Scaling approach to anomalous diffusion

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Outline

- Introduction
- MD experiments on normal diffusion and Brownian dynamics
- Scaling approach to anomalous diffusion - theory and illustrations
- Conclusions

Einstein's diffusion model

5. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen;
von A. Einstein.

In dieser Arbeit soll gezeigt werden, daß nach der molekularkinetischen Theorie der Wärme in Flüssigkeiten suspendierte Körper von mikroskopisch sichtbarer Größe infolge der Molekularbewegung der Wärme Bewegungen von solcher Größe ausführen müssen, daß diese Bewegungen leicht mit dem Mikroskop nachgewiesen werden können. Es ist möglich, daß die hier zu behandelnden Bewegungen mit der sogenannten „Brownschen Molekularbewegung" identisch sind; die mir erreichbaren Angaben über letztere sind jedoch so ungenau, daß ich mir hierüber kein Urteil bilden konnte.

A. Einstein, *Ann. Phys.*, vol. 322, no. 8, 1905.

f(x,t) is a concentration

$$f(x, t+\tau)\,dx = dx \cdot \int_{\Delta=-\infty}^{\Delta=+\infty} f(x+\Delta)\,\varphi(\Delta)\,d\Delta$$

→

$$\frac{\partial f}{\partial t} = D\,\frac{\partial^2 f}{\partial x^2}.$$

$$f(x,t) = \frac{n}{\sqrt{4\pi D}}\,\frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{t}}.$$

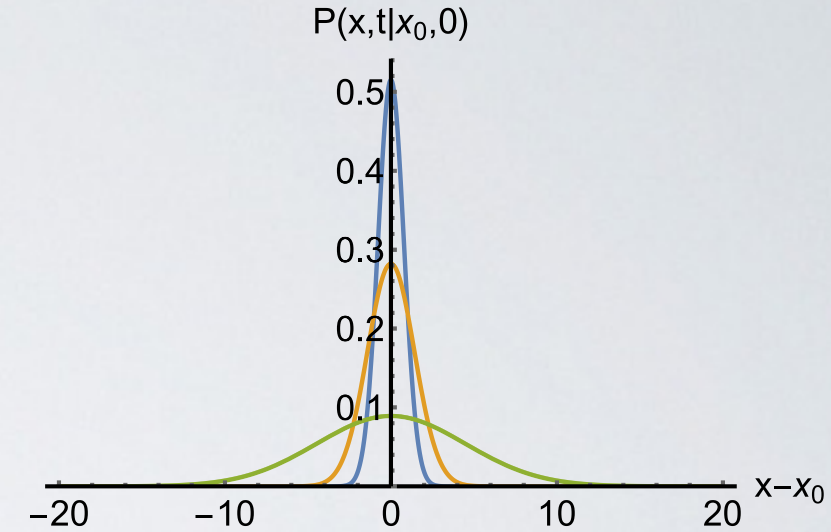
→

$$\lambda_x = \sqrt{\overline{x^2}} = \sqrt{2Dt}.$$

The Wiener process

$p(x,t|x_0,0)$ is a transition probability

$$\partial_t P(x,t|x_0,0) = D\frac{\partial^2}{\partial x^2}P(x,t|x_0,0)$$

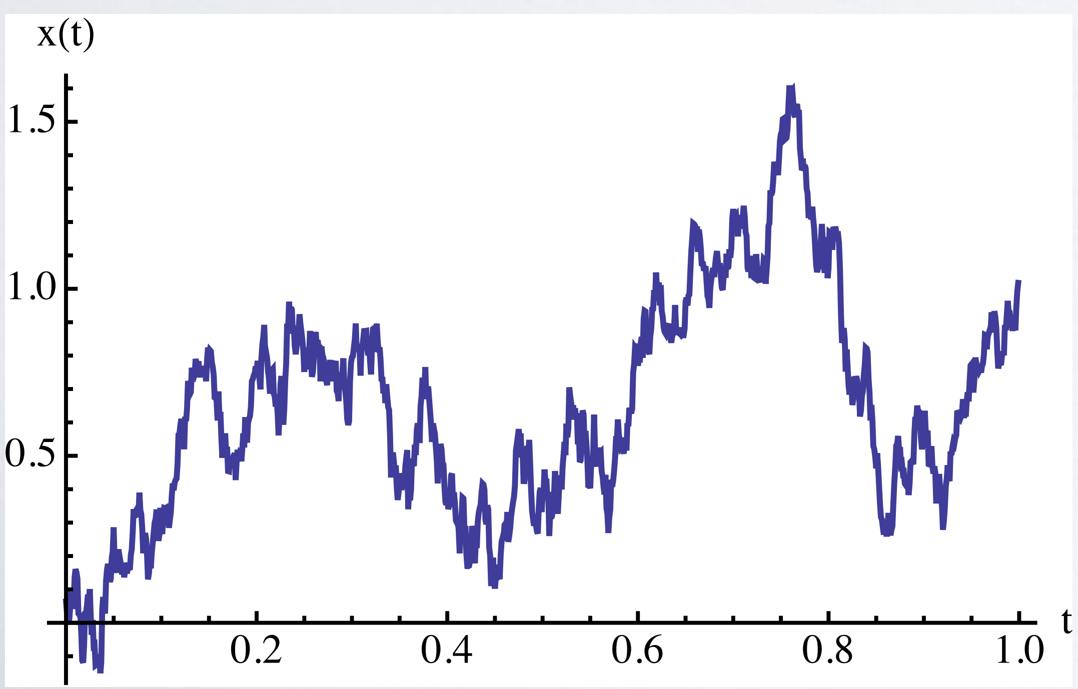


$$x(t_0+\Delta t) = x(t_0) + \xi$$

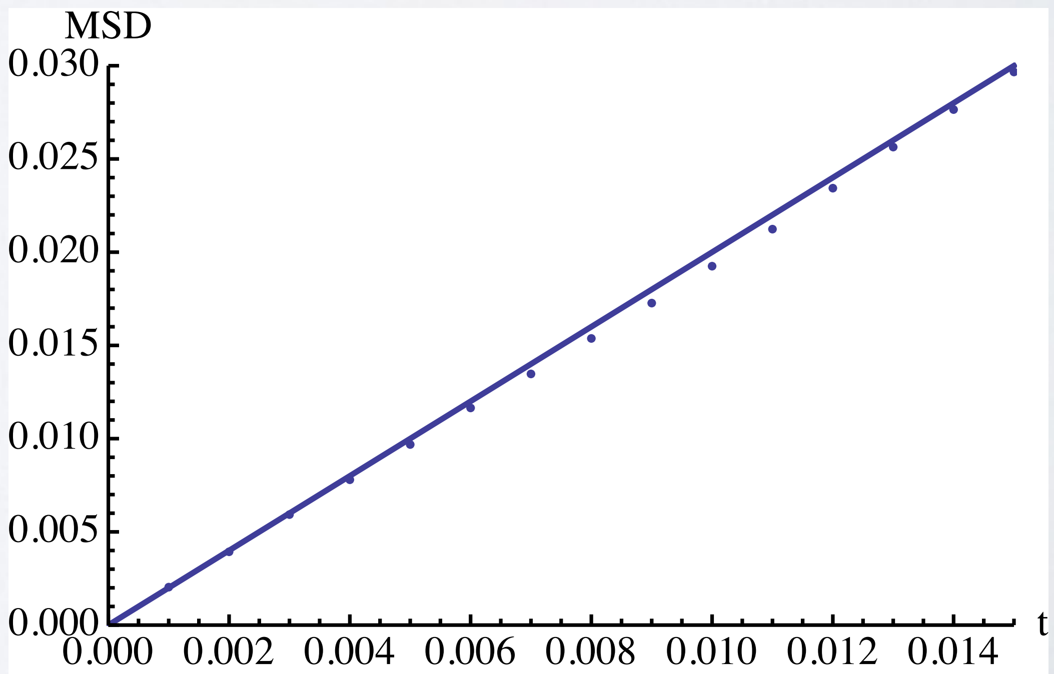
$$\overline{\xi} = 0$$
$$\overline{\xi^2} = 2D\Delta t$$

white noise

Trajectory



$$W(t) := \langle (x(t)-x(0))^2\rangle = 2Dt$$



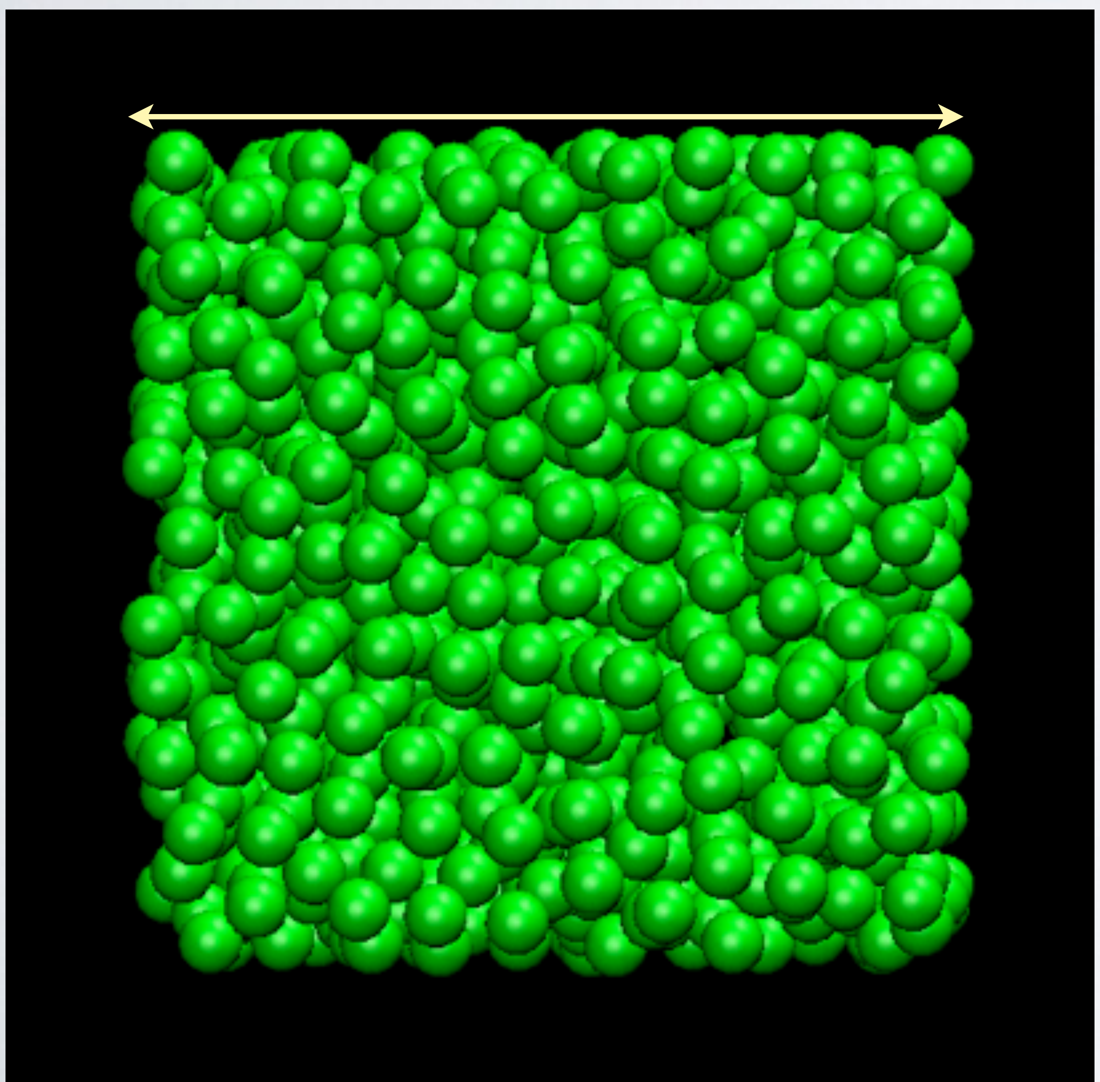
A molecular dynamics view of diffusion

PHYSICAL REVIEW VOLUME 136, NUMBER 2A 19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN
Argonne National Laboratory, Argonne, Illinois
(Received 6 May 1964)

~ 3.6 nm



- Solve Newton's equation of motion

$$M_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

$$U = \sum_{ij} 4\epsilon \left(\left[\frac{\sigma}{r_{ij}} \right]^{12} - \left[\frac{\sigma}{r_{ij}} \right]^{6} \right)$$

- Discretization and iterative solution itérative yields trajectories = time series (< 100 ns)

$$\mathbf{r}_i(n+1) \leftarrow 2\mathbf{r}_i(n) - \mathbf{r}_i(n-1) + \frac{\Delta t^2}{M_i}\mathbf{F}_i(n)$$

$$\mathbf{v}_i(n) \leftarrow \frac{\mathbf{r}_i(n+1) - \mathbf{r}_i(n-1)}{2\Delta t}.$$

$$\text{Forces:} \quad \mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

Mean square displacement

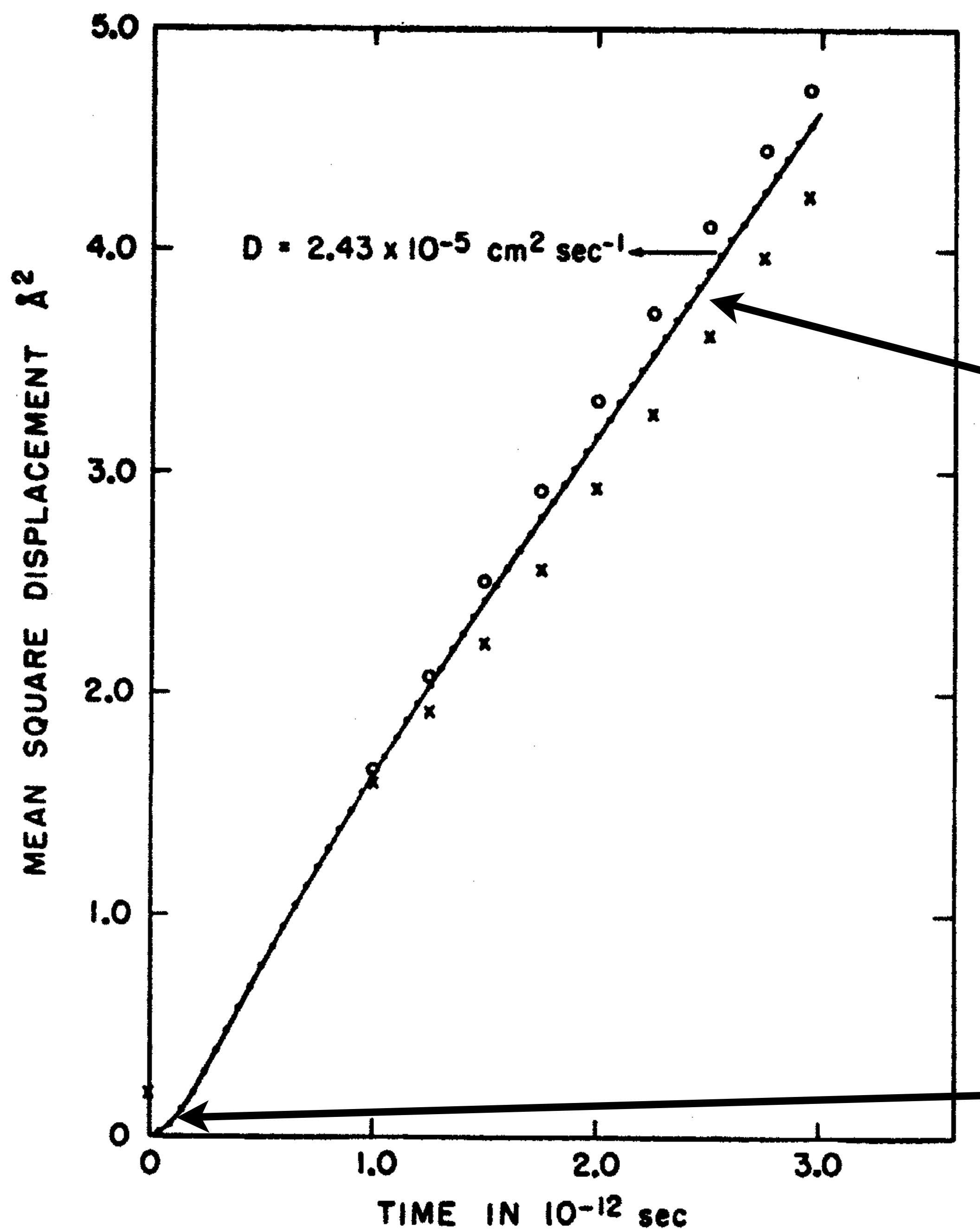


FIG. 3. Mean-square displacement of particles. The continuous curve is the mean of a set of 64 curves; the two members of the set which have *maximum* departures from the mean are shown as circles and as crosses. The asymptotic form of the continuous curve is $6Dt+C$, with D as shown on the figure and $C=0.2$ Å^2.

