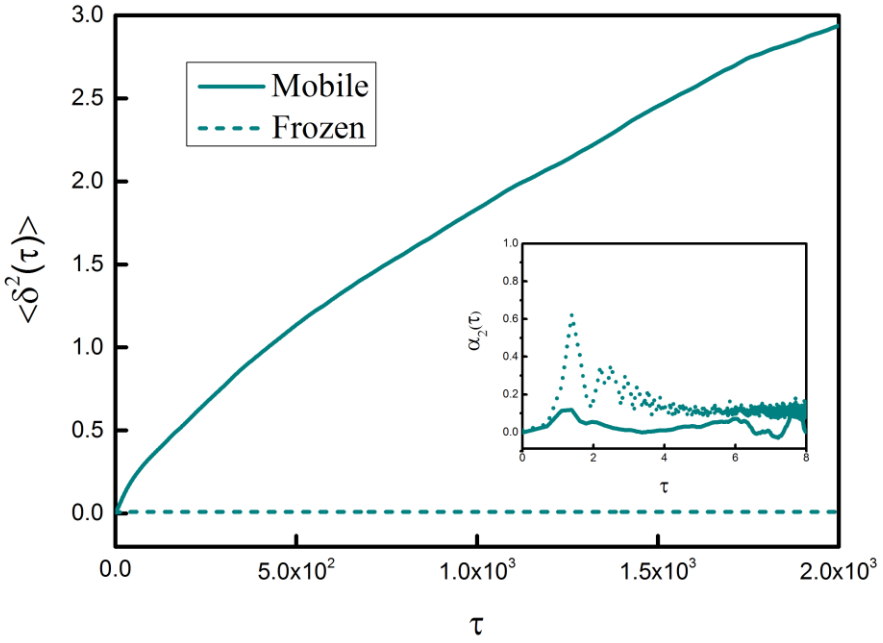
Binding Affinity, $e=2$	$\langle t_{trap} \rangle$	$\langle t_{trap} \rangle$
Vol. Fraction, f	Mobile	Frozen
5%	1.22	1.38
10%	1.3	1.84
15%	1.39	1.81

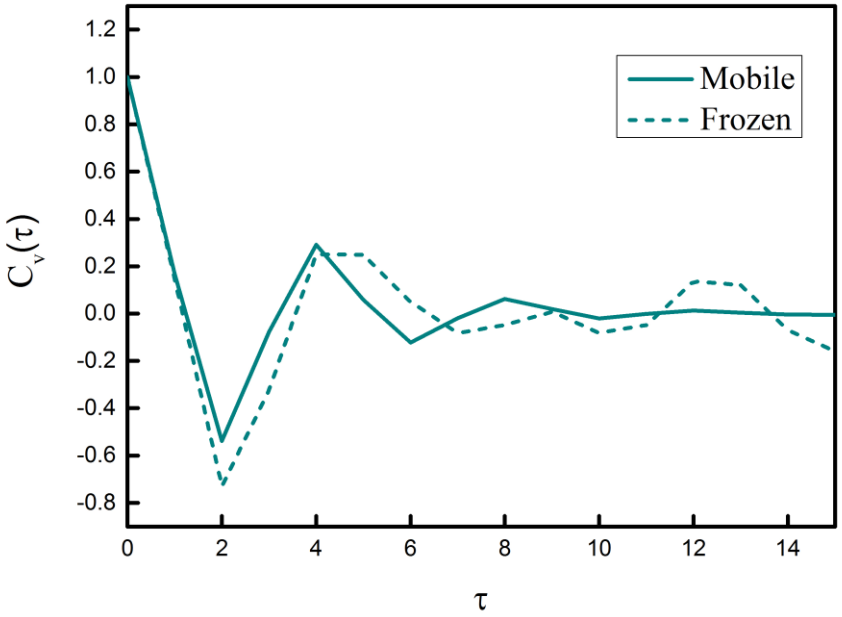
Bigger tracer: more Gaussian like distribution.....



Because of its bigger size it experiences Homogeneous distribution of polymers around (Jee et al. JPCLett (2016)).

Only when the polymers are frozen it experiences heterogeneous distribution of traps.





Conclusions…..

- Crowding and stickiness affect the tracer dynamics profoundly.

- Frozen polymeric environment slows down the diffusion more efficiently than the mobile environment.

- As the traps are frozen (or sluggish) tracer dynamics remains non-Gaussian even for moderately longer times. However it becomes Gaussian eventually.

- This connects to a large number of problems on tracer diffusion in polymeric materials.

Samanta & Chakrabarti, Soft Matter, 12, 8554 (2016)

The Team…..

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Poster: Self-propelled Janus tracer in sticky polymeric environment….

Nairhita Samanta