Simulation-based modeling of neutron scattering data

Linking neutron scattering and MD simulations

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Content

- Elements of neutron scattering theory
- Linking MD simulations and neutron scattering
- Basic analysis of MD simulations
- Modeling MD time series and correlation functions

Elements of neutron scattering theory

Properties of the neutron

The neutron is a particle of mass $m = 1.6749 \times 10^{-27}$kg with zero charge. A free neutron is not stable and decays after a mean life time of 885.6 s into a proton, an electron, and an electronic anti-neutrino,

$$n \longrightarrow p^+ + e^- + \overline{\nu}_e.$$

A thermal neutron is a non-relativistic article of thermal energy, $E \approx k_B T$. [1] After its generation by nuclear fission or a spallation process, it attains this energy after multiple collisions with the atoms of a moderator (H_20, D_20,...) at temperature T.

Wave length of thermal neutrons

Using the De Broglie relations[2]

$$\vec{p} = \hbar\vec{k}, \qquad |\vec{k}| = \frac{2\pi}{\lambda},$$

one finds for $E = \vec{p}^{\,2}/2m = k_B T$ et $T = 300\,\mathrm{K}$ a wavelength of

$$\lambda = 1.778\,\text{Å}.$$

The wave length is this compatible with typical interatomic distances between the atoms in condensed matter systems. Since $E \approx k_B T$ is comparable with their energy, thermal neutron scattering is a unique tool for studying the structure and the dynamics of condensed matter.

[2] $\hbar = h/(2\pi) = 1.05457 \times 10^{34}$ Js is the reduced Planck constant.

Interaction of neutrons with matter

Neutrons interact with matter primarily through a short-ranged (fm) neutron-nucleus interaction, which is described through Fermi's pseudo-potential,

$$T = \frac{2\pi\hbar^2}{m} b\,\delta(\vec{r} - \vec{R}).$$

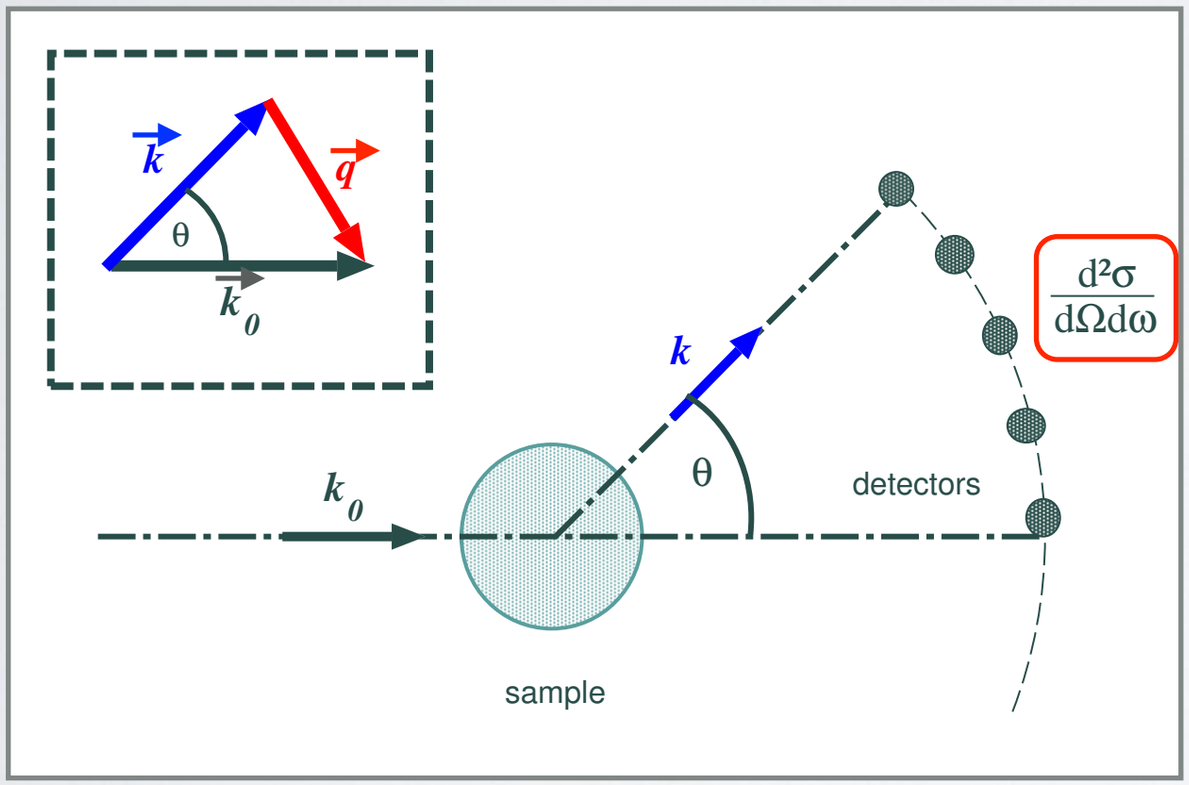
Here $\vec{r}$ and $\vec{R}$ is, respectively, the position operator of the neutron and the nucleaus of the scattering atom and the (generally complex) scattering length b takes values in the fm range. It depends on the relative orientation of the neutron and the nuclear spin. The symbol m denotes the neutron mass. The scattering cross section of a fixed atom is

$$\sigma = 4\pi|b|^2.$$

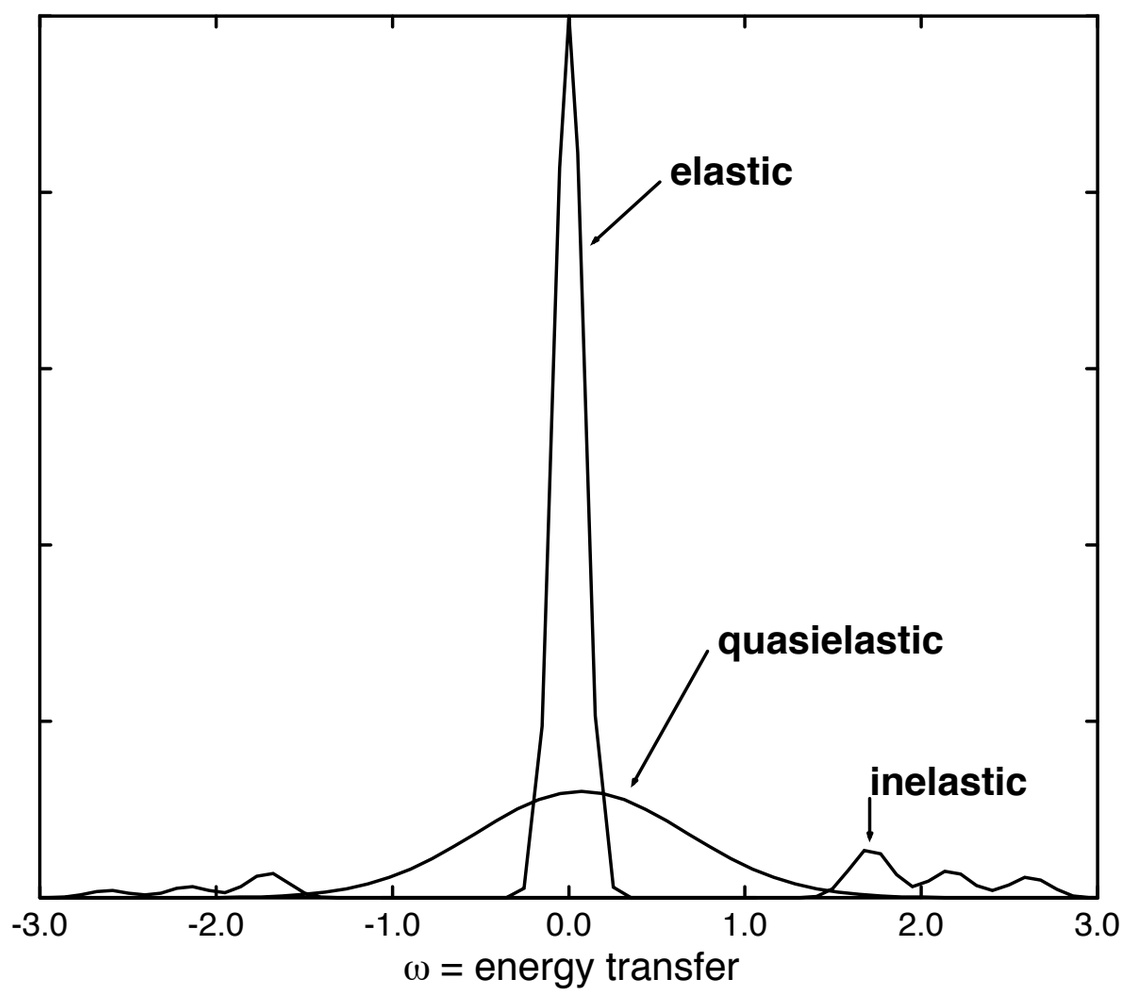
Scattering experiment

Exploring the structural dynamics of condensed matter on the atomic scale (0.1-10 nm, sub ps - 10 ns)

Setup for a neutron scattering experiment



Energy spectrum



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

Energy transfer:
$\omega = (E_0 - E)/\hbar$

Differential scattering cross section

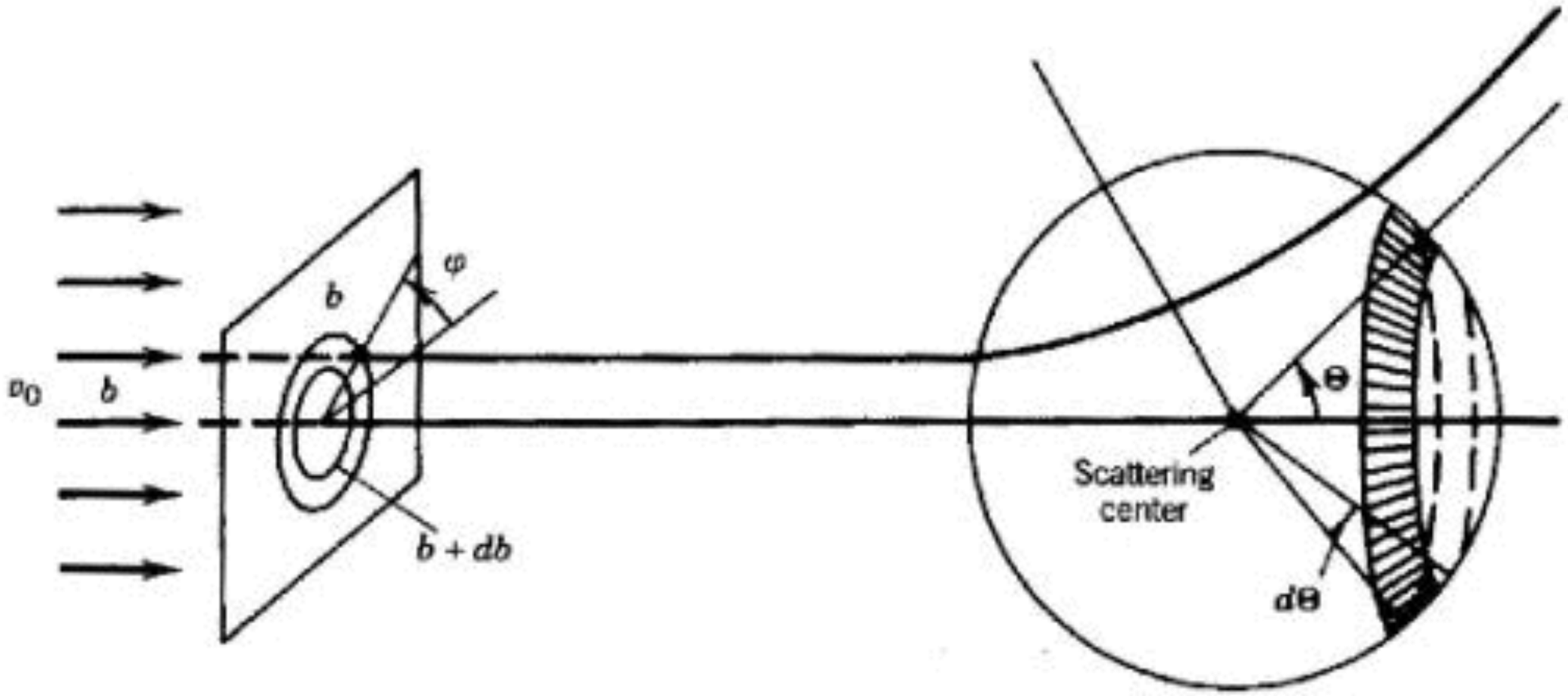


Figure 1-2-5. Relation between the impact parameter b and the CM scattering angle Θ for the one-particle equivalent problem of a purely repulsive Coulomb potential $V_{coul}(r)$. The outer circle in the plane at the left corresponds to the values b and Θ, the inner circle to the values $b - |db|$ and $\Theta + |d\Theta|$. [Adapted from Goldstein (1980).]

The (normalized) differential scattering cross section for N scattering atoms and an unpolarized neutron beam/sample is

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{|\vec{k}|}{|\vec{k}_0|}\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\,\frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\overline{b_\alpha^* b_\beta}\left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}\, e^{i\vec{q}\cdot\vec{R}_\beta(t)}\right\rangle$$

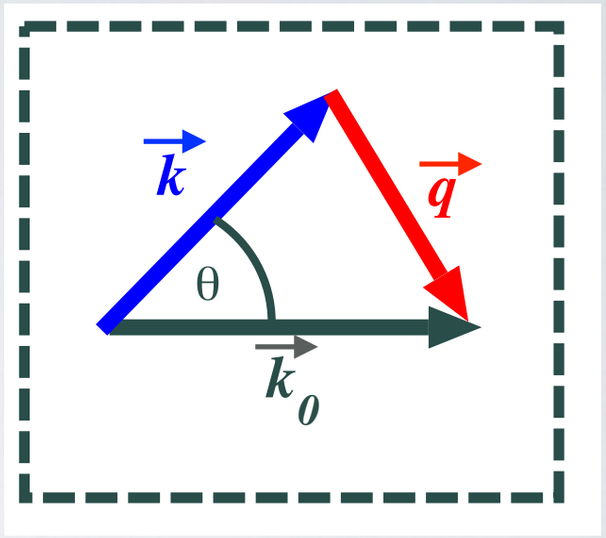
where

$$\langle A(0)B(t)\rangle = \frac{1}{Z}\mathrm{tr}\left\{Ae^{iHt/\hbar}Be^{-iHt/\hbar}\right\}$$

denotes a quantum time correlation function. Here H is the Hamilton operator of the scattering system and $Z = \mathrm{tr}\{e^{-\beta H}\}$ is the partition function, with $\beta = (k_B T)^{-1}$. The overline denotes an average over relative neutron-nucleus spin orientations. The incident and scattered neutron have the momenta $\hbar\vec{k}_0$ and $\hbar\vec{k}$, respectively.

Dynamic structure factor

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{|\vec{k}|}{|\vec{k}_0|}\mathcal{S}(\vec{q},\omega)$$



$$\mathcal{S}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\mathcal{I}(\vec{q},t)$$

Dynamic structure factor

$$\mathcal{I}(\vec{q},t) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\overline{b_\alpha^* b_\beta}\left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}\, e^{i\vec{q}\cdot\vec{R}_\beta(t)}\right\rangle$$

Intermediate scattering function

Coherent and incoherent scattering

The intermediate scattering function is split into a coherent part, reflecting collective motions, and and incoherent part, reflecting single particle motions,

$$\boxed{\mathcal{I}(\vec{q},t) = \mathcal{I}_{\mathsf{coh}}(\vec{q},t) + \mathcal{I}_{\mathsf{inc}}(\vec{q},t)}$$

Defining $b_{\alpha\,\mathsf{coh}} = \overline{b_\alpha}$ and $b_{\alpha\,\mathsf{inc}} = \sqrt{\overline{|b_\alpha|^2} - \left|\overline{b_\alpha}\right|^2}$, one has

$$\mathcal{I}_{\mathsf{coh}}(\vec{q},t) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} b^*_{\alpha\,\mathsf{coh}}\, b_{\beta\,\mathsf{coh}} \left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}\, e^{i\vec{q}\cdot\vec{R}_\beta(t)} \right\rangle$$

$$\mathcal{I}_{\mathsf{inc}}(\vec{q},t) = \frac{1}{N}\sum_{\alpha=1}^{N} |b_{\alpha\,\mathsf{inc}}|^2 \left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}\, e^{i\vec{q}\cdot\vec{R}_\alpha(t)} \right\rangle$$

Scattering cross sections for neutrons and photons

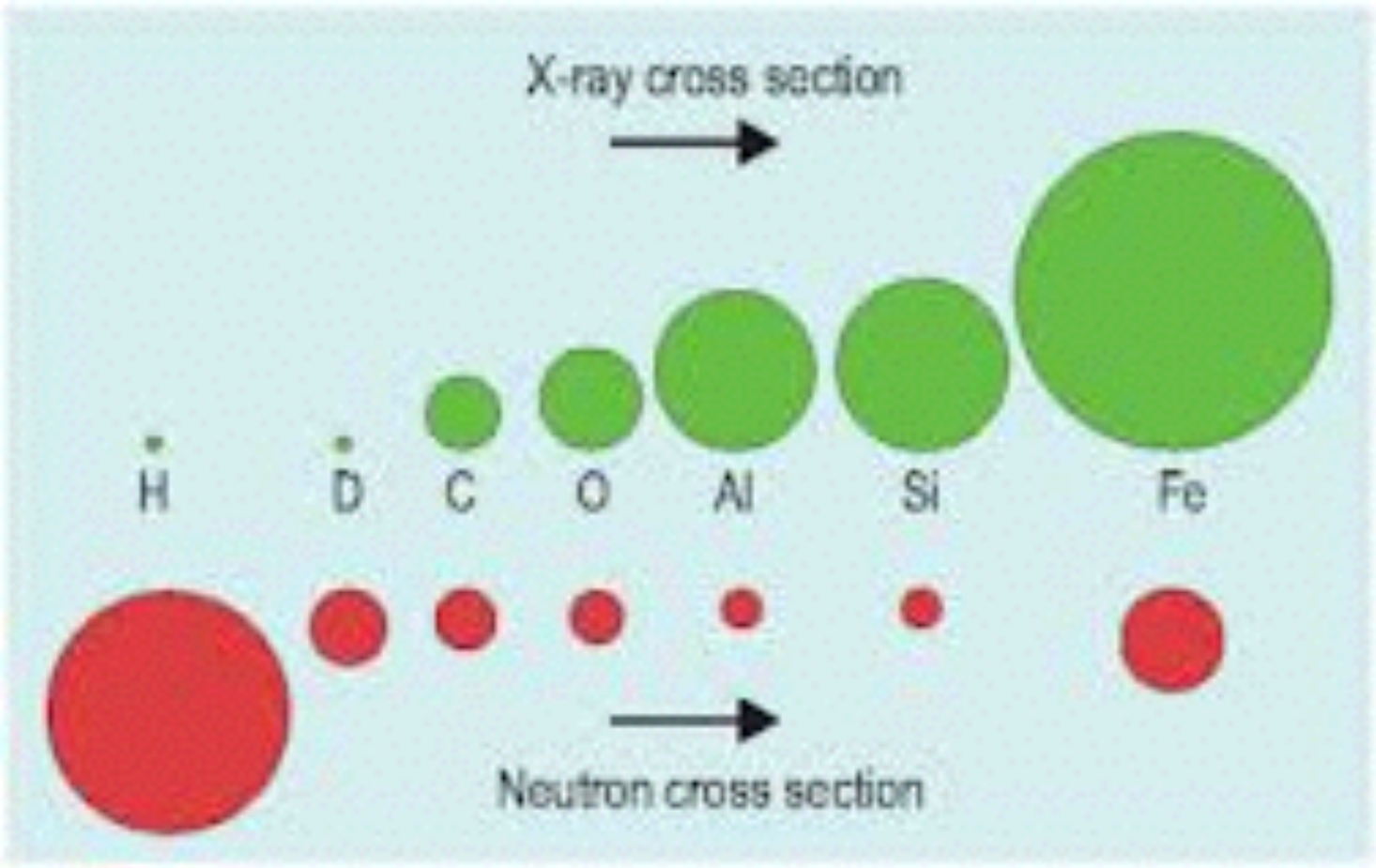


Fig. 2. Neutron and x-ray scattering cross-sections compared. Note that neutrons penetrate through Al much better than x rays do, yet are strongly scattered by hydrogen.