$$W(t) := \langle (x(t) - x(0))^2 \rangle$$

Long-time limit

$$W(t) \approx 2Dt$$

Short-time limit

$$W(t) \approx \langle v^2 \rangle t^2 = \frac{k_B T}{M} t^2$$

Kubo formula for the diffusion coefficient

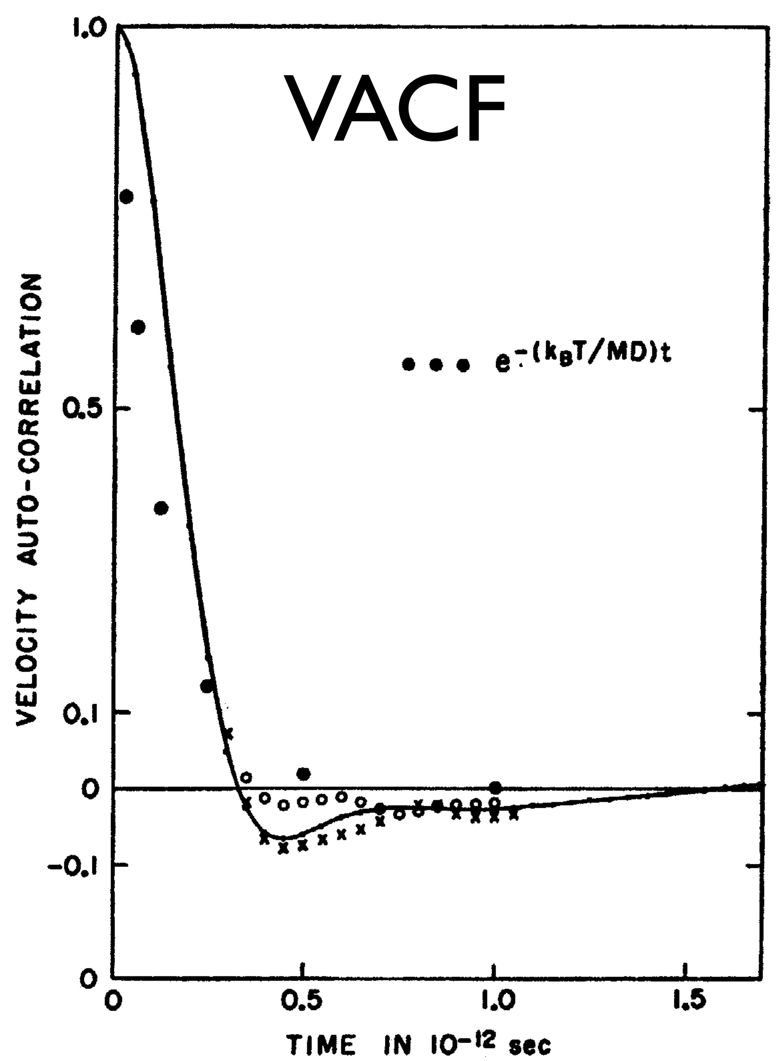
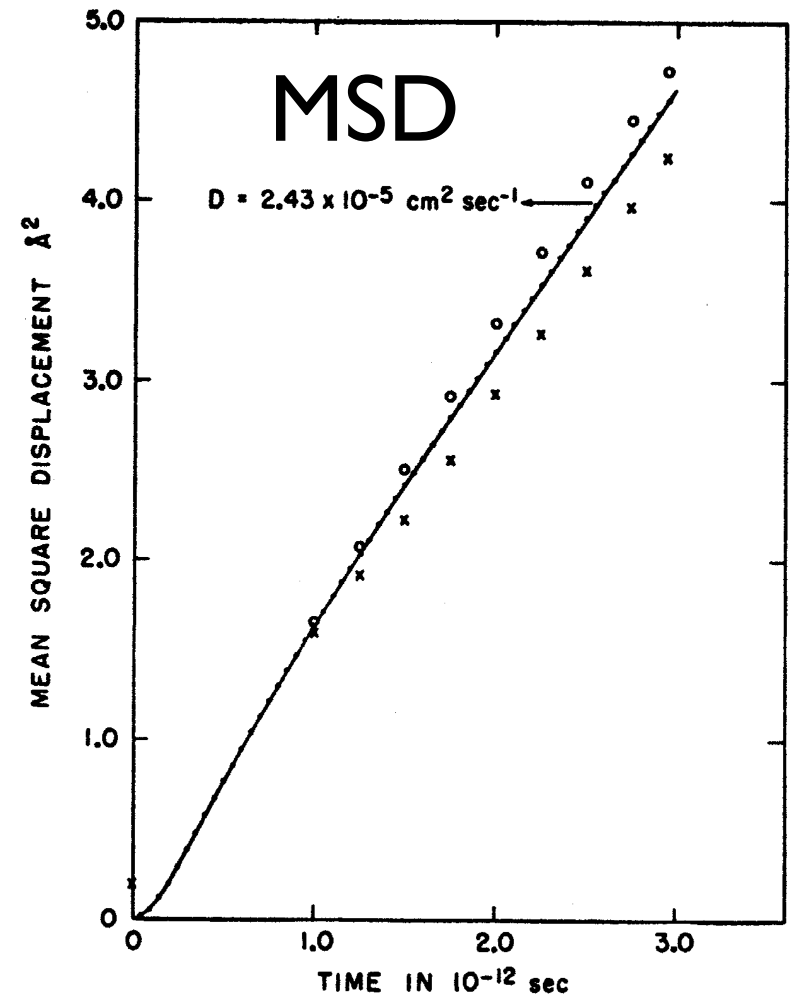


FIG. 4. The velocity autocorrelation function. The Langevin-type exponential function is also shown. The continuous curve, the circles, and the crosses correspond to the curves shown in Fig. 3.



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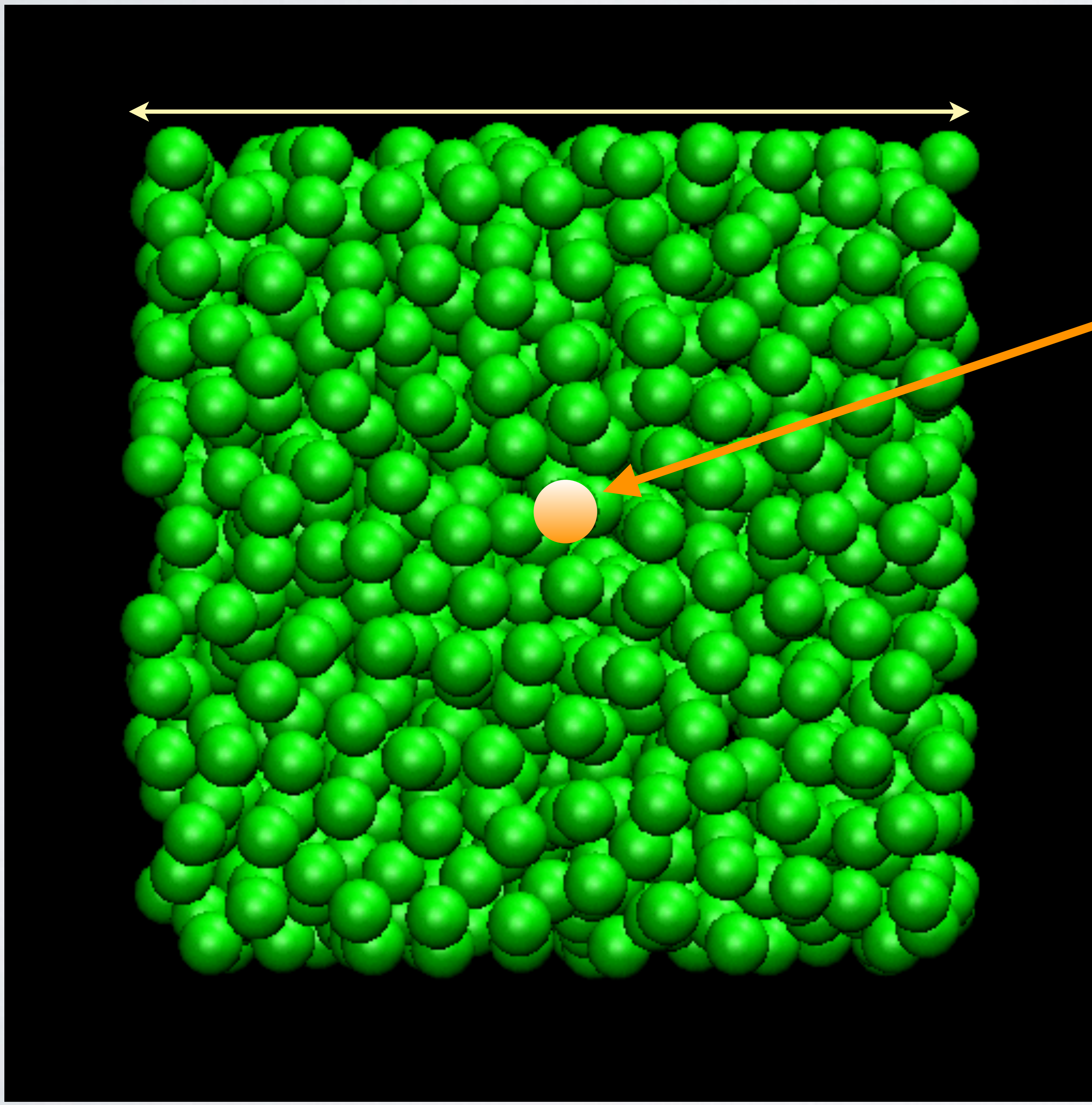
$$W(t) = 2\int_0^t dt'\,(t-t')\langle v(t')v(0)\rangle$$

$$D = \int_0^\infty dt\,\langle v(t)v(0)\rangle$$

Towards Brownian dynamics

G.R. Kneller, K. Hinsen, and G. Sutmann, J Chem Phys 118, 5283 (2003).

~ 3.6 nm



One particle with mass $M > m$ and size $d > d_0$

Generalized Langevin equation

$$\frac{d}{dt}v(t) = -\int_0^t d\tau\, \xi(t-\tau)v(\tau) + f^+(t)$$

Memory function

$$\langle v(0) f^+(t) \rangle = 0$$

In the memoryless case one retrieves the Langevin equation

$$\xi(t) = \gamma\delta(t) \quad \Rightarrow \quad \frac{d}{dt}v(t) = -\gamma v(t) + f_r(t)$$

[1] R. Zwanzig. *Statistical mechanics of irreversibility*, pages 106–141. Lectures in Theoretical Physics. Wiley-Interscience, New York, 1961.

Microscopic description of the memory function

Projector:

$$\mathcal{P}f = v\langle v f\rangle / \langle v^2\rangle.$$

$$\xi(t) = \frac{\langle \dot{v}\exp(i(1-\mathcal{P})\mathcal{L}t)(1-\mathcal{P})\dot{v}\rangle}{\langle v^2\rangle}$$

Liouville operator

$$\mathcal{L} = i\sum_\alpha \frac{\partial H}{\partial x_\alpha}\frac{\partial}{\partial p_\alpha} - \frac{\partial H}{\partial p_\alpha}\frac{\partial}{\partial x_\alpha}$$

Memory function equation

$$\frac{d\psi}{dt} = -\int_0^t d\tau \xi(t-\tau)\psi(\tau)$$

$$\hat{\psi}(s) = \int_0^t dt \exp(-st)\psi(t)$$

Laplace transform

$$\hat{\psi}(s) = \frac{1}{s + \hat{\xi}(s)}$$

Solving the discrete memory function equation

G.R. Kneller and K. Hinsen, J Chem Phys 115, 11097 (2001).

$$\frac{\psi(n+1)-\psi(n)}{\Delta t} = -\sum_{k=0}^{n} \Delta t\, \xi(n-k)\,\psi(k)$$

unilateral z-transform

$$F_>(z) = \sum_{n=0}^{\infty} f(n) z^{-n}$$

$$\Psi_>(z) = \frac{1}{z-1+\Delta t^2 \Xi_>(z)}$$

$$\Xi_>(z) = \frac{1}{\Delta t^2}\left(\frac{z}{\Psi_>(z)} + 1 - z\right)$$

- Compute $\xi(n)$ in a time window $T = N\Delta t$ by **polynomial division,** using

$$\Xi_>(z) = \sum_{n=0}^{\infty} \xi(n) z^{-n} \quad \text{and} \quad \Psi_>(z) \approx \sum_{n=0}^{N} \psi(n) z^{-n}$$

- Estimate $\psi(n)$ by **autoregressive (AR) modeling**

Autoregressive model for the VACF

- AR model

$$v(t) = \sum_{n=1}^{P} a_k^{(P)} v(t - n\Delta t) + \epsilon_P(t)$$

Fit coefficients to MD time series

$$\langle \epsilon_P(t)\epsilon_P(t')\rangle = \sigma_P^2 \delta(t - t')$$

- Characteristic polynomial

$$p(z) = z^P - \sum_{k=1}^{P} a_k z^{(P-k)}$$

with poles $z_k \quad (|z_k| < 1)$

- z-transformed VACF

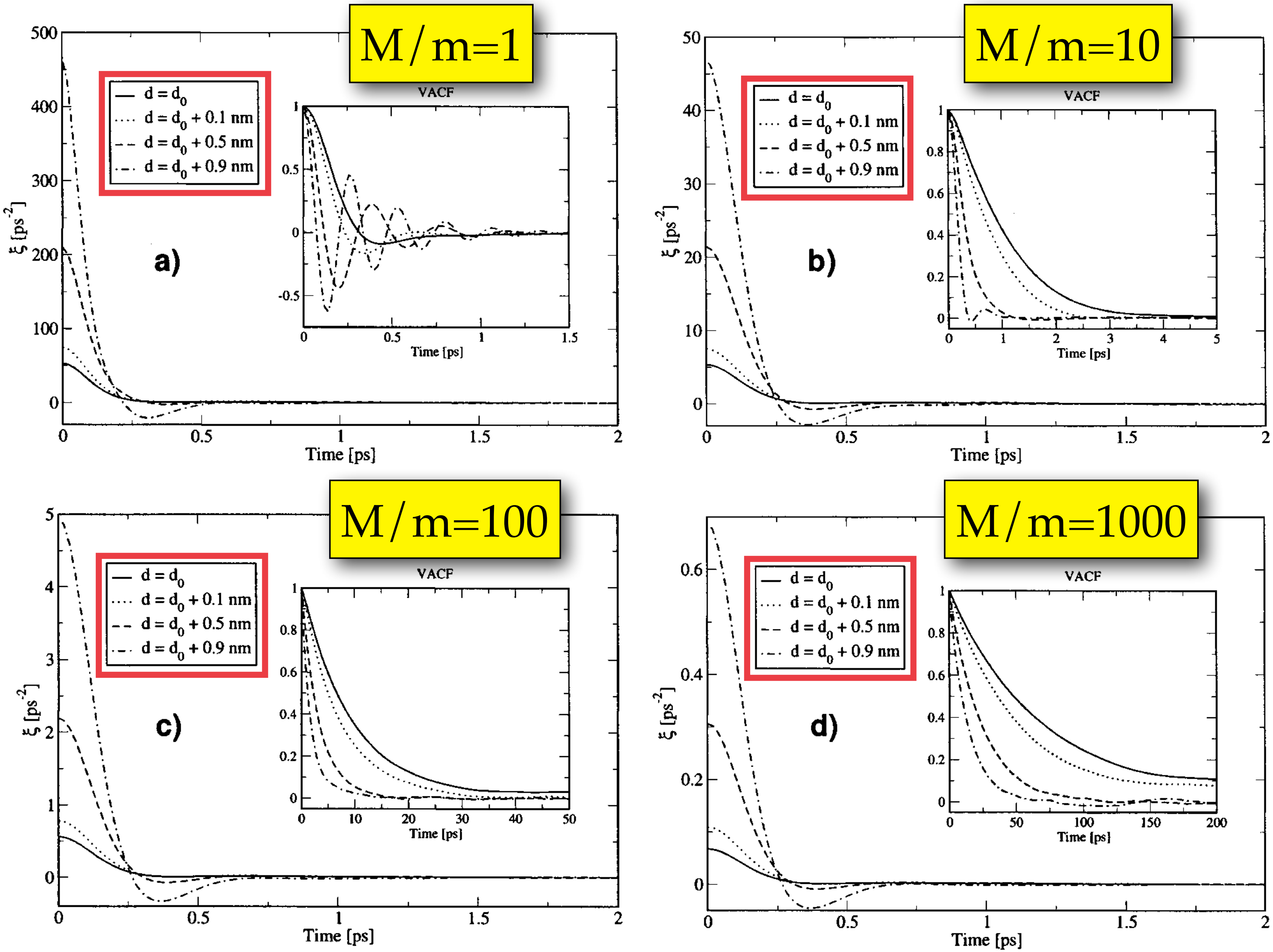
$$\Psi_>^{(AR)}(z) = \sum_{j=1}^{P} \beta_j \frac{z}{z - z_j},$$

$$\beta_j = \frac{1}{a_P^{(P)}} \frac{-z_j^{P-1}\sigma_P^2}{\prod_{k=1,k\neq j}^{P}(z_j - z_k)\prod_{l=1}^{P}(z_j - z_l^{-1})}$$

- VACF

$$\psi(n) = \frac{1}{2\pi i}\oint_C dz\, z^{n-1}\Psi_>^{(AR)}(z) = \sum_{j=1}^{P} \beta_j z_j^n$$

Tracer particle in liquid argon



Scaling of the memory function

TABLE III. Values of the memory function at $t=0$ compared to the negative curvature of the VACF, $-\ddot{\psi}(0)$. The latter has been obtained by numerical differentiation.

