Probing anomalous diffusion in frequency space

Numerical experiments with MD simulations

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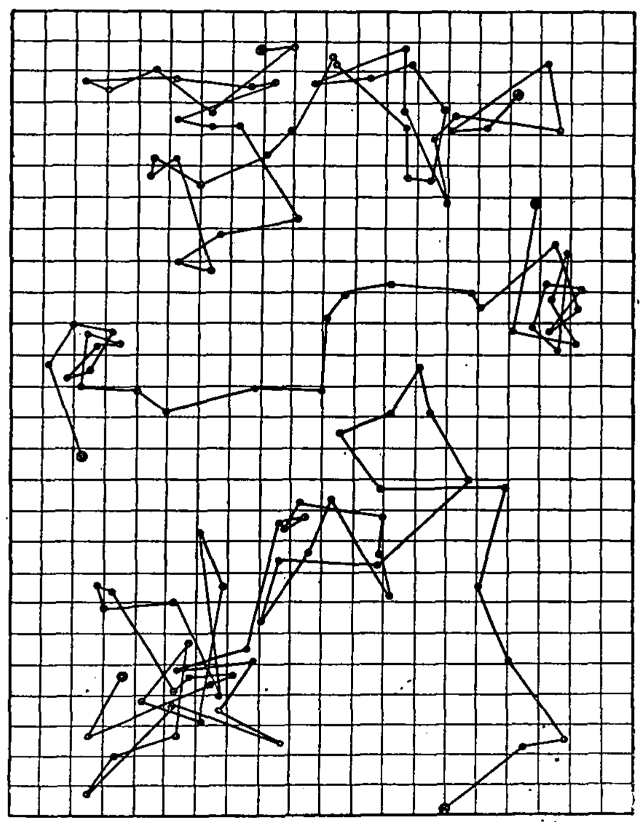
Diffusion and many-particle dynamics

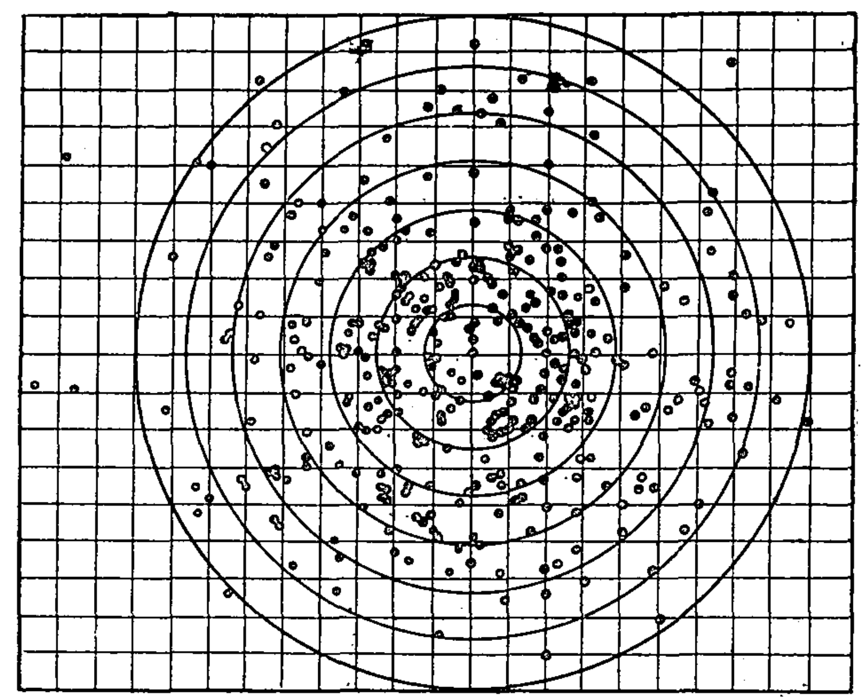
MOUVEMENT BROWNIEN ET RÉALITÉ MOLÉCULAIRE;

PAR M. JEAN PERRIN.



$$\xi^2 = \tau \frac{RT}{N} \frac{1}{3\pi a \zeta}$$

Fig. 7.



Ici encore le contrôle de la loi de répartition peut être quantitatif. Si, en effet, on admet la loi de probabilité donnée pour une composante x, il est facile de voir que la probabilité pour qu'un déplacement horizontal ait une longueur comprise entre r et $r + dr$ est donnée par l'expression

$$\frac{1}{2\pi\xi^2} e^{-\frac{r^2}{2\xi^2}} 2\pi r\, dr,$$

Annales de Chimie et de Physique, vol. 18, p. 5 (1909)

Diffusion models

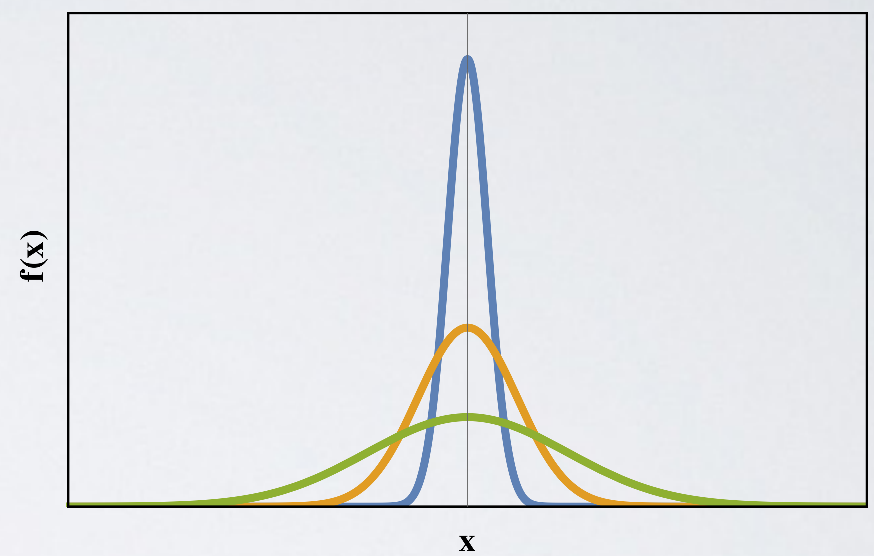
Diffusion equation

$$\frac{\partial}{\partial t} f(\boldsymbol{r},t) = D\Delta f(\boldsymbol{r},t)$$

A. Einstein, Annalen Der Physik 322, 549 (1905).

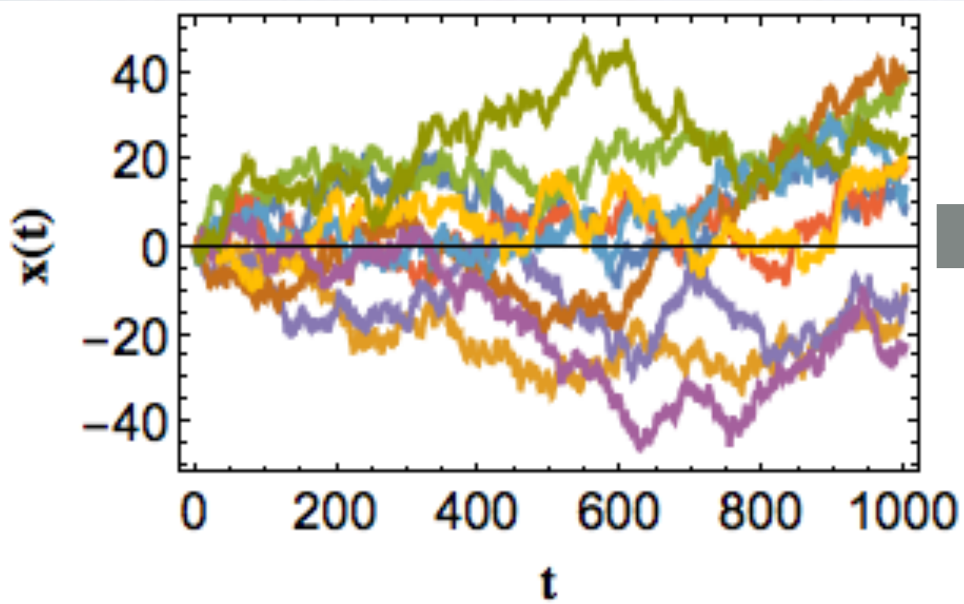
M. Von Smoluchowski, Annalen Der Physik 326, 756 (1906).

Distribution/spread



Stochastic process

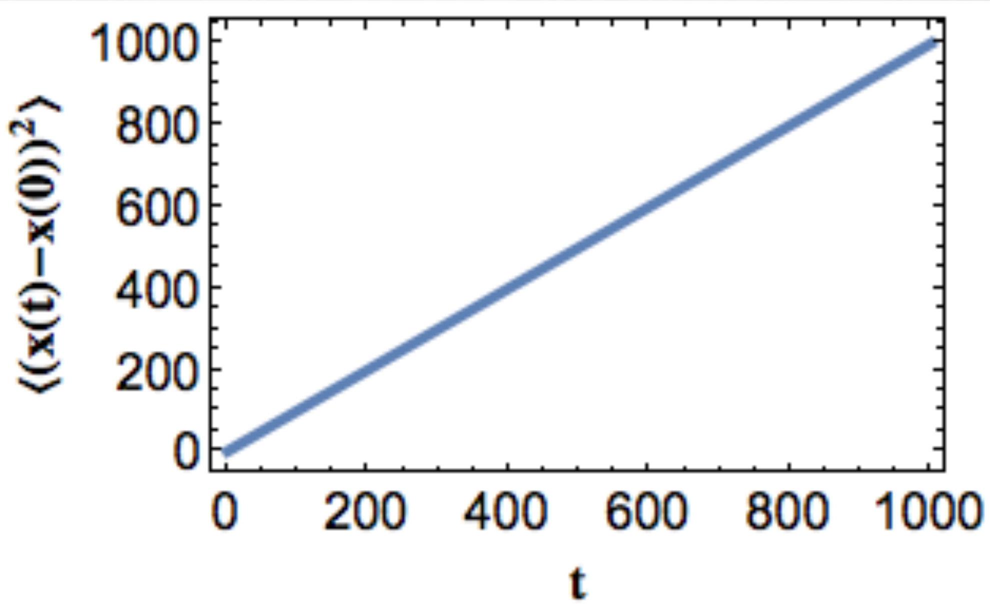
(1d Brownian Motion)



N. Wiener, Journal of Mathematics and Physics 2, 131 (1923).

Mean square displacement

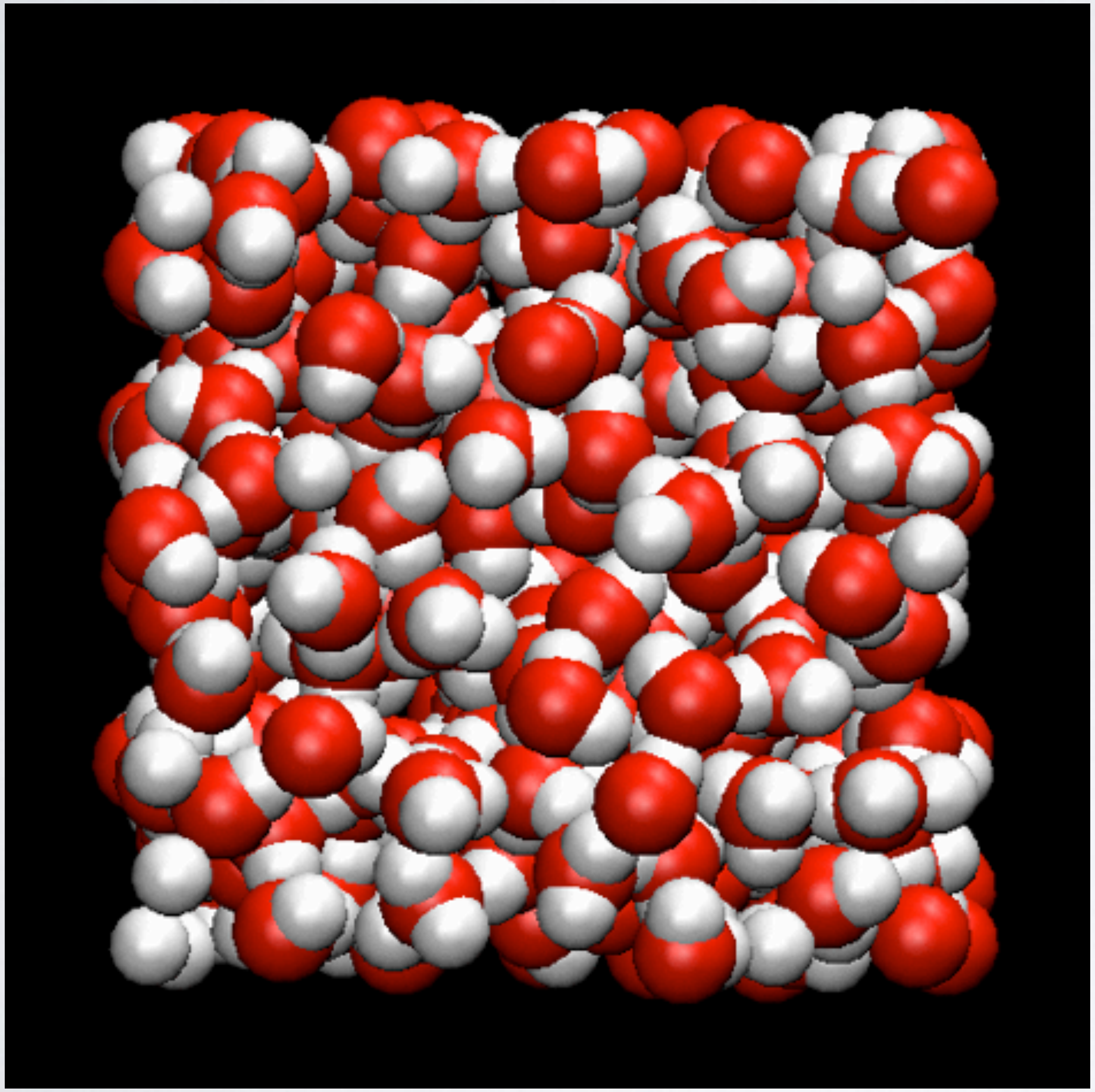
$$W(t) \equiv \langle (x(t) - x(0))^2 \rangle = 2Dt$$