$$\sigma_{tot} = \int\int d\Omega d\omega \frac{d^2\sigma}{d\Omega d\omega}$$

Source: http://www.ncnr.nist.gov/AnnualReport/FY2003_html/RH2/

Hydrogenous samples

Element	H	D	C	O	N	S
b_{coh}	-3.741	6.674	6.648	5.805	9.300	2.847
b_{inc}	25.217	4.022	0.285	0.000	2.241	0.188

Due to the dominant incoherent scattering cross section of hydrogen, soft matter samples (polymers, biomolecules), which contain typically 50 % hydrogen atoms, scatter essentially incoherently. Therefore

$$\mathcal{I}(\vec{q},t) \approx \frac{|b_{H\,\mathrm{inc}}|^2}{N_H} \sum_{\alpha\in\mathbb{H}} \left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)} e^{i\vec{q}\cdot\vec{R}_\alpha(t)} \right\rangle .$$

Classical approximation of the scattering law

In the (usual) classical approximation, quantum time correlation functions are replaced by their classical counterparts, such that

$$\mathcal{I}(\vec{q},t) \approx \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\overline{b_\alpha^* b_\beta}\left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}e^{i\vec{q}\cdot\vec{R}_\beta(t)}\right\rangle_{cl}$$

Here

$$\langle A(0)B(t)\rangle_{cl} \equiv \frac{1}{Z_{cl}}\int d^{6N}\Gamma e^{-\beta H(\Gamma)}A(\Gamma)e^{t\mathcal{L}}B(\Gamma)$$

is an ensemble average over the $6N$ phase space coordinates Γ, with $Z_{cl} = \int d^{6N}\Gamma e^{-\beta H(\Gamma)}$, and $\mathcal{L} = \sum_{i=1}^{3N}\left\{\frac{\partial H}{\partial p_i}\frac{\partial}{\partial x_i} - \frac{\partial H}{\partial x_i}\frac{\partial}{\partial p_i}\right\}$ is the Liouville operator of the scattering system.

Van Hove functions and QENS

Within the classical approximation, the spatial Fourier transforms of the atomic contributions to the intermediate scattering function,[3]

$$G_{\alpha\beta}(\vec{r},t) \equiv \frac{1}{(2\pi)^3}\int d^3q\, e^{i\vec{q}\cdot\vec{r}}\left\langle e^{-i\vec{q}\cdot\left(\vec{R}_\alpha(0)-\vec{R}_\beta(t)\right)}\right\rangle_{cl},$$
$$= \langle\delta(\vec{r}-[\vec{R}_\alpha(0)-\vec{R}_\beta(t)])\rangle_{cl}$$

have a simple interpretation: They give the probability to find atom β at time t at position $\vec{r}$, given atom α was at time 0 at position $\vec{0}$. With the above definition

$$\mathcal{I}(\vec{q},t) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\overline{b_\alpha^* b_\beta}\int d^3r\, e^{-i\vec{q}\cdot\vec{r}}G_{\alpha\beta}(\vec{r},t).$$

[3] L. Van Hove, Physical Review 95, 249 (1954).

[4] L. Van Hove, Physica 24, 404 (1958).

Van Hove function for a freely diffusing atom

In case of free diffusion, the Van Hove self-correlation function fulfills the diffusion equation

$$\partial_t G_s(\mathbf{r}, t) = D \left\{ \partial_x^2 + \partial_y^2 + \partial_z^2 \right\} G_s(\mathbf{r}, t),$$

where D is the diffusion constant. The solution is a Gaussian

$$G(\mathbf{r}, t) = \frac{e^{-\frac{|r|^2}{4\mathrm{D}|t|}}}{2\sqrt{\pi \mathrm{D}\,|t|}^3}$$

The mean square displacement grows linearly with time

$$W(t) = \int d^3 r\, |r|^2 G(\mathbf{r}, t) = 6Dt.$$

Historical articles about diffusion

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

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

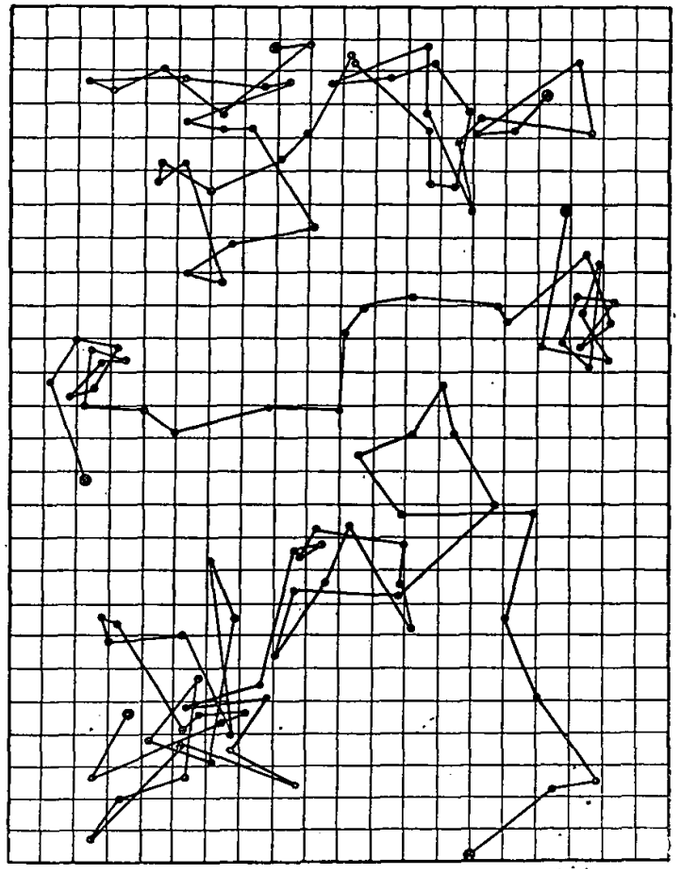
$$\frac{\partial f}{\partial t} = D\,\frac{\partial^2 f}{\partial x^2}.$$

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

$$\lambda_x = \sqrt{\overline{x^2}} = \sqrt{2\,D\,t}.$$

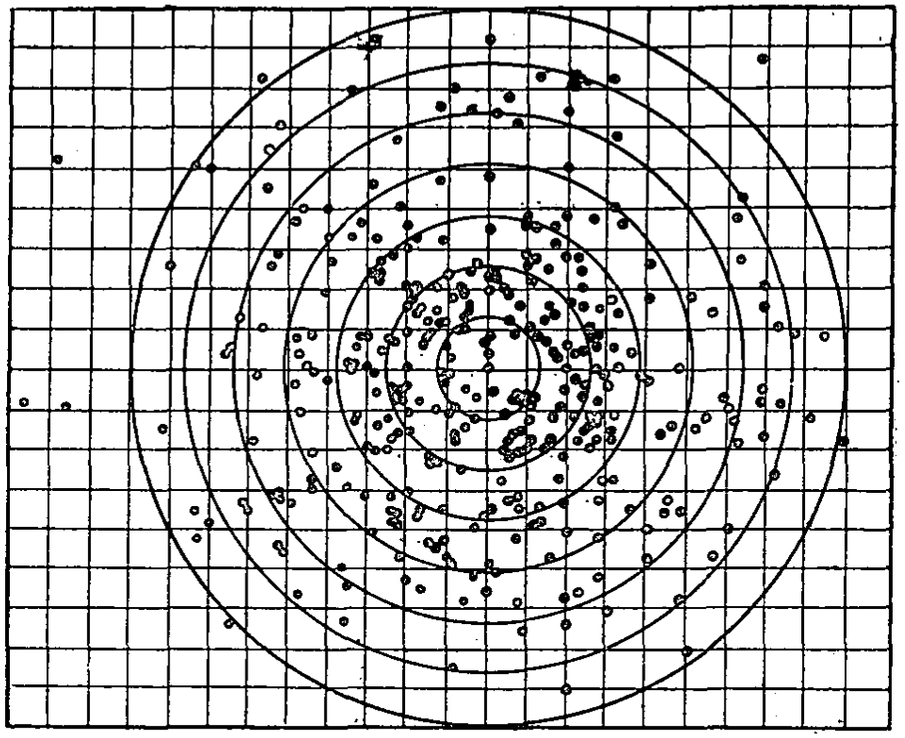
MOUVEMENT BROWNIEN ET RÉALITÉ MOLÉCULAIRE;

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)

Dynamic structure factor for QENS

The intermediate scattering function for a freely diffusing particle is

$$\mathcal{F}(\mathbf{q},t) = |b_H|^2 \int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} G(\mathbf{r},t) = |b_H|^2 e^{-\mathrm{D}|q|^2|t|}$$

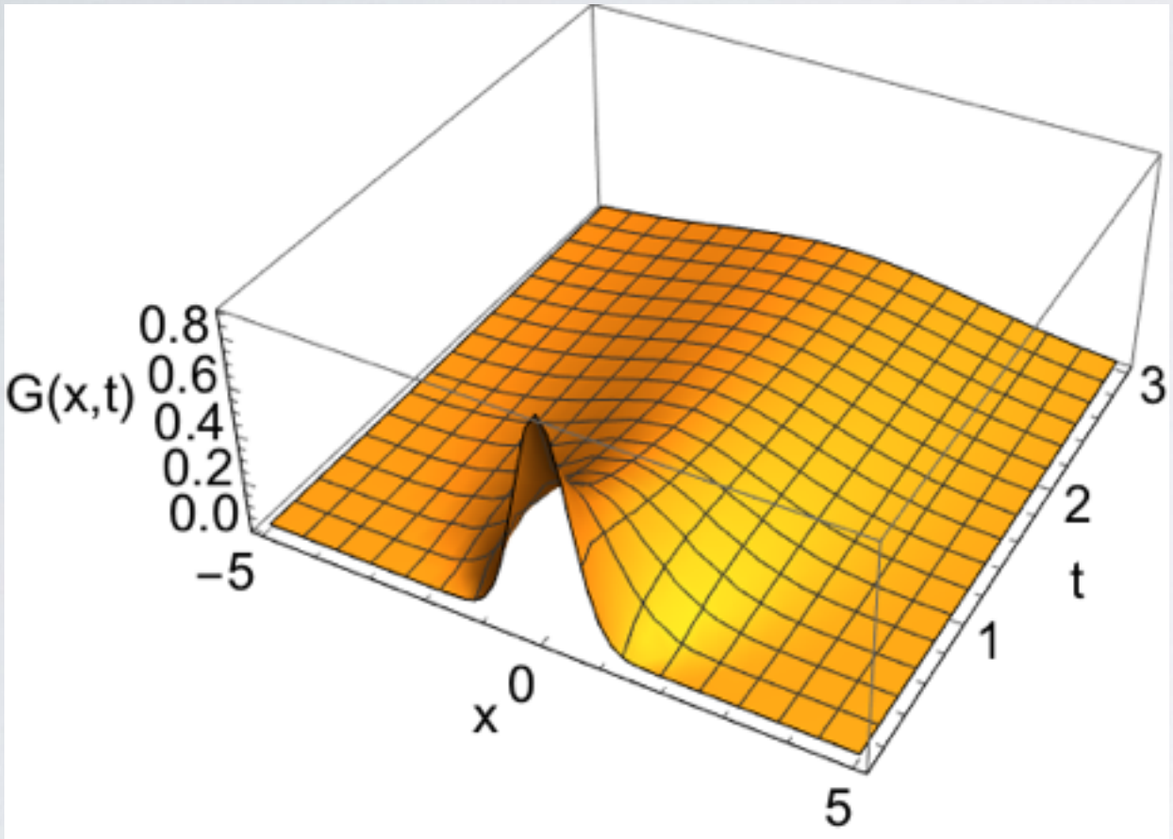
and the corresponding dynamic structure factor

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

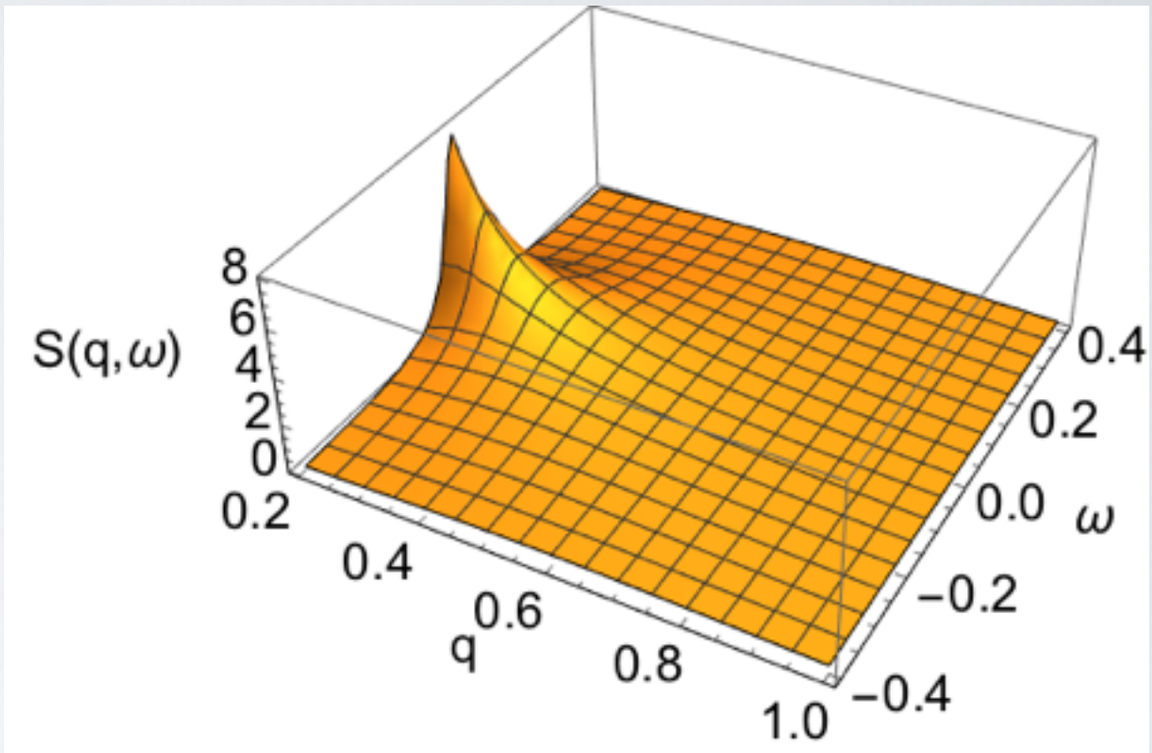
$$= |b_H|^2 \frac{\mathrm{D}|q|^2}{\pi\left(\mathrm{D}^2|q|^4+\omega^2\right)}$$

Lorentzian quasielastic scattering profile

Van Hove function



Dynamic structure factor



In oder to describe QENS from more complex systems, various diffusion models have been developed (see e.g. [1]).

M. Bée. Quasielastic Neutron Scattering, Adam Hilger, Bristol, 1988.

Limits of the classical approximation in neutron scattering

There are two conditions for the validity of the classical approximation:

1. The intrinsic quantum properties of the scattering system must be negligible.
2. The recoil effect on the scattering atom must be negligible,

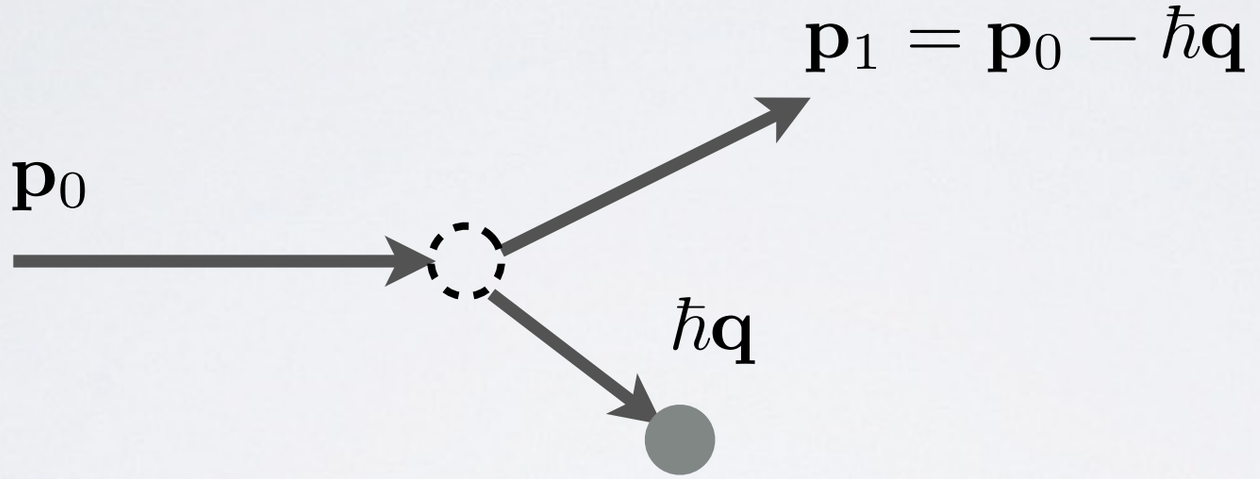
$$\frac{\hbar^2|\vec{q}|^2}{2M} \ll k_B T,$$

where M is the mass of the scattering atom.

1 A. Rahman, Physical Review 130, 1334 (1963).
2 G.R. Kneller, Mol Phys 83, 63 (1994).

Recoil effects

In simulating neutron scattering spectra on the basis of classical molecular dynamics simulations one implicitly assumes the absence of strong recoil effects



Condition for the validity of S(q,w) calculated from MD

$$\frac{\hbar^2 q^2}{2m} \ll k_B T$$

G. Kneller, *Mol. Phys.*, vol. 83, no. 1, pp. 63–87, 1994.

Two very different representations of the same correlation function...