$\frac{M}{m}$	$\frac{\delta}{nm}$: 0	0.1	0.5	0.9
1	53.2532	74.8534	210.4775	467.7310
	53.2721	74.7491	210.2601	467.7315
10	5.3438	7.5191	21.4838	47.2131
	5.2980	7.5034	21.2139	47.1845
100	0.5591	0.7797	2.1962	4.9542
	0.5283	0.7779	2.1960	4.9534
1000	0.0675	0.1091	0.3066	0.6887
	0.0587	0.1080	0.3105	0.6897

$$\xi(0) = \frac{\langle F^2 \rangle}{\mu k_B T}$$

Here μ is the reduced mass of the system solute/solvent

[1] G.R. Kneller, K. Hinsen, and G. Sutmann. Mass and size effects on the memory function of tracer particles. *J. Chem. Phys.*, 118(12):5283–5286, 2003.

Mathematical scaling approach

G.R. Kneller and G. Sutmann, J Chem Phys 120, 1667 (2004).

$$\psi_\lambda(t) = \frac{1}{2\pi i}\oint_C ds\, \frac{\exp(st)}{s+\lambda\hat{\xi}(s)},$$

Scaling the memory function

$$\stackrel{s\rightarrow s/\lambda}{=} \frac{1}{2\pi i}\oint_{C'} ds\, \frac{\exp(s\lambda t)}{s+\hat{\xi}(\lambda s)}.$$

Scaling the arguments

$$\int_0^\infty dt\,\xi(t) \equiv \gamma > 0$$

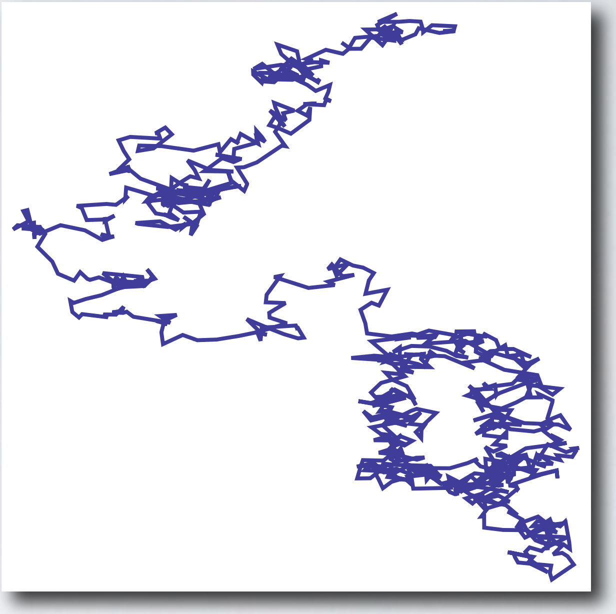
$$\xi(t) \longrightarrow \frac{1}{\lambda}\,\xi\left(\frac{t}{\lambda}\right)$$

$$\psi_\lambda(t) \stackrel{\lambda\rightarrow 0}{\approx} \exp(-\lambda\gamma t)$$

For small λ the memory function approaches a Dirac distribution and the VACF approaches an exponential function

Anomalous diffusion in biological systems

$$W(t) = \langle [x(t) - x(0)]^2 \rangle \stackrel{t\to\infty}{\to} 2D_\alpha t^\alpha$$



$0 < \alpha < 1$: **sub**diffusion
(diffusion of molecules in membranes)

$\alpha = 1$: **normal** diffusion
(diffusion of molecules in liquids)

$1 < \alpha < 2$: **super**diffusion
(target-site search by DNA-binding proteins)

more examples for anomalous diffusion

PHYSICAL REVIEW A VOLUME 9, NUMBER 1 JANUARY 1974

Anomalous self-diffusion for one-dimensional hard cores

J. K. Percus*
Courant Institute of Mathematical Sciences, and
Department of Physics, New York University, New York, New York 10012
(Received 27 August 1973)

PHYSICAL REVIEW B VOLUME 12, NUMBER 6 15 SEPTEMBER 1975

Anomalous transit-time dispersion in amorphous solids

Continuous time random walk

Harvey Scher
Xerox Webster Research Center, 800 Phillips Road, Webster, New York 14580

Elliott W. Montroll
Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627*
(Received 13 January 1975)

PHYSICAL REVIEW B **73**, 045407 (2006)

Temperature dependent normal and anomalous electron diffusion in porous TiO_2 studied by transient surface photovoltage

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Iván Mora-Seró, Germà García-Belmonte, and Juan Bisquert
Departament de Ciències Experimentals, Universitat Jaume I, 12071 Castello, Spain
(Received 21 September 2005; revised manuscript received 19 October 2005; published 11 January 2006)

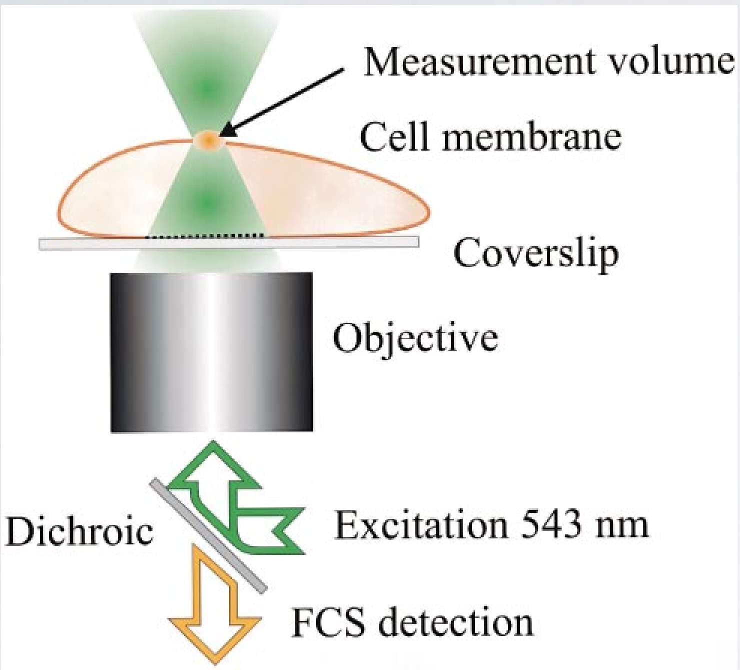
THE JOURNAL OF CHEMICAL PHYSICS **130**, 184709 (2009)

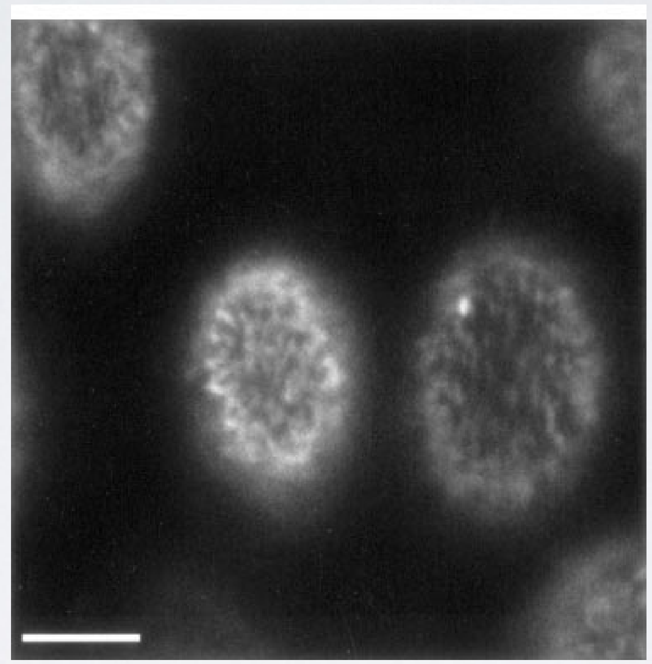
Anomalous diffusion of chains in semicrystalline ethylene polymers

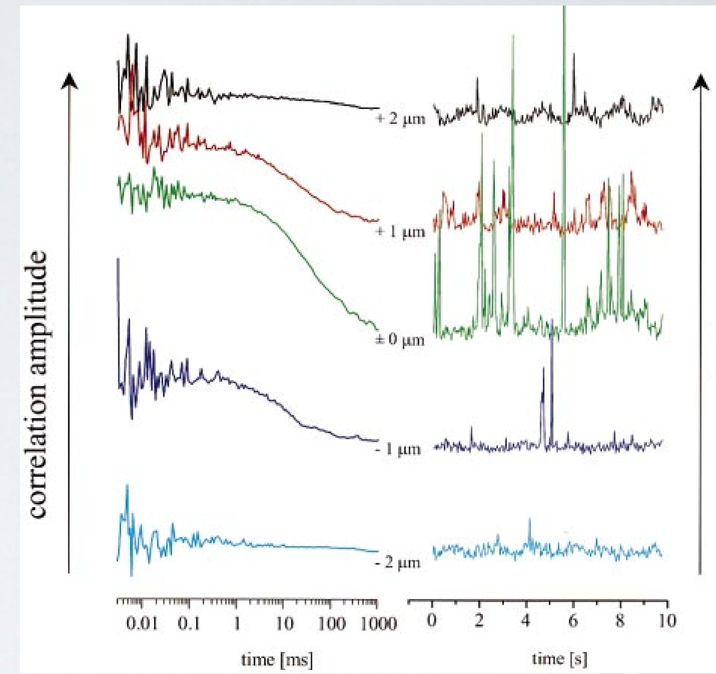
Liying Wang, Xiuzhi Gao, Zhibo Sun, and Jiwen Feng[a)]
State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Science, Wuhan 430071, China
(Received 18 November 2008; accepted 3 April 2009; published online 12 May 2009)

Subdiffusion of lipids observed by Fluorescence Correlation Spectroscopy

P. Schwille, J. Korlach, and W. Webb, Cytometry 36, 176 (1999).





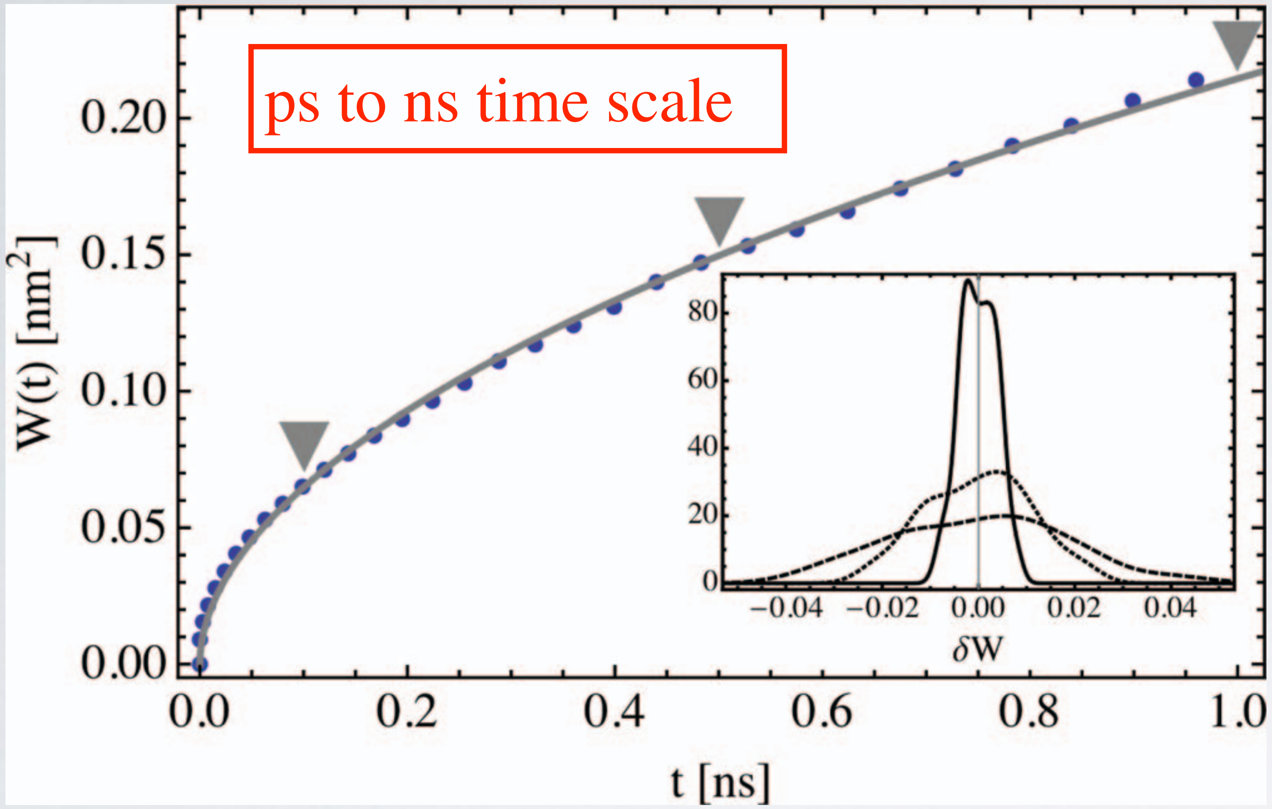


ms to s time scale

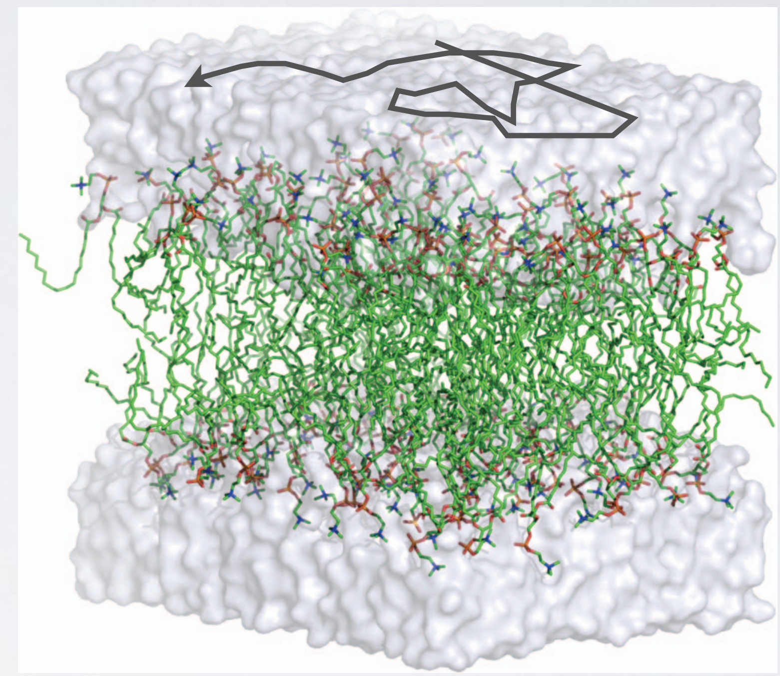
$$P_{anom}[\underline{r}', (t+\tau) | \underline{r}, t] = \frac{1}{(\pi \Gamma \tau^{\alpha})^{n/2}} e^{\frac{-(\underline{r}-\underline{r}')^2}{\Gamma \tau^{\alpha}}}$$

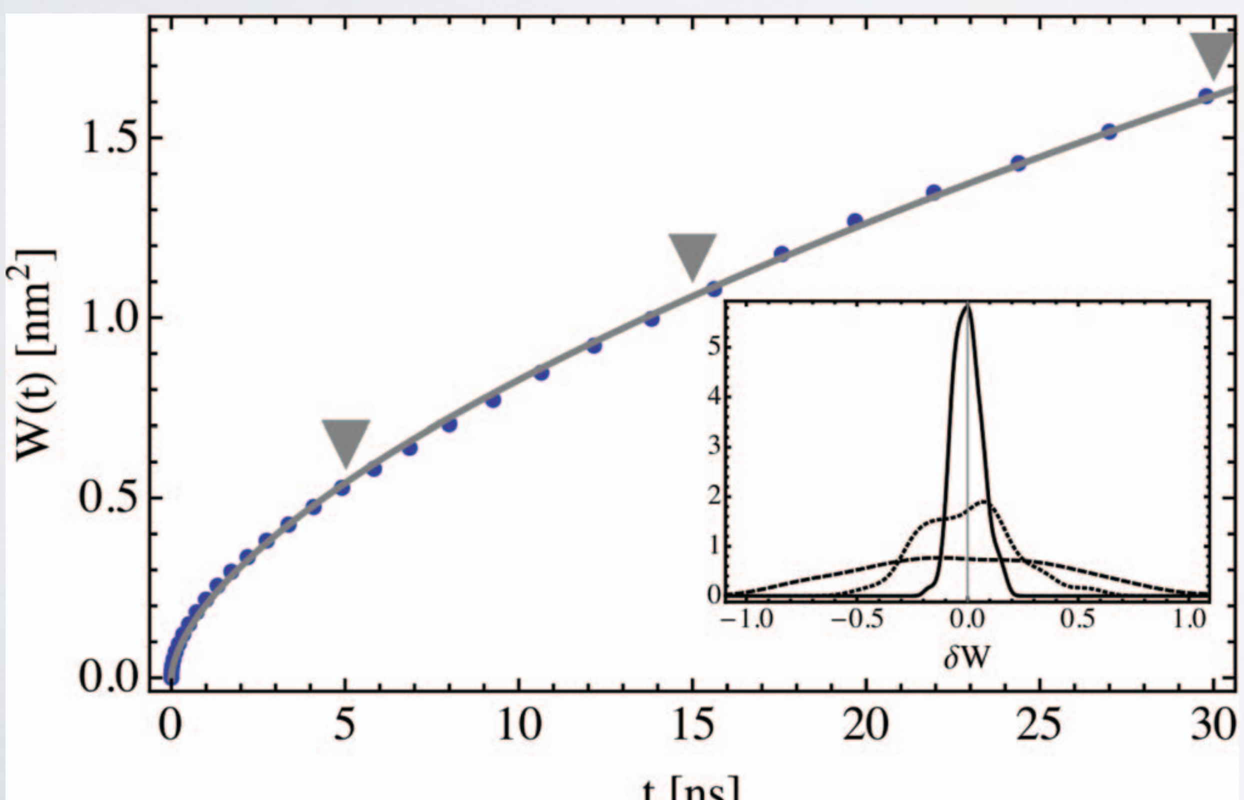
$$W(t) := 2D_{\alpha} t^{\alpha} \qquad \alpha \approx 0.74$$

Subdiffusion of DOPC lipids observed by MD simulation



$D_\alpha = 0.107\ nm^2/ns^\alpha$ for $\alpha = 0.52$.