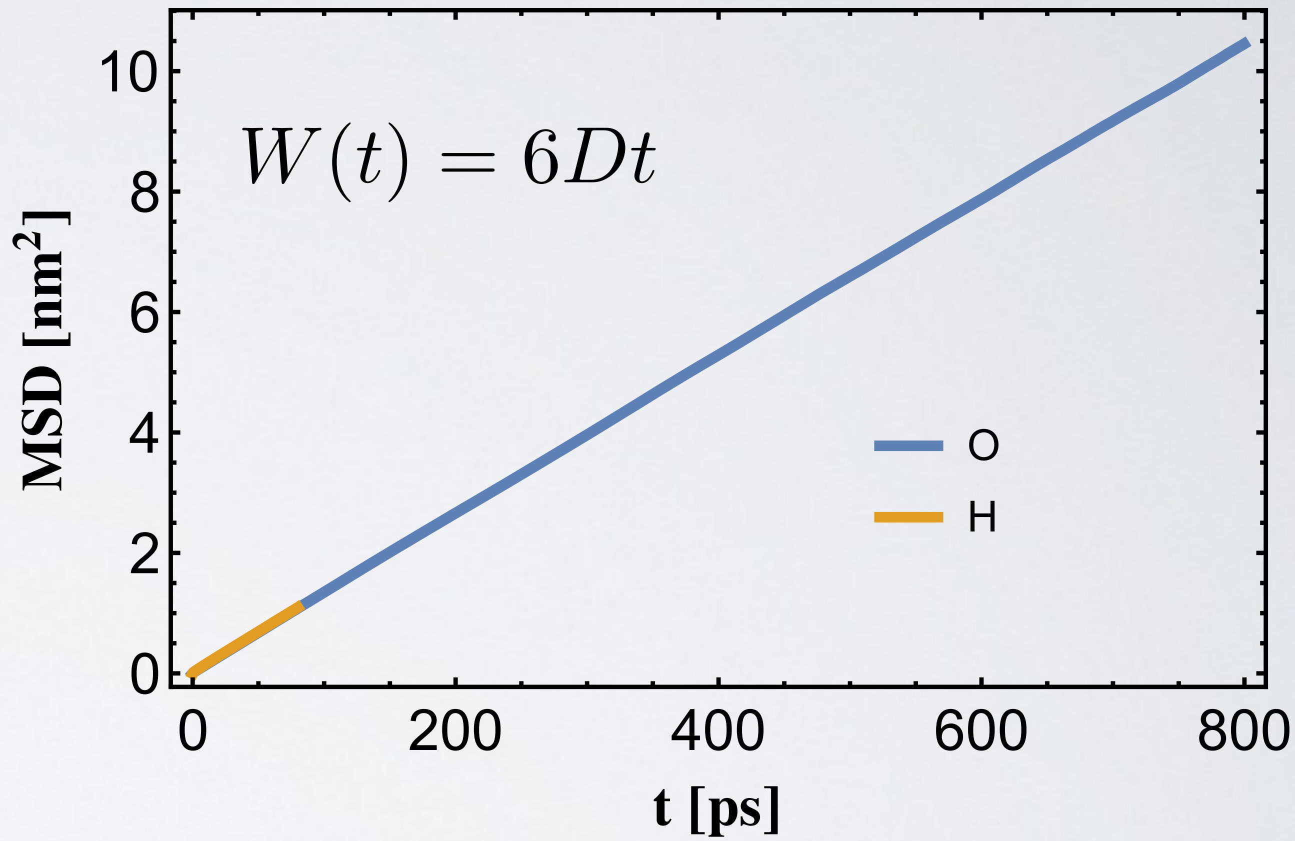
Diffusion of water molecules by MD simulations

Molecular dynamics simulation
SPC/E model, T = 300 K, p = 1 atm

H.J.C. Berendsen, et al, J Chem Phys 81, 3684 (1984).



$$W(n) \approx \frac{1}{N_t - |n|} \sum_{k=0}^{N_t-|n|-1} |\mathbf{x}(k+n) - \mathbf{x}(k)|^2$$



$$D = 2.17 \times 10^{-5} \mathrm{cm}^2/\mathrm{s}$$

$$D_{\mathrm{exp}} = 2.30 \times 10^{-5} \mathrm{cm}^2/\mathrm{s} \;\; [1]$$

[1] K. Krynicki, C. D. Green, and D. W. Sawyer, Faraday Discuss. Chem. Soc. 66, 199, (1978)

Relating diffusion to microscopic dynamics

$$x(t) - x(0) = \int_0^t dx(\tau) \overset{v(t)=\dot{x}(t)}{=} \int_0^t d\tau v(\tau)$$

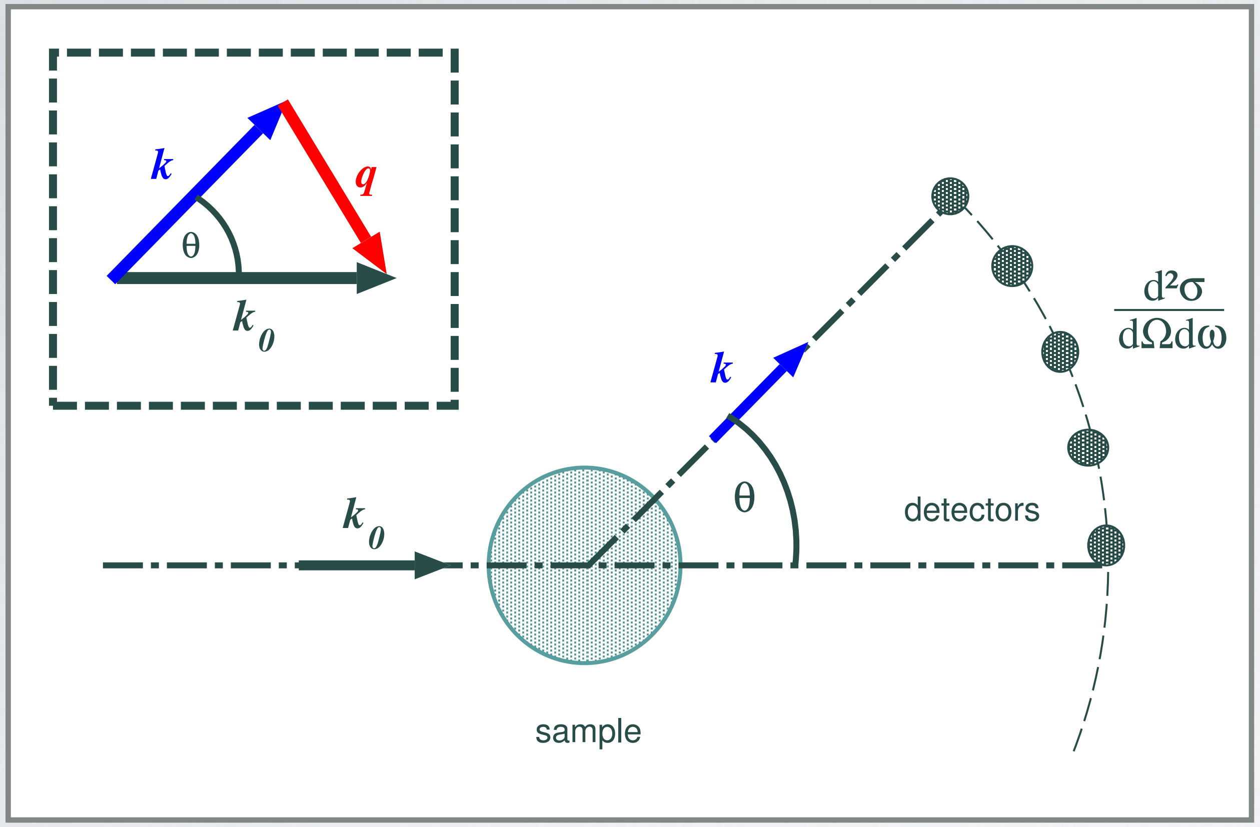
$$\boxed{\underbrace{\langle (x(t) - x(0))^2 \rangle}_{W(t)} = 2 \int_0^t d\tau \, (t - \tau) \, \underbrace{\langle v(\tau) v(0) \rangle}_{c_{vv}(\tau)}}$$

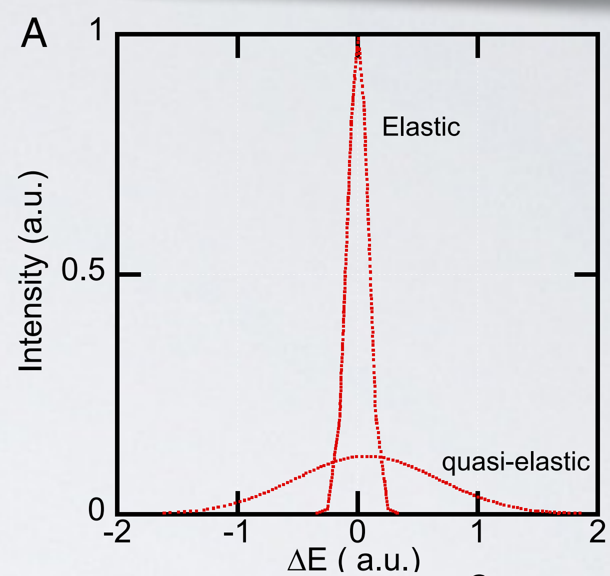
The Fourier-transformed VACF (Density of States=**DOS**)

$$g(\omega) \equiv \int_0^\infty dt \, \cos \omega t \, \langle v(t) v(0) \rangle$$

is accessible by **neutron scattering** and **MD « experiments »**

DOS from neutron scattering experiments





momentum transfer:

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k} = (\mathbf{p}_0 - \mathbf{p})/\hbar$$

energy transfer:

$$\omega = (E_0 - E)/\hbar$$

$$\frac{d^2\sigma}{d\Omega dw} = \frac{k}{k_0} S(\mathbf{q},\omega)$$

$$\boxed{g(\omega) = \lim_{q\to 0} \frac{\omega^2}{q^2} S(q,\omega)}$$

$$S(\mathbf{q},\omega) \approx \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\left\langle e^{-i\mathbf{q}\cdot(\mathbf{r}(t)-\mathbf{r}(0))}\right\rangle$$

GHz-THz freq. scale
ps-ns time scale

VACF long time tails from neutron scattering experiments

VOLUME 58, NUMBER 18 PHYSICAL REVIEW LETTERS 4 MAY 1987

Experimental Evidence for the Long-Time Decay of the Velocity Autocorrelation in Liquid Sodium

Chr. Morkel, Chr. Gronemeyer, and W. Gläser [(a)]
Physik-Department, Technische Uiversität München, D-8046 Garching, West Germany

and

J. Bosse
Fachbereich Physik, Freie Universität Berlin, D-1000 Berlin 33, West Germany
(Received 22 December 1986)

Incoherent inelastic neutron-scattering experiments on liquid sodium at high temperature revealed that atomic motions in simple liquids are governed by hydrodynamic shear modes leading to measurable deviations from Fick's law of diffusion. The experiments for the first time verify earlier predictions of a "long-time tail" behavior of the velocity-autocorrelation function of liquid particles as derived from computer-simulation data and theory. A proper analysis of the experimental data demonstrates the existence of a corresponding low-frequency cusp in the velocity-autocorrelation spectrum.

PHYSICAL REVIEW A VOLUME 39, NUMBER 5 MARCH 1, 1989

Velocity autocorrelation function of simple dense fluids from neutron scattering experiments

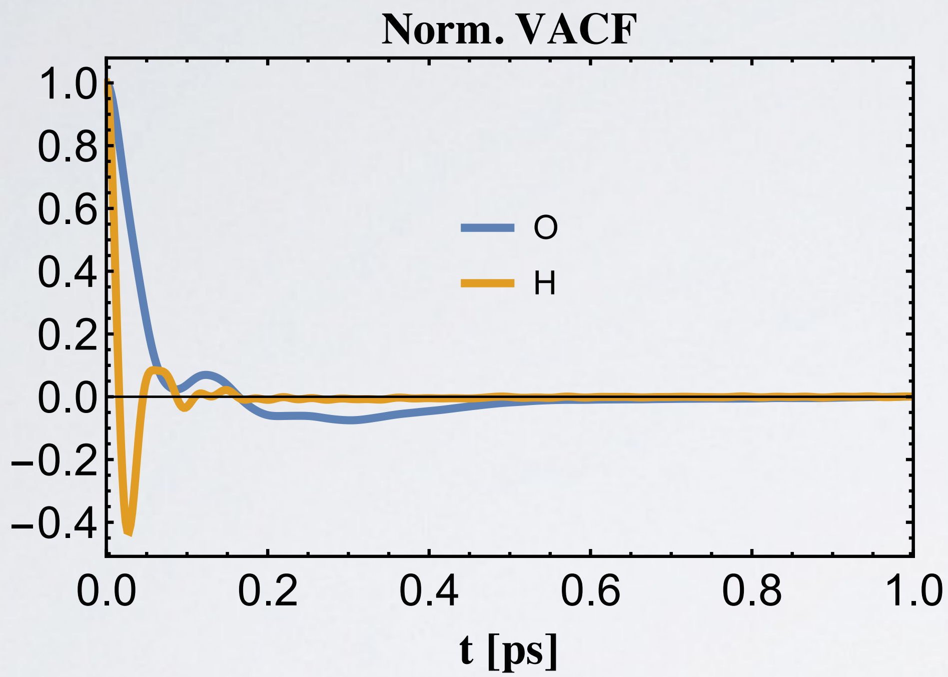
Wouter Montfrooij and Ignatz de Schepper
Interfaculty Reactor Institute, Delft University of Technology, 2629 JB Delft, The Netherlands
(Received 12 October 1988)

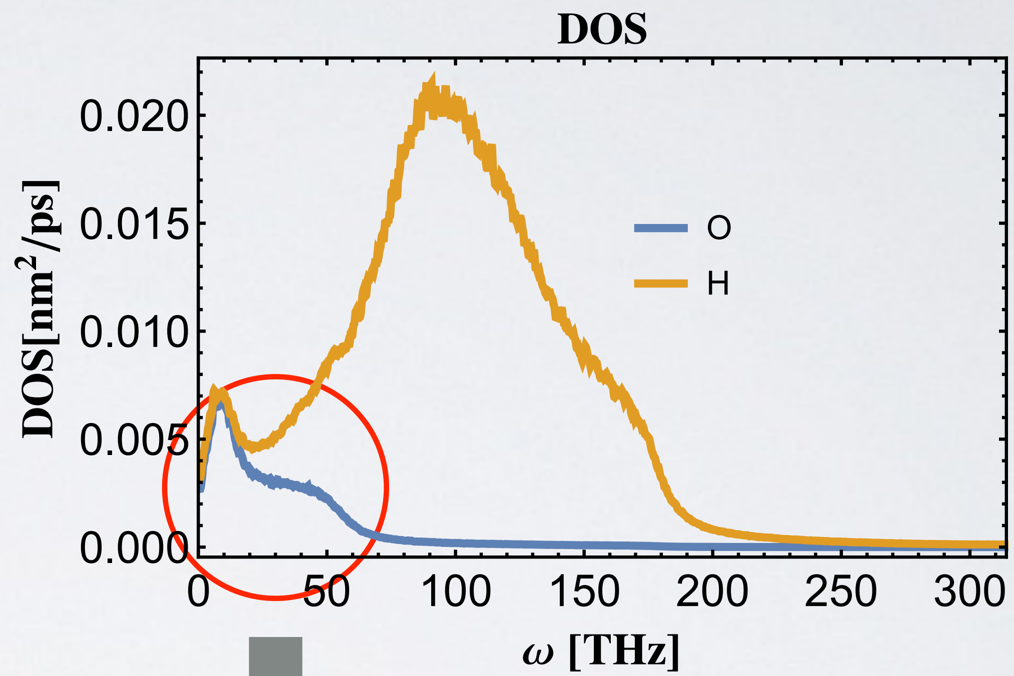
By molecular dynamics for a Lennard-Jones fluid at $n^* = 0.55$ and $T^* = 3.2$ we determine both the Fourier-transformed velocity autocorrelation function $z(\omega)$ and the incoherent neutron scattering functions $S_s(k,\omega)$. $z(\omega)$ (including the "long-time-tail" singularity near $\omega = 0$) can be obtained from $S_s(k,\omega)$ by extrapolation to $k = 0$, only when data for $S_s(k,\omega)$ are included with k smaller than $(\omega/2D)^{1/2}$, with D the self-diffusion coefficient.