The impact of the neutron on the scattering system can be highlighted through the identity[4]

$$\boxed{\left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)} e^{i\vec{q}\cdot\vec{R}_\alpha(t)} \right\rangle = \left\langle e^{iH_\alpha(\vec{q})t/\hbar} e^{-iHt/\hbar} \right\rangle}$$

where $H_\alpha(\vec{q})$ is the "kicked Hamiltonian"

$$H_\alpha(\vec{q}) = \sum_{\gamma=1}^{N} \frac{(\vec{p}_\gamma + \delta_{\gamma\alpha}\hbar\vec{q})^2}{2M_\gamma} + V(\vec{R}_1, \ldots, \vec{R}_N).$$

One uses here that $e^{-i\vec{q}\cdot\vec{R}_\alpha} e^{iHt/\hbar} e^{i\vec{q}\cdot\vec{R}_\alpha} = e^{iH_\alpha(\vec{q})t/\hbar}$. The usual classical approximation neglects not only quantum effects in the scattering system, but also its perturbation through the neutron.[5]

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[4] G. Wick, Physical Review 94, 1228 (1954)

[5] G.R. Kneller, Mol Phys 83, 63 (1994)

Linking MD simulations and neutron scattering

- MD simulations and neutron scattering cover comparable length and time scales.
- Due to the point-like neutron-nucleus interaction, neutron scattering probes the space-time correlations of the same objects which are simulated in MD simulations - the atomic nuclei.
- Compute time correlation functions from MD trajectories, using the classical approximation.

$$\mathcal{I}(\vec{q},t) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\overline{b_\alpha^* b_\beta}\left\langle e^{-i\vec{q}\cdot\vec{R}_\alpha(0)}\, e^{i\vec{q}\cdot\vec{R}_\beta(t)}\right\rangle$$

from MD

Time correlation functions from MD simulations

Time correlation functions, such as $\mathcal{I}(\vec{q}, t)$, can be computed from time series, assuming ergodicity ($t \geq 0$),

$$\langle A(0)B(t)\rangle_{cl} = \lim_{T\to\infty} \frac{1}{T-t} \int_0^{T-t} d\tau\, A(\tau + t)B(\tau).$$

For discrete time series (MD trajectories) one uses the approximation ($m = 0, 1, 2, \ldots$)

$$\langle A(0)B(m)\rangle_{cl} \approx \frac{1}{N_t - m} \sum_{k=0}^{N_t-m-1} A(k + m)B(k),$$

where N_t is the number of available time frames in the series.

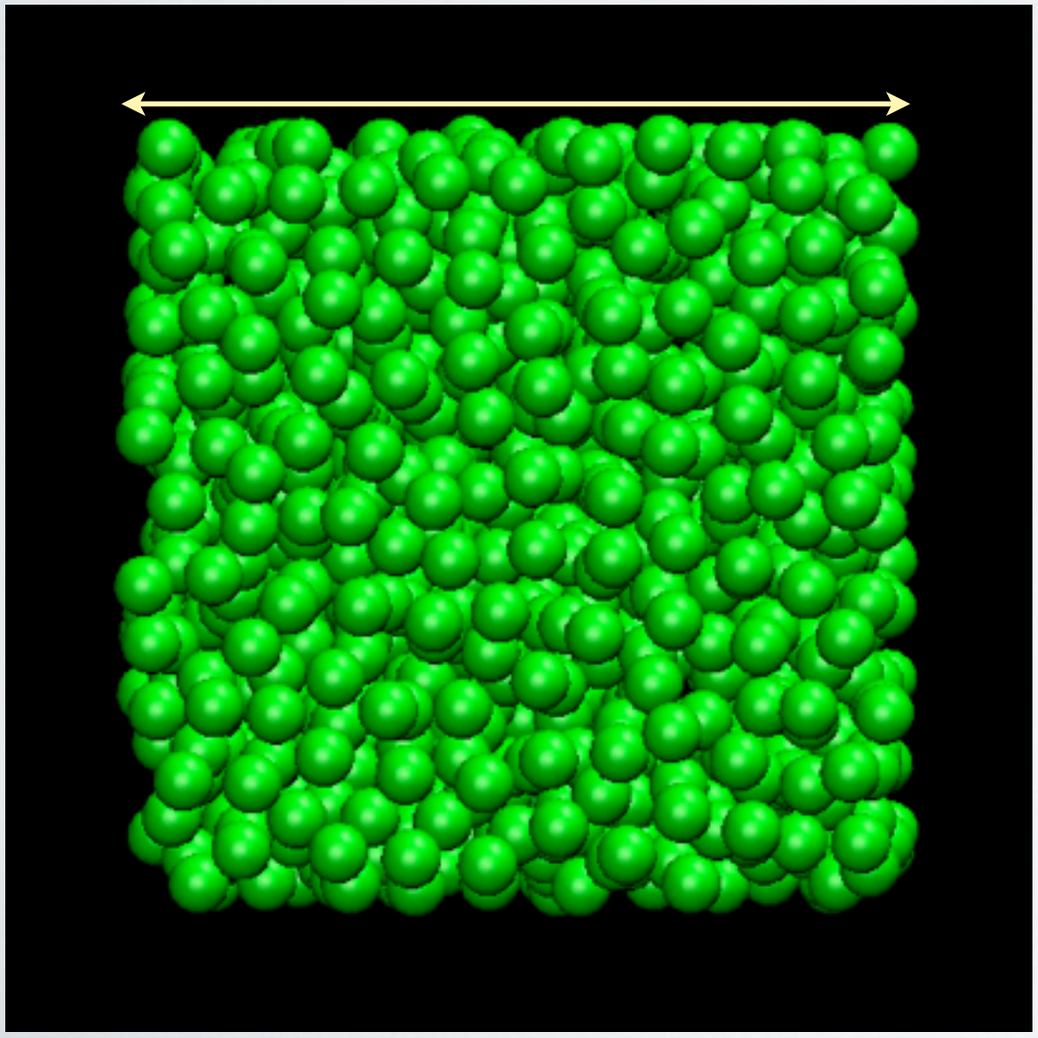
Principle of MD simulations

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

$$M_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \qquad U = \sum_{ij} 4\epsilon \left(\left[\frac{\sigma}{r_{ij}}\right]^{12} - \left[\frac{\sigma}{r_{ij}}\right]^{6} \right)$$

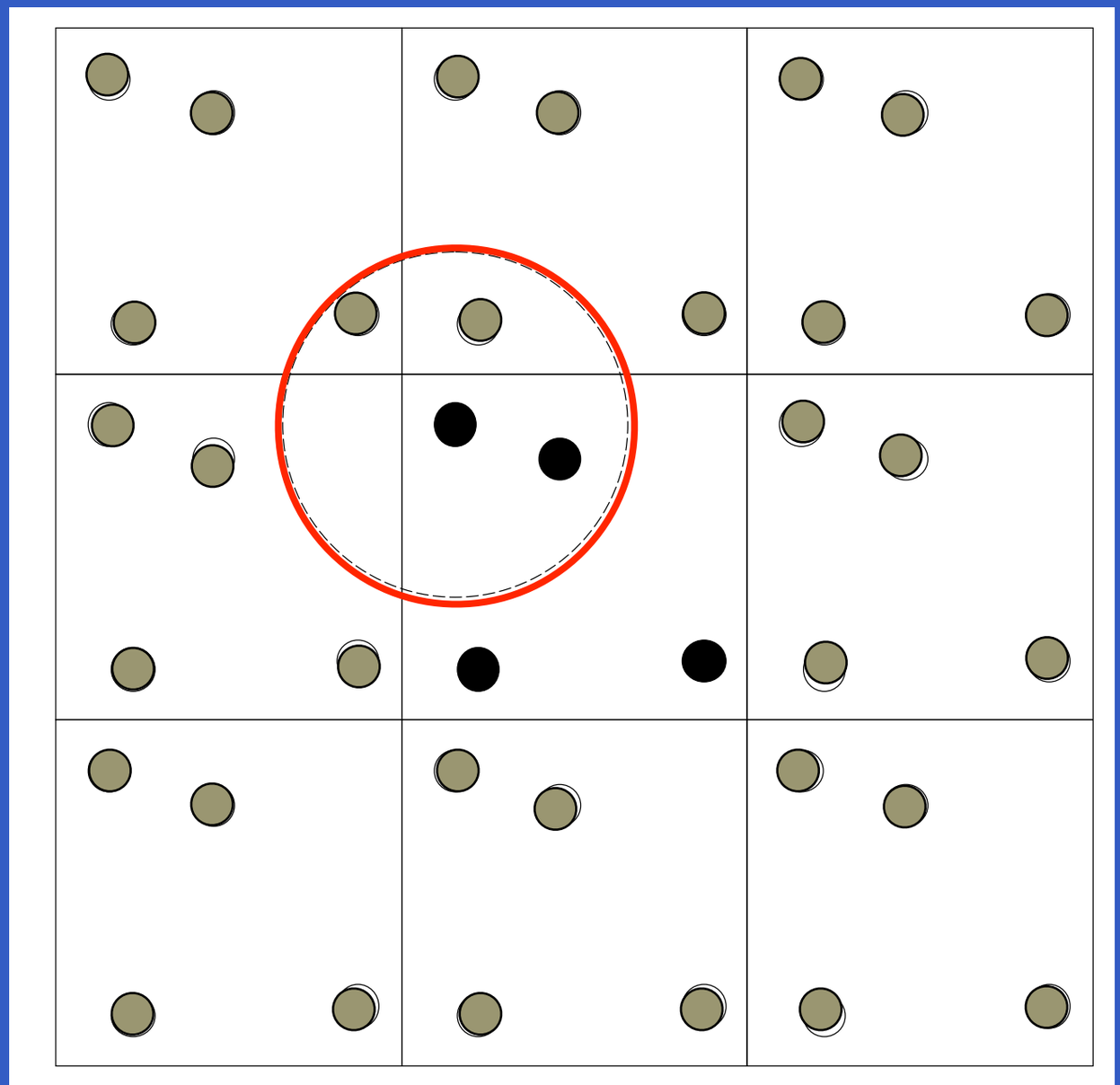
- Discretization and iterative solution itérative yields trajectories = time series (< 100 ns)

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

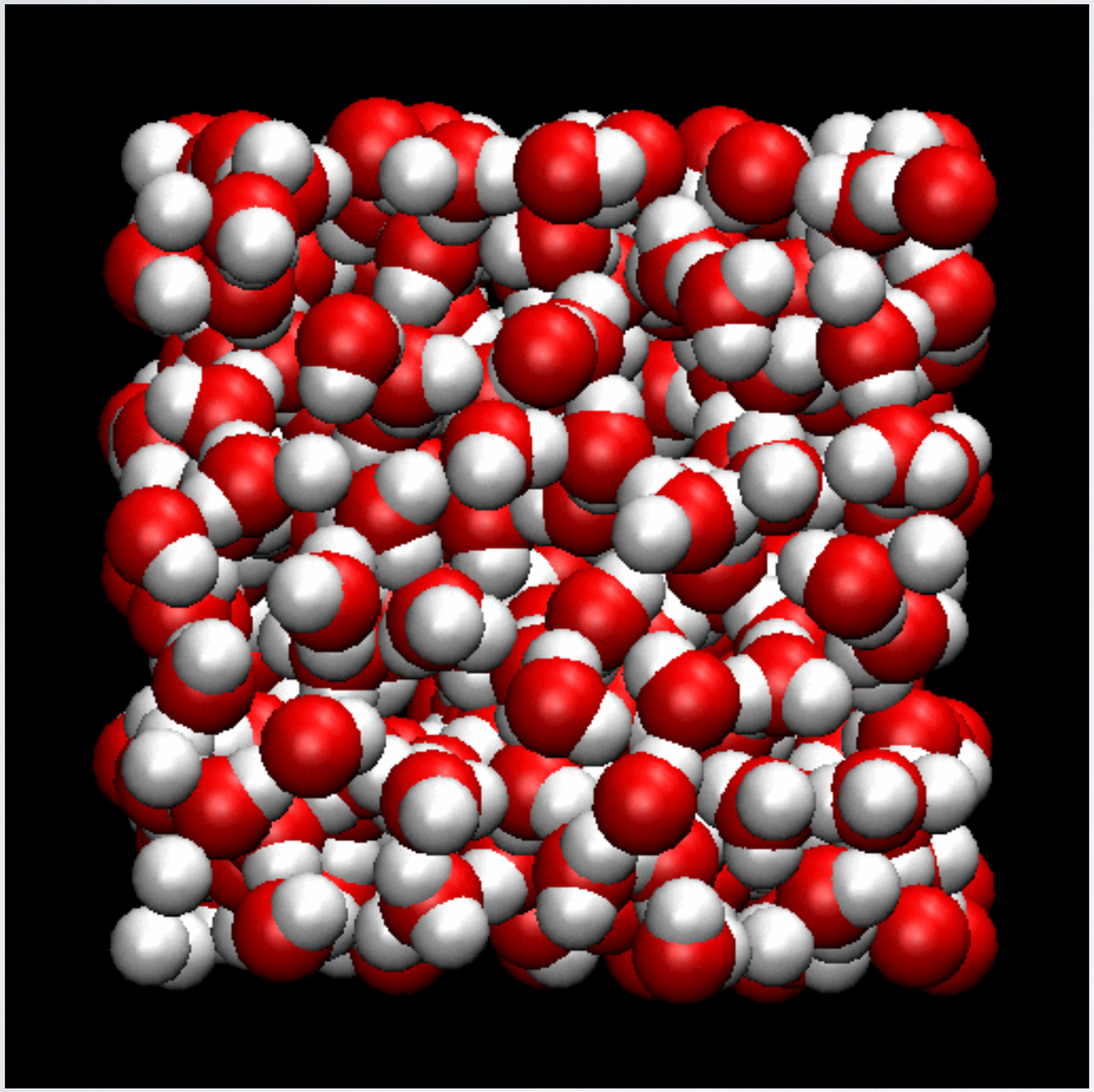
$$\mathbf{v}_i(n) \leftarrow \frac{\mathbf{r}_i(n+1) - \mathbf{r}_i(n-1)}{2\Delta t}.$$

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

Periodic boundary conditions



Dynamics of water



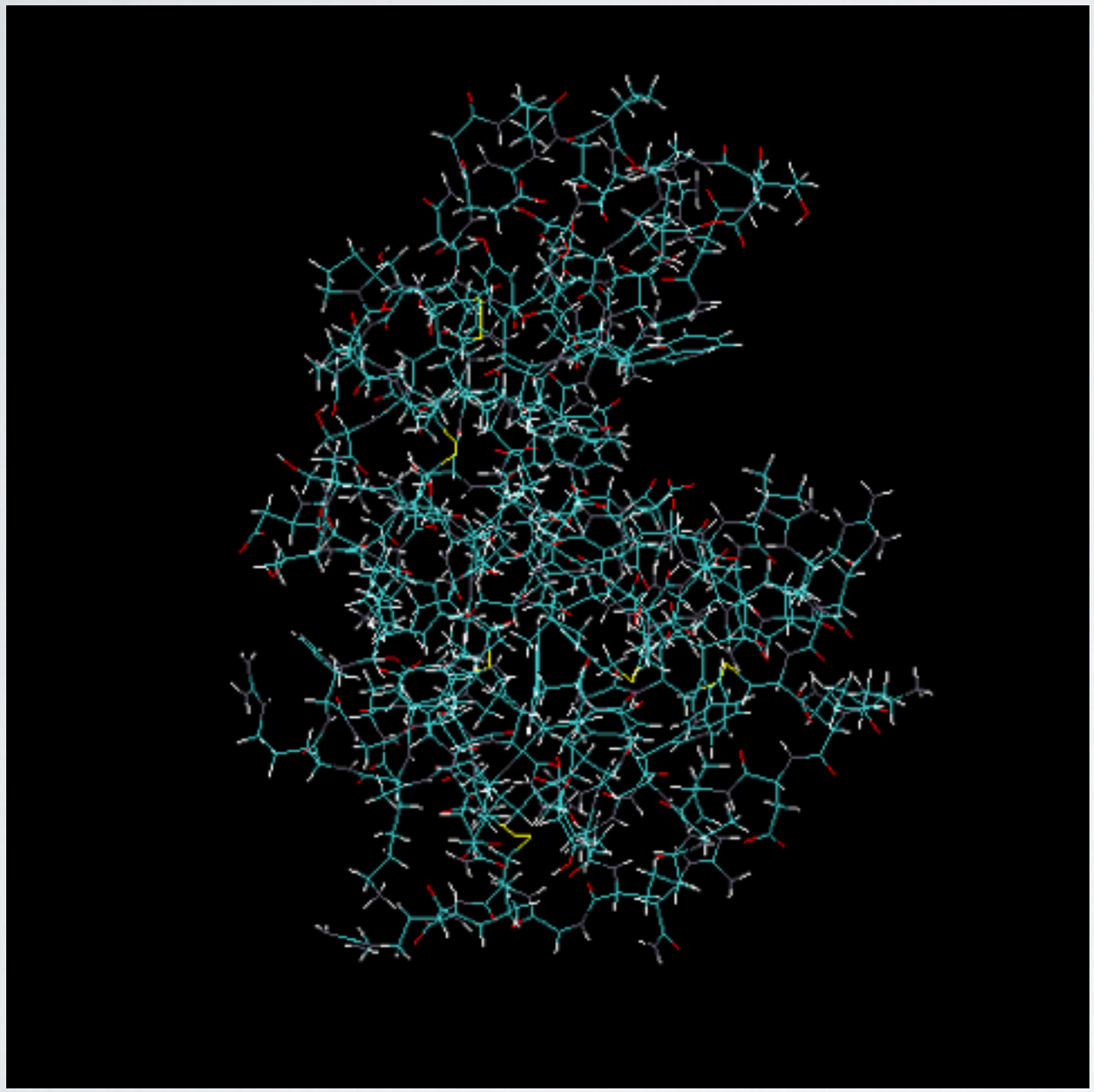
Dynamics of 256 water molecules with in a cibic box with periodic boundary conditions and Ewald summation for the Coulomb forces

SPC/E potential [1]:

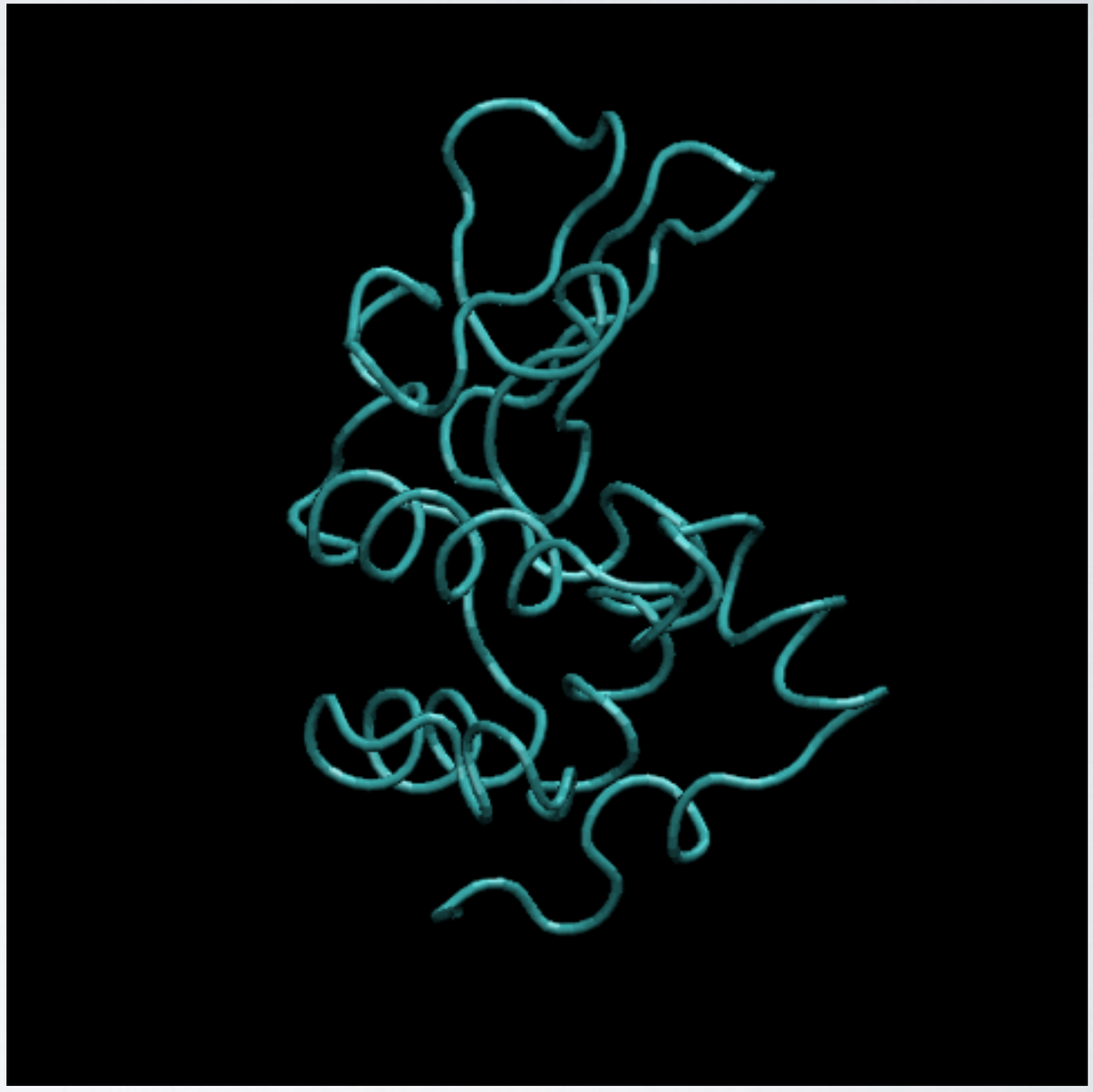
- O-O interactions of Lennard-Jones type
- **Coulomb interactions** for O-O, H-H, O-H

[1] H. Berendsen, J.R. Grigera, and T.P. Straatsma, J Phys Chem-Us 91, 6269 (1987).