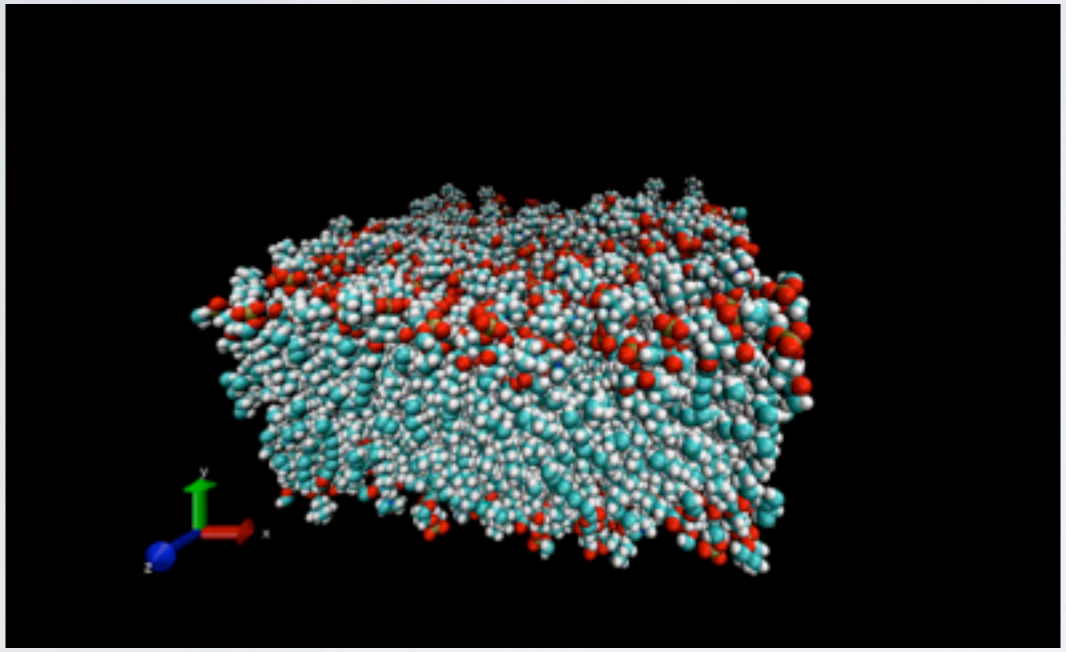
$D_\alpha = 0.101\ nm^2/ns^\alpha$ for $\alpha = 0.61$.

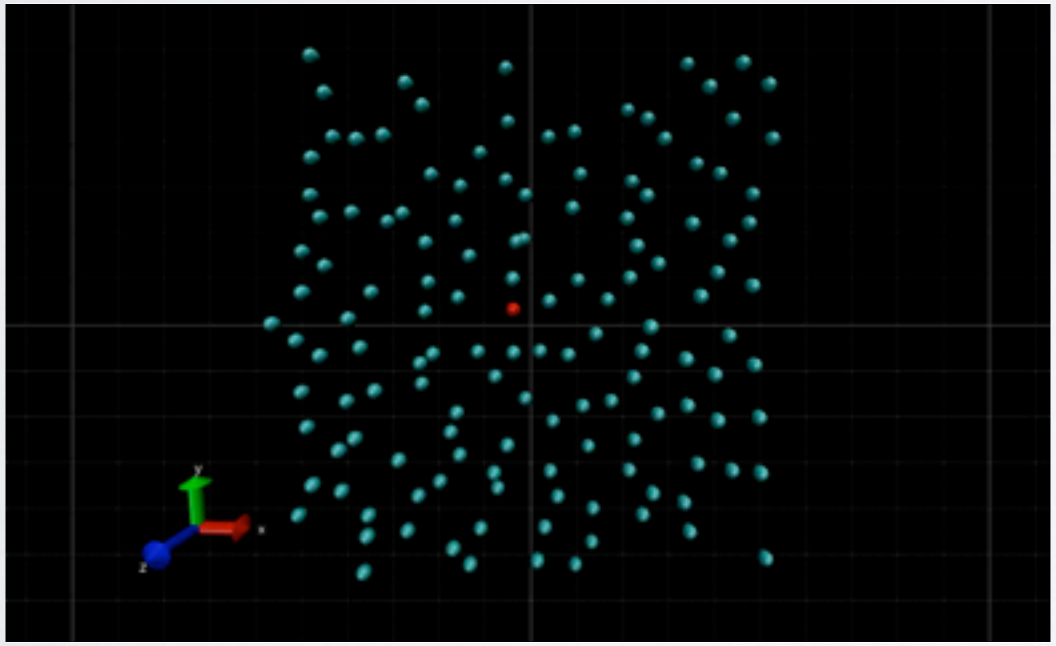
Experimental value for DLPC:
$D_\alpha = 0.088 \pm 0.007\ nm^2/ns^\alpha$
for $\alpha = 0.74 \pm 0.08$.

G. R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula. *J. Chem. Phys.*, 135(14):141105, 2011.

slower subdiffusion in a POPC bilayer….

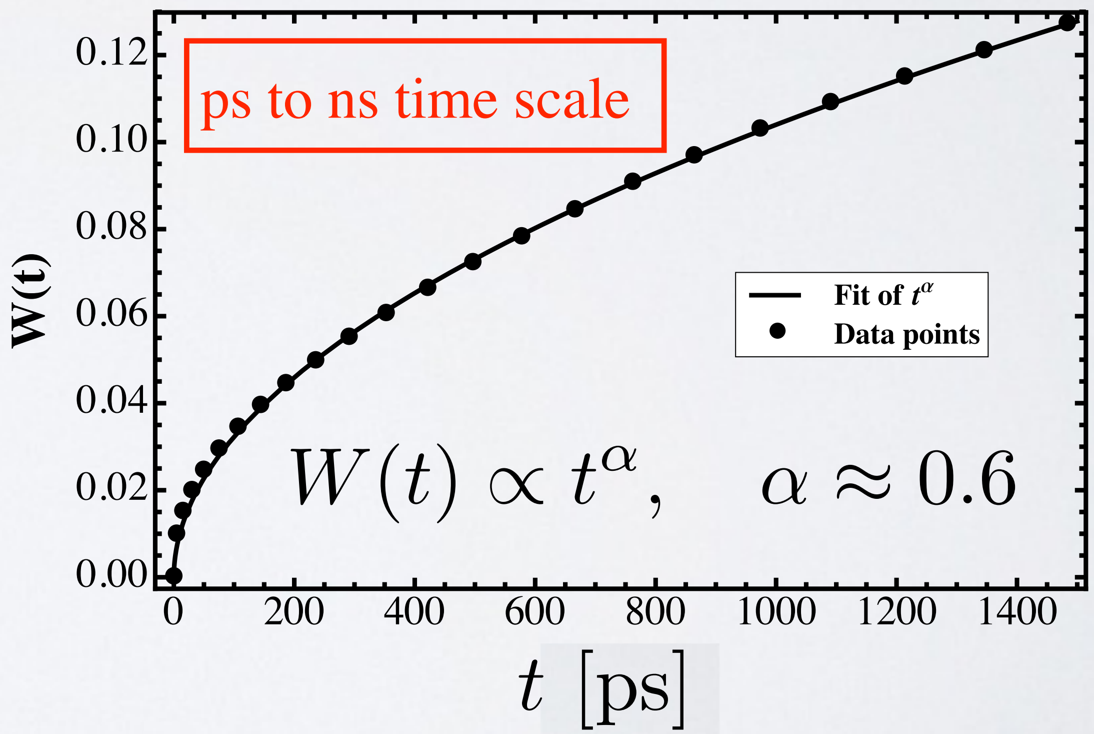
S. Stachura and G.R. Kneller, Mol Sim. 40, 245 (2013).





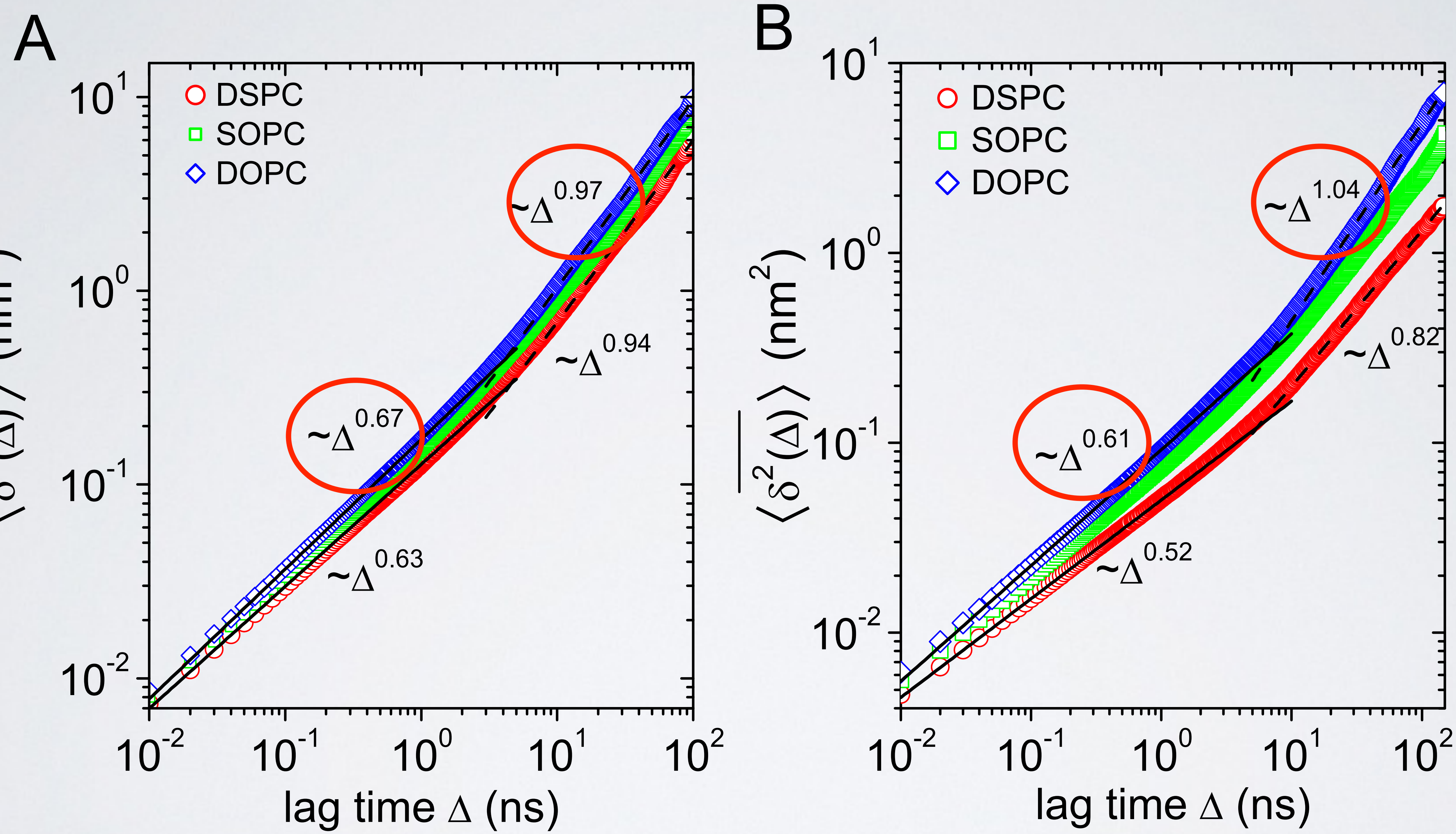
- 2x137 POPC molecules (10 nm X 10 nm in the XY-plane)
- 10471 water molecules (fully hydrated)
- OPLS force field
- T=310 K

MSD for lateral diffusion



See also G.R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula, J Chem Phys 135, 141105 (2011).

Jeon, J. H., Monne, H., Javanainen, M. & Metzler, R. *Phys Rev Lett* 109, 188103 (2012)



Fractional diffusion equation

See e.g. Metzler and Klafter. Phys Rep (2000) vol. 339 (1) pp. 1-77

$$\partial_t P(\mathbf{x}, t|\mathbf{x}_0, 0) = {}_0\partial_t^{1-\alpha} \left\{ D_\alpha \frac{\partial^2}{\partial \mathbf{x}^2} \right\} P(\mathbf{x}, t|\mathbf{x}_0, 0) \quad (0 < \alpha < 2)$$

$${}_0\partial_t^{1-\alpha} = \frac{d}{dt} \int_0^t d\tau \, \frac{(t-\tau)^{\alpha-1}}{\Gamma(\alpha)} f(\tau)$$

Fractional Riemann-Liouville derivative of order 1-α

$$\Rightarrow \quad W(t) = 2D_\alpha t^\alpha$$

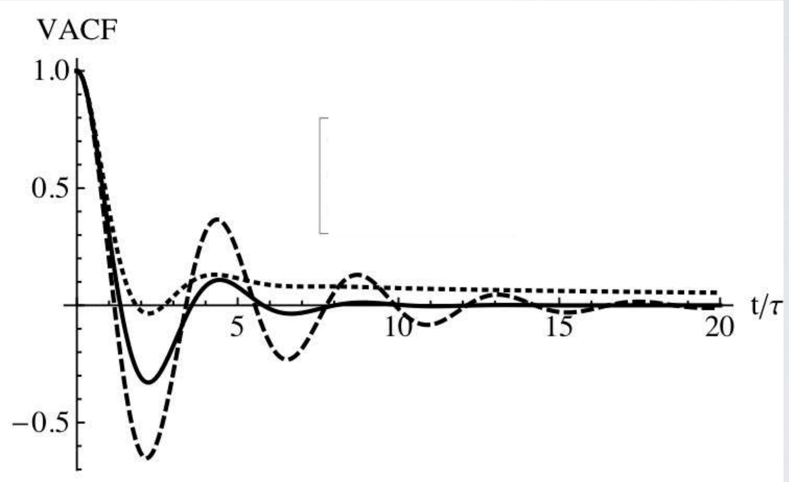
On *all* time scales!

But: diffusion concerns the *asymptotic* regime of the MSD

$$W(t) = 2\int_0^t dt'\,(t-t')c_{vv}(t')$$

Velocity autocorrelation function

$$c_{vv}(t) = \langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$$



$t \to 0$

$$W(t) \overset{t\to 0}{\sim} \langle \mathbf{v}^2\rangle t^2$$

For small times the MSD grows quadratically with time!

$t \to \infty$

$$W(t) \overset{t\to\infty}{\sim} 2D_\alpha t^\alpha$$

Asymptotic regime

Anomalous diffusion in velocity space

E. Barkai and R. Silbey, J Phys Chem B 104, 3866 (2000).

$$\partial_t p(v,t|v_0,0) = \eta_{\rho}\, {}_0\partial_t^{1-\rho} \left\{ \frac{\partial}{\partial v} v + \frac{k_B T}{m} \frac{\partial^2}{\partial v^2} \right\} p(v,t|v_0,0)$$

$$c(t) = \langle v^2 \rangle E_\rho(-\eta_\rho t^\rho)$$

Mittag-Leffler function

$$E_\rho(z) = \sum_{k=0}^{\infty} z^k / \Gamma(1+\rho k)$$

$$W(t) \overset{t\to\infty}{\sim} 2D_\alpha t^\alpha$$

$$D_\alpha = \frac{\langle v^2 \rangle \eta_{2-\alpha}^{-1}}{\Gamma(1+\alpha)}.$$

$$W(t) \overset{t\to 0}{\sim} \langle v^2 \rangle t^2$$

Asymptotic analysis of diffusion

Neuer Beweis und Verallgemeinerung der Tauberschen Sätze, welche die Laplacesche und Stieltjessche Transformation betreffen.

Von *J. Karamata* in Belgrad.

Journal für die Reine und Angewandte Mathematik (Crelle's Journal) **1931,** 27–39 (1931).

$$h(t) \overset{t\to\infty}{\sim} L(t)t^{\rho} \Leftrightarrow \hat{h}(s) \overset{s\to 0}{\sim} L(1/s)\frac{\Gamma(\rho+1)}{s^{\rho+1}} \quad (\rho > -1).$$

$\hat{h}(s) = \int_0^\infty dt\ \exp(-st)h(t) \quad (\Re\{s\} > 0)$ Laplace transform

$\lim_{t\to\infty} L(\lambda t)/L(t) = 1$, with $\lambda > 0$. Slowly growing function

What can be learned from diverging integrals?