Density of states and diffusion coefficient

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

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

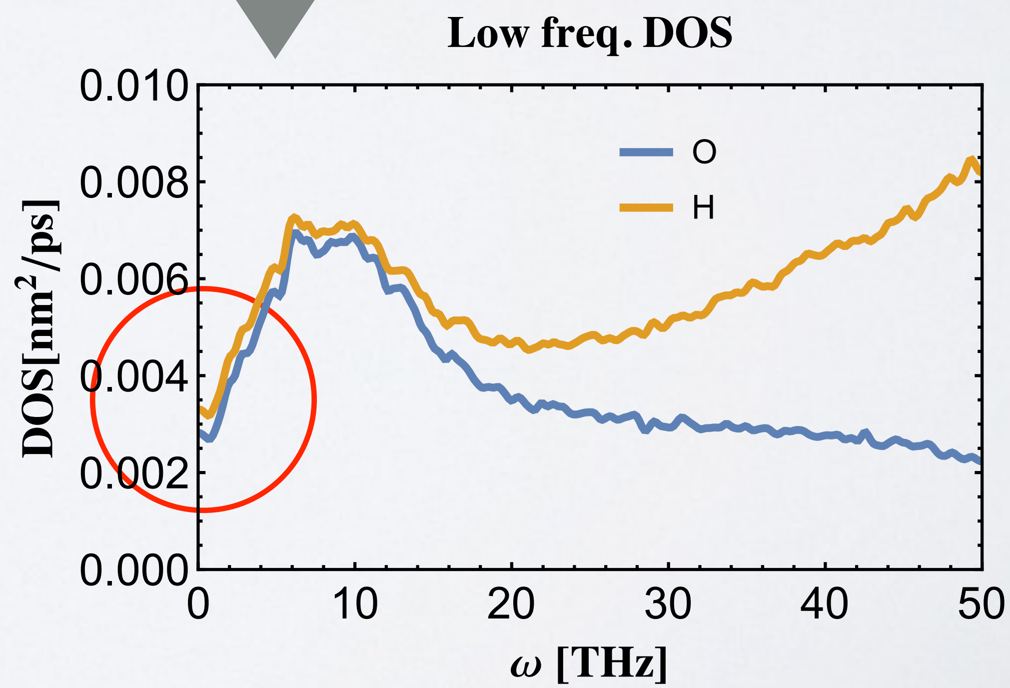




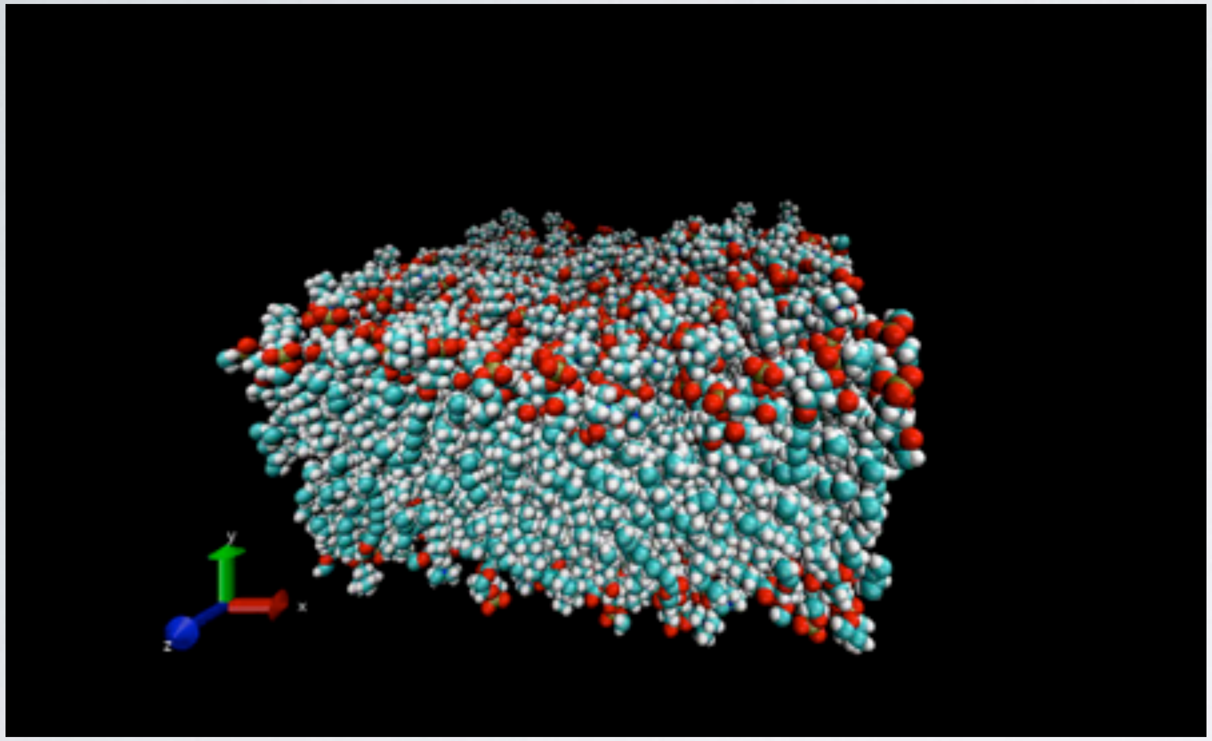
$$D = \int_0^\infty c_{vv}(t) = g(0)$$

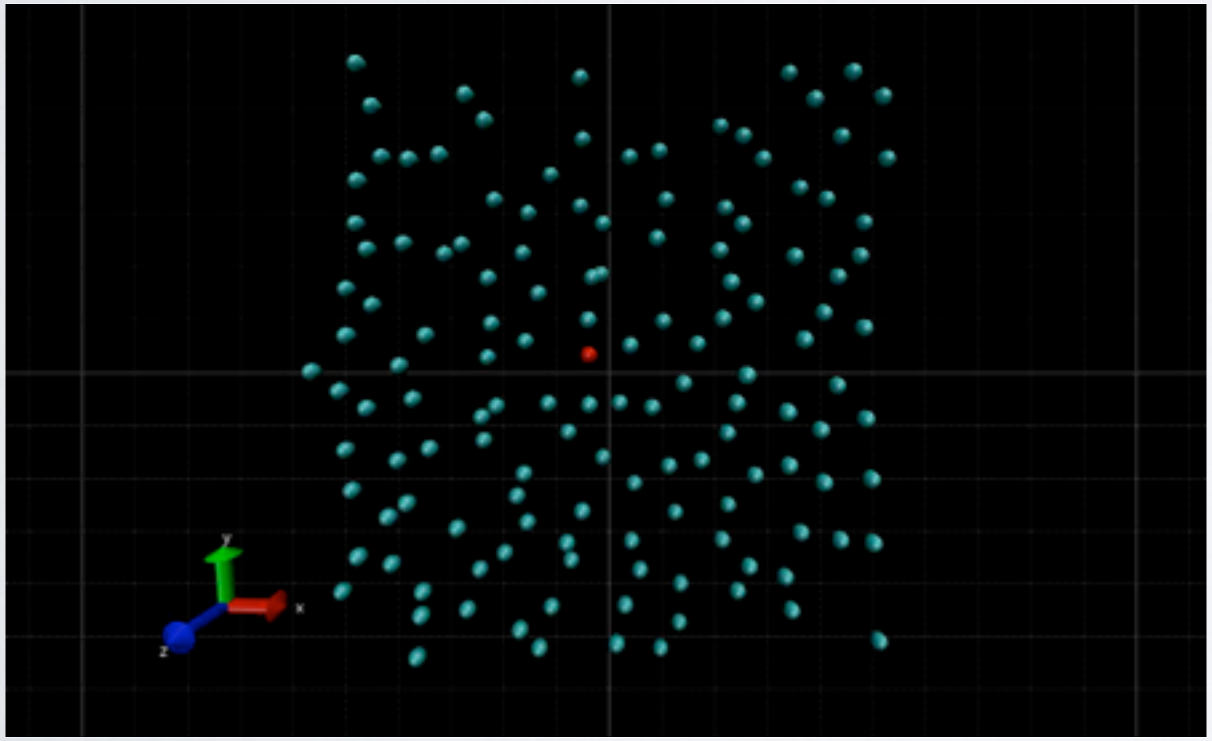
$$D_O \approx 2.8 \times 10^{-5} \mathrm{cm}^2/\mathrm{s}$$