Dynamics of lysozyme

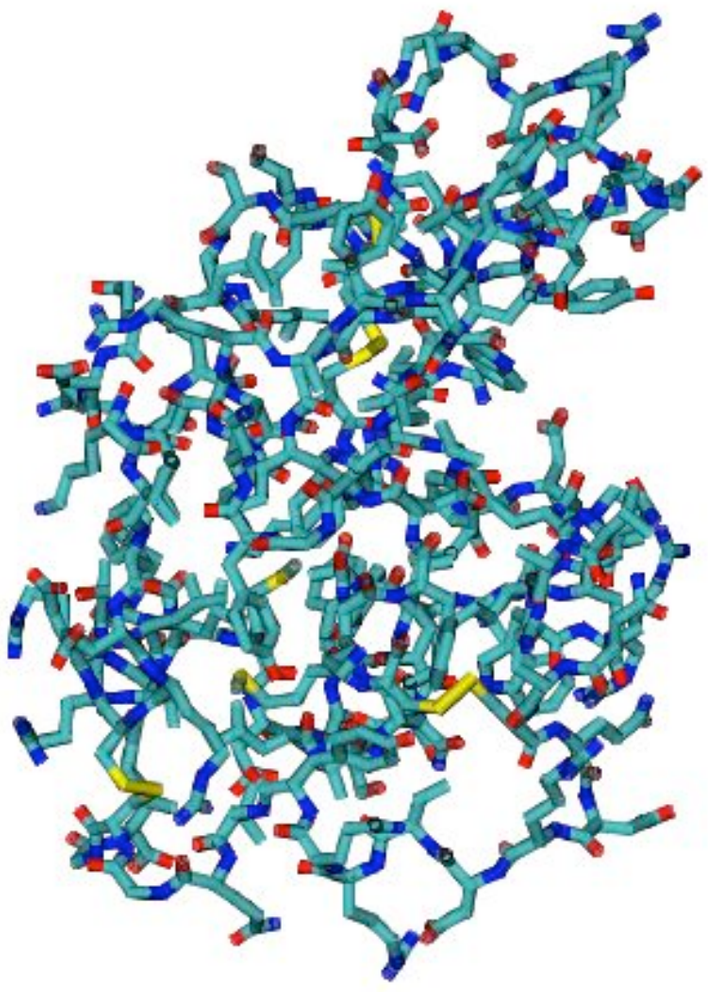


All atoms



backbone

Force field for biomolecular simulations



Lysozyme

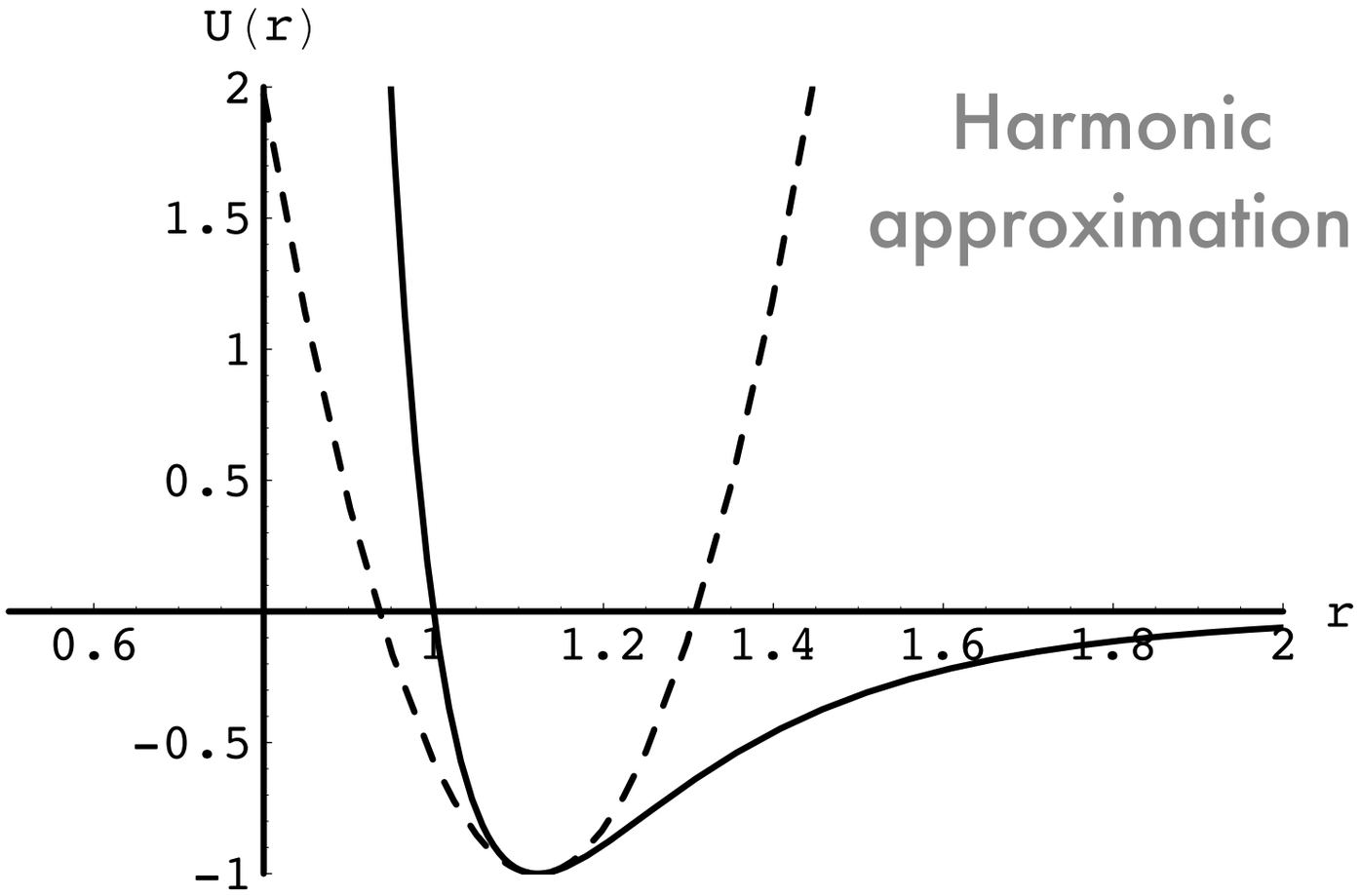
$$U = \sum_{\text{bonds } ij} k_{ij}(r_{ij} - r_{ij}^{(0)})^2 + \sum_{\text{angles } ijk} k_{ijk}(\phi_{ijk} - \phi_{ijk}^{(0)})^2$$

$$+ \sum_{\text{dihedrals } ijkl} k_{ijkl}\cos(n_{ijkl}\theta_{ijkl} - \delta_{ijkl})$$

$$\left.\begin{aligned} &+ \sum_{\text{all pairs } ij} 4\epsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r^{12}} - \frac{\sigma_{ij}^{6}}{r^{6}}\right) \\ &+ \sum_{\text{all pairs } ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \end{aligned}\right\} \text{non-bonded.}$$

The force field (Amber)

The limit of classical MD



Harmonic approximation

$$\hbar\omega_0 \ll k_B T$$

Argon :

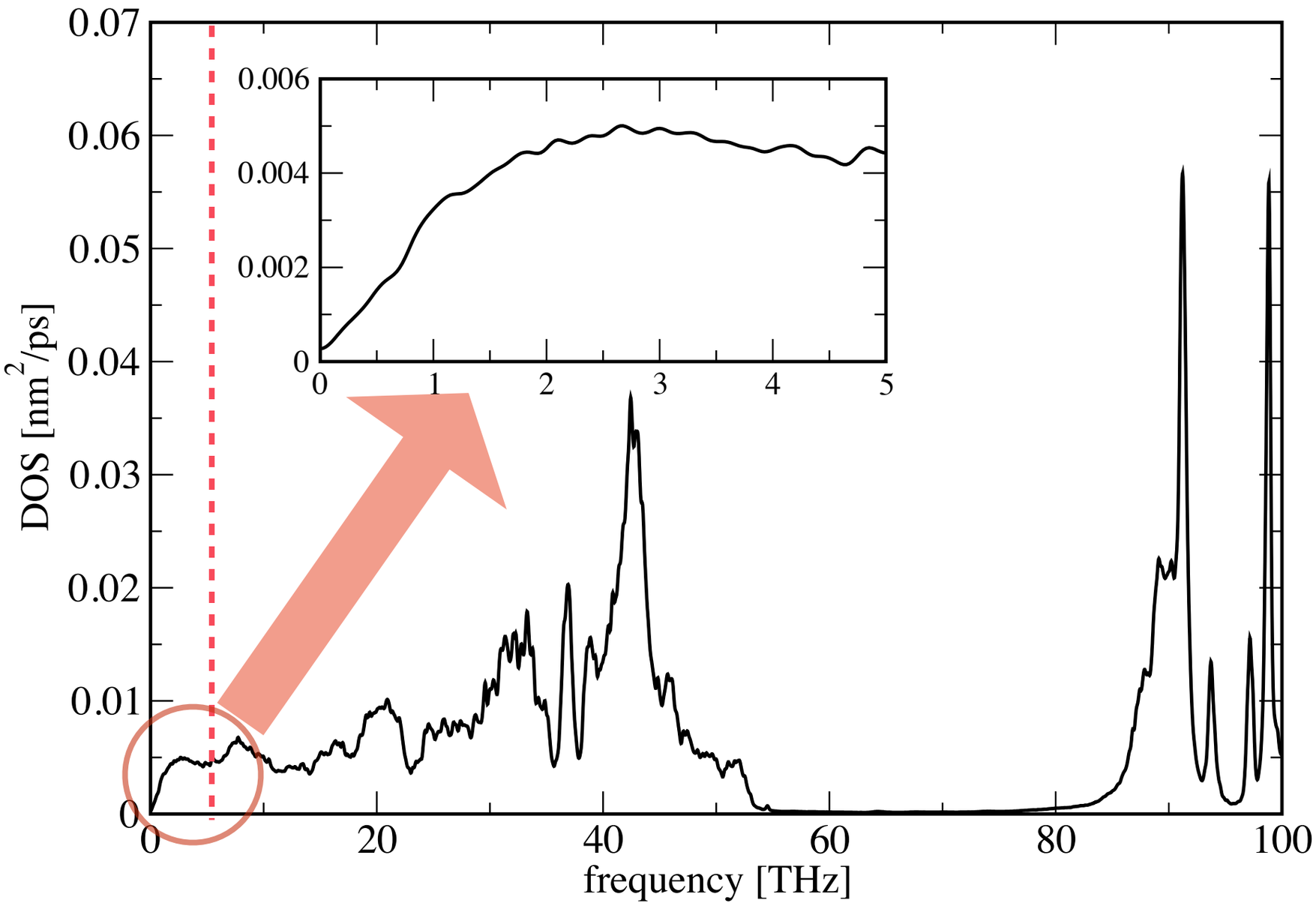
$$T = 94.4\,K$$

$$\hbar\omega_0 = 0.4\,k_B T$$

$$U_{LJ}(r) = 4\epsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right) \approx -\epsilon + \frac{18\cdot 2^{2/3}\epsilon\left(r-r_0\right)^2}{\sigma^2}$$

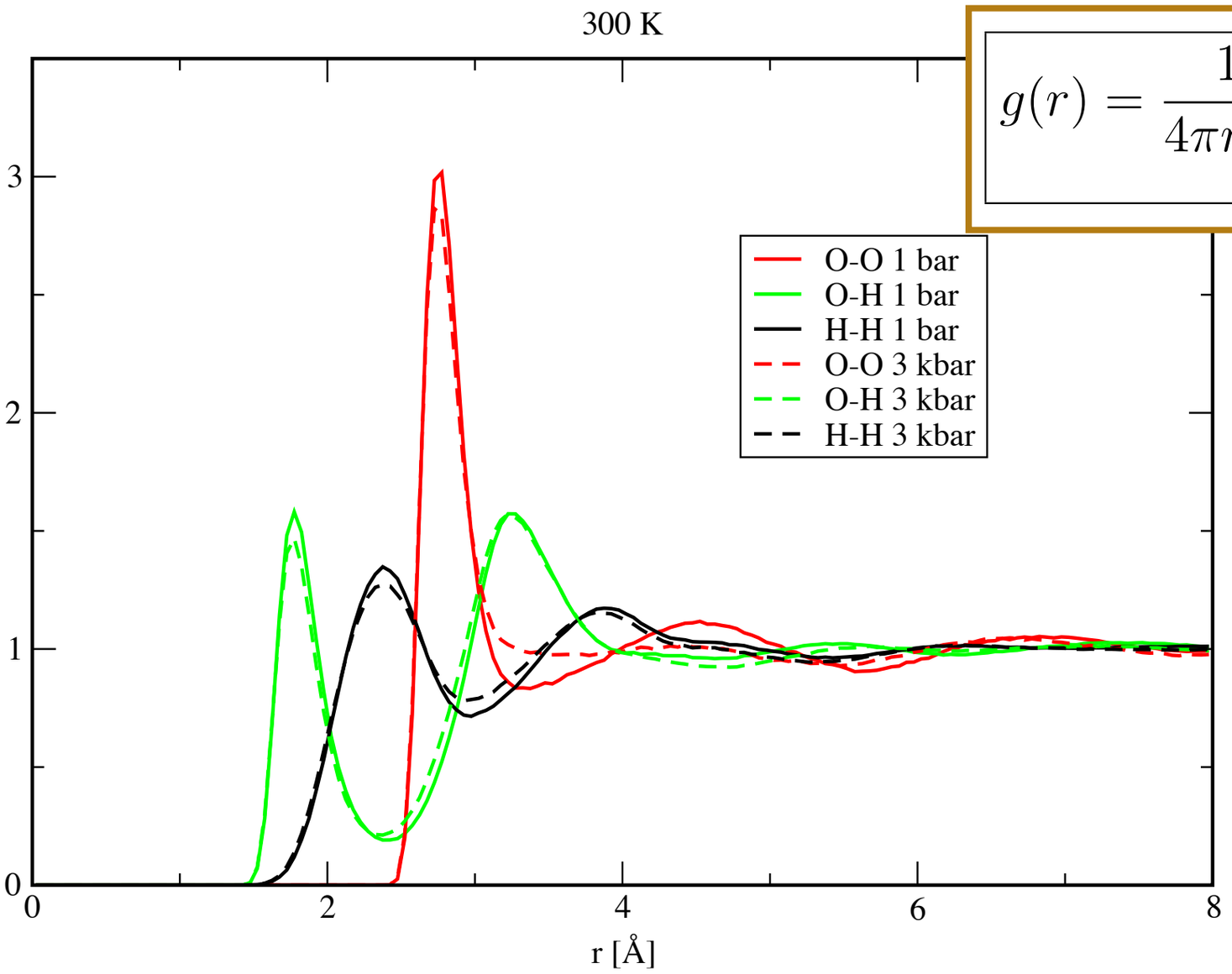
$$\omega_0 = \sqrt{\frac{18\cdot 2^{2/3}\epsilon}{\mu\sigma^2}}$$

For macromolecules like proteins only a small part of the motional frequency spectrum is accessible to classical MD!