Combining

1. Mathematics (α is given)

$$W(t) \overset{t\to\infty}{\sim} 2D_\alpha L(t)t^\alpha \longleftrightarrow \hat{W}(s) \overset{s\to 0}{\sim} 2D_\alpha L(1/s)\frac{\Gamma(\alpha+1)}{s^{\alpha+1}}.$$

$$\lim_{t\to\infty} L(t) = 1 \qquad \lim_{t\to\infty} t\frac{dL(t)}{dt} = 0$$

Special choice of L(t)

2. Physics

$$W(t) = 2\int_0^t d\tau\,(t-\tau)c_{vv}(\tau)$$

$$\frac{dc_{vv}(t)}{dt} = -\int_0^t d\tau\,\kappa(t-\tau)c_{vv}(\tau)$$

$$\hat{W}(s) = \frac{2\hat{c}_{vv}(s)}{s^2} = \frac{2\langle v^2\rangle}{s^2(s+\hat{\kappa}(s))}$$

Obtain asymptotic forms for Laplace transforms of the VACF and its memory function

Kneller, G. R. , J Chem Phys 134, 224106 (2011).

Laplace transformed VACF

$$\hat{c}_{vv}(s) \stackrel{s\to 0}{\sim} D_\alpha \Gamma(\alpha+1) L(1/s) s^{1-\alpha}.$$

Laplace transformed memory function

$$\hat{\kappa}(s) \stackrel{s\to 0}{\sim} \frac{\langle \mathbf{v}^2 \rangle}{D_\alpha \Gamma(\alpha+1)} \frac{s^{\alpha-1}}{L(1/s)}.$$

Generalized Kubo expressions and FD-theorem

Kneller, G. R. , J Chem Phys 134, 224106 (2011).

$$D_\alpha = \frac{1}{\Gamma(1+\alpha)} \int_0^\infty dt \; {}_0\partial_t^{\alpha-1} c_{vv}(t).$$

Generalized Kubo formula for the **diffusion coefficient**

$${}_0\partial_t^{\alpha-1} = \frac{d}{dt}\int_0^t d\tau \, \frac{(t-\tau)^{1-\alpha}}{\Gamma(2-\alpha)} f(\tau)$$

$$\eta_\alpha = \Gamma(1+\alpha) \int_0^\infty dt \; {}_0\partial_t^{1-\alpha} \kappa(t)$$

Generalized Kubo formula for the **relaxation coefficient**

$${}_0\partial_t^{1-\alpha} = \frac{d}{dt}\int_0^t d\tau \, \frac{(t-\tau)^{\alpha-1}}{\Gamma(\alpha)} f(\tau)$$

$$D_\alpha = \frac{\langle \mathbf{v}^2 \rangle}{\eta_\alpha}$$

Fluctuation-Dissipation theorem

Long time tails

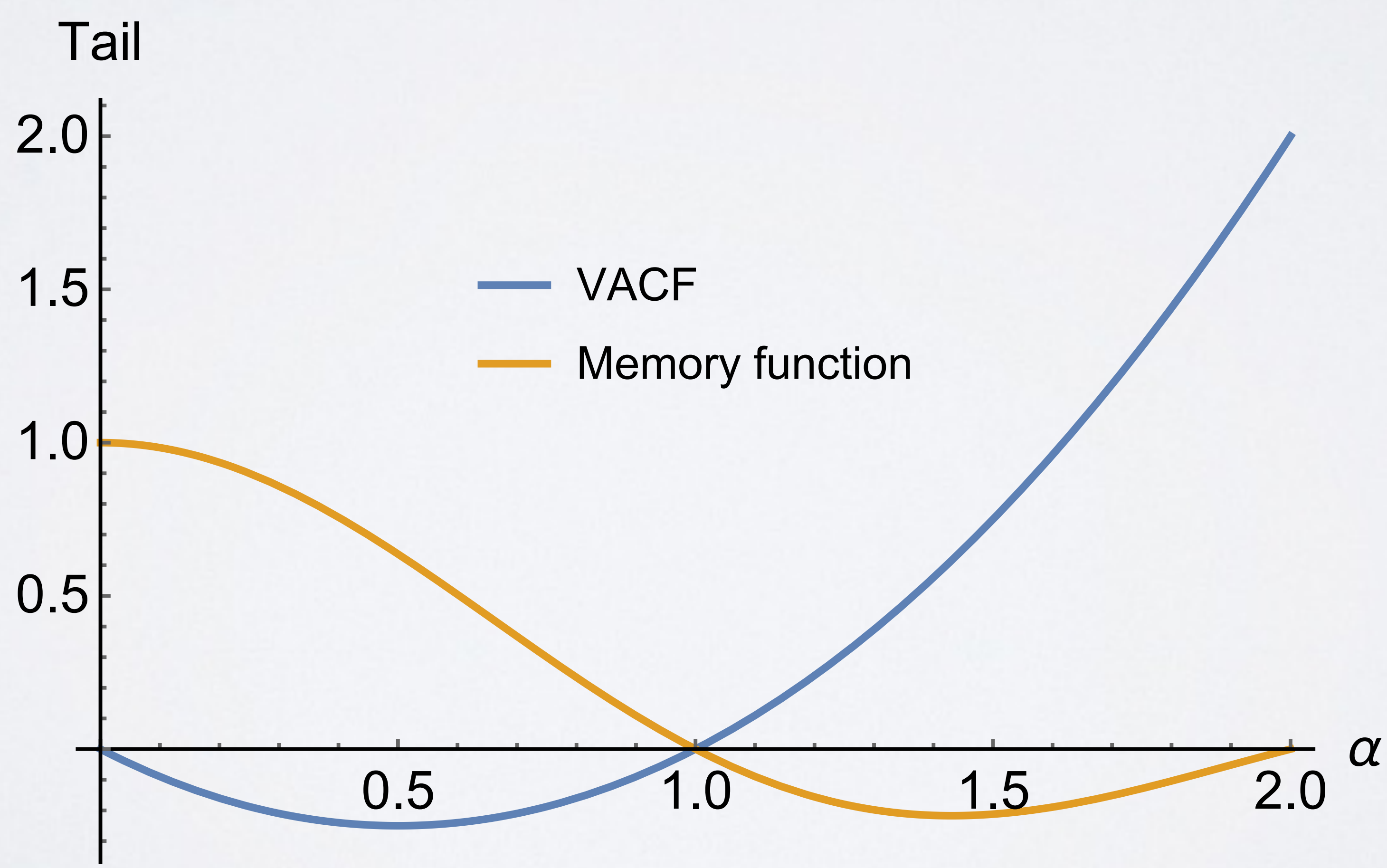
$$\lim_{t\to\infty} L(t) = 1 \qquad \lim_{t\to\infty} t\frac{dL(t)}{dt} = 0$$

$$c_{vv}(t) \overset{t\to\infty}{\sim} D_\alpha \alpha(\alpha-1)L(t)t^{\alpha-2},$$

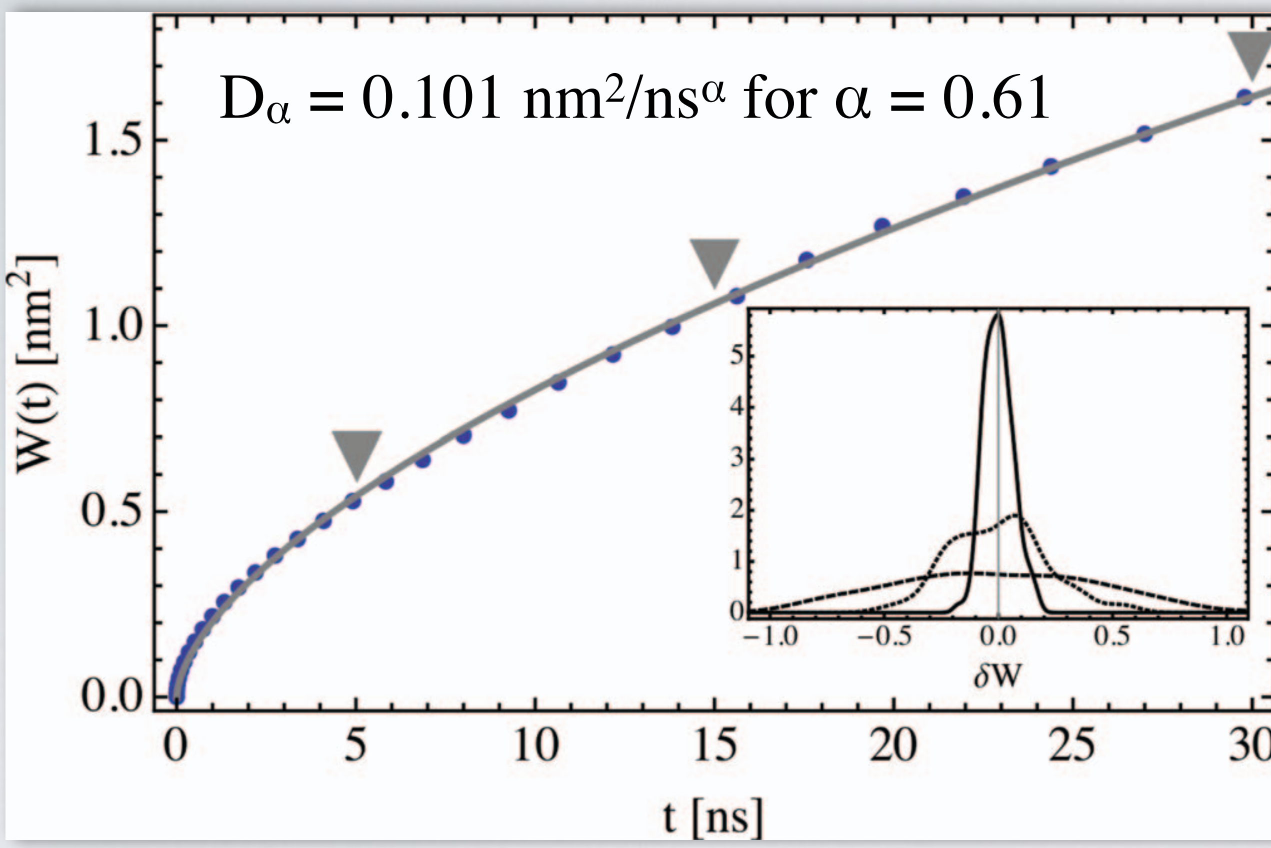
also sufficient for $1 < \alpha < 2$

$$\kappa(t) \overset{t\to\infty}{\sim} \frac{\langle \mathbf{v}^2 \rangle}{D_\alpha} \frac{\sin(\pi\alpha)}{\pi\alpha} \frac{1}{L(t)} t^{-\alpha}.$$

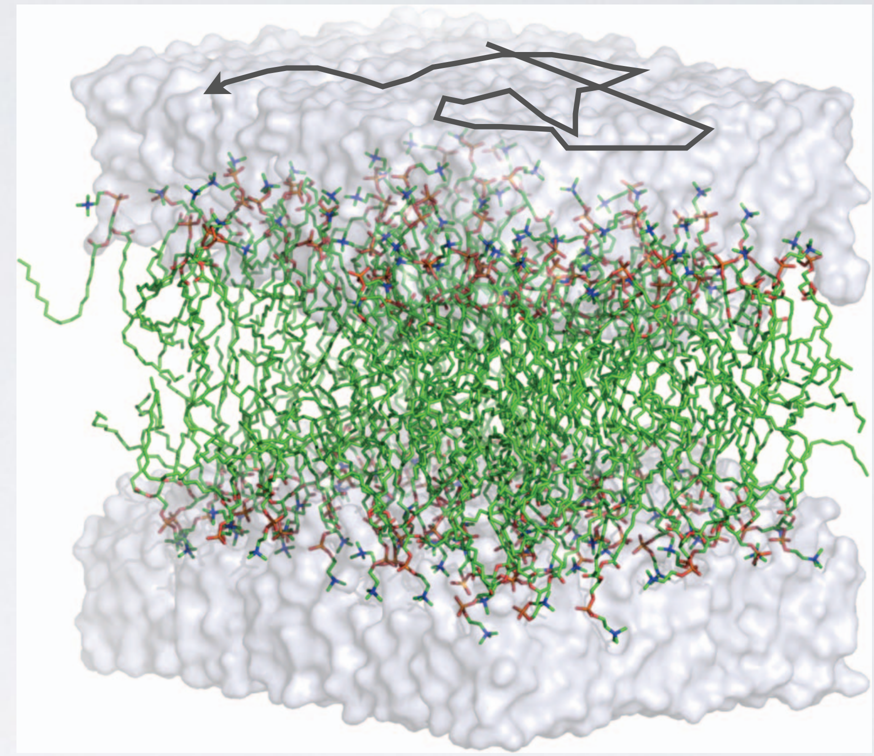
also sufficient for $0 < \alpha < 1$

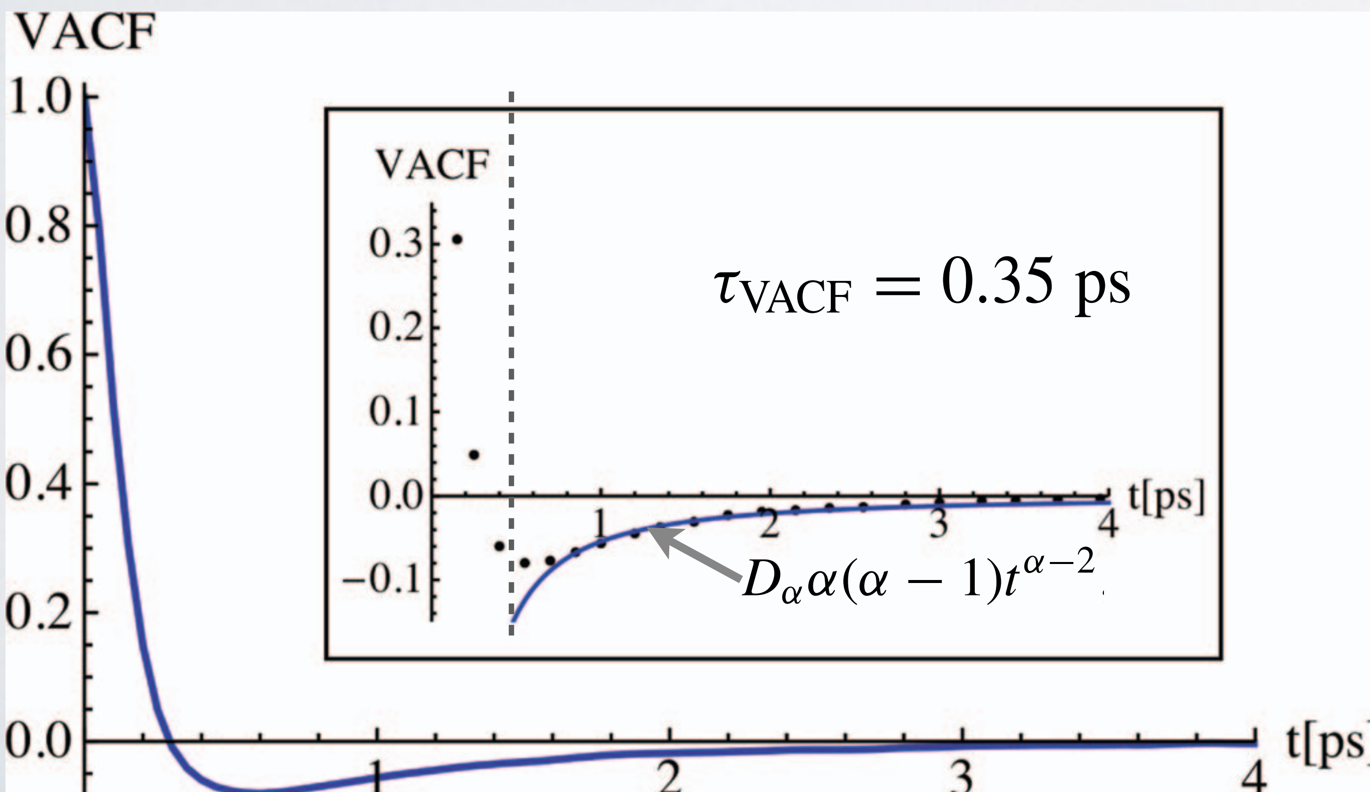


VACF long time tail in a DOPC bilayer



Simulated DOPC system





$$\tau_{\mathrm{VACF}} = \left(\frac{D_\alpha \Gamma(1+\alpha)}{\langle v^2 \rangle}\right)^{1/(2-\alpha)}$$

$$D_\alpha = \frac{\langle v^2 \rangle \tau_{\mathrm{VACF}}^{2-\alpha}}{\Gamma(1+\alpha)}$$

G. R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula. *J. Chem. Phys.*, 135(14):141105, 2011.

"Cage effect" and memory function

$$\dot{\mathbf{v}}(t) = -\int_0^t dt'\,\kappa(t-t')\mathbf{v}(t') + \mathbf{f}^{(+)}(t)$$

$$\kappa(t) \equiv \Omega^2 \Rightarrow c_{vv}(t) = \langle v^2 \rangle \cos \Omega t$$