$$D_H \approx 3.3 \times 10^{-5} \mathrm{cm}^2/\mathrm{s}$$



Anomalous diffusion

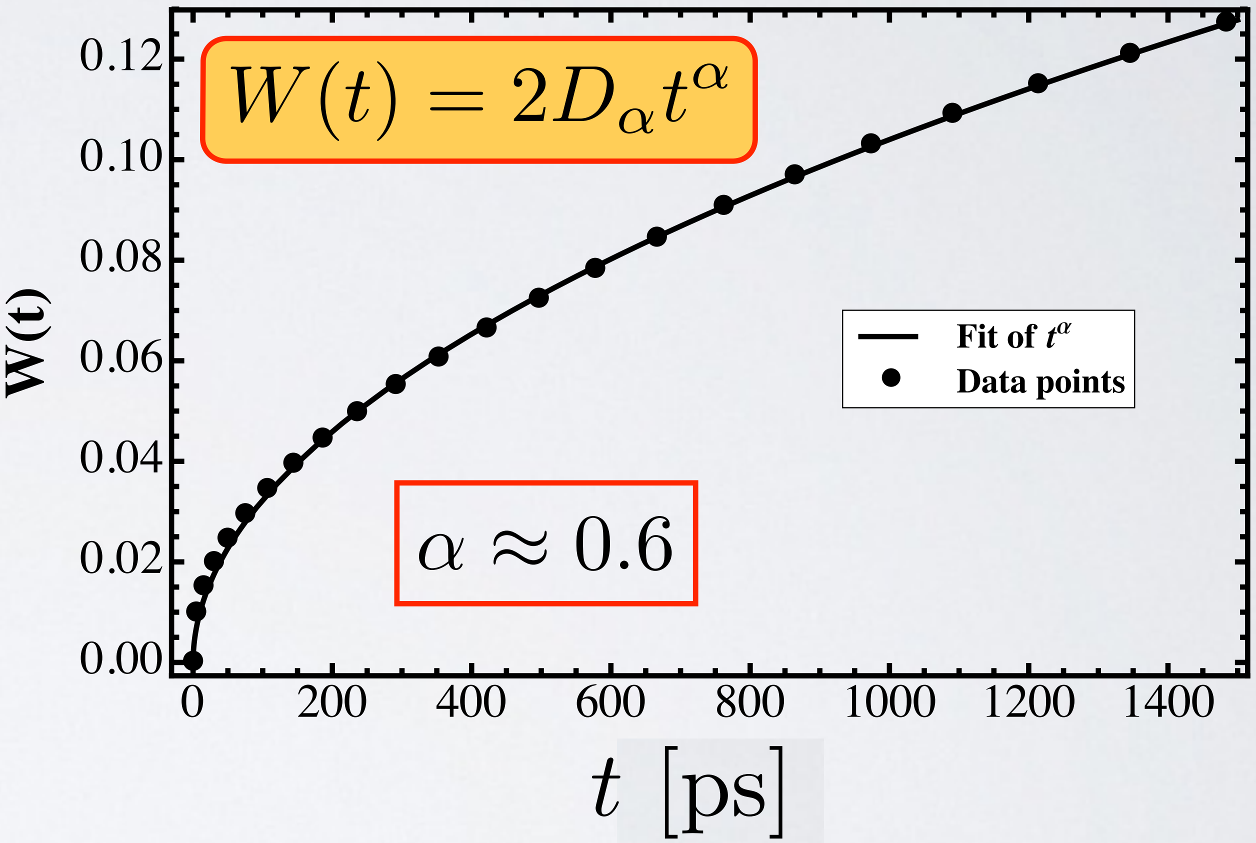




Molecular dynamics simulation of a POPC bilayer

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

MSD for lateral diffusion



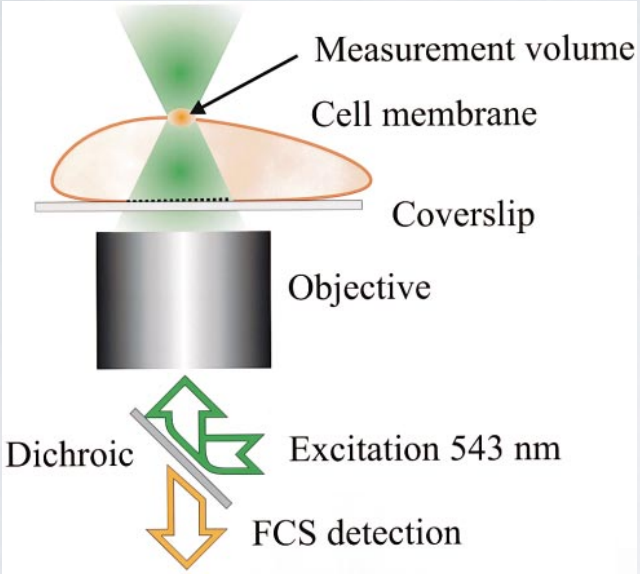
ps-ns time scale

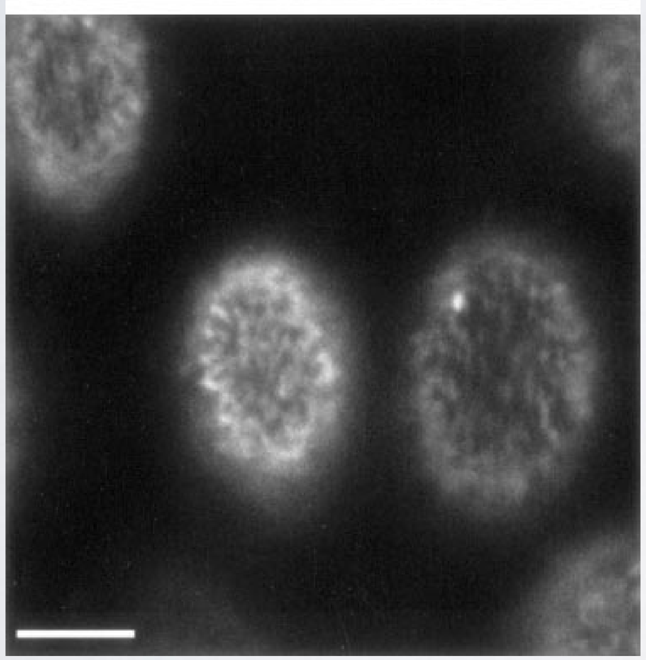
See also

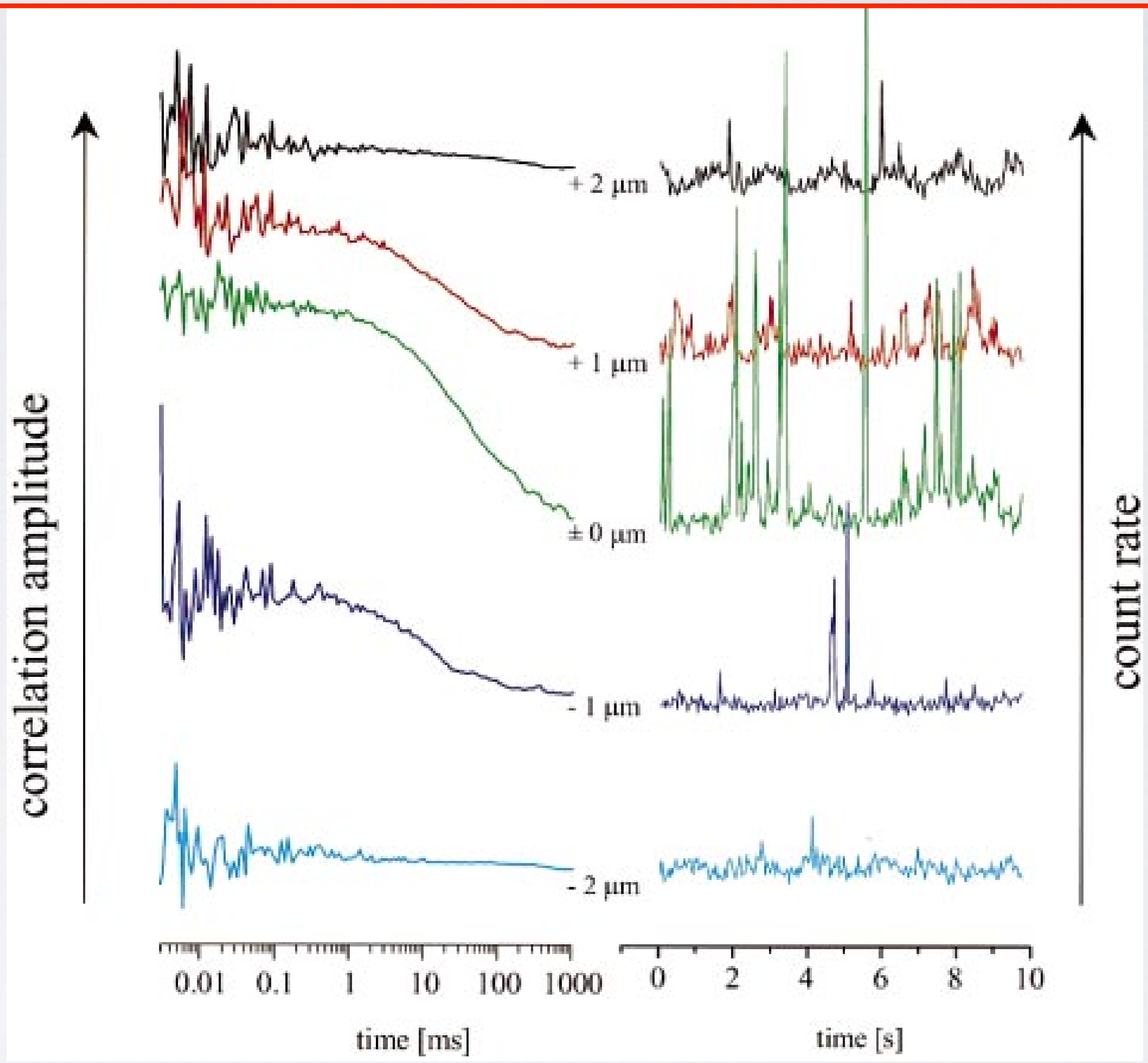
E. Flenner, J. Das, M. Rheinstädter, and I. Kosztin, Phys Rev E 79, 11907 (2009).
G.R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula, J Chem Phys 135, 141105 (2011).
J.H. Jeon, H. Monne, M. Javanainen, and R. Metzler, Phys Rev Lett (2012).

Anomalous diffusion of lipids observed by FCS

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







$$\boxed{\sigma^2(t) \propto t^\alpha}$$

$0 < \alpha < 1$
(subdiffusion)

ms-s time scale

Some numbers ....

- $D_\alpha = 0.088\,\mathrm{nm}^2/\mathrm{ns}^\alpha$, $\alpha = 0.74$, for DLPC

FCS: ms-s time scale

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

- $D_\alpha = 0.101\,\mathrm{nm}^2/\mathrm{ns}^\alpha$, $\alpha = 0.55$, for DOPC

MD: ps-ns time scale

G.R. Kneller, K. Baczynski, and M. Pasenkiewicz-Gierula, JCP 135, 141105 (2011)

- $D_\alpha = 0.018\,\mathrm{nm}^2/\mathrm{ns}^\alpha$, $\alpha = 0.67$, for POPC

MD: ps-ns time scale

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

☞ Self-similarity; Measure the same phenomenon on different time scales

Extending the diffusion models (0<α<2)

Fractional diffusion equation

$$\frac{\partial}{\partial t} f(\boldsymbol{r},t) = \partial_t^{1-\alpha} \{D_\alpha \Delta f(\boldsymbol{r},t)\}$$

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

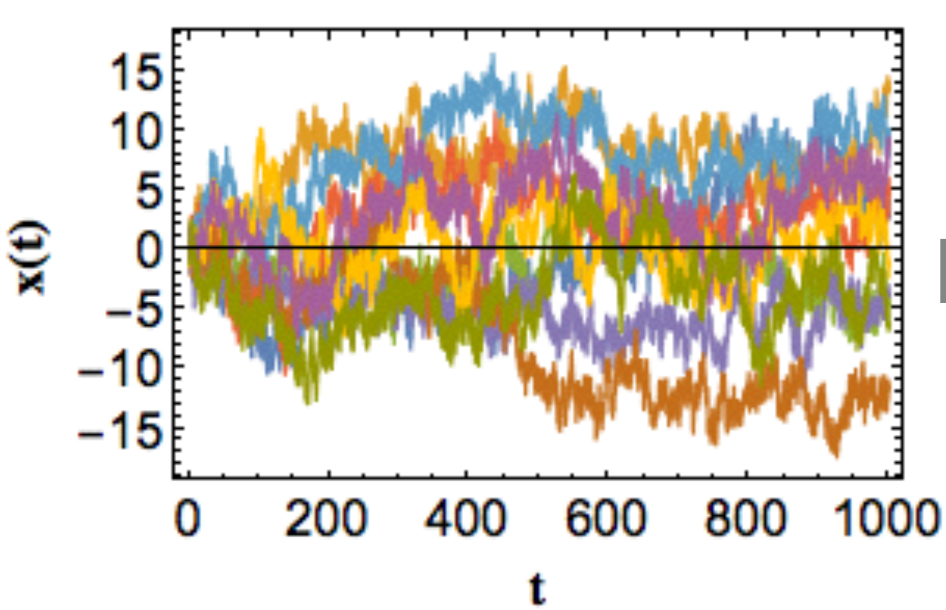
Spread

$$\sigma^2(t) := \frac{\int d^n r\, |\boldsymbol{r}|^2 f(\boldsymbol{r},t)}{\int d^n r\, f(\boldsymbol{r},t)} = \frac{2nD_\alpha t^\alpha}{\Gamma(1+\alpha)}$$

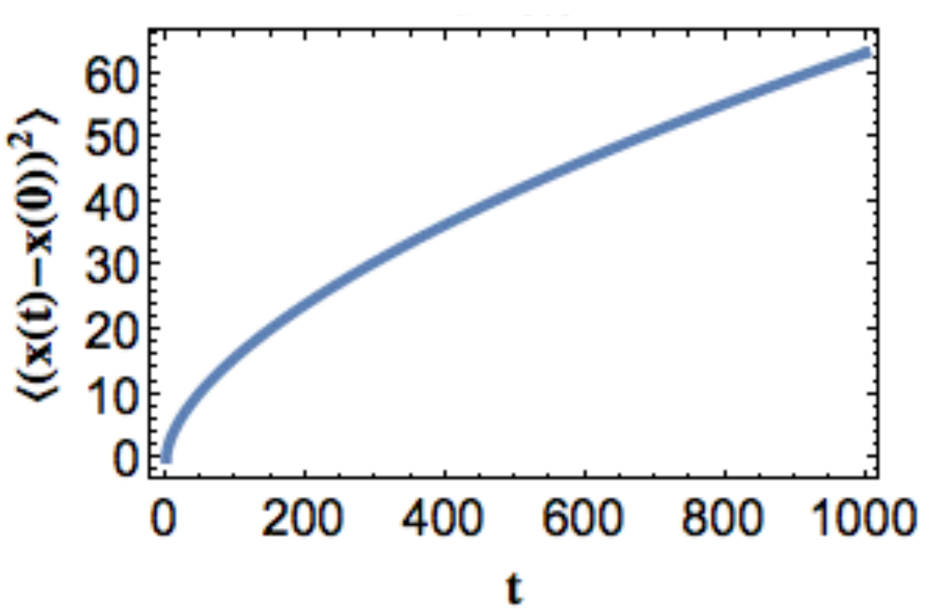
fractional Brownian motion

$$W(t) \equiv \langle (x(t)-x(0))^2 \rangle = 2D_\alpha t^\alpha$$

$\alpha = 0.6$



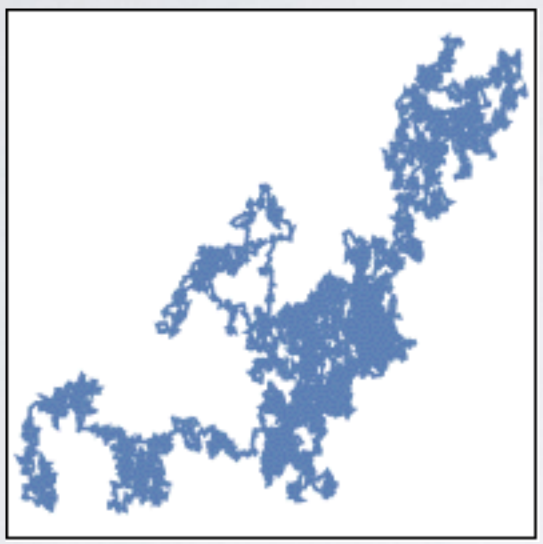
$\alpha = 0.6$



1 R. Metzler and J. Klafter, Phys Rep 339, 1 (2000).
2 I.M. Sokolov, Soft Matter 8, 9043 (2012).

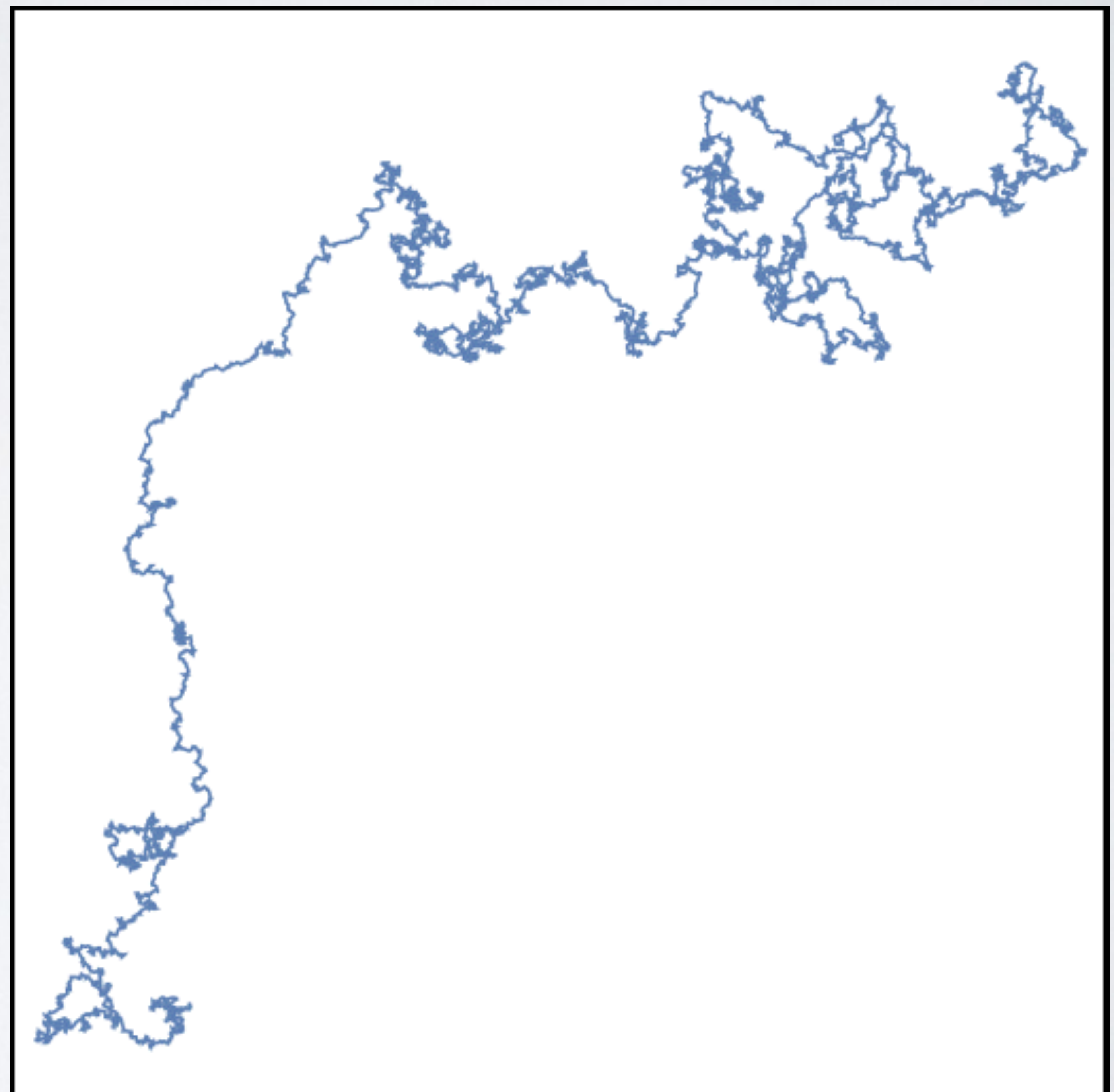
Exploring space (10^4 steps fBM)

$\alpha = 1$



$\alpha = 0.6$

$\alpha = 1.4$



Exploring low-frequency spectra

☞ How to relate the fractional diffusion exponent and constant in a « model-free way » to the low-frequency DOS?