Basic analysis of MD simulations

Static site pair correlation functions of water

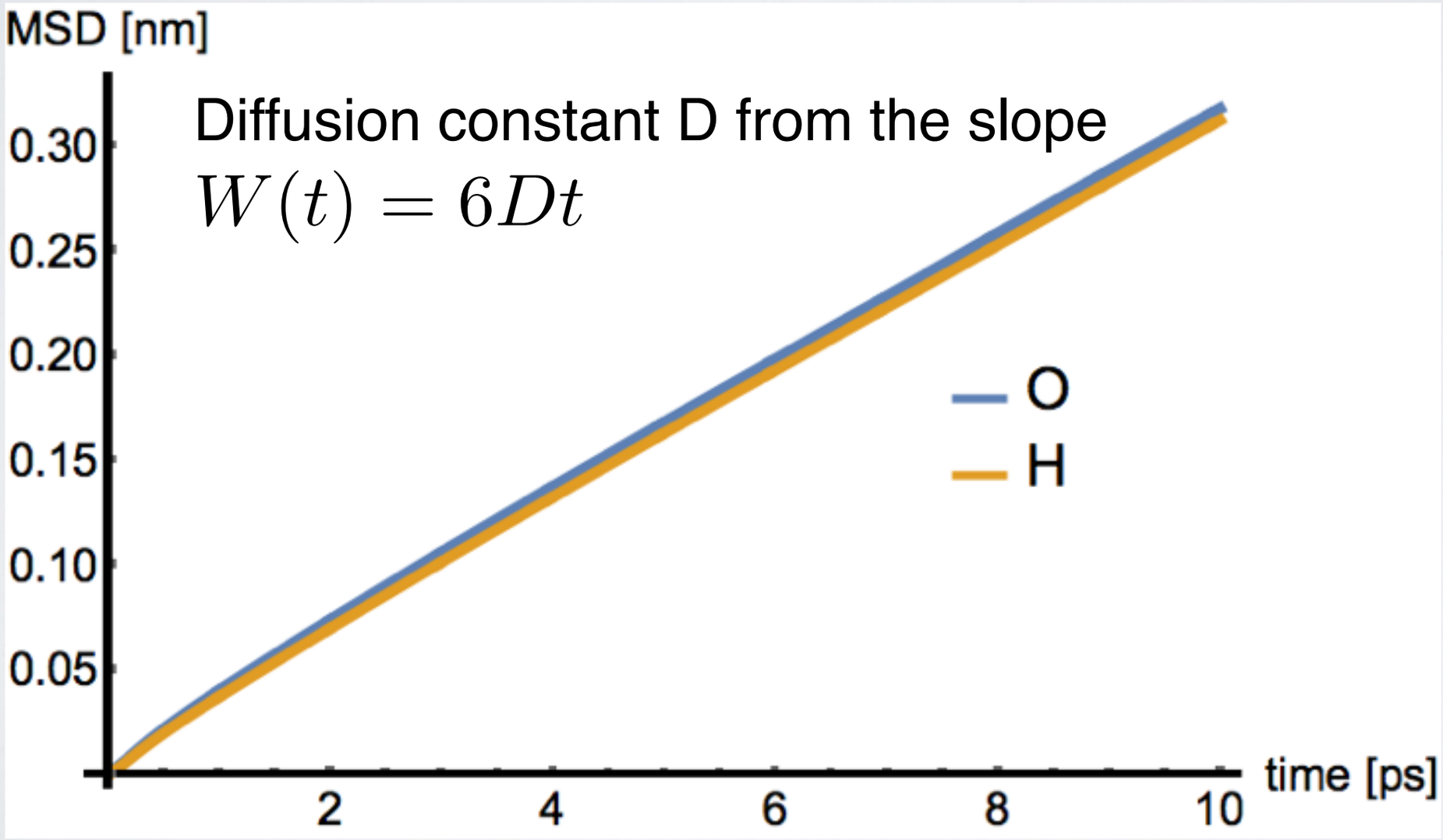


$$g(r) = \frac{1}{4\pi r^2 \rho} \frac{1}{N} \sum_{\alpha} \sum_{\beta \neq \alpha} \langle \delta(r - |R_\alpha - R_\beta|) \rangle$$

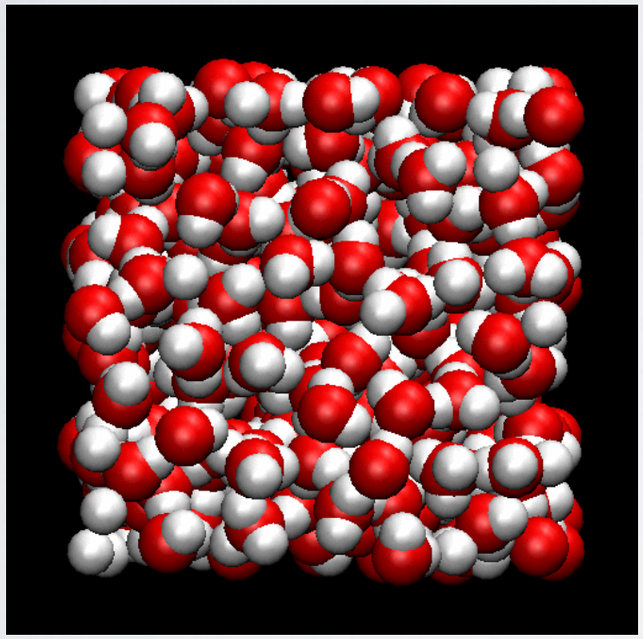
Atomic mean square displacements

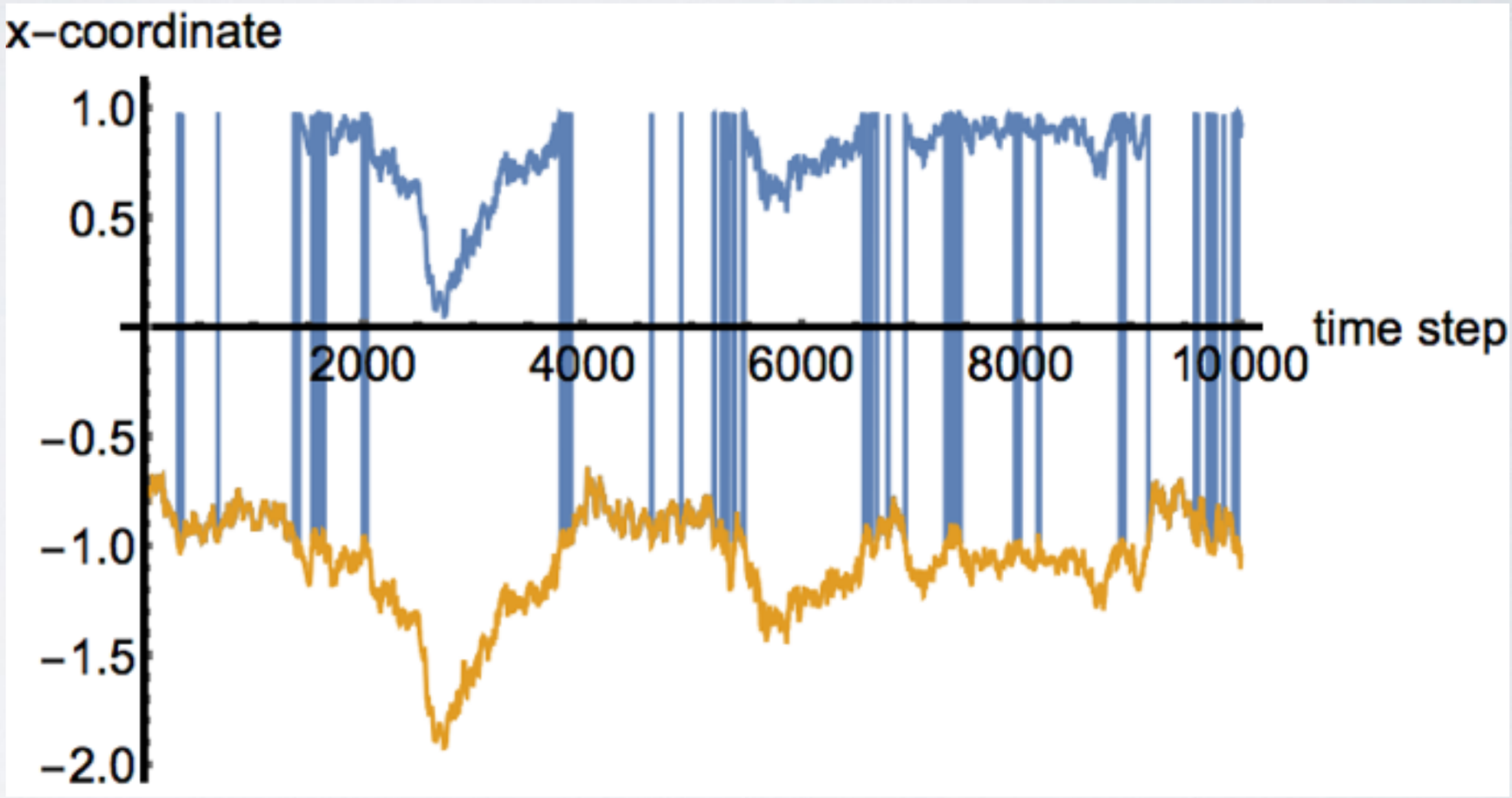
$$W^{(\alpha)}(n) \approx \frac{1}{N_t - |n|} \sum_{k=0}^{N_t-|n|-1} \left| \mathbf{x}^{(\alpha)}(k+n) - \mathbf{x}^{(\alpha)}(k) \right|^2$$

$$W(n) = \frac{1}{N} \sum_{\alpha=1}^{N} W_{vv}^{(\alpha)}(n) \quad \text{average over molecules}$$



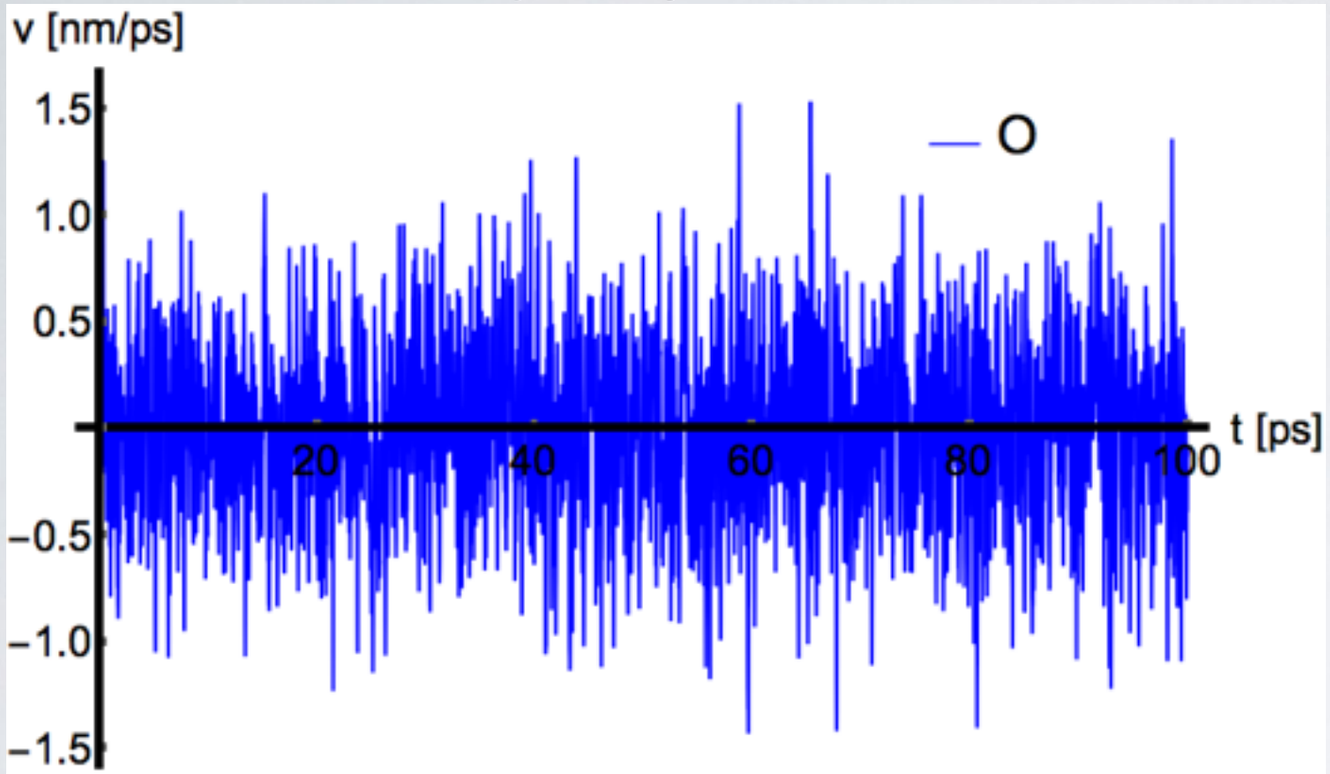
Remove first jumps due to p.b.c. !



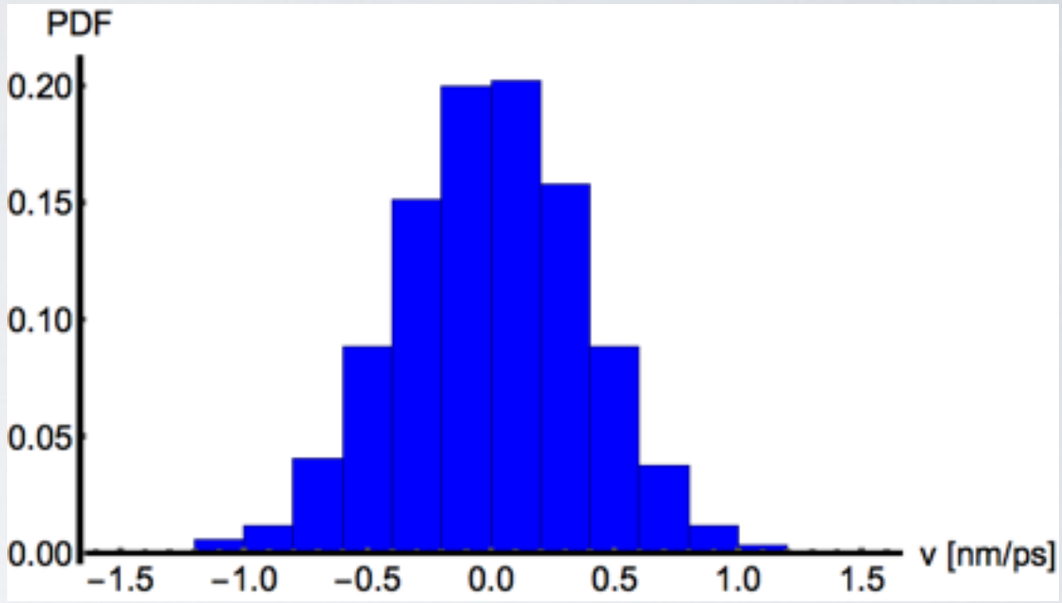


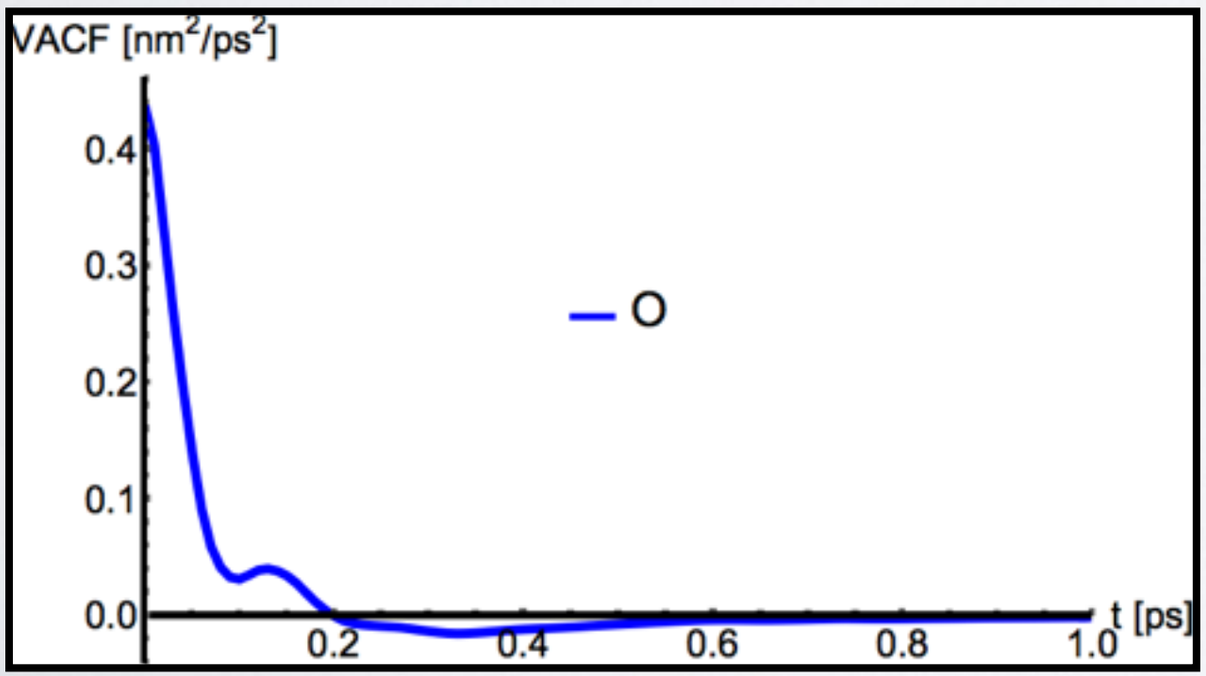
Velocity autocorrelation function (oxygen)

Trajectory



Maxwell distribution





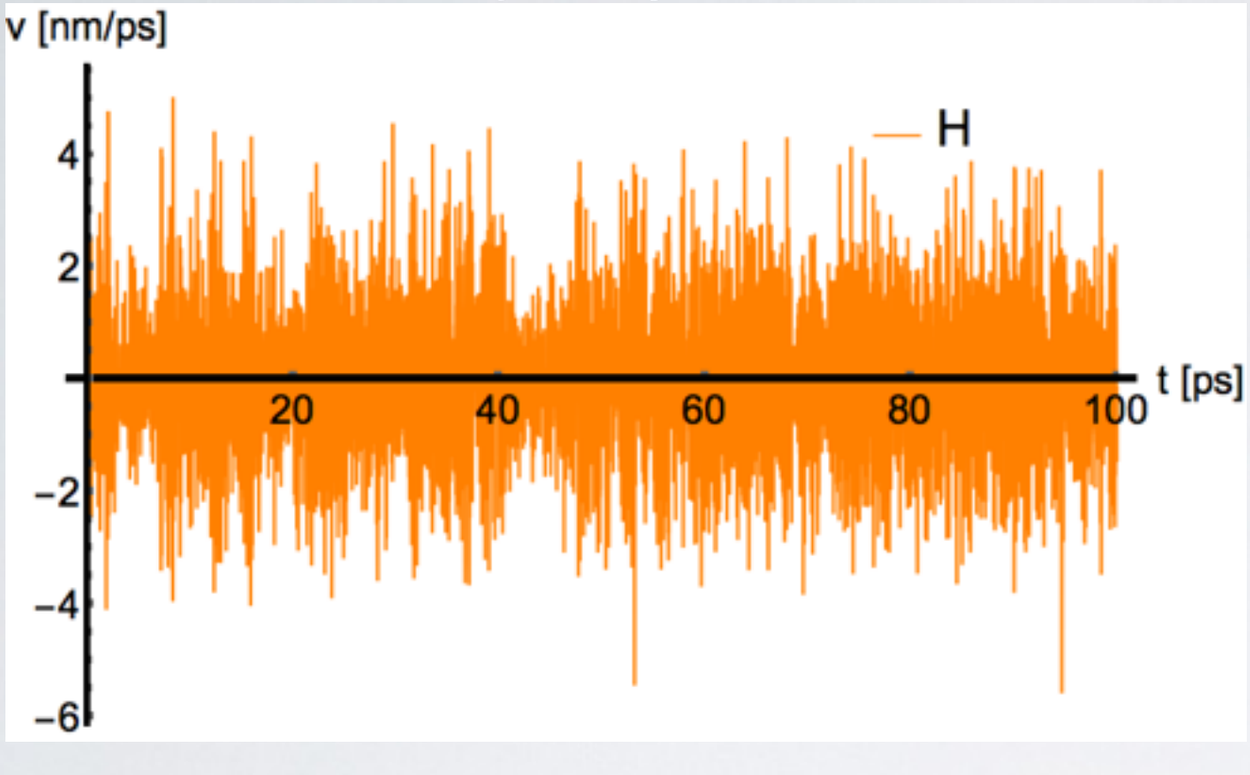
$$c_{vv}^{(\alpha)}(n) \approx \frac{1}{N_t - |n|} \sum_{k=0}^{N_t-|n|-1} \mathbf{v}^{(\alpha)}(k) \cdot \mathbf{v}^{(\alpha)}(k+n)$$