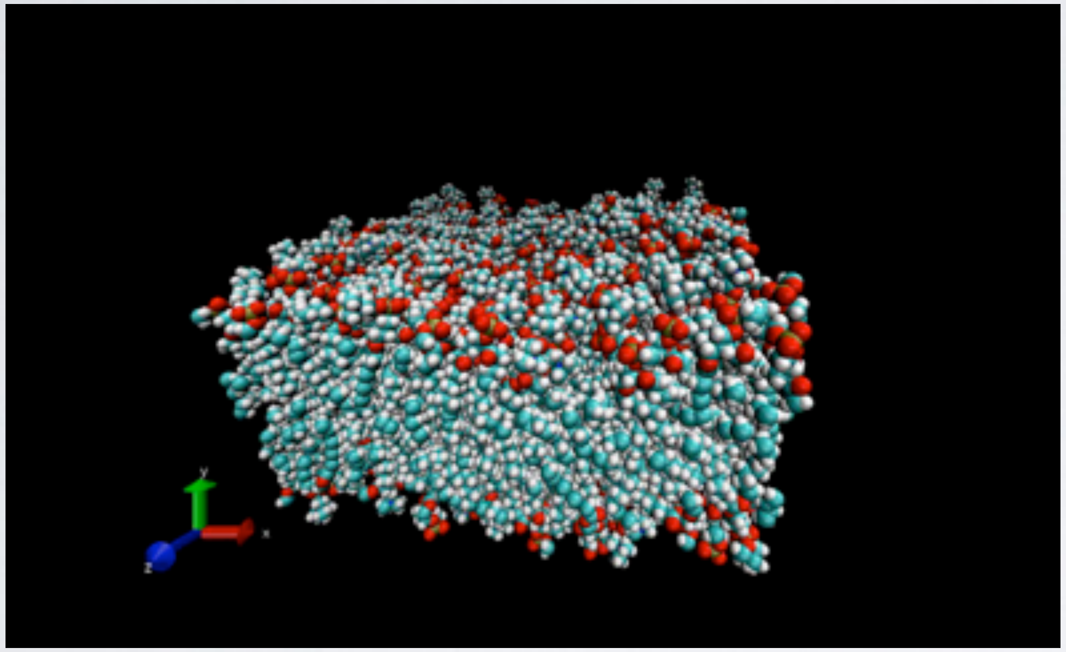
special choice of constant memory

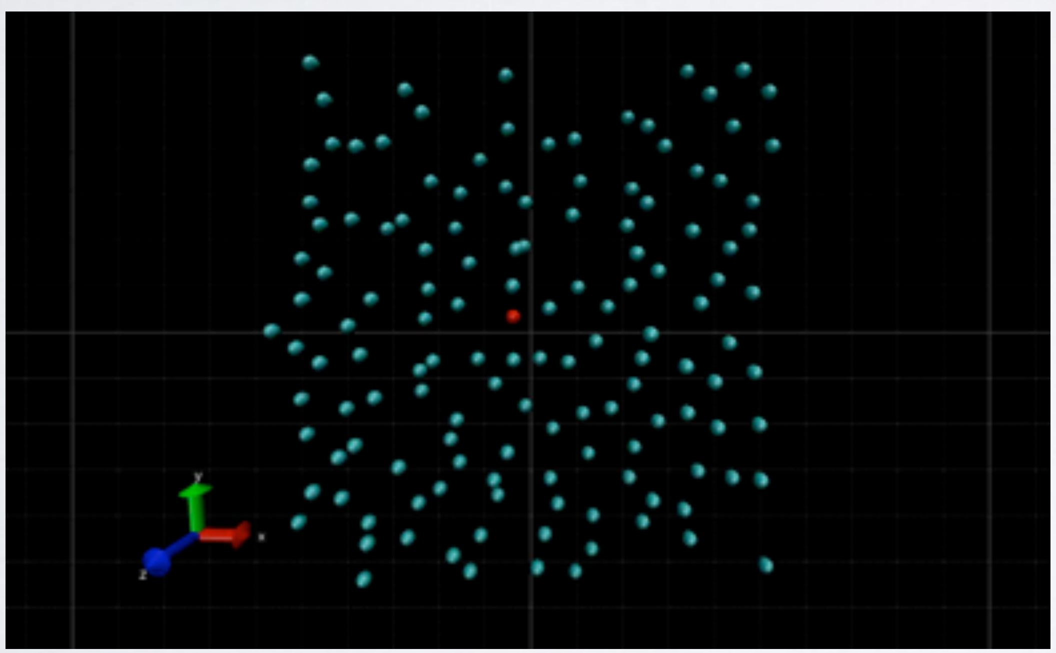
oscillatory «rattling» motions in the «cage» of nearest neighbors

☛ The asymptotic decay of this cage determines the type of diffusion which is observed (normal, anomalous).

Visualizing the cage effect in a POPC bilayer

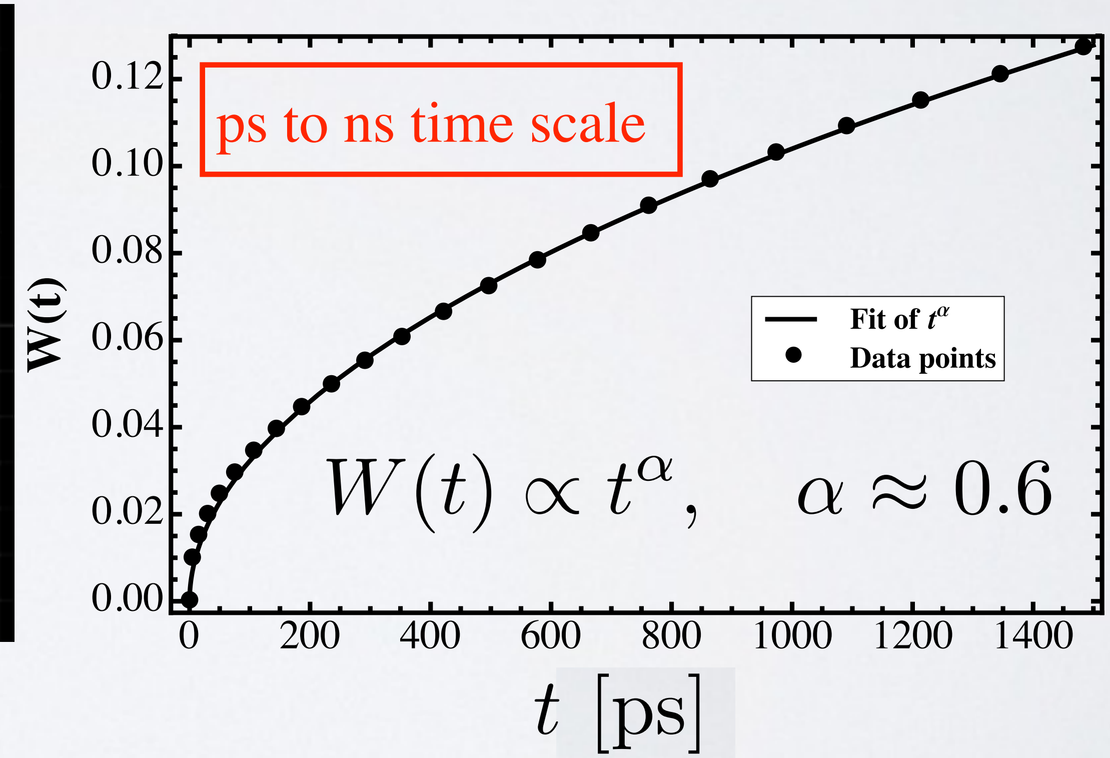
S. Stachura and G.R. Kneller, Mol Sim. 40, 245 (2013).





- 2x137 POPC molecules (10 nm × 10 nm in the XY-plane)
- 10471 water molecules (fully hydrated)
- OPLS force field
- T=310 K

MSD for lateral diffusion



See also G.R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula, J Chem Phys 135, 141105 (2011).
J.H. Jeon, H. Monne, M. Javanainen, and R. Metzler, Phys Rev Lett (2012).

Van Hove correlation function and the „cage" of nearest neighbours

* The pair Distribution Function (PDF), g(r), is proportional to the probability of finding a particle between distances „r+dr", from a tagged central particle in a liquid.
* Time-dependent PDFs (van Hove PDFs), $G_D(r,t)$, display the dynamic structure in a liquid.

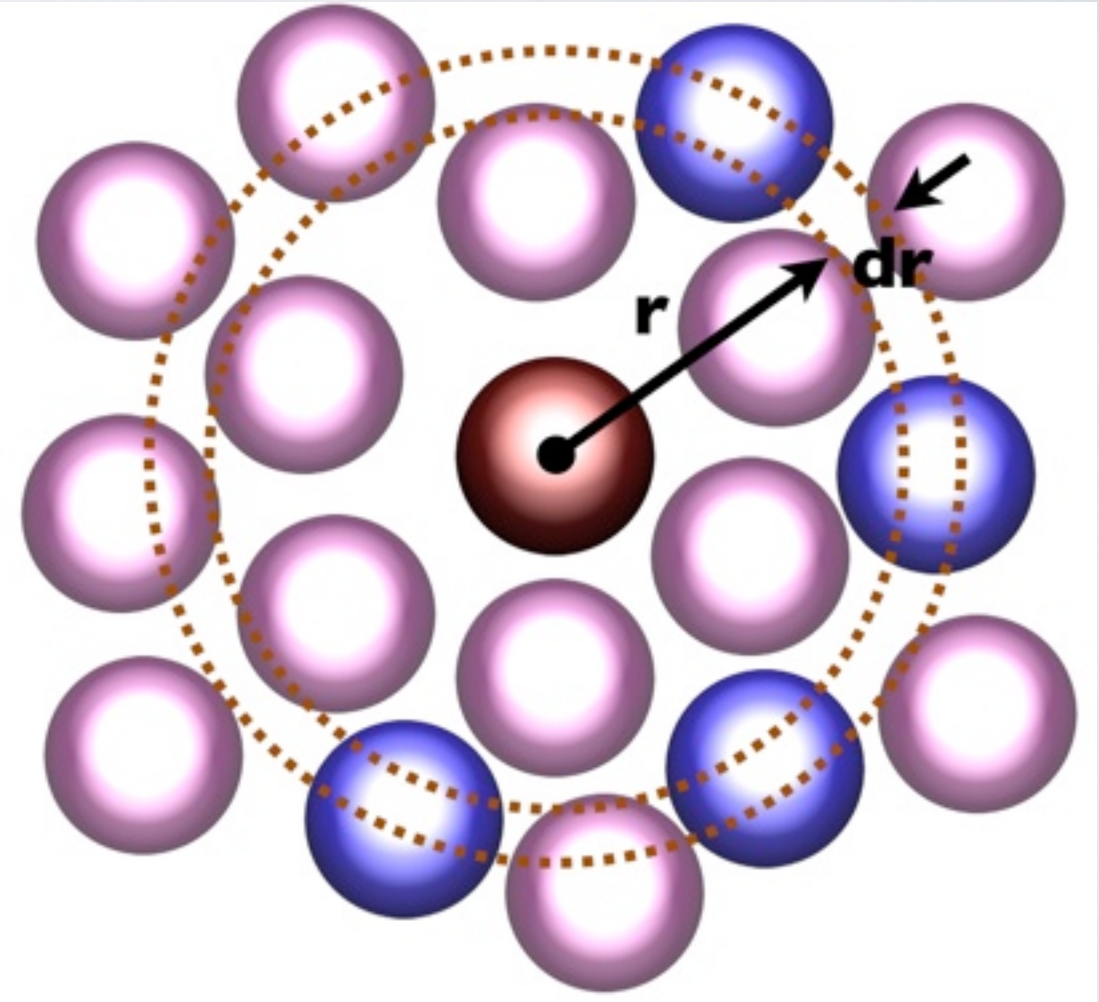
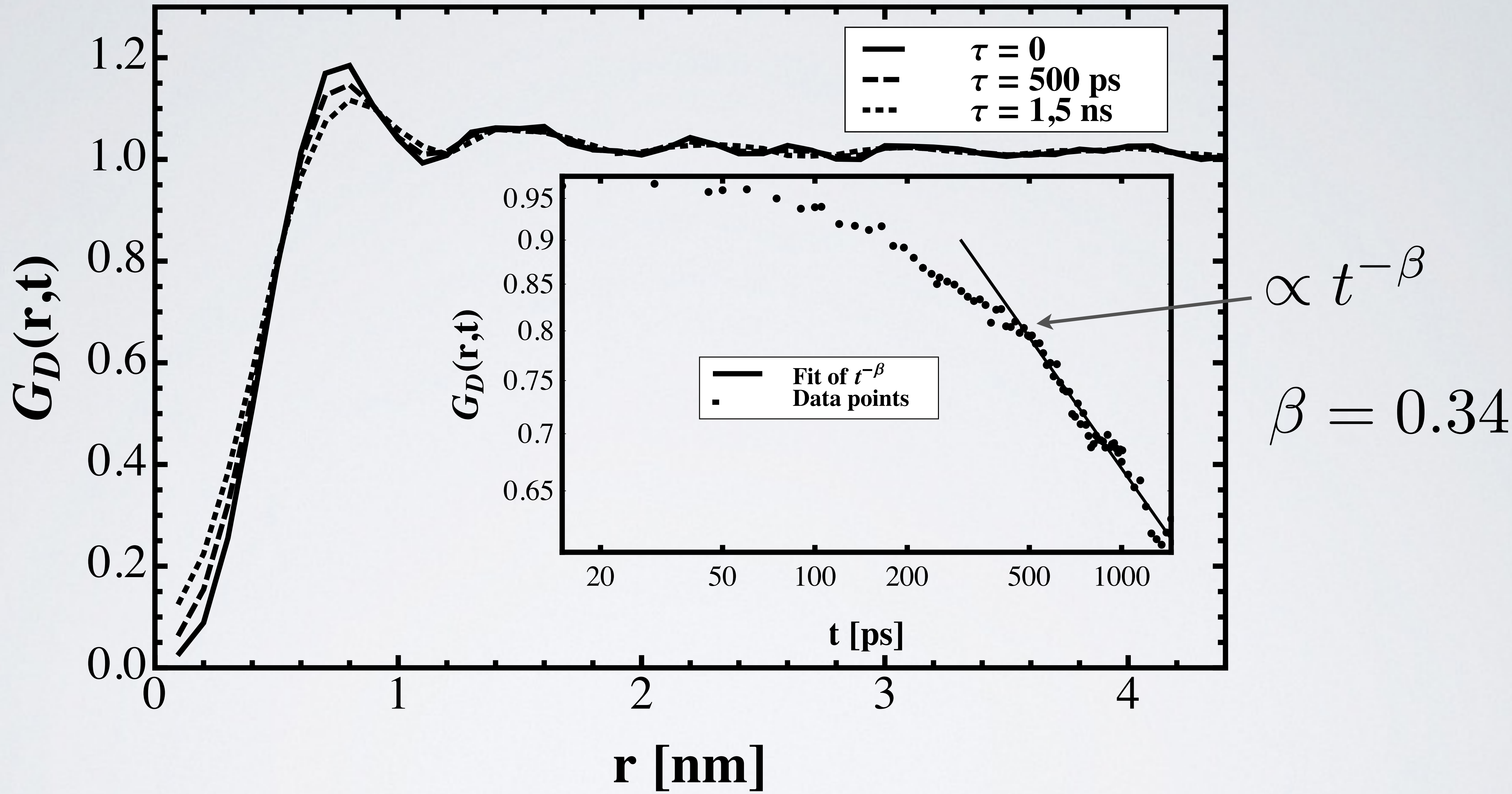


Image: "The structure of the cytoplasm" from Molecular Biology of the Cell. Adapted from D.S. Goodsell, Trends Biochem. Sci. 16:203-206, 1991.