☞ Estimate the frequency range where this is approach is valid.

A remark on van Hove functions

$$S(\mathbf{q},\omega) \approx \frac{1}{2\pi}\int_{-\infty}^{+\infty}\int d^3r dt\, e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}G(\mathbf{r},t)$$

$$G(\mathbf{r},t)\frac{1}{(2\pi)^3}\int d^3q\, e^{-i\mathbf{q}\cdot\mathbf{r}}\left\langle e^{i\mathbf{q}\cdot(\mathbf{R}(t)-\mathbf{R}(0))}\right\rangle$$

Diffusion models

$$\frac{\partial}{\partial t}G(\mathbf{r},t) = \partial_t^{1-\alpha}\,\{D_\alpha \Delta\, G(\mathbf{r},t)\}\,, \quad 0<\alpha<2$$

There is no universal asymptotic (long time) expression for the full G(r,t) !

Low-frequency DOS from long-time MSD

$$W(t) = 2\int_0^t d\tau\,(t-\tau)c_{vv}(\tau) \Leftrightarrow \hat{W}(s) = \frac{2\hat{c}_{vv}(s)}{s^2}$$

$$\boxed{W(t) \overset{t\to\infty}{\sim} 2D_\alpha t^\alpha \Leftrightarrow \hat{W}(s) \overset{s\to 0}{\sim} 2D_\alpha \Gamma(\alpha+1)s^{-(\alpha+1)}}$$

$$\Leftrightarrow \quad \boxed{\hat{c}_{vv}(s) \overset{s\to 0}{\sim} \Gamma(\alpha+1)D_\alpha s^{1-\alpha}}$$

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

Karamata, Journal Für Die Reine Und Angewandte Mathematik (Crelle's Journal) 1931, 27 (1931).

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

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

Low frequency DOS

$$g(\omega) \equiv \int_0^\infty dt\, \cos\omega t\, c_{vv}(t) = \Re\{\hat{c}_{vv}(i\omega)\} \quad \boxed{(0 < \alpha \leq 1)}$$

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

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

$$g(0) \overset{\alpha\to 1}{=} \int_0^\infty dt\, c_{vv}(t) = D$$

VACF long-time tails

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

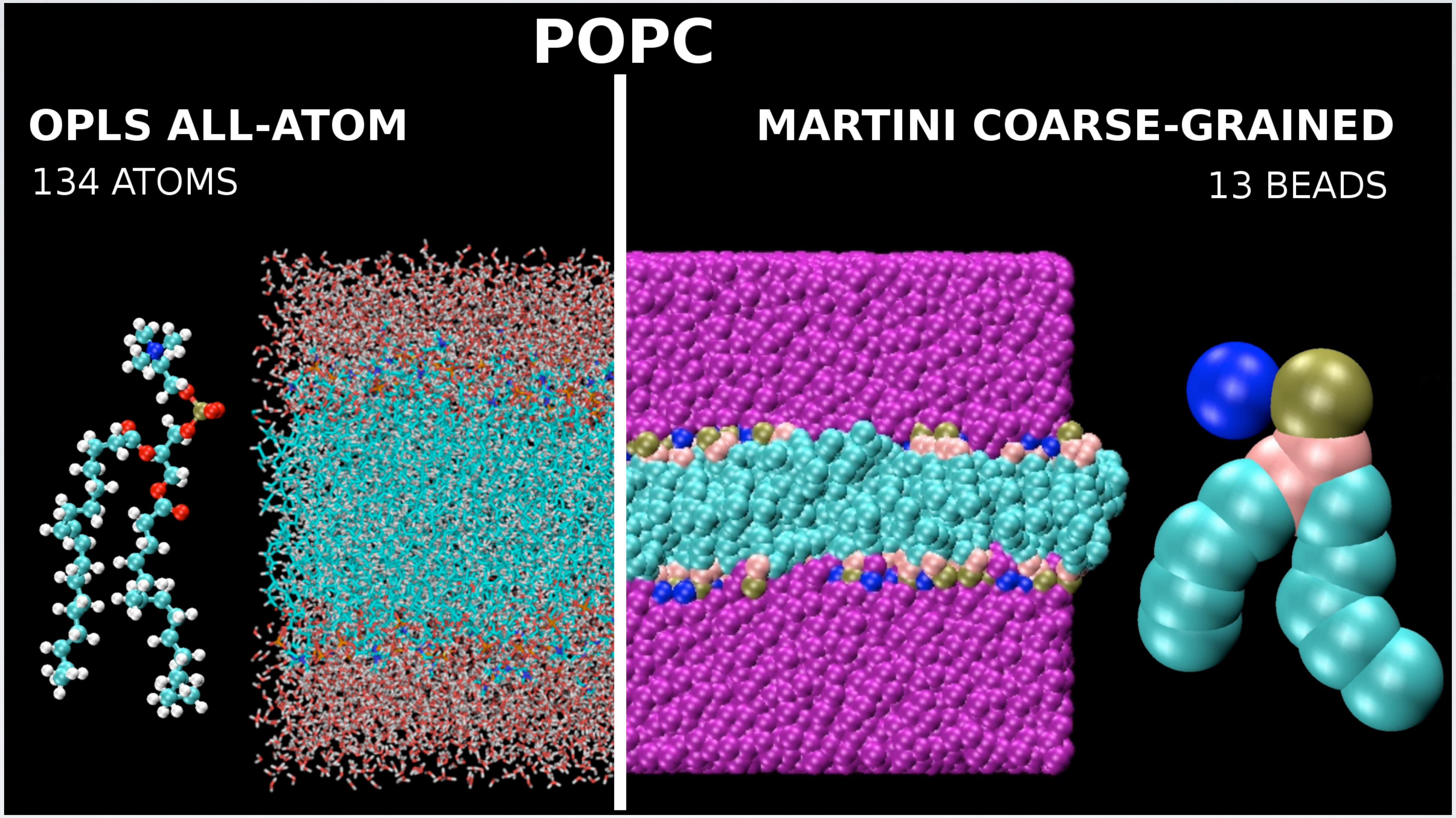
$$\frac{\hat{c}_{vv}(s)}{s} \overset{s\to 0}{\sim} \Gamma(\alpha+1) D_\alpha s^{-\alpha} \Leftrightarrow \int_0^t d\tau\, c_{vv}(\tau) \overset{t\to\infty}{\sim} D_\alpha\, \alpha\, t^{\alpha-1}$$

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

- Necessary for $0 < \alpha < 2$
- Necessary and sufficient for $1 < \alpha < 2$

$$\Rightarrow \quad D_\alpha = \frac{1}{\Gamma(1+\alpha)} \int_0^\infty dt\ {}_0\partial_t^{\alpha-1} c_{vv}(t) \quad (0 < \alpha < 2)$$

Simulation studies



T = 310 K, p = 1 atm, 150 ns,

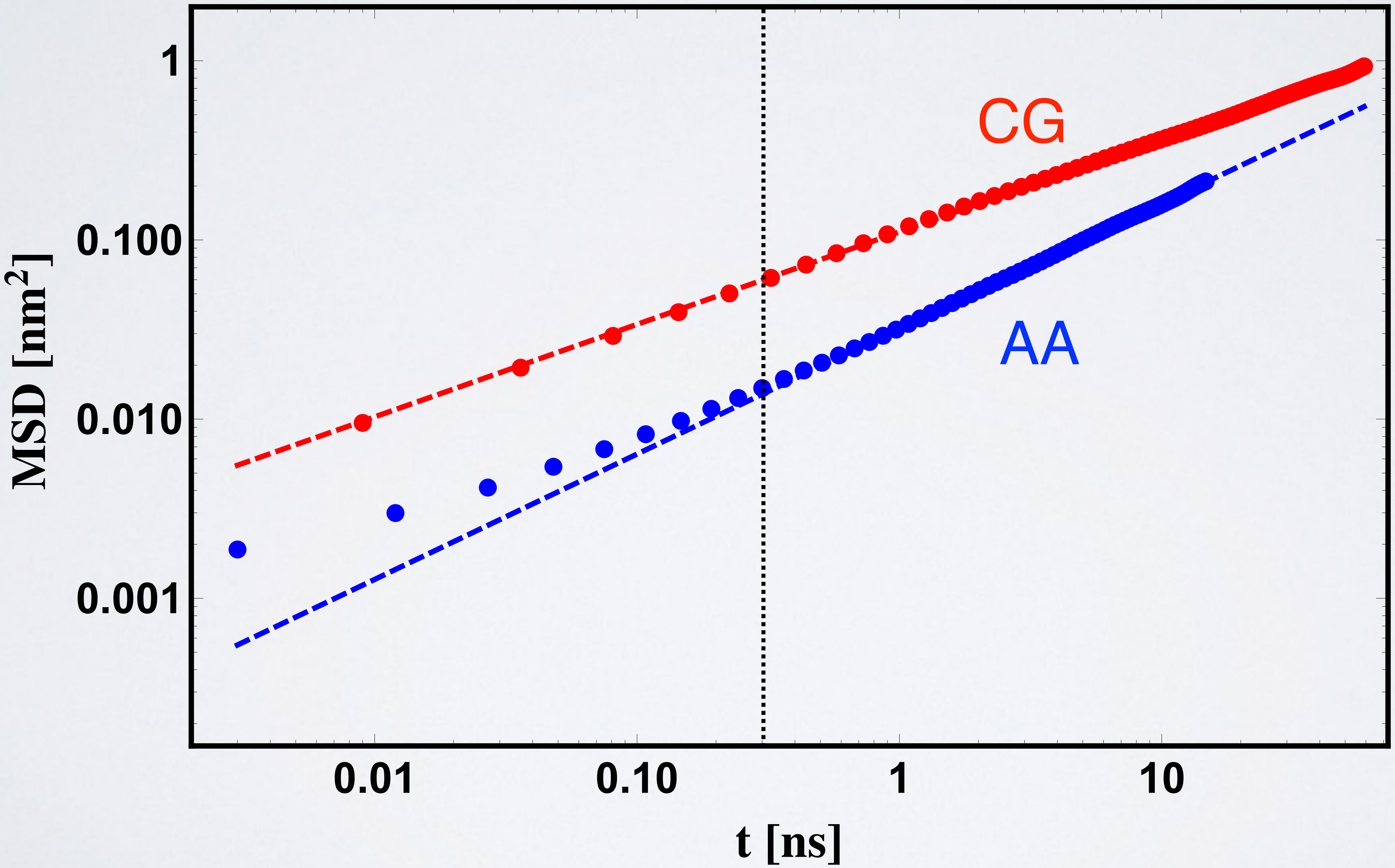
274 POPC lipid molecules
+ 10471 water molecules

T = 320 K, p = 1 atm, 600 ns,

2033 POPC lipid molecules
+ 231808 water molecules

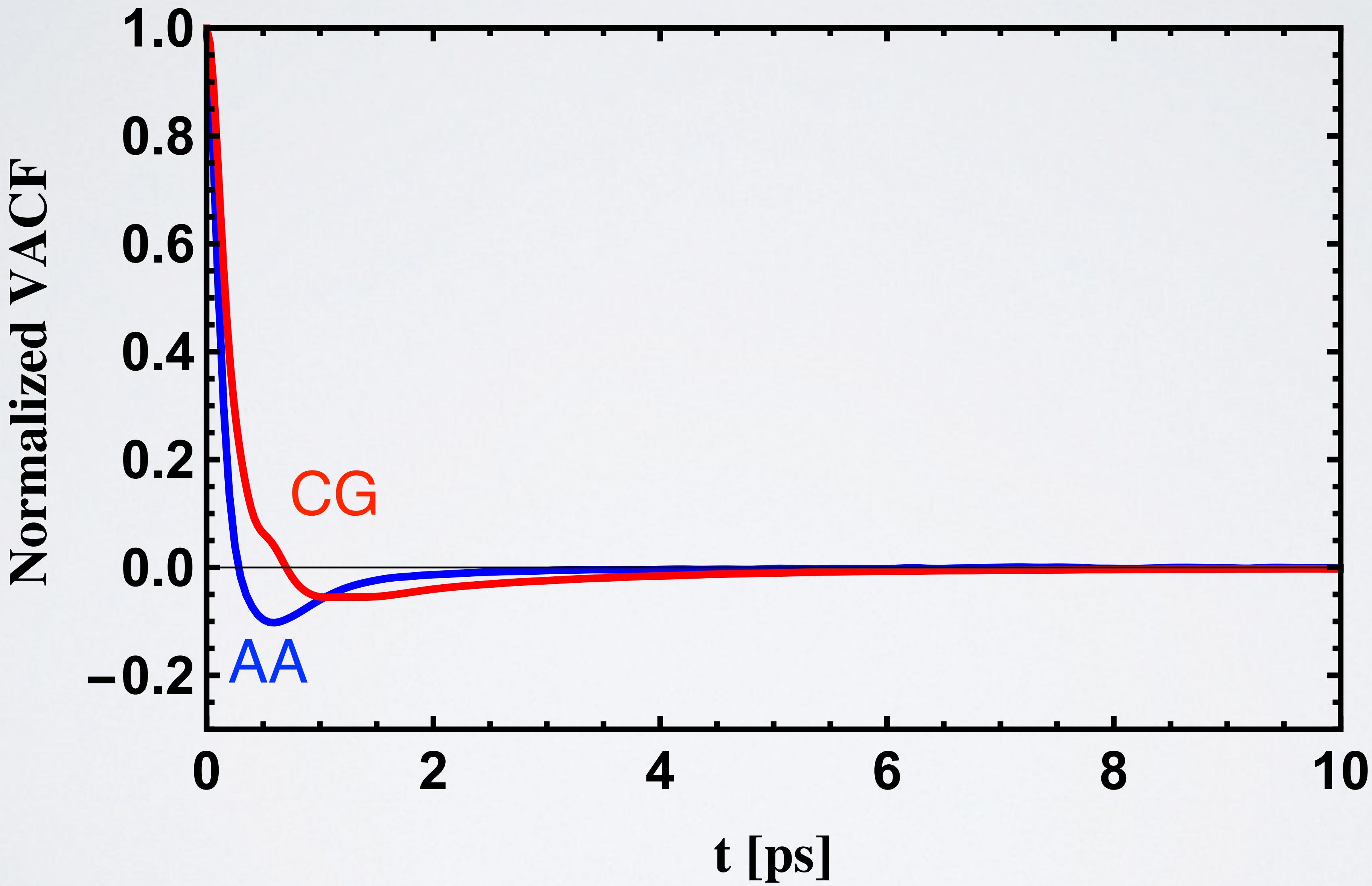
MSD

$$W(n) \approx \frac{1}{N_t - |n|} \sum_{k=0}^{N_t - |n| - 1} |\mathbf{x}(k+n) - \mathbf{x}(k)|^2$$



VACF

$$c_{vv}(n) \approx \frac{1}{N_t - |n|} \sum_{k=0}^{N_t-|n|-1} \mathbf{v}(k) \cdot \mathbf{v}(k+n)$$



☞ The max. lag time for the VACF is 500 ps.