$$c_{vv}(n) = \frac{1}{N} \sum_{\alpha=1}^{N} c_{vv}^{(\alpha)}(n)$$

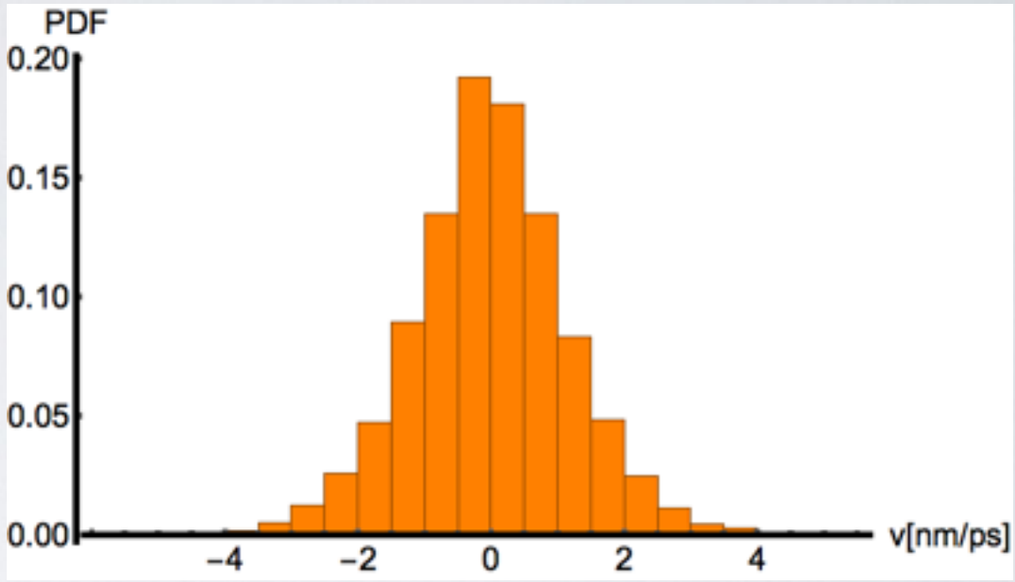
average over molecules

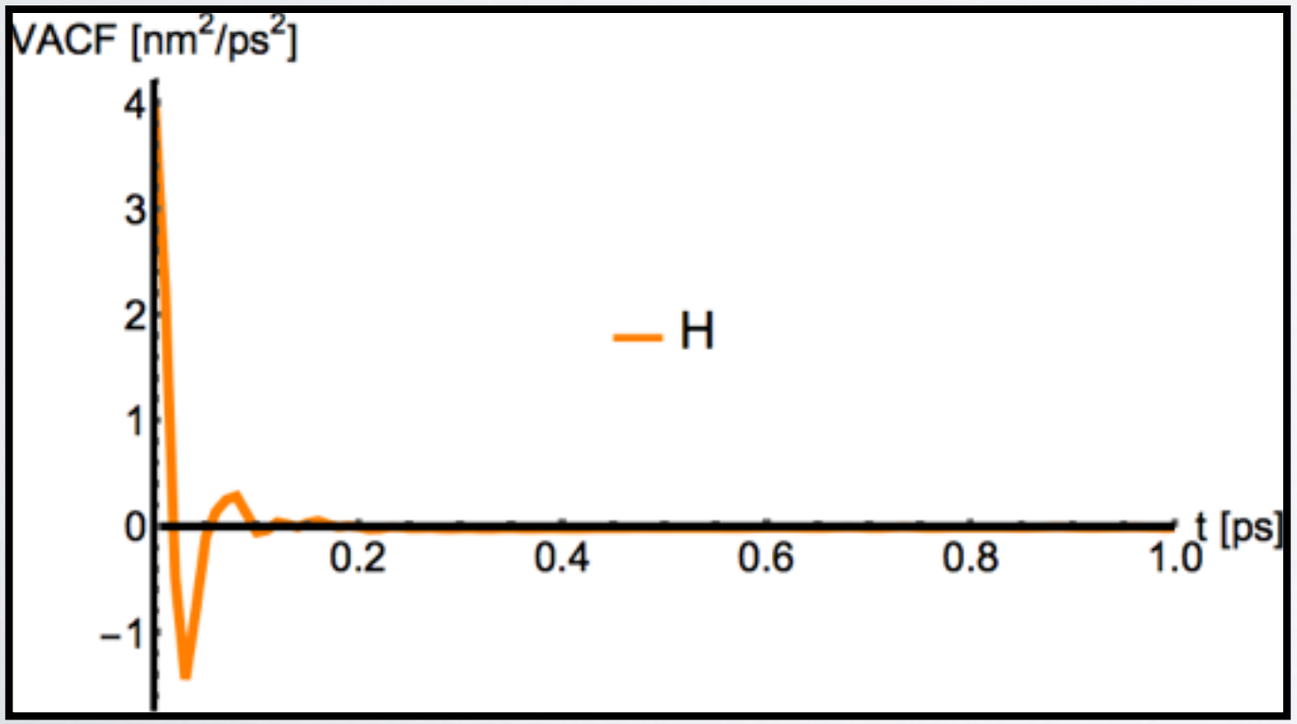
Velocity autocorrelation function (hydrogen)

Trajectory



Maxwell distribution

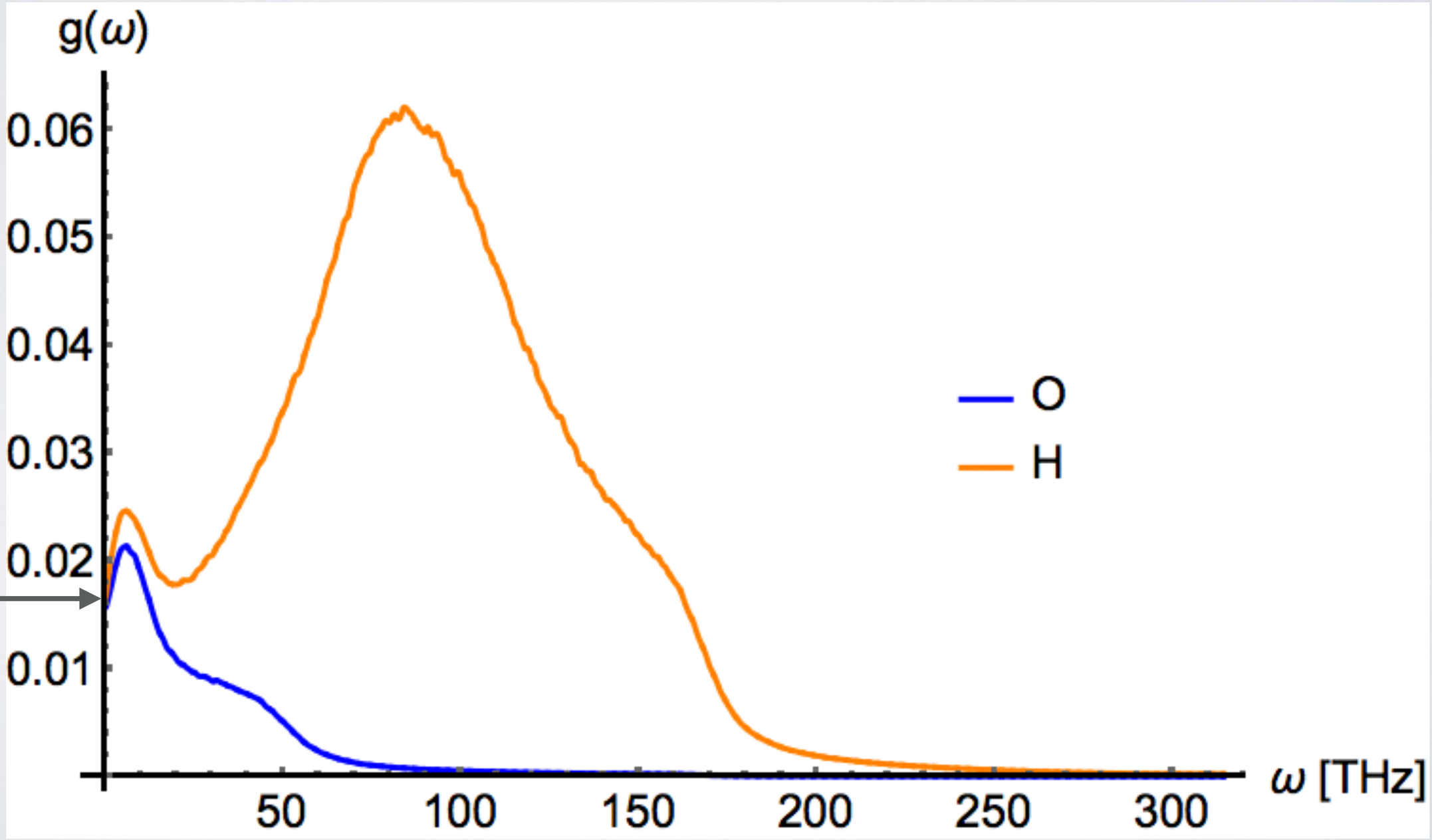




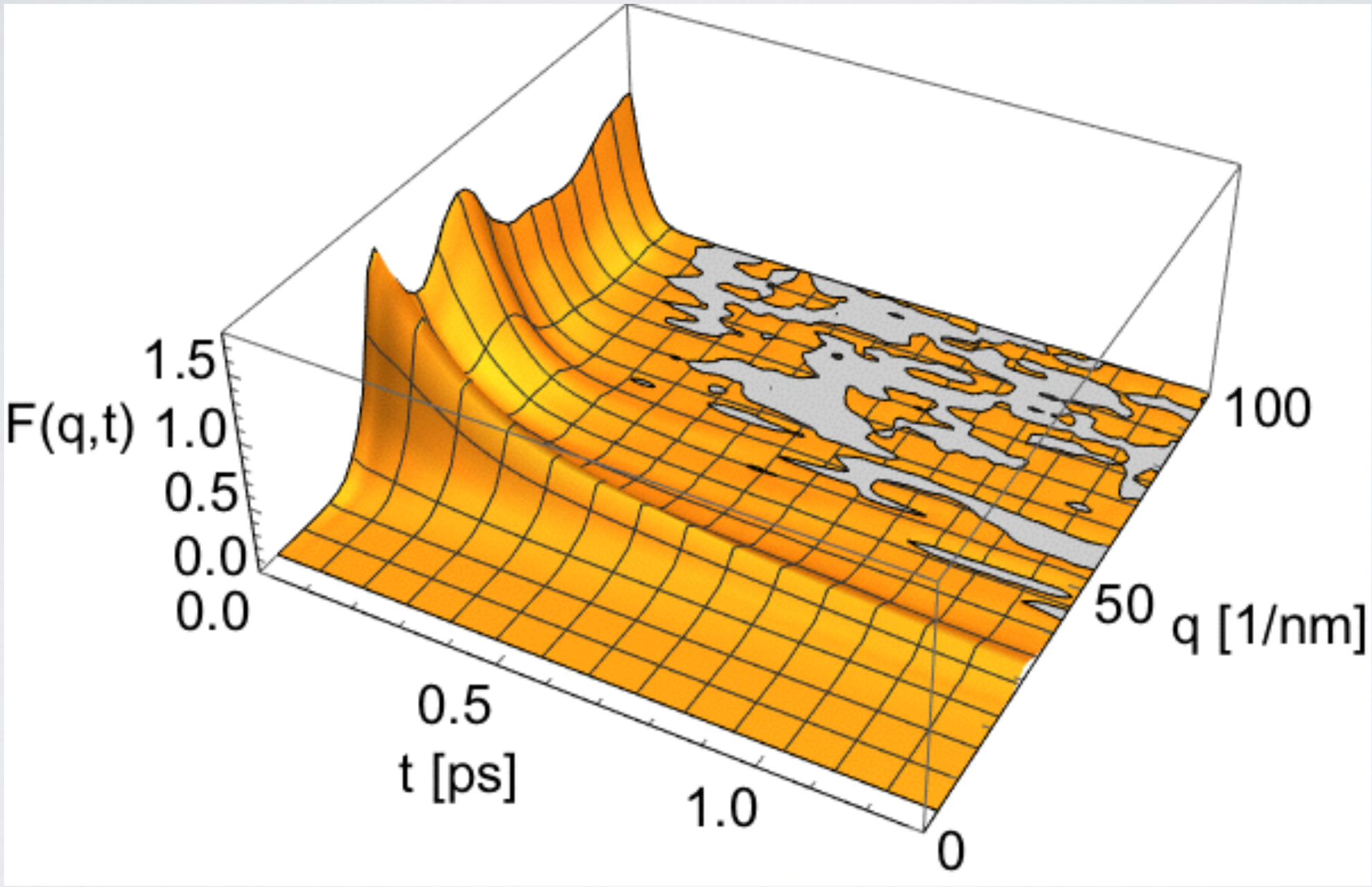
Density of States, VACF, and diffusion coefficient

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

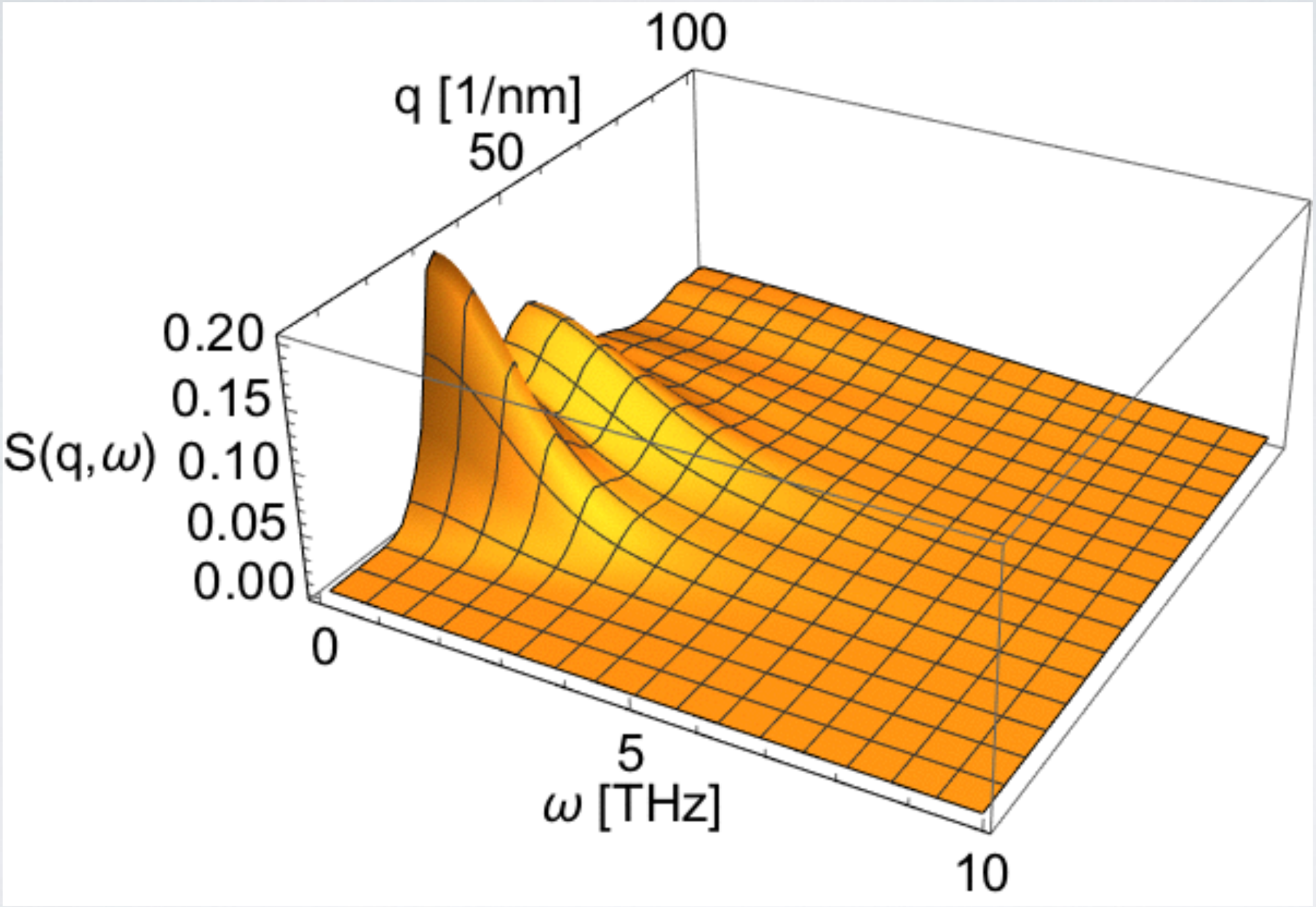
$$D = \int_0^\infty dt \, c_{vv}(t) = g(0),$$



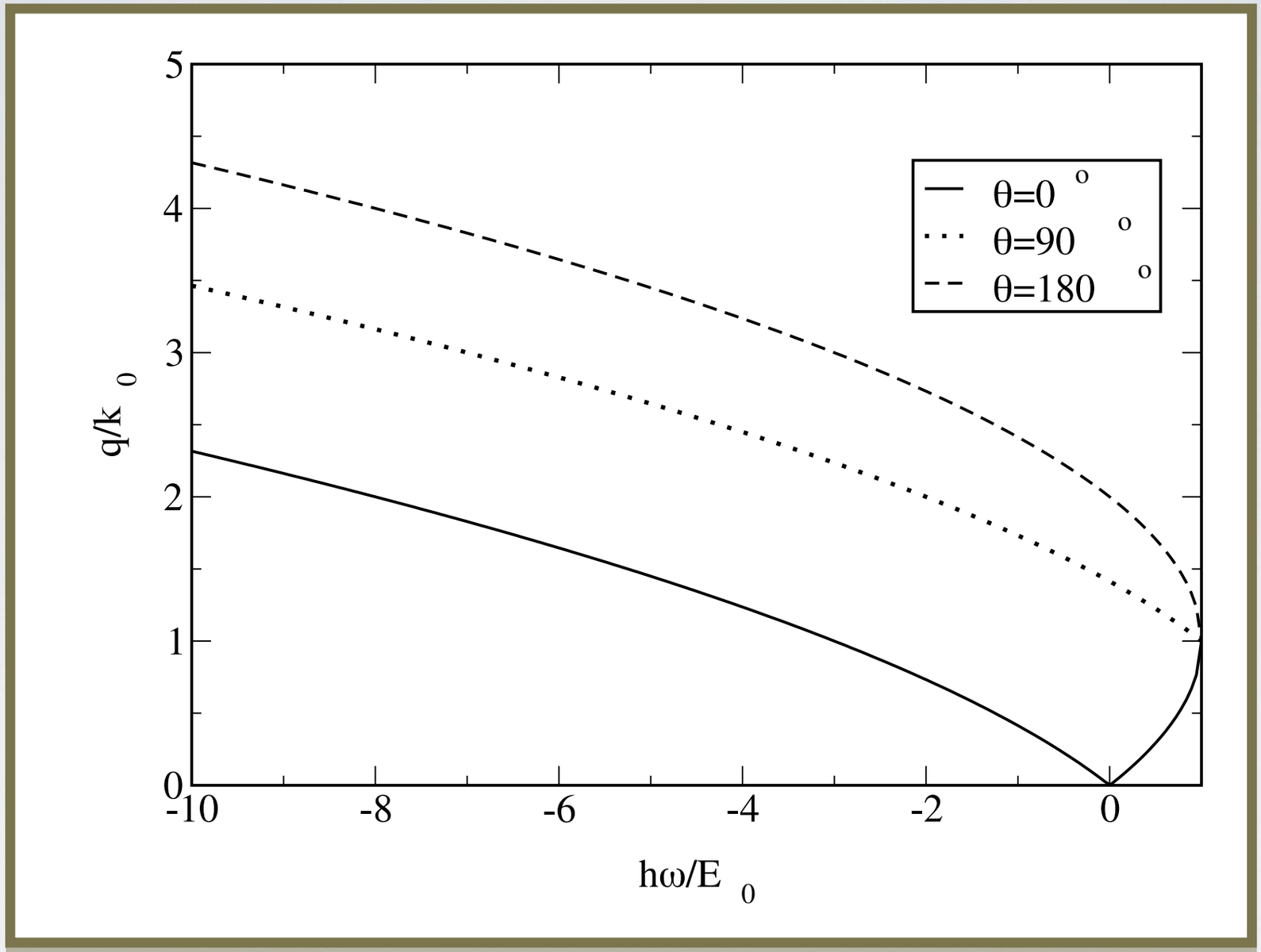
Coherent intermediate scattering function



Coherent dynamic structure factor



Experimentally accessible (q,ω)-range



$$|\vec{q}| = k_0 \sqrt{2 - \frac{\hbar\omega}{E_0} - 2\sqrt{1 - \frac{\hbar\omega}{E_0}}\cos\theta}$$

Calculation of time correlation functions - an « efficient detour » via Fourier space

The correlation theorem of the Fourier transform reads

$$\int_{-\infty}^{+\infty} dt\, f(t+\tau)g^*(\tau) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \tilde{f}(\omega)\tilde{g}^*(\omega)e^{i\omega t}$$

where

$$\tilde{f}(\omega) = \int_{-\infty}^{+\infty} d\omega\, f(t)e^{-i\omega t},$$

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \tilde{f}(\omega)e^{i\omega t},$$

is the Fourier transform pair of f.