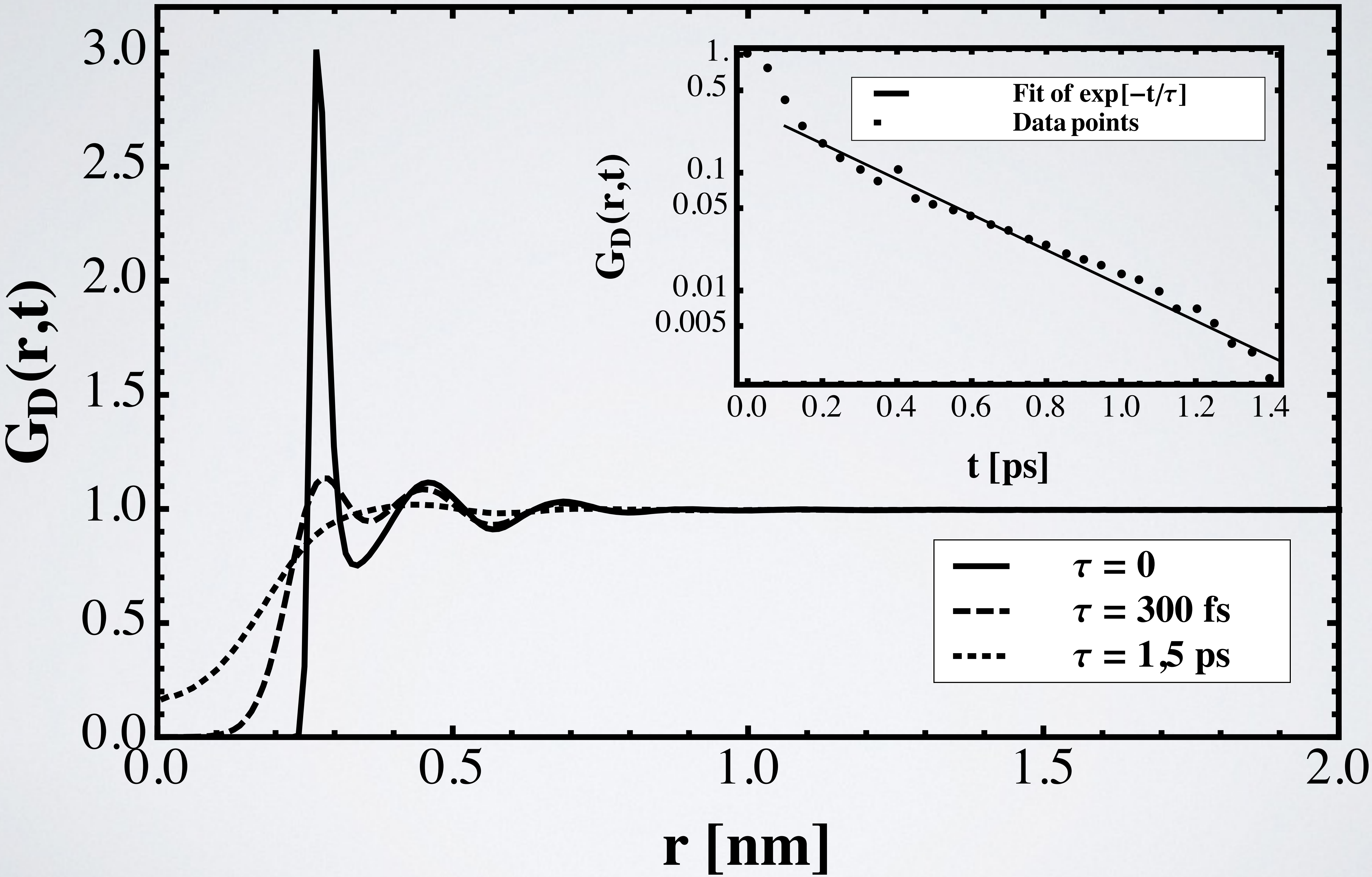
* (Van Hove) PDFs can be obtained from scattering experiments (neutron scttering, inelastic X-ray scattering)

Time-dependent pair correlation function for POPC



Time-dependent Pair Correlation Function $G_d(r,t)$ of POPC lipids (CM) for three time slices : t=0 (thick line), t=500 ps (dashed line) and for t=1.5 ns (dotted line). **Inset:** Log-log plot for the decay of Gd(r,t) as a function of time for r =0.8 nm.

Bulk water for comparison....



Scaling approach to anomalous diffusion

G.R. Kneller, J Chem Phys 141, 041105 (2014).

- Consider a tagged particle in a liquid whose MSD grows as $W(t) \sim t^\alpha$
- Scale its memory function according to

$$\kappa(t) \to \lambda\kappa(t)$$

where $\lambda \to 0$. This corresponds to increasing its mass according to $m \to m/\lambda$.

Scaling procedure

- The normalized VACF corresponding to the scaled memory function is

$$\psi_\lambda(t) = \frac{1}{2\pi i}\oint ds\, \frac{\exp(st)}{s + \lambda\hat{\kappa}(s)}$$
$$\overset{s\to s/\lambda}{=} \frac{1}{2\pi i}\oint ds\, \frac{\exp(s\lambda t)}{s + \hat{\kappa}(\lambda s)}.$$

- Use that $\kappa(s) \overset{s\to 0}{\sim} s^{\alpha-1}$ such that $\hat{\kappa}(\lambda s) \overset{\lambda\to 0}{=} \lambda^{\alpha-1}\hat{\kappa}(s)$ and iterate the scaling procedure. After n iterations one obtains

$$\psi_\lambda(t) \overset{\lambda\to 0}{\sim} \frac{1}{2\pi i}\oint du\, \frac{\exp\left(\lambda\,\lambda^{\alpha-1}\ldots\lambda^{(\alpha-1)^{n-1}}(t/\tau)u\right)}{u + K(\lambda^{(\alpha-1)^{n-1}}u)}$$

where

$$K(u) = u^{\alpha-1} \quad \text{and} \quad \tau = \left(\frac{D_\alpha\Gamma(\alpha+1)}{\langle v^2\rangle}\right)^{1/(2-\alpha)}.$$

- For $n \to \infty$ one obtains the VACF of a Rayleigh particle

$$\psi_\lambda(t) \overset{\lambda\to 0}{\sim} E_{2-\alpha}\left(-\lambda[t/\tau]^{2-\alpha}\right) \quad \text{where} \quad E_\rho(z) = \sum_{k=0}^{\infty} z^k/\Gamma(1+\rho k).$$

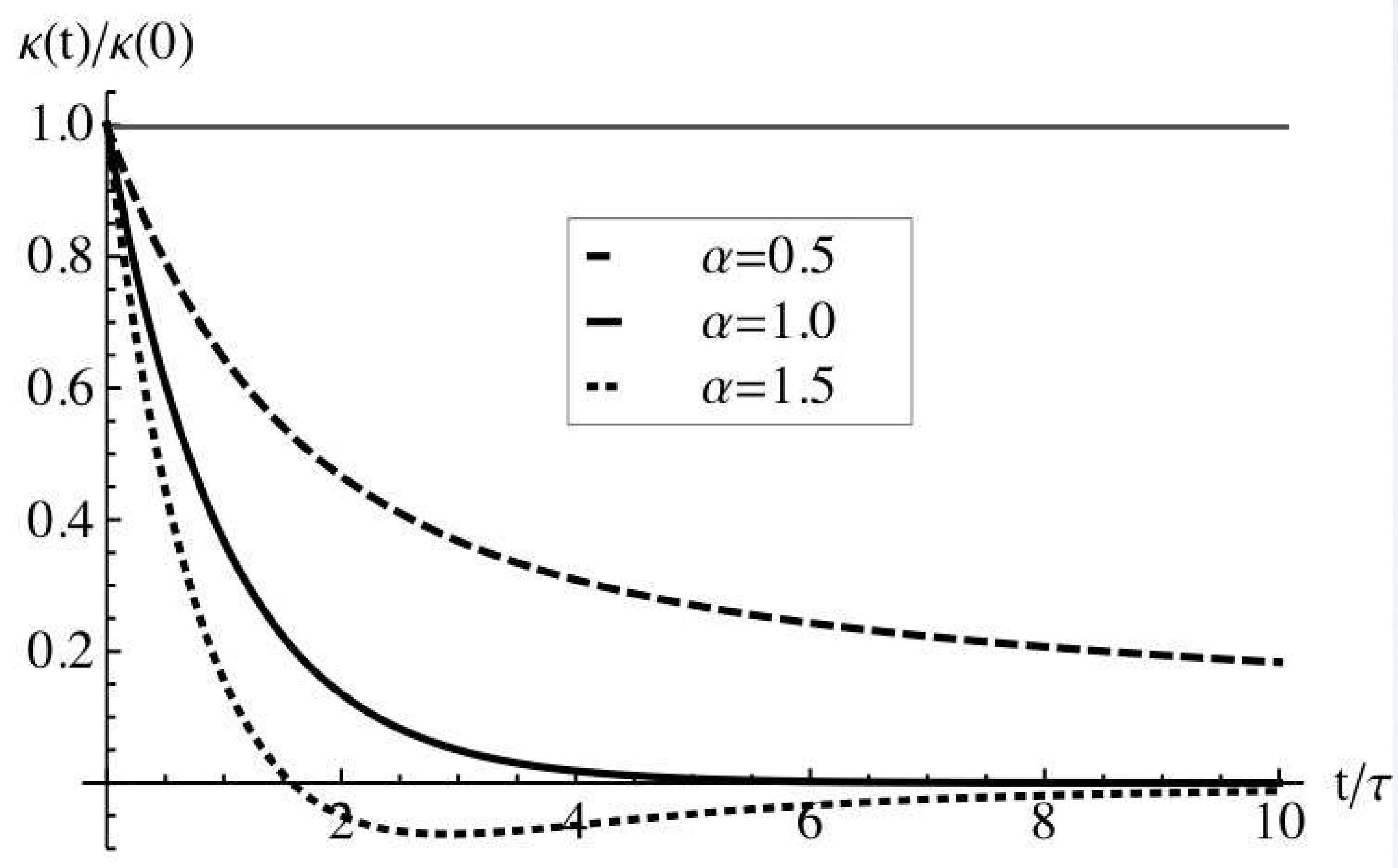
Simple model for the memory function

model memory function

$$\kappa_f(t) = \Omega^2 M(\alpha, 1, -t/\tau)$$

Kummer function

$$\hat{\kappa}_f(s) = \Omega^2 \left\{ \frac{\tau^\alpha}{s^{1-\alpha}} \frac{1}{(s\tau + 1)^\alpha} \right\}$$

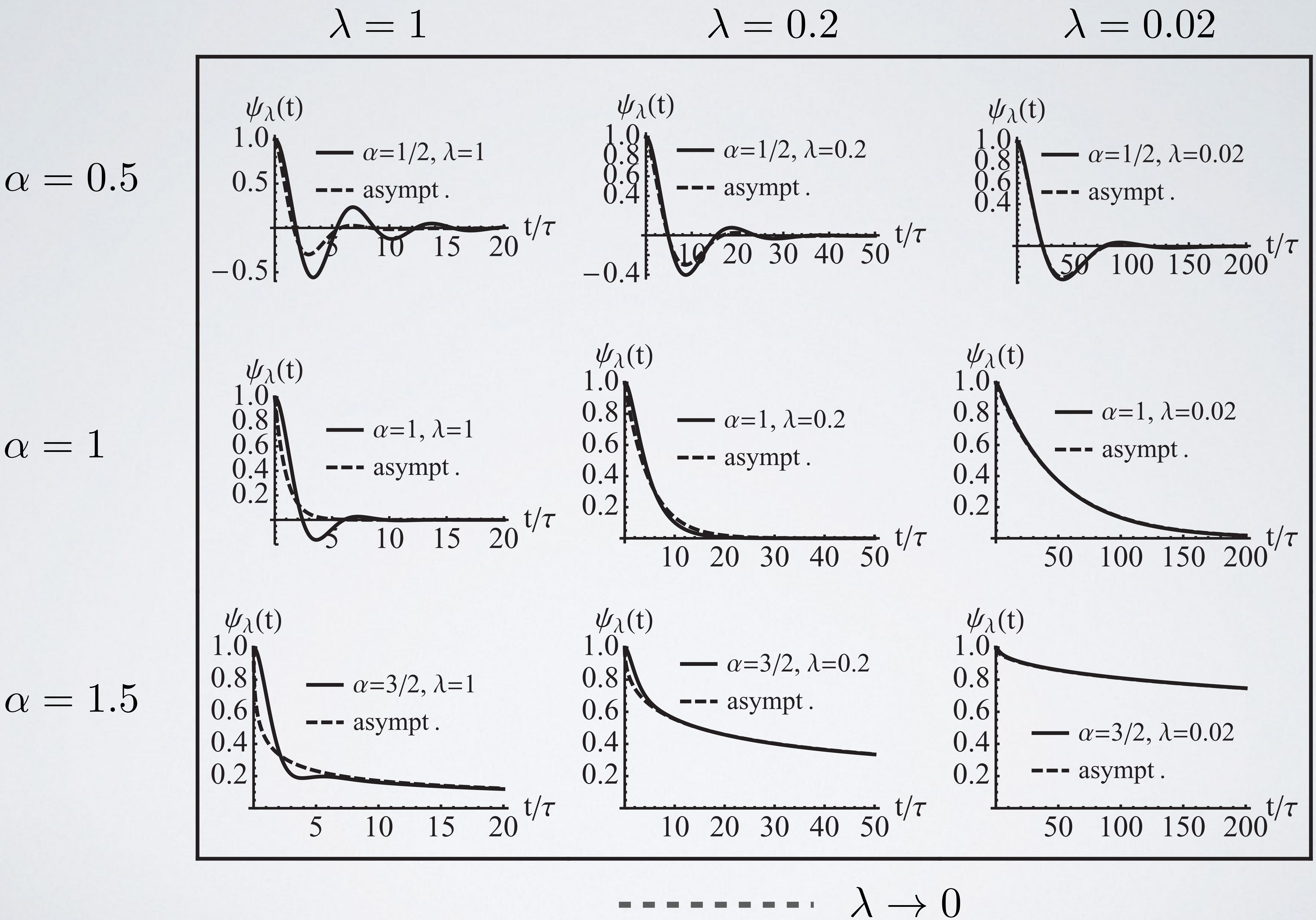


asymptotic form

$$\kappa_f(t) \overset{t\to\infty}{\sim} \begin{cases} \Omega^2 \frac{(t/\tau)^{-\alpha}}{\Gamma(1-\alpha)}, & \alpha \neq 1, \\ \Omega^2 \exp(-t/\tau), & \alpha = 1. \end{cases}$$

G. Kneller, *J. Chem. Phys.*, vol. 134, p. 224106, 2011.

Approaching the limiting VACF



Anomalous confined diffusion

- The limiting form for the VACF of a massive Brownian particle in a solvent of light molecules is
$$\psi(t) \sim E_{2-\alpha}\left(-[t/\tau_\lambda]^{2-\alpha}\right), \quad 0 < \alpha < 2,$$
where $\tau_\lambda = \tau/\lambda^{1/(2-\alpha)}$ and
$$\tau = \left(\frac{\Gamma(\alpha+1)D_\alpha}{\langle v^2\rangle}\right)^{1/(2-\alpha)}.$$

- **The case $\alpha \to 0$ corresponds to confined diffusion**. Here
$$\psi(t) \sim \cos(t/\tau_\lambda),$$
where $\tau_\lambda = \tau/\sqrt{\lambda}$, with
$$\tau = \sqrt{\langle u^2\rangle/\langle v^2\rangle}.$$
Here $\langle u^2\rangle \equiv D_0$ is the mean square position flotation of the Brownian particle.

The limit α→0 for the memory function

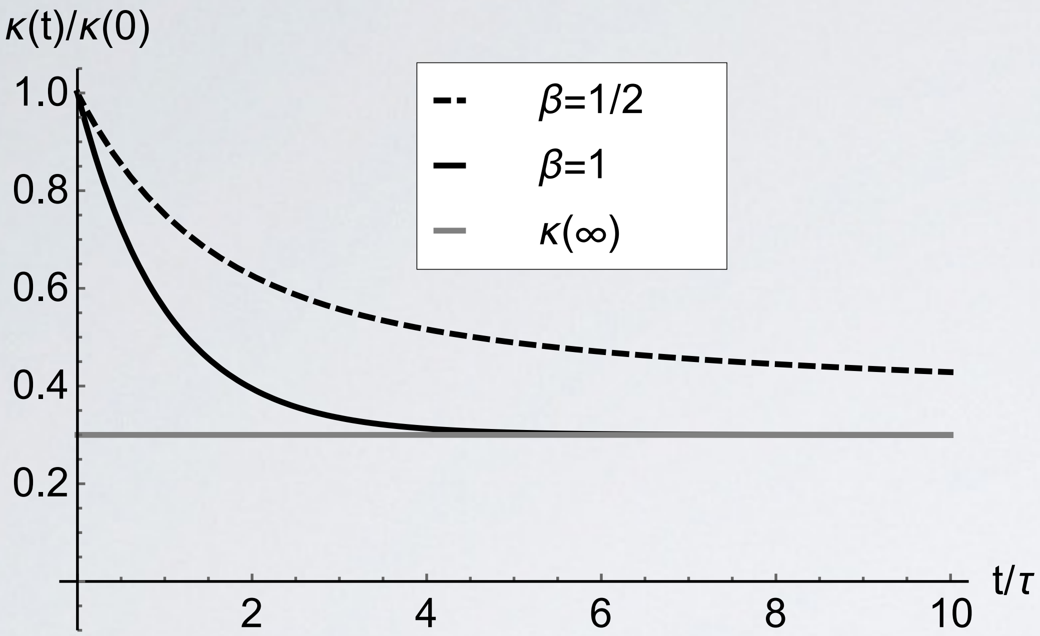
$$\hat{\kappa}(s) \overset{s\to 0}{\sim} \frac{\langle v^2\rangle}{D_\alpha \Gamma(1+\alpha)} s^{\alpha-1} \overset{\alpha\to 0}{\rightarrow} \frac{\langle v^2\rangle}{\langle u^2\rangle}\frac{1}{s}$$

where $\langle u^2\rangle$ is the mean square position fluctuation.

$$\Rightarrow \quad \kappa(t) \overset{t\to\infty}{\sim} \frac{\langle \mathbf{v}^2\rangle}{\langle \mathbf{u}^2\rangle}$$