DOS by windowed discrete FT

$$g(n) \approx \frac{\Delta t}{2} \sum_{k=-(N_t-1)}^{N_t-1} e^{-\frac{2\pi i n k}{2N_t-1}} w(k) c_{vv}(k)$$

$$w(t) = \exp\left(-t^2/(2\sigma_t^2)\right)$$

DOS by maximum entropy estimation

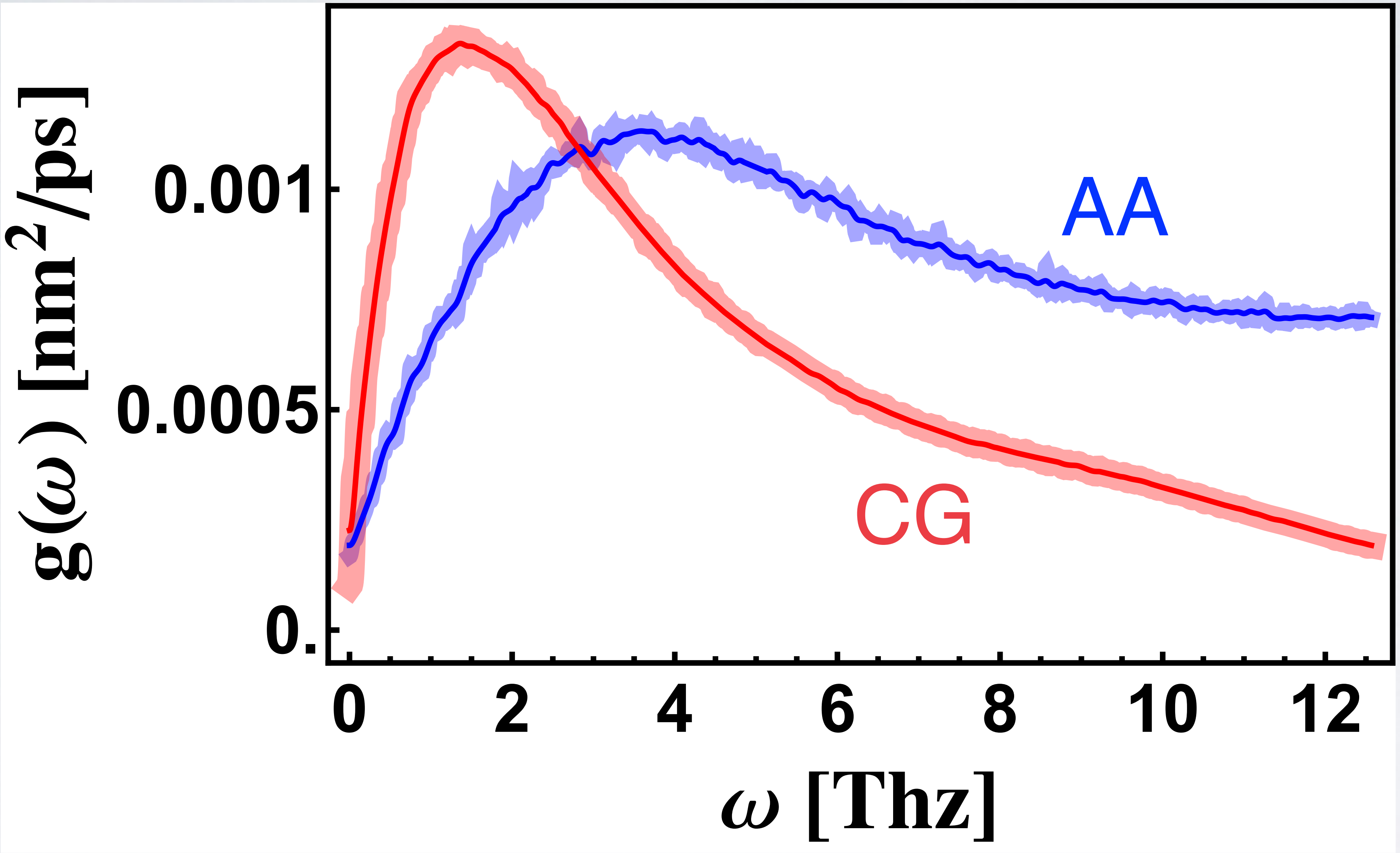
$$v(n) = \sum_{j=1}^{P} a_j^{(P)} v(n-j) + \epsilon(n)$$

Autoregressive process

$$\langle \epsilon(n)\epsilon(k)\rangle = \sigma_P^2 \delta_{nk}$$

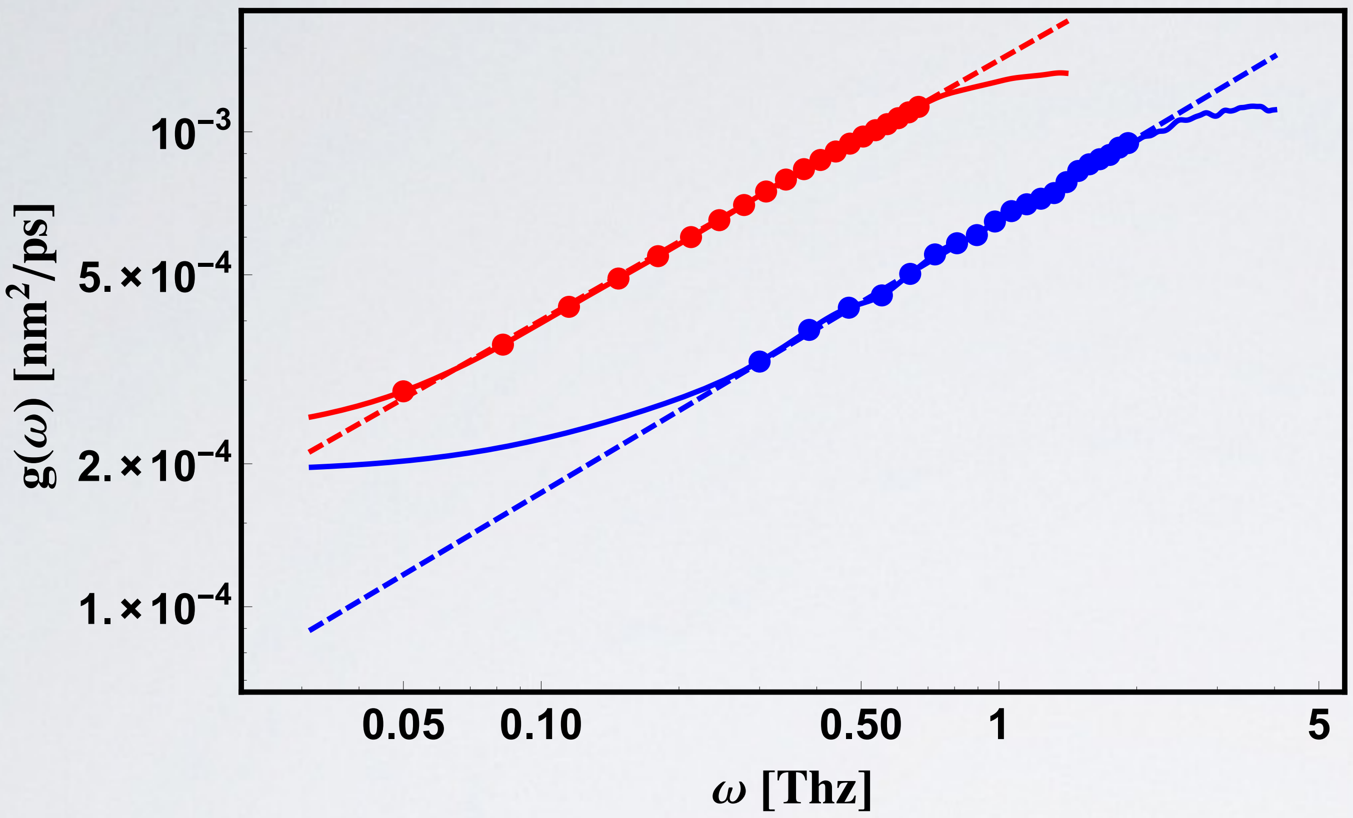
$$g(\omega) \approx \frac{\sigma_P^2 \Delta t}{2\left|1 - \sum_{k=1}^{P} a_k^{(P)} \exp(-i\omega k \Delta t)\right|^2}$$

DOS

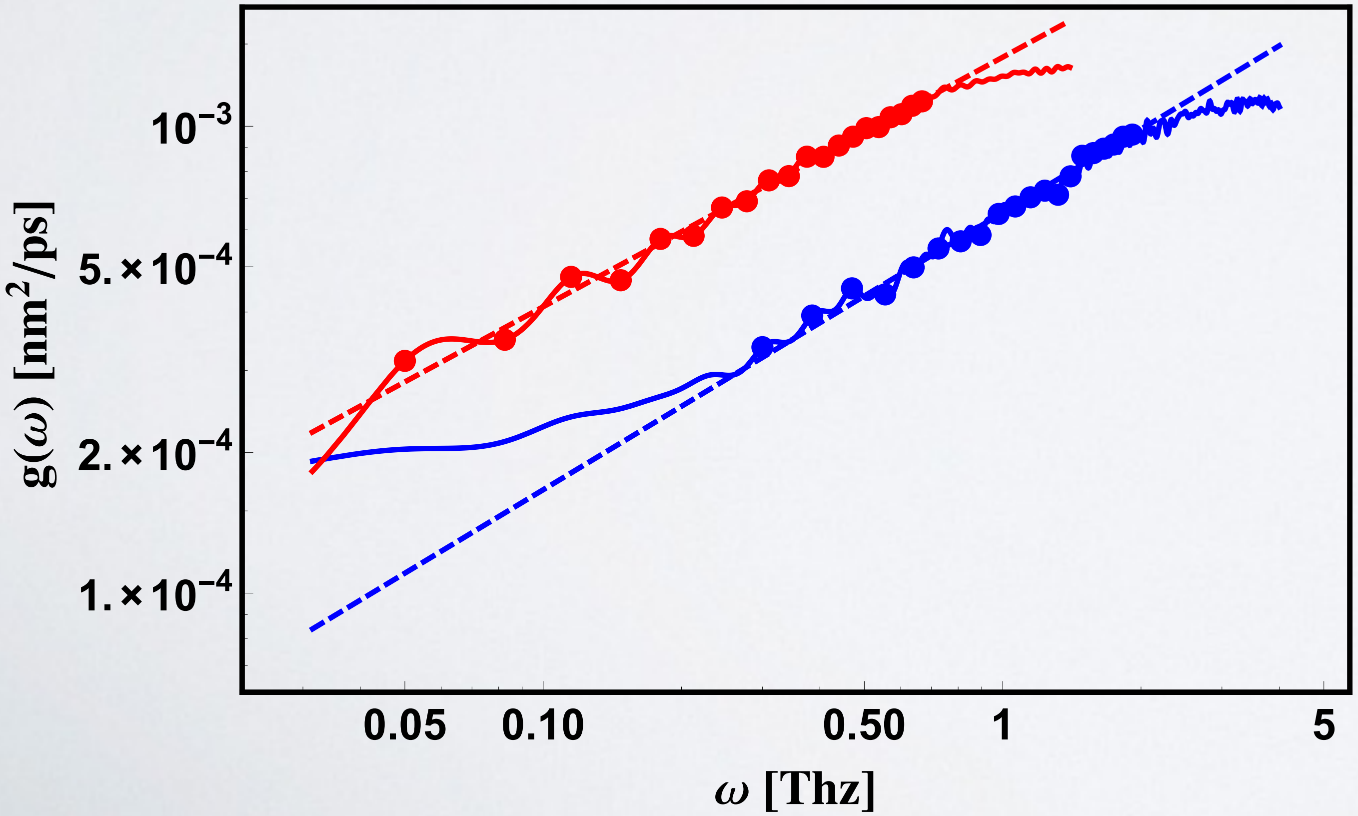


WDFT (thin lines) and MEE (blurred lines) give quad-identical results

Low-frequency DOS



Windowed discrete FT
(log-log plot)



Maximum entropy estimation
(log-log plot)

Low-frequency condition

$$\omega\tau_v \ll 1, \quad \text{with} \quad \tau_v = \left(\frac{D_\alpha}{\langle|\mathbf{v}^2|\rangle}\right)^{\frac{1}{2-\alpha}}$$

in the ps regime

☞ ω is in the sub-THz region

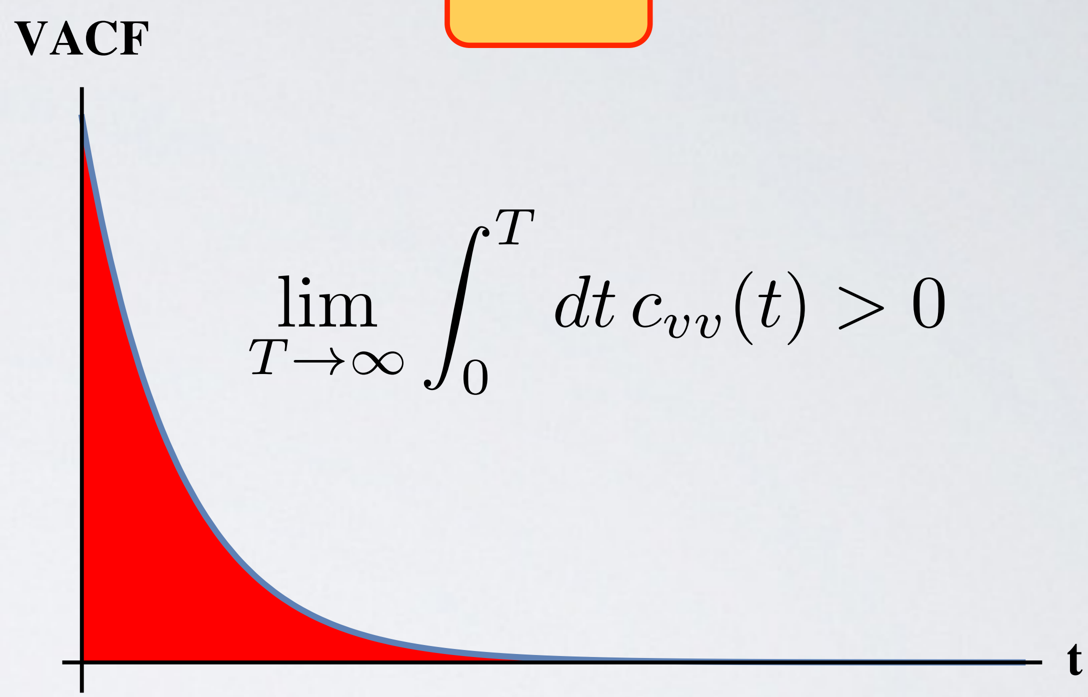
☞ The resolution of the best QENS spectrometers is in the GHz region and the new ESS spectrometers have even much better resolution.