Fast Correlation algorithm

The discrete version of the correlation theorem,

$$\sum_{k=0}^{N_t-1} f(n+k)g^*(k) = \frac{1}{N_t}\sum_{k=0}^{N_t-1} F(k)G^*(k)e^{2\pi i\frac{nk}{N_t}}$$

$$F(k) \stackrel{FFT}{=} \sum_{n=0}^{N_t-1} f(n)e^{-2\pi i\frac{nk}{N_t}},$$

can be used to compute correlation functions by a "detour" via a Fast Fourier Transform (FFT), which reduces the complexity from N_t^2 to $N_t \log_2 N_t$, N_t being the number of frames in the discrete signals. To avoid spurious correlations due to periodicity, use zero padding,

$$f(n) \to f_p(n) = \begin{cases} f(n) & \text{if} \quad 0 \le n \le N_t - 1, \\ 0 & \text{if} \quad N_t \le n \le 2N_t - 1. \end{cases}$$

Computing MSDs

Use here that [6]

$$\left\langle \left(x(n+k)-x(k)\right)^2 \right\rangle = 2\underbrace{\langle x(n+k)x(k)\rangle}_{\text{FCA}} + \underbrace{\left\langle x(n+k)^2 \right\rangle}_{\text{recursively}} + \underbrace{\left\langle x(k)^2 \right\rangle}_{\text{recursively}}.$$

[6] G.R. Kneller *et al.*, Comput Phys Commun 91, 191 (1995).

Modeling MD time series and correlation functions

Autoregressive time series model

$$v(n) \equiv v(n\Delta t), \quad n \in \mathbb{Z}.$$

time series

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

AR model of order P

$$\begin{aligned} \langle \epsilon_P(n) \rangle &= 0, \\ \langle \epsilon_P(n) \epsilon_P(n') \rangle &= \sigma_P^2 \delta_{nn'}. \end{aligned}$$

"white noise"

parameters of the model: $\alpha_1^{(P)}, \ldots, \alpha_P^{(P)}, \sigma_P$

Wiener-Hopf equations for the coefficients

$$\langle \epsilon_P(n) v(n-k) \rangle = 0 \qquad (k = 1, \ldots, P)$$

$$\sum_{k=1}^{P} c_{vv}(|j-k|) a_k^{(P)} = c_{vv}(j), \qquad j = 1 \ldots P$$

yields the coefficients $a_k^{(P)}$

$$\sigma_P^2 = c_{vv}(0) - \sum_{k=1}^{P} a_k^{(P)} c_{vv}(k)$$

Wiener-Khintchin theorem for discrete signals

- **Finite sample of a signal**

$$v_M(n) = \begin{cases} v(n) & \text{si} \quad -M \leq n \leq M \\ 0 & \text{sinon} \end{cases}$$

- **z-Transform**

$$f(n) = \frac{1}{2\pi i} \oint_C dz\, z^{n-1} F_{(>)}(z) \quad \longleftrightarrow \quad F(z) = \sum_{n=-\infty}^{+\infty} f(n) z^{-n}.$$

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

$$(f \circ g)(n) = \sum_{j=-\infty}^{+\infty} f(n+j) g^*(j) \quad \longleftrightarrow \quad F(z) G^*(1/z^*)$$

- **Correlation function**

$$c_{vv}(n) = \lim_{M \to \infty} \frac{1}{2M+1} \sum_{k=-M}^{M} v(n+k) v^*(k)$$

$$\boxed{C_{vv}(z) = \lim_{M \to \infty} \frac{1}{2M+1} V_M(z) V_M^*(1/z^*)}$$

Analytical form of the z-transformed correlation function

AR model

$$V(z) = \frac{\mathcal{E}_P(z)}{1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}}$$

$$\lim_{M\to\infty} \frac{1}{2M+1} V(z)V^*(1/z^*) = \frac{\lim_{M\to\infty} \frac{1}{2M+1} \mathcal{E}_P(z)\mathcal{E}_P^*(1/z^*)}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

$$C_{vv}^{(AR)}(z) = \frac{C_{\epsilon\epsilon}(z)}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

$$C_{vv}^{(AR)}(z) = \frac{\sigma_P^2}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

"all pole" model

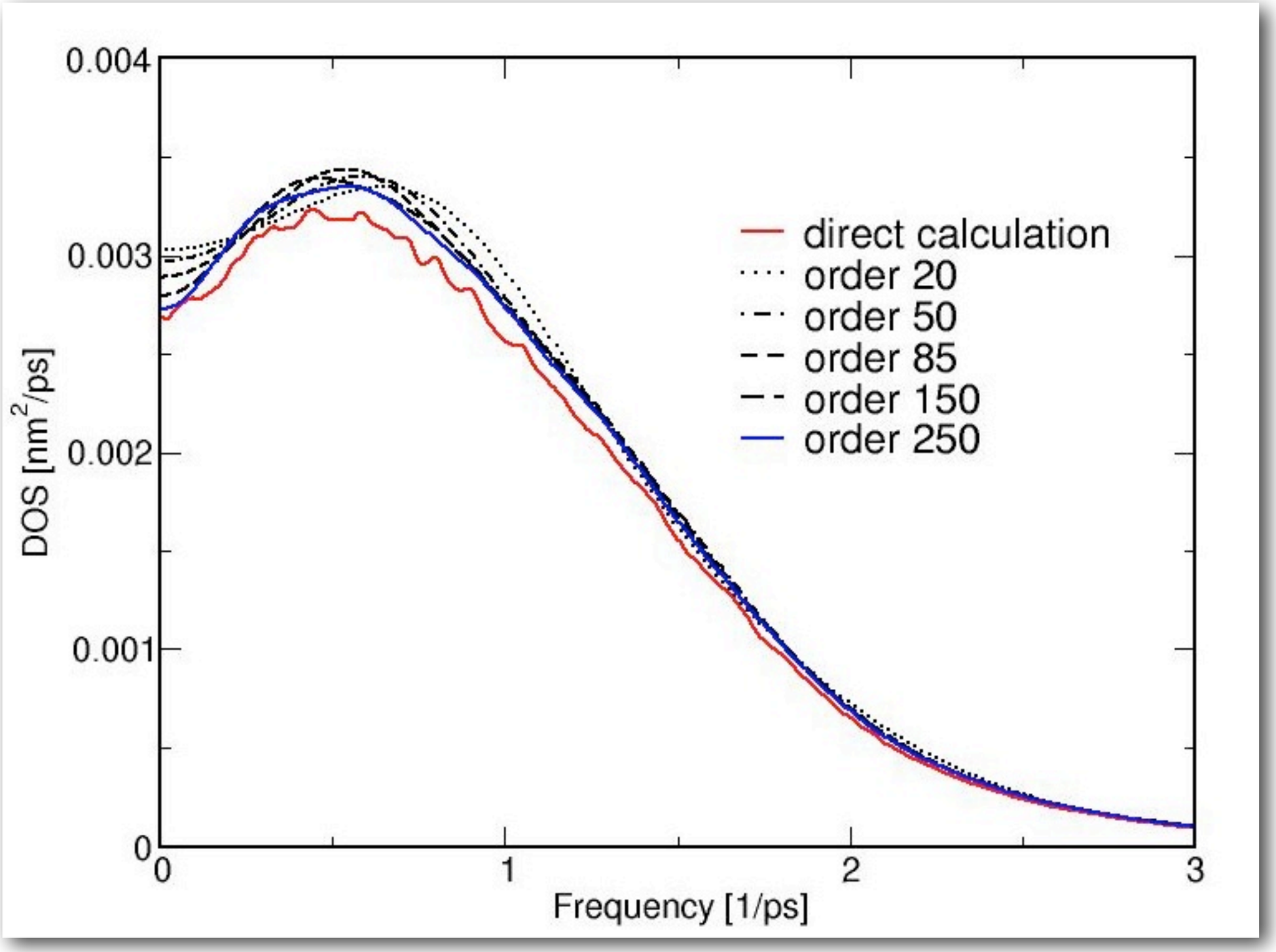
Analytical form of the Fourier-transformed correlation function

$$\tilde{c}_{vv}^{(AR)}(\omega) = \Delta t \sum_{n=-\infty}^{+\infty} c_{vv}^{(AR)}(n) \exp[-in\omega\Delta t] \approx \tilde{c}_{vv}(\omega)$$

$$\boxed{\tilde{c}_{vv}^{(AR)}(\omega) = \Delta t \, C_{vv}^{(AR)}\left(\exp[i\omega\Delta t]\right)}$$

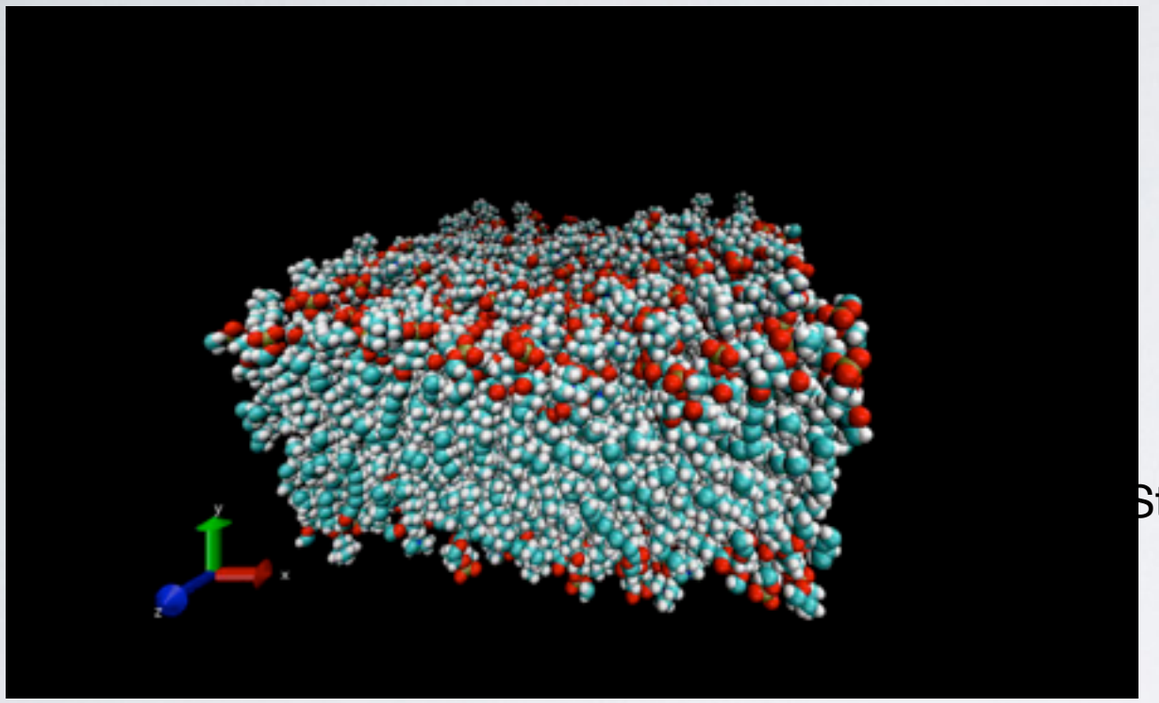
$$g(\omega) \approx \frac{\sigma_P^2 \Delta t}{2\left|1 - \sum_{k=1}^{P} a_k^{(P)} \exp(-i\omega k \Delta t)\right|^2}.$$

Application to a simple liquid (argon)



G.R. Kneller and K. Hinsen. *J. Chem. Phys.*, 115(24):11097–11105, 2001.

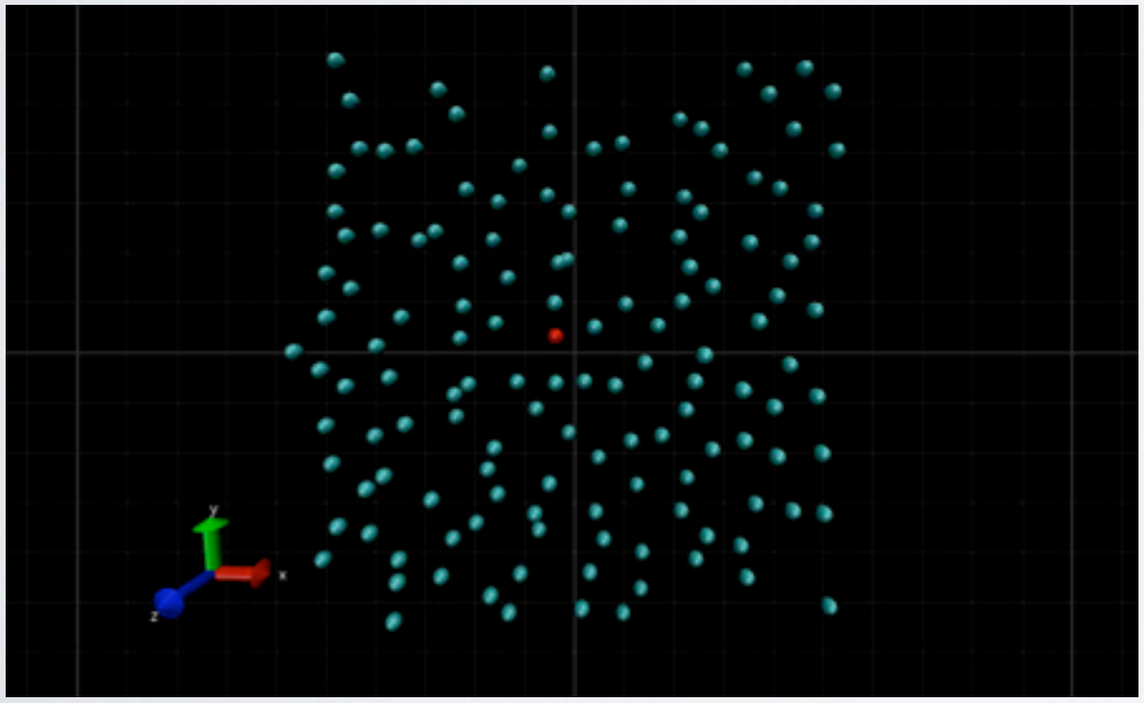
Anomalous diffusion of molecules in a lipid bilayer



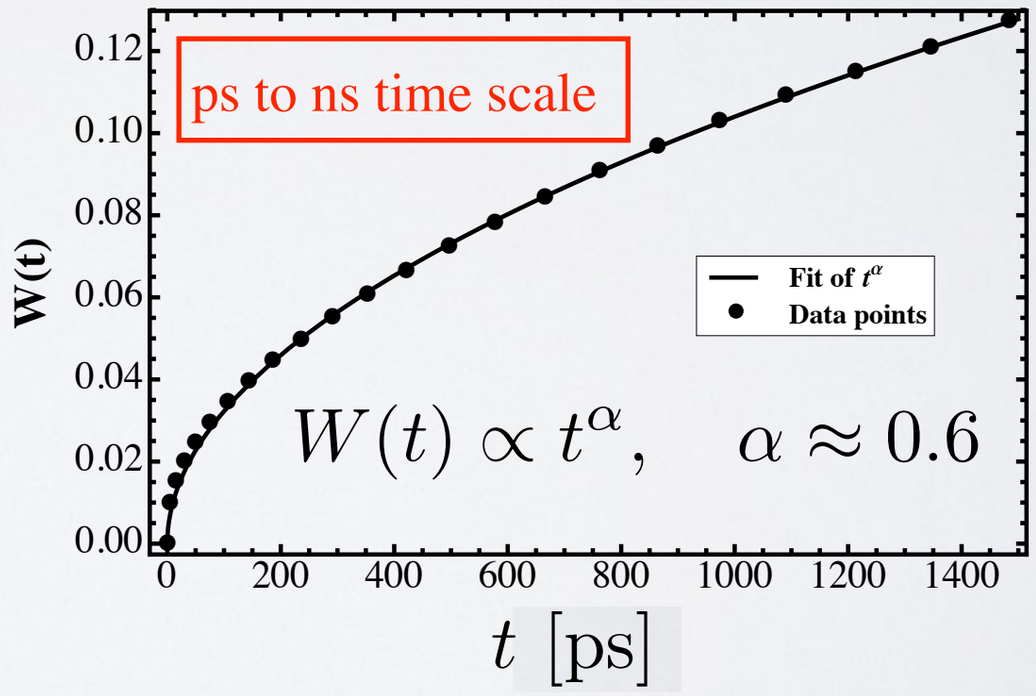
S. Stachura and G.R. Kneller, Mol Sim. 40, 245 (2013).
S. Stachura and G.R. Kneller, J Chem Phys in rint .

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

Stachura and G. R. Kneller. Probing anomalous diffusion in frequ



MSD for lateral diffusion



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 is known since long time

ANOMALOUS DIFFUSION IN TRUE SOLUTION.

By Herbert Freundlich and Deodata Krüger.

Received 30th April, 1935.

H. Freundlich and D. Krüger, Trans. Faraday Soc. 31, 906 (1935).

$$\sigma^2(t) := \frac{\int d^n r\, |\mathbf{r}|^2 f(\mathbf{r},t)}{\int d^n r\, f(\mathbf{r},t)}$$

Anomalous Diffusion of Acetone into Cellulose Acetate*

F. A. Long, E. Bagley, and J. Wilkens
Department of Chemistry, Cornell University, Ithaca, New York
(Received May 18, 1953)

F.A. Long, E. Bagley, and J. Wilkens,
The Journal of Chemical Physics 21, 1412 (1953).