Plateau value

Scaling for a simple model

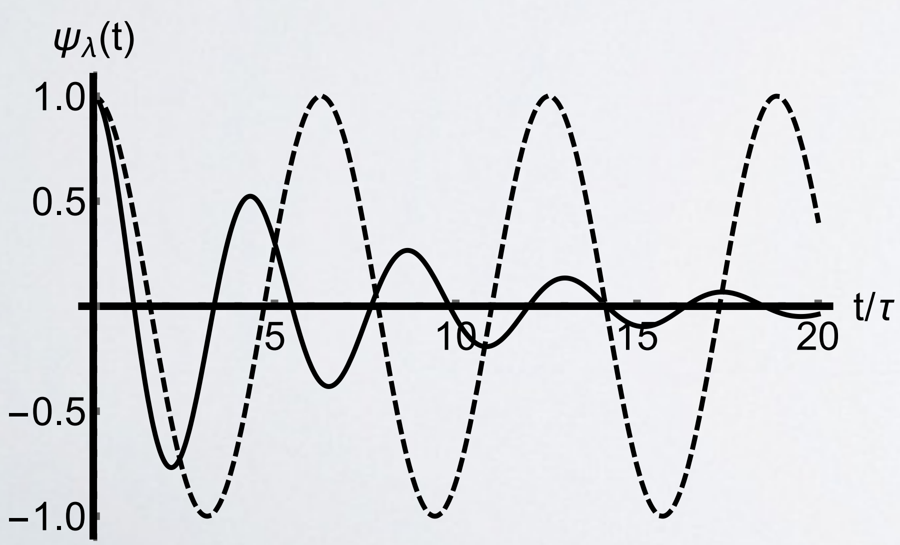


The memory function tends to a plateau

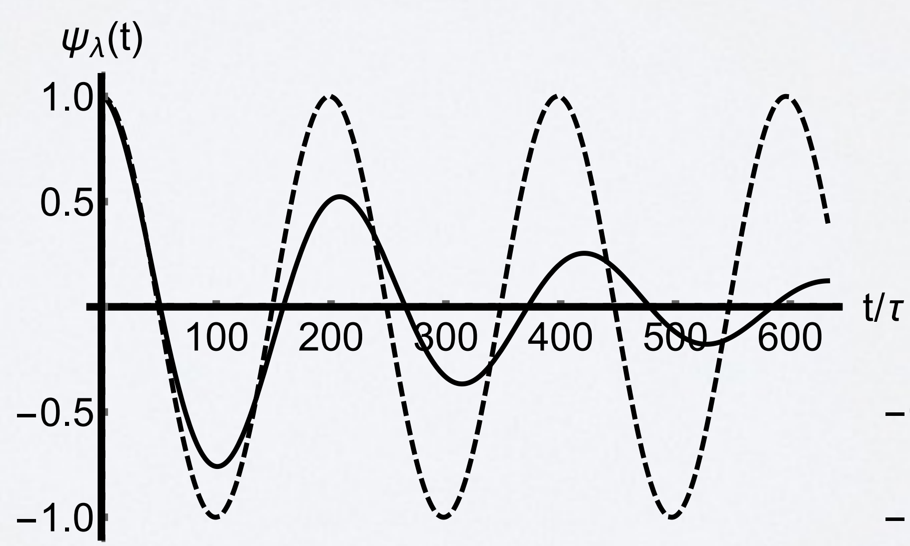
$$\kappa_c(t) = \Omega^2 \left\{ r + (1-r) M(\beta, 1, -t/\tau) \right\},$$

The description of (slow power law) demping implies a refined description of the anomalous form of the MSD

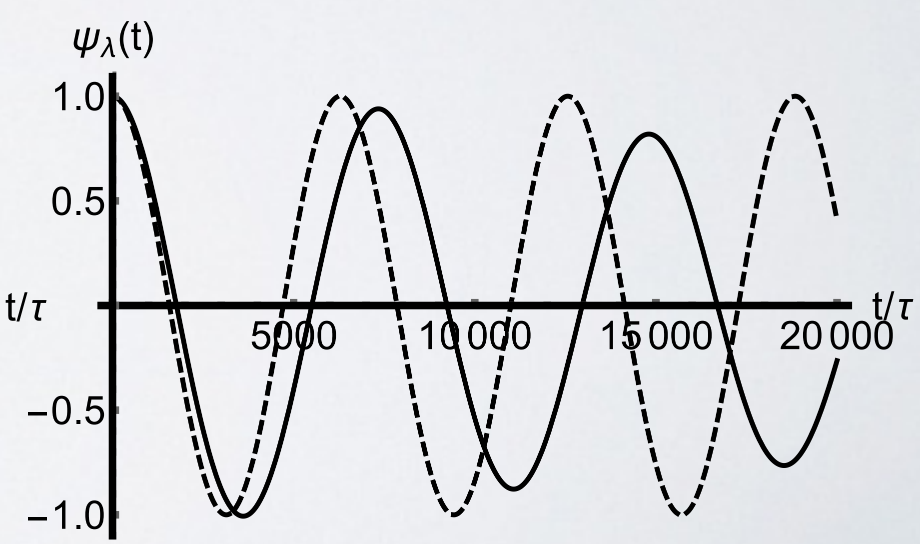
λ=1



λ=10^-3



λ=10^-6



Probing anomalous diffusion in velocity space

Defining

$$g(\omega) = \int_0^\infty dt\ \cos(\omega t) c_{vv}(t),$$

it follows from $W(t) \overset{t\to\infty}{\sim} 2D_\alpha t^\alpha$ that

$$g(\omega) \overset{\omega\to 0}{\sim} \omega^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) \Gamma(\alpha+1) D_\alpha.$$

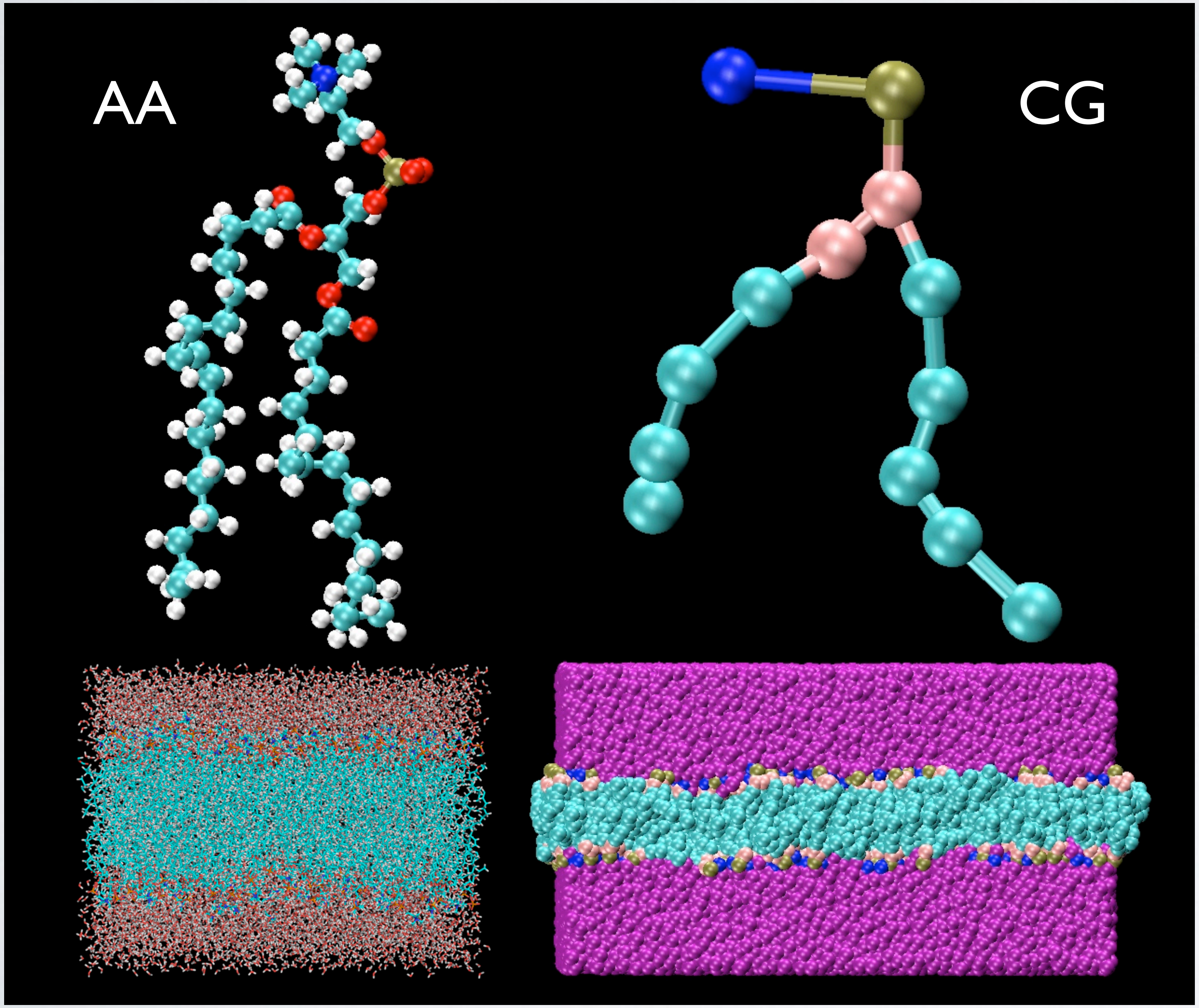
The fractional diffusion constant is thus obtained through

$$D_\alpha = \lim_{\omega\to 0} \frac{\omega^{\alpha-1} g(\omega)}{\sin\left(\frac{\pi\alpha}{2}\right)\Gamma(\alpha+1)}.$$

For $\alpha = 1$ the Kubo formula $D = \int_0^\infty dt\, c_{vv}(\omega)$ is retrieved.

Comparing all-atom (OPLS) and coarse-grained (MARTINI) force field for POPC

Thesis Slawomir Stachura, TBP



All atom (AA):

274 POPC lipids in 10 471 water molecules (OPLS)

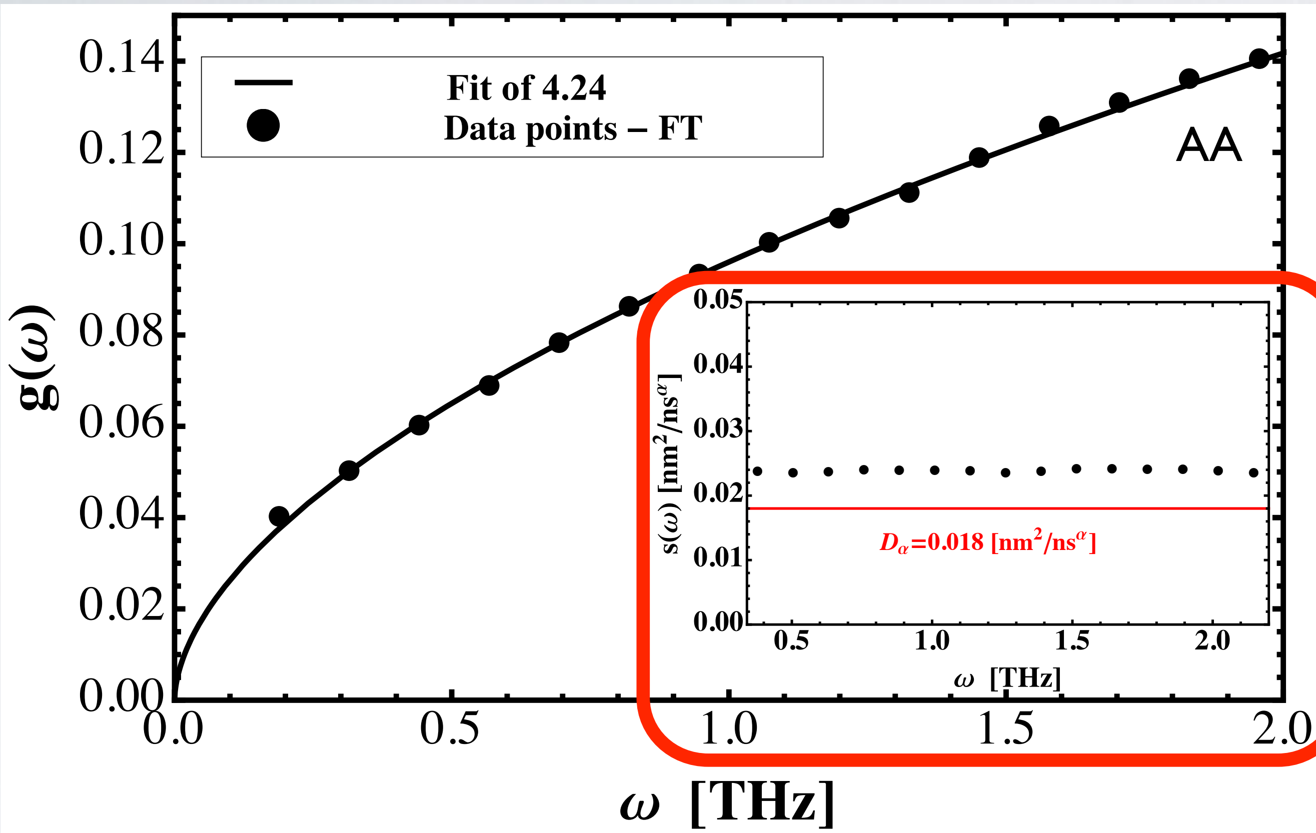
Coarse Grained (CG):

2033 POPC lipids in 231 808 water molecules (MARTINI)

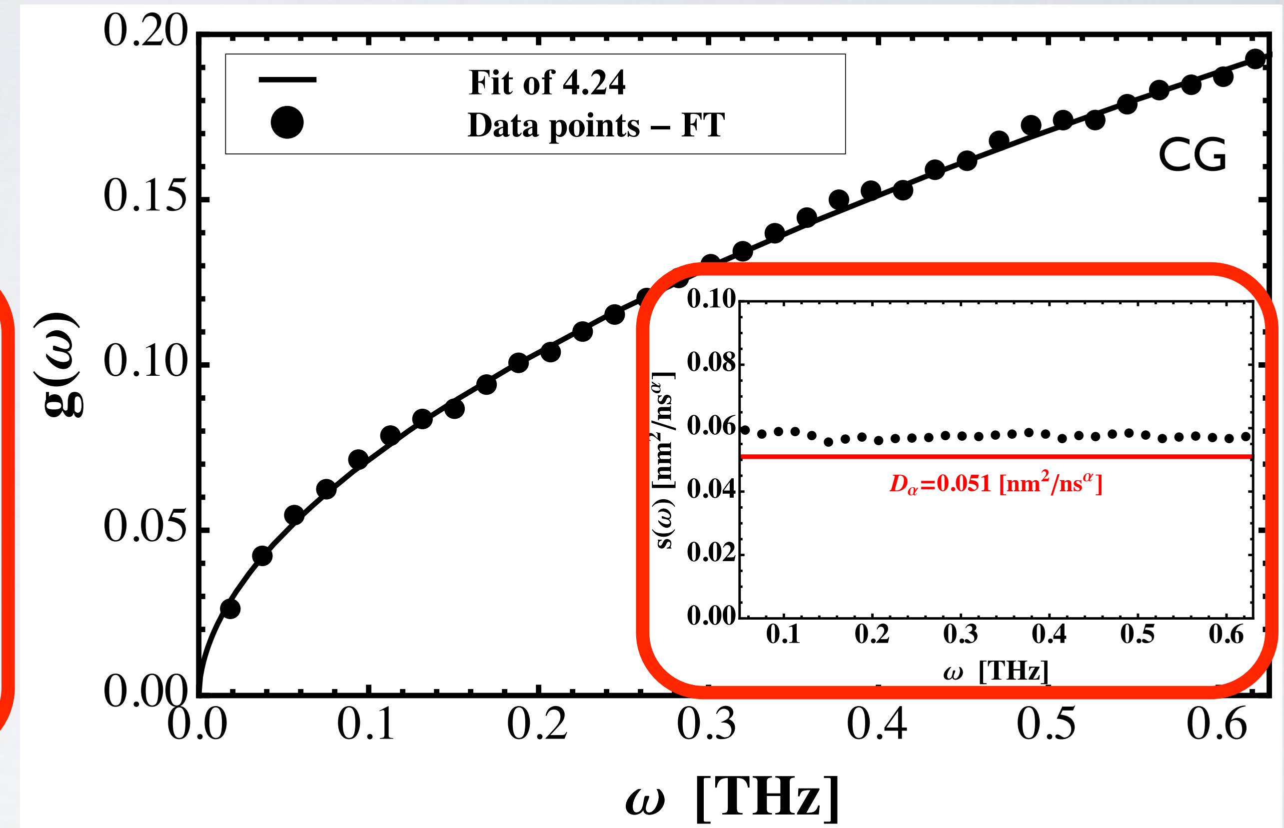
1. Marrink, et al. J Phys Chem B 111, 7812–7824 (2007).
2. de Jong, D. H. et al. JCTC 9, 687–697 (2012).

Density of states g(ω)

all atom



coarse grained



$$s(\omega) = \frac{\omega^{\alpha-1} g(\omega)}{\sin\left(\frac{\pi\alpha}{2}\right)\Gamma(\alpha+1)}$$

Remark: The Martini force field leads to ≈ 4 x faster diffusion!

CONCLUSIONS

- The combination of physical models (GLE) and **asymptotic analysis yields** insight into the origin anomalous diffusion : The decay of the local cage of neighbors represented by a memory function defines the type of diffusion.
- Time scale separation through scaling of the memory function leads to exact VACFs for normal and anomalous diffusion.
- Anomalous diffusion can be probed in frequency space and is accessible to spectroscopic experiments (neutron scattering).

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http://dirac.cnrs-orleans.fr/sputnik/home/