A simple model for the VACF of sub-diffusing lipids

$$c_{vv}(t) = \langle v^2 \rangle {}_1F_1(2-\alpha, 1, -t/\tau)$$

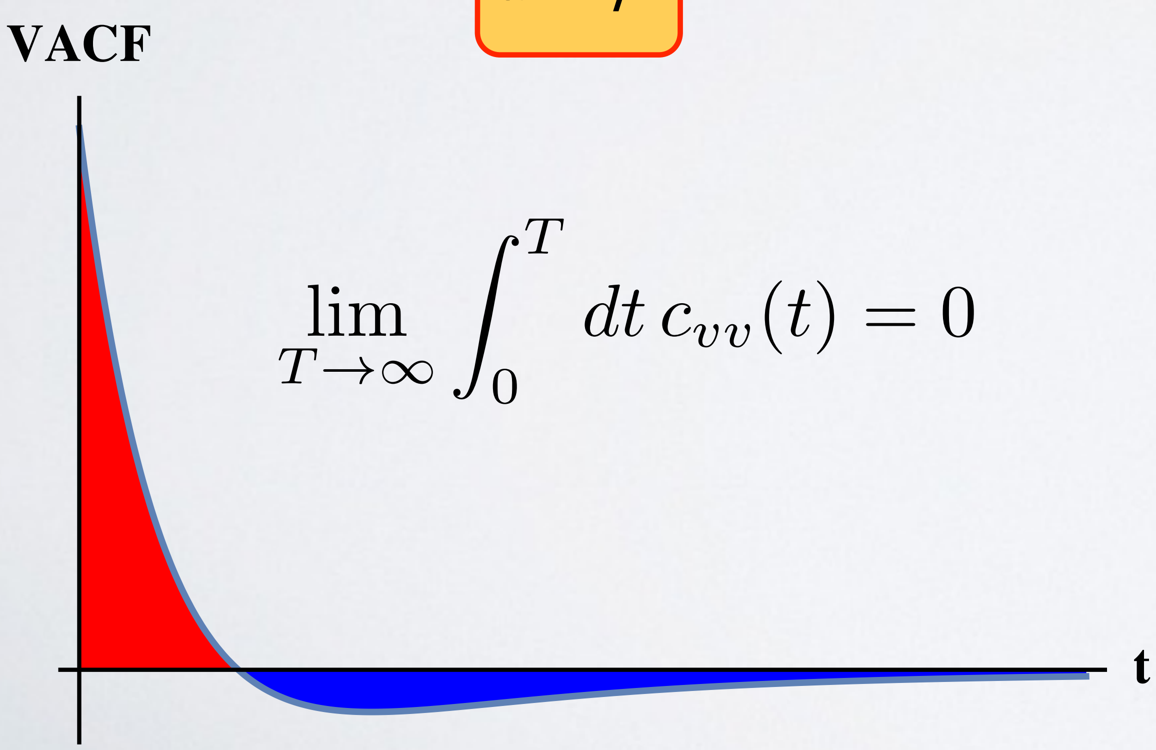
$$\hat{c}_{vv}(s) \overset{s\to 0}{\sim} s^{1-\alpha}$$

α=1



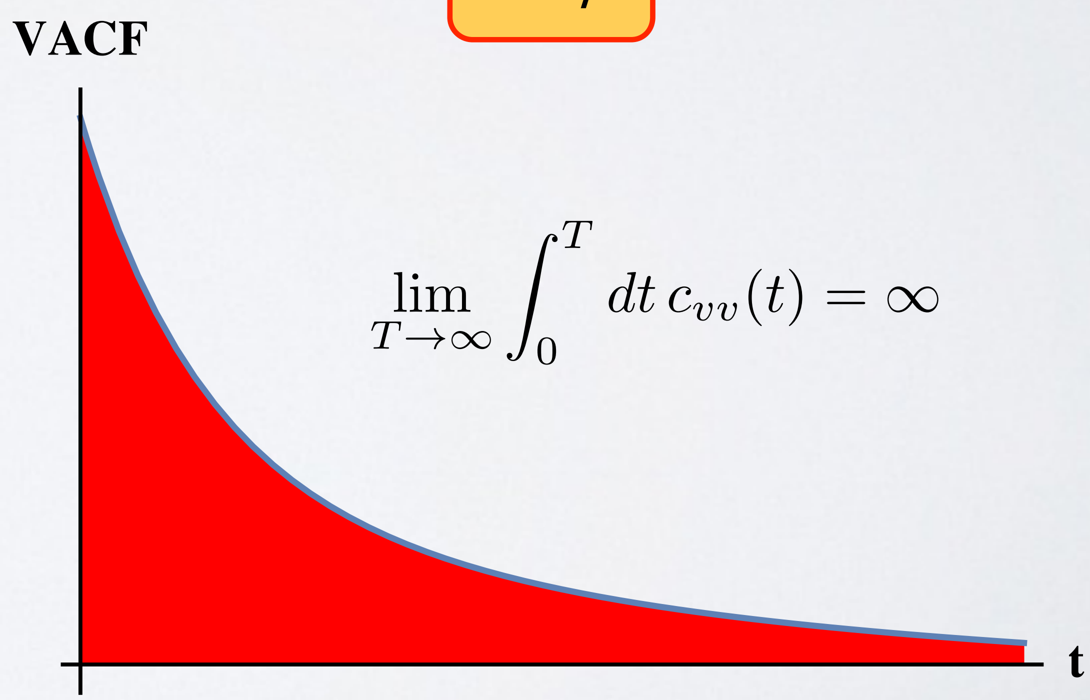
$$\lim_{T\to\infty} \int_0^T dt\, c_{vv}(t) > 0$$

α=1/2



$$\lim_{T\to\infty} \int_0^T dt\, c_{vv}(t) = 0$$

α=3/2



$$\lim_{T\to\infty} \int_0^T dt\, c_{vv}(t) = \infty$$

Regular short time behavior (power series)

$$c_{vv}(t) = \langle v^2 \rangle \left(1 + (\alpha - 2)(t/\tau) + \frac{1}{4}\left(\alpha^2 - 5\alpha + 6\right)(t/\tau)^2 + \ldots \right)$$

short time relaxation

Desired small s behavior of the Laplace transform

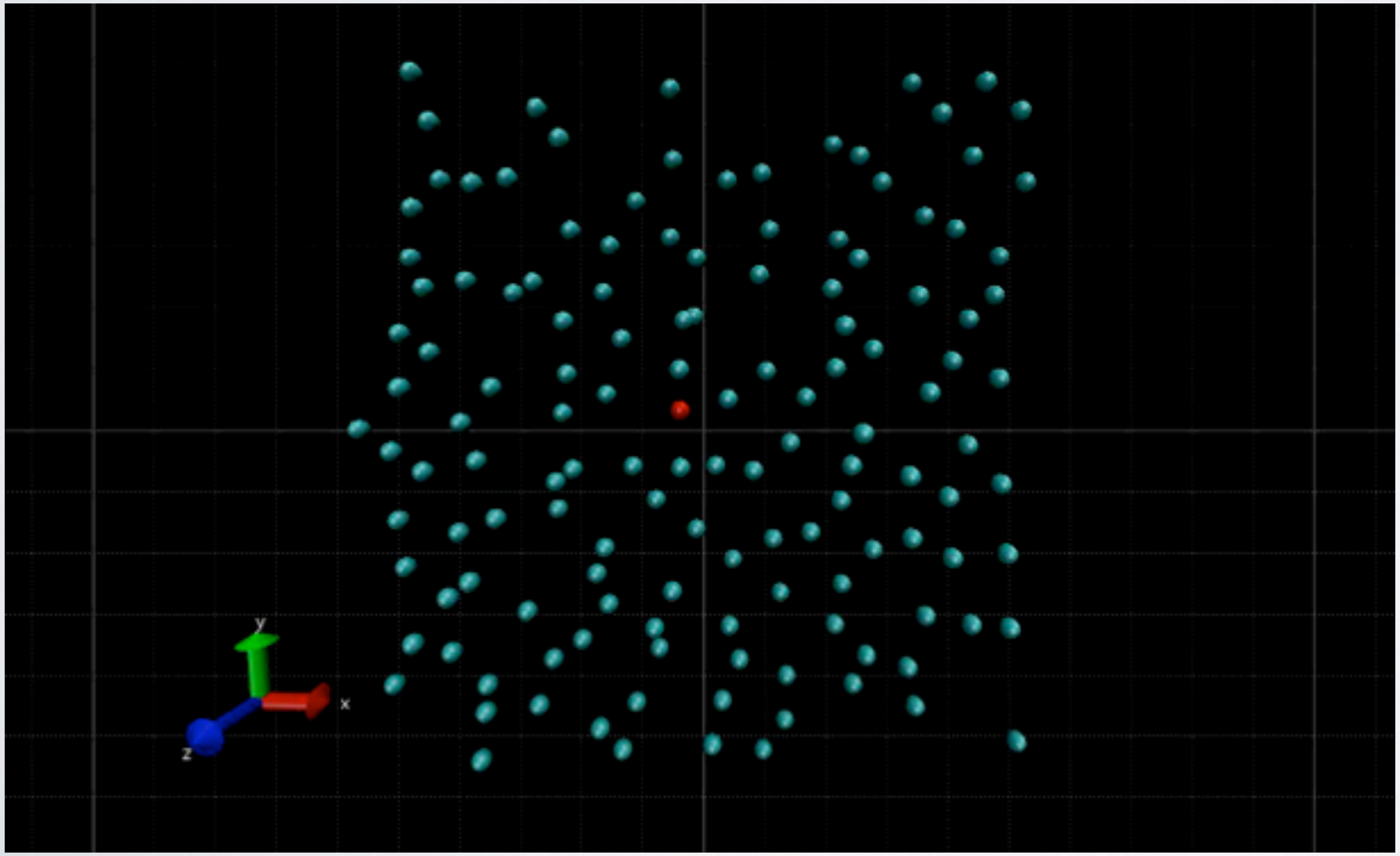
$$\hat{c}_{vv}(s) = \langle v^2 \rangle \frac{\tau(s\tau)\left(\frac{1}{(s\tau)} + 1\right)^{\alpha}}{\left((s\tau) + 1\right)^2} \overset{s \to 0}{\sim} \underbrace{\langle v^2 \rangle \tau^{2-\alpha}}_{\Gamma(1+\alpha) D_\alpha} s^{1-\alpha}$$

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

Remark: The VACF of an anomalously diffusing Rayleigh particle is **not** an appropriate model,

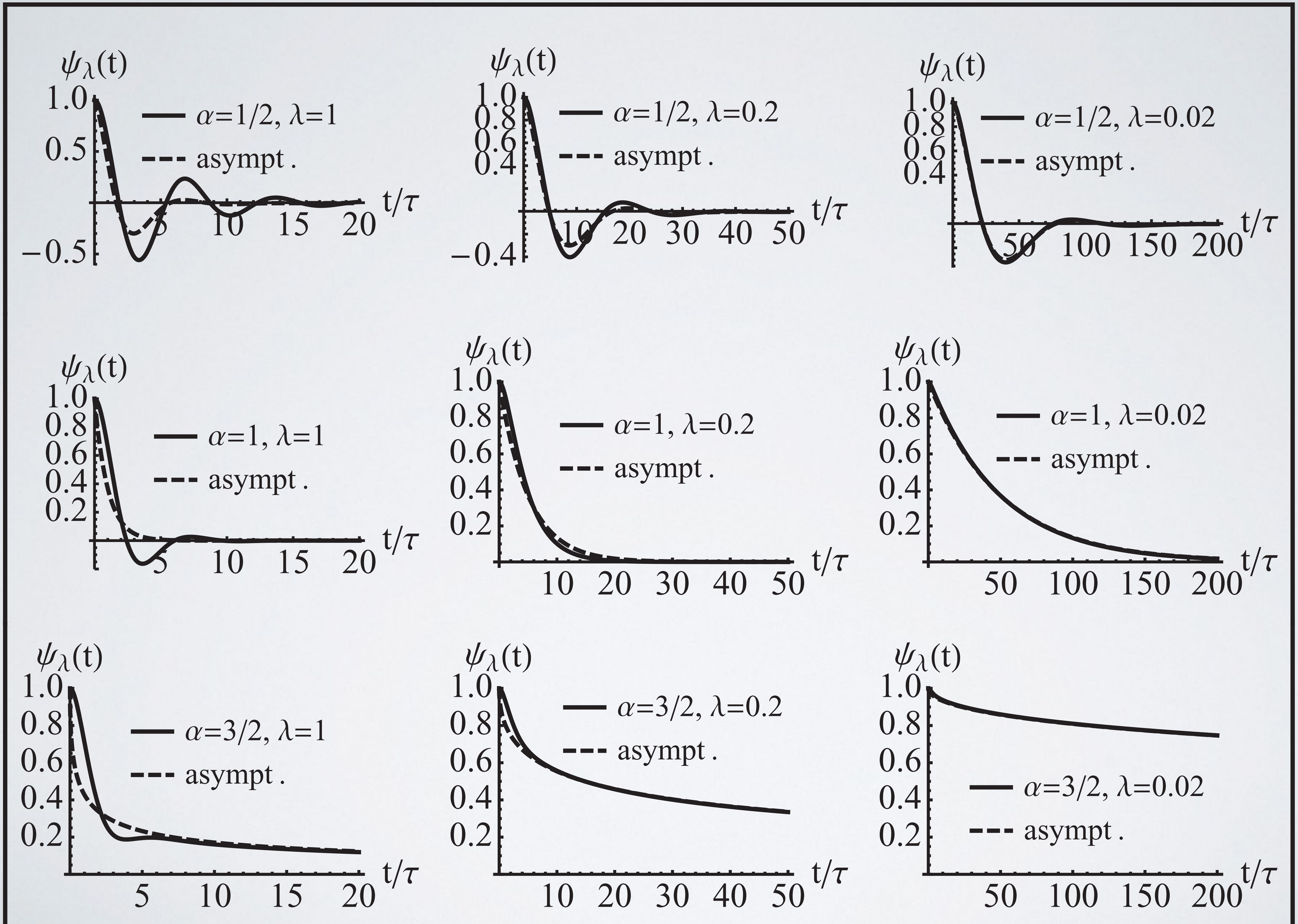
$$c_{vv}(t) = \langle v^2 \rangle E_{2-\alpha}(-[t/\tau]^\alpha)$$

since here a tagged diffusing molecule is supposed to move on much slower time scales as this in the surrounding solvent. The above VACF is moreover not regular at t=0.