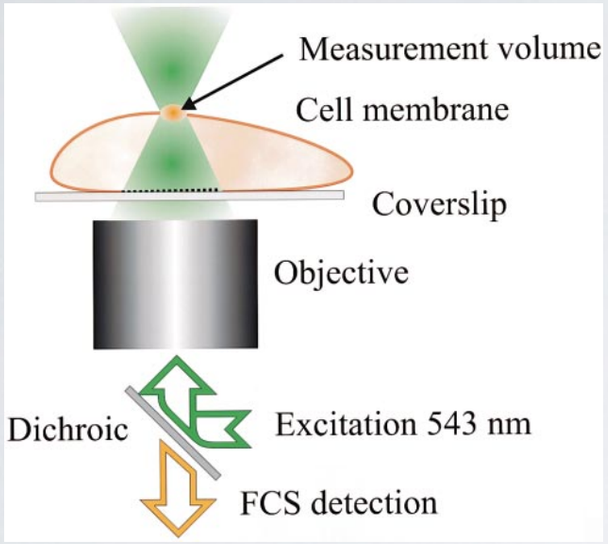
$$\sigma^2(t) \propto t^{\alpha}$$

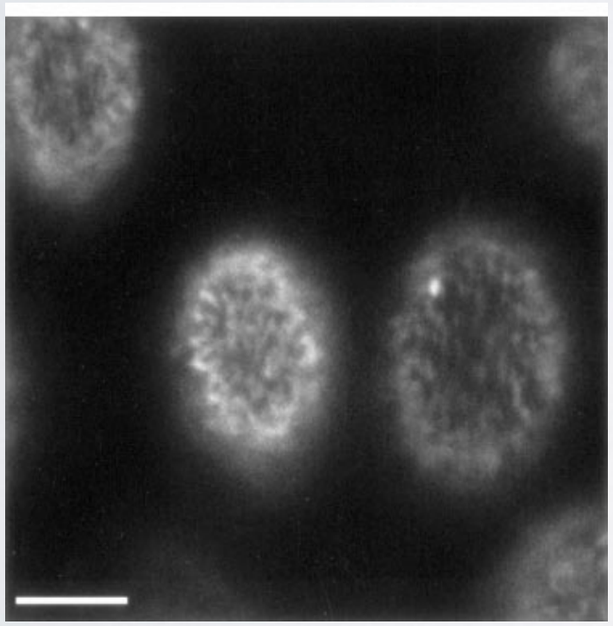
$$0 < \alpha < 1$$

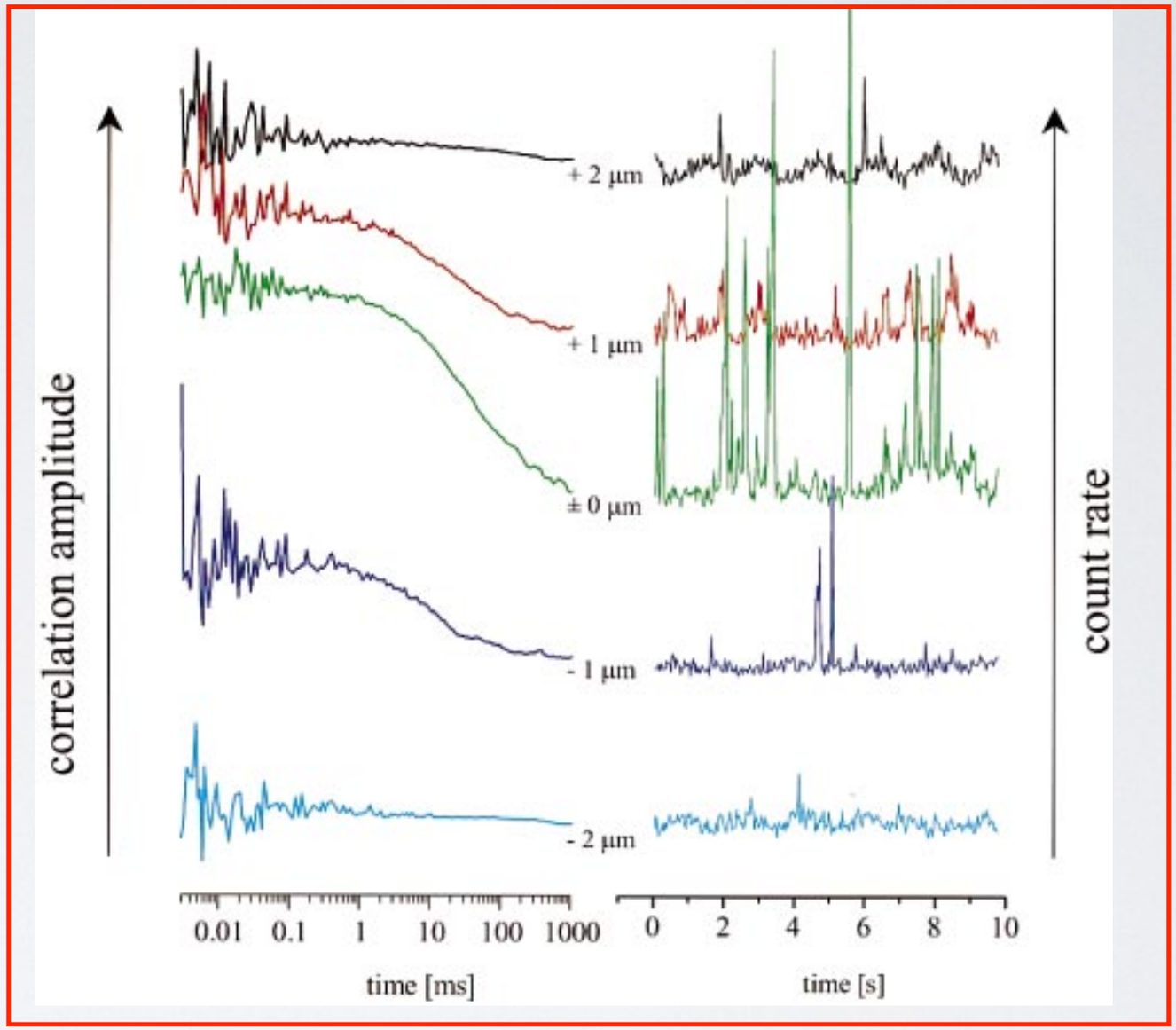
(subdiffusion)

Subdiffusion of lipids observed by FCS

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







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

ms to s time scale

Fractional diffusion/Fokker Planck equation

W. Wyss, Journal of Mathematical Physics 27, 2782 (1986).
R. Metzler, E. Barkai, and J. Klafter, Phys Rev Lett 82, 3563 (1999).

$$\frac{\partial}{\partial t}p(\mathbf{r},t|\mathbf{r}_0,0) = \partial_t^{1-\alpha}\, D_\alpha \Delta p(\mathbf{r},t|\mathbf{r}_0,0)$$

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

Fractional derivative

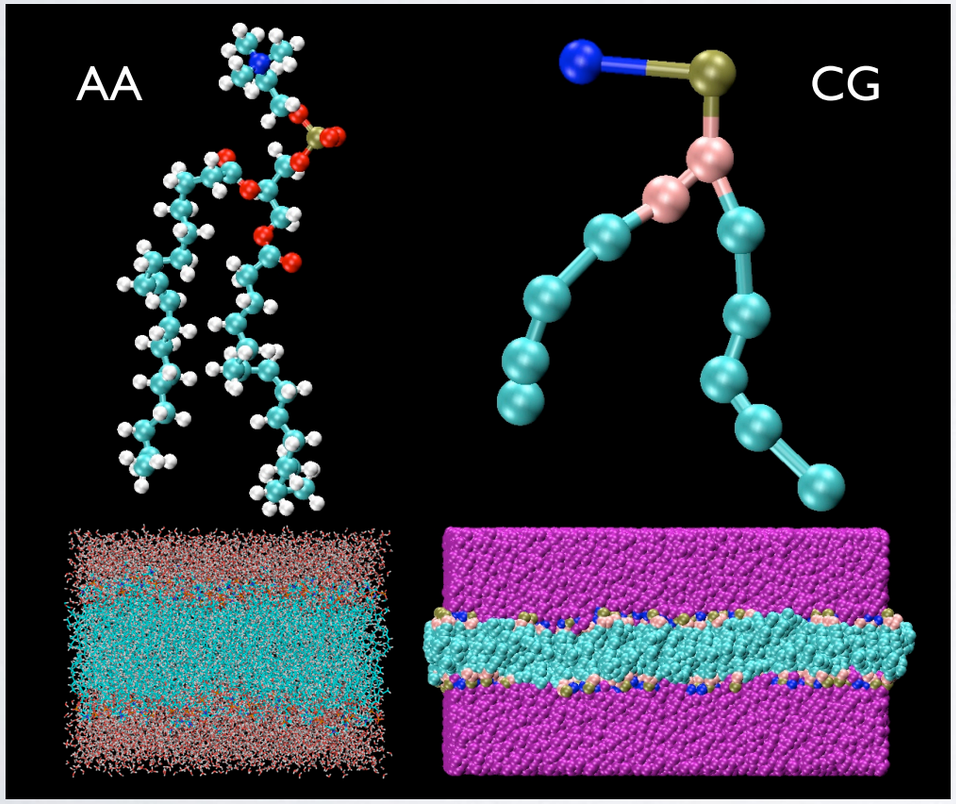
$$W(t) = \frac{2nD_\alpha t^\alpha}{\Gamma(1+\alpha)}.$$

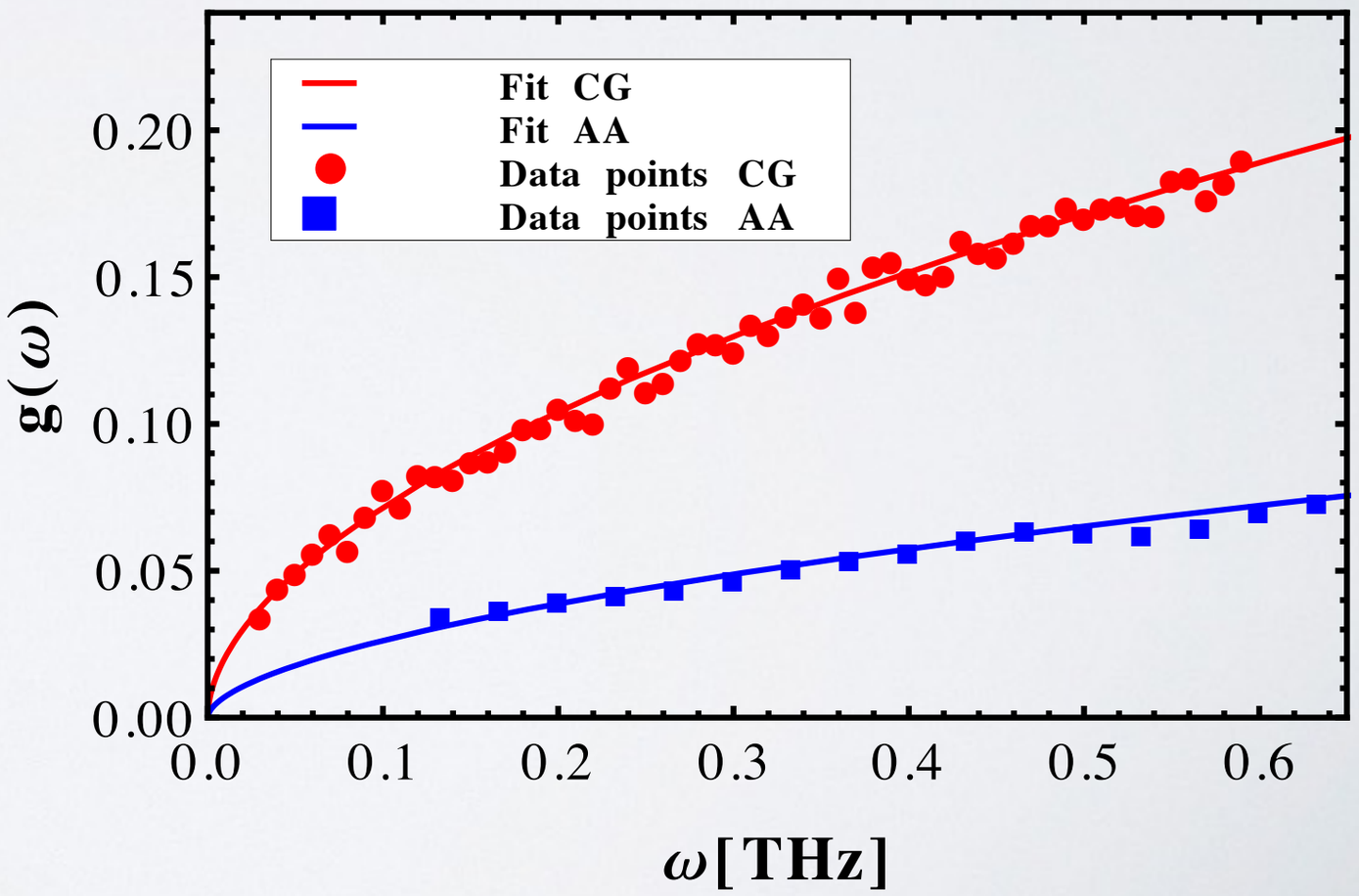
Precise calculation of the low-frequency DOS

S. Stachura and G.R. Kneller, J .Chem. Phys., vol. 143, p. 191103, 2015.

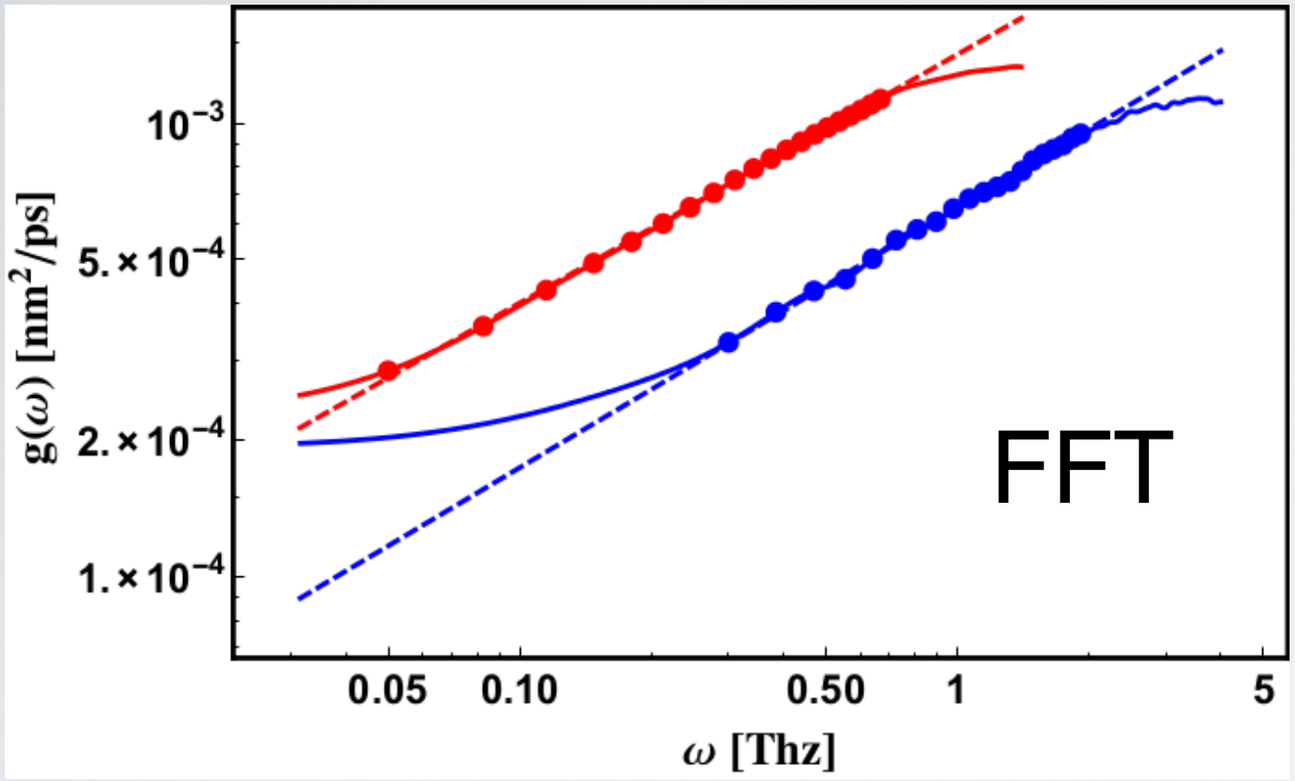
$$g(\omega) = \int_0^\infty dt\, \cos(\omega t) c_{vv}(t) \overset{\omega \ll 1/\tau_v}{\sim} D_\alpha\, \omega^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right)$$

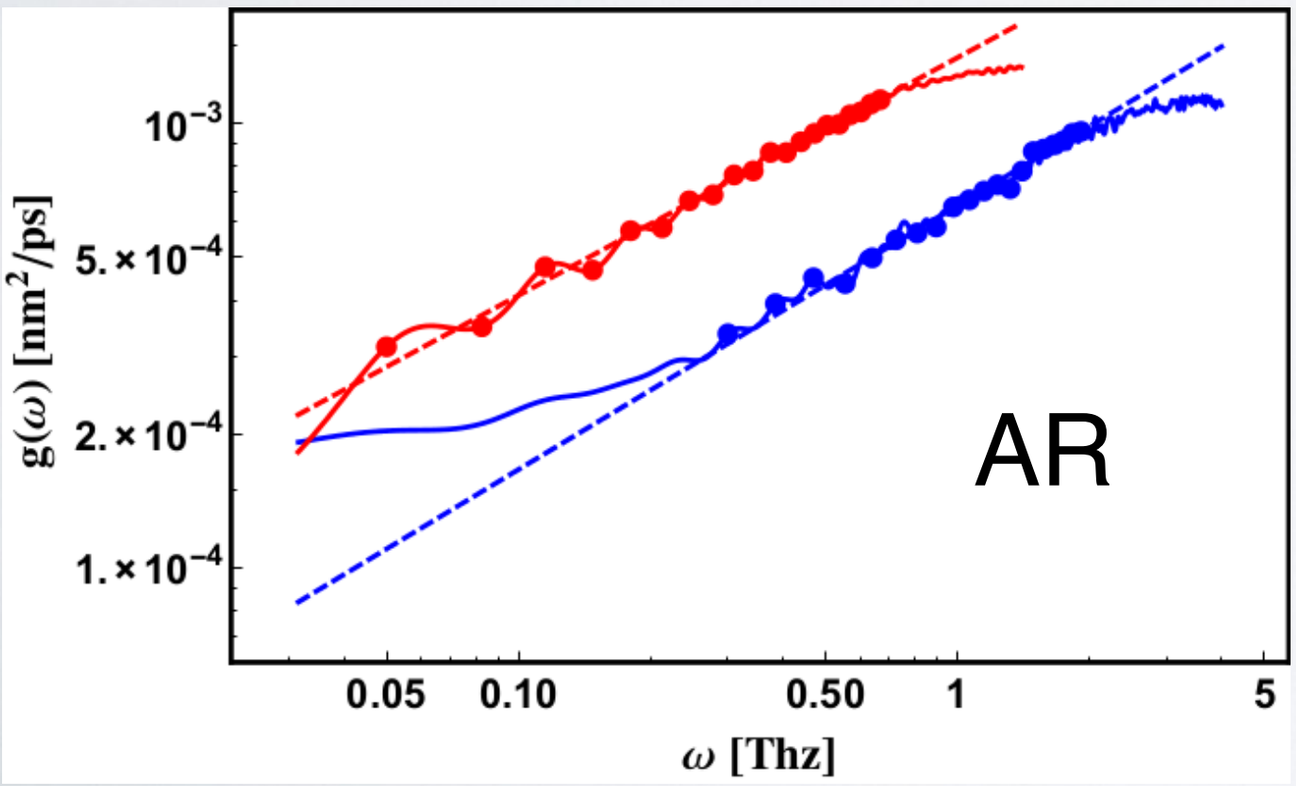
Compare the low freq. DOS for POPC simulations with an all-atom (OPLS) and a coarse-grained (MARTINI) force field:





Low frequency DOS - FFT versus AR estimation