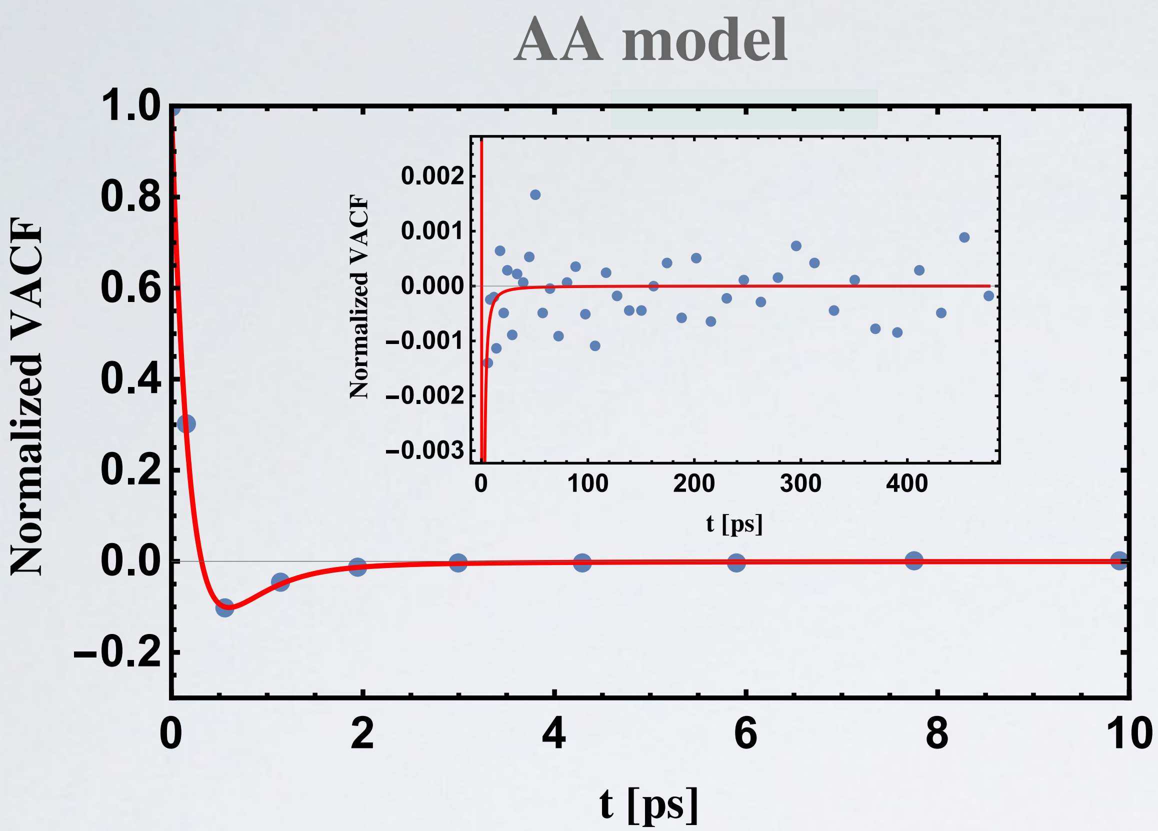


Any VACF takes the ML form as the mass of the diffusing tracer particle becomes large.

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



Fits of $c_{vv}(t) = \langle v^2 \rangle {}_1F_1(2-\alpha, 1, -t/\tau)$



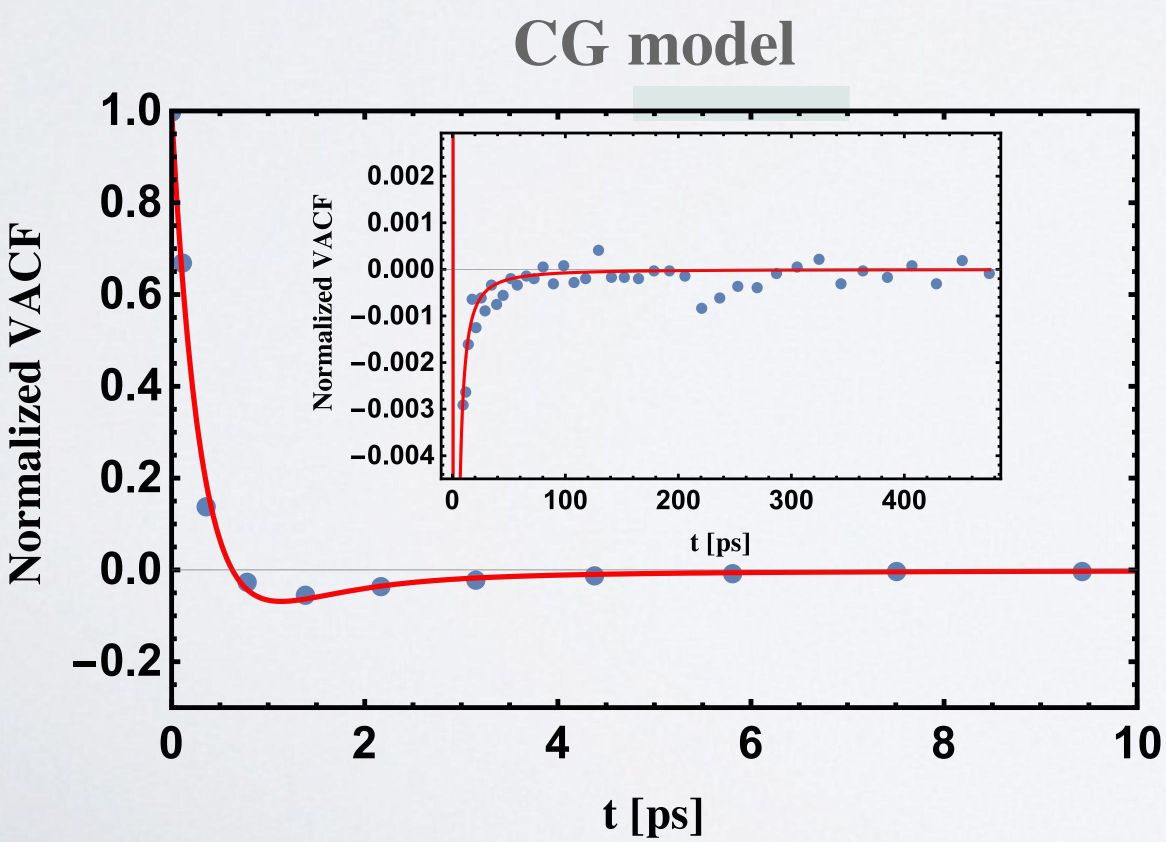
$$\alpha = 0.30$$

$$D_\alpha = 0.0048\,\mathrm{nm}^2/\mathrm{ns}^\alpha$$

From MSD:

$$\alpha = 0.70$$

$$D_\alpha = 0.016\,\mathrm{nm}^2/\mathrm{ns}^\alpha$$



$$\alpha = 0.52$$

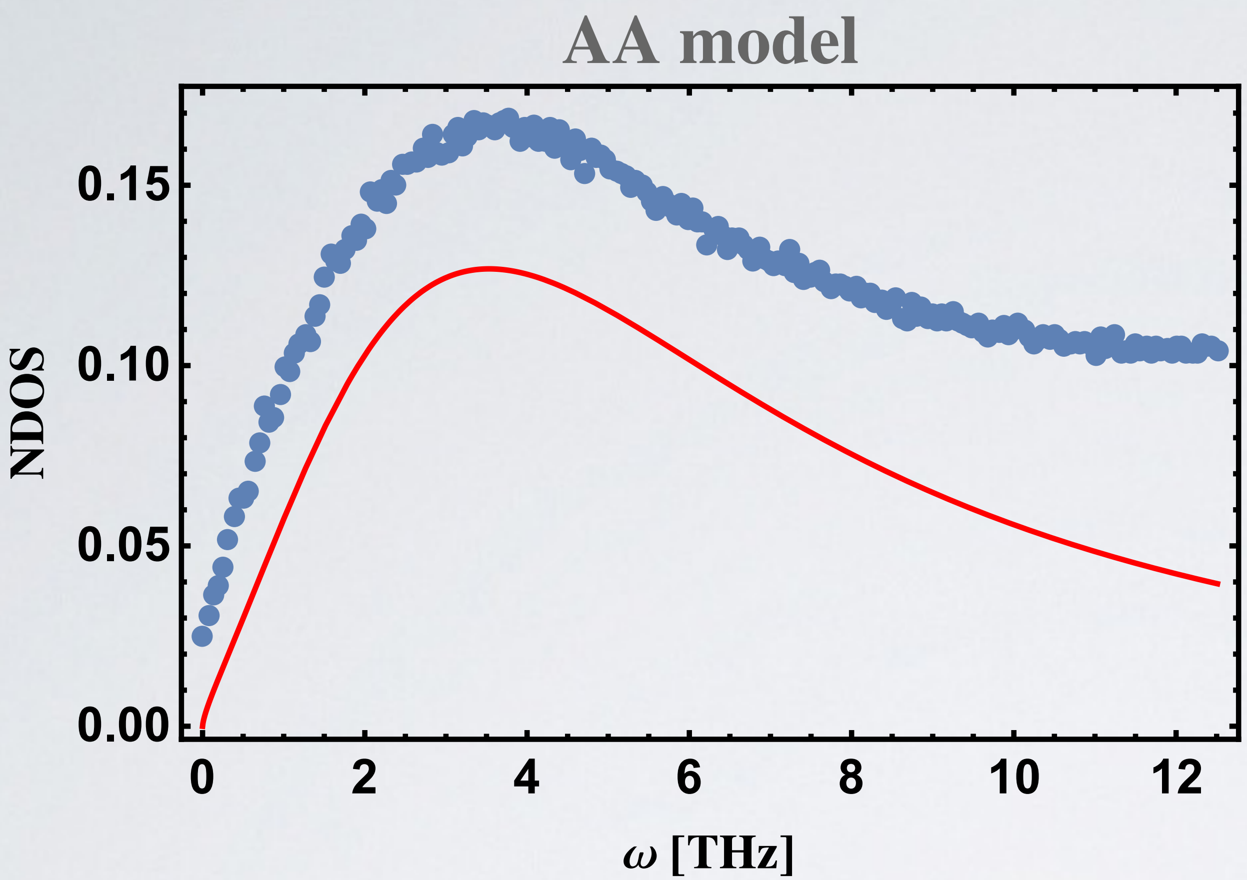
$$D_\alpha = 0.056\,\mathrm{nm}^2/\mathrm{ns}^\alpha$$

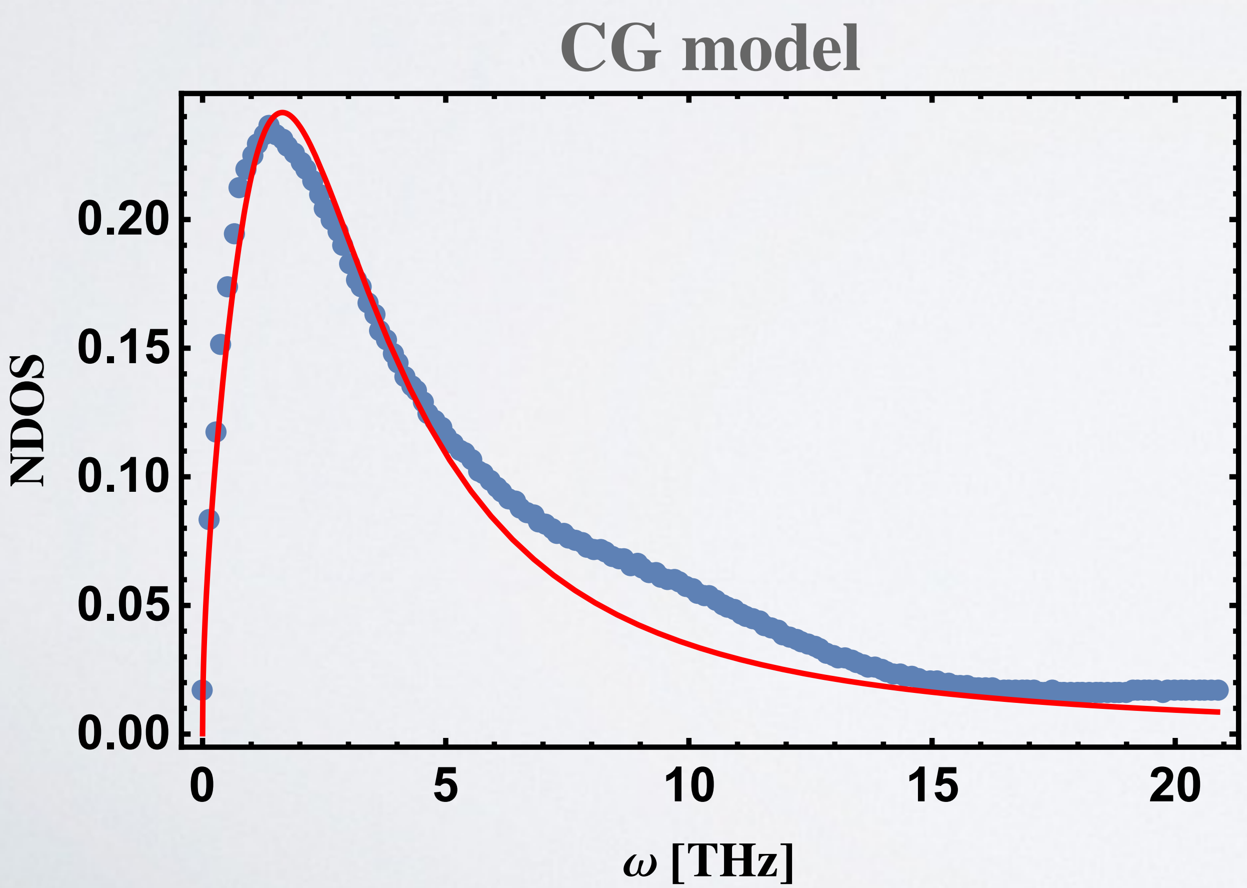
From MSD:

$$\alpha = 0.52$$

$$D_\alpha = 0.056\,\mathrm{nm}^2/\mathrm{ns}^\alpha$$

Corresponding normalized DOS





CONCLUSIONS

- A simple algebraic form for the low-frequency DOS can be derived from the asymptotic form of the MSD, if $0<\alpha\leq 1$.

- Reliable values for the fractional exponent and diffusion coefficient can be obtained by fitting this form to simulated data, provided the statistics is good enough.

- The method provides a simple mean for the interpretation of QENS data, given that the resolution of the best instruments is in the GHz range.

- Hypergeometric functions provide a mean to develop VACF models which are regular for small at $t=0$ and which have the desired long-time behavior.

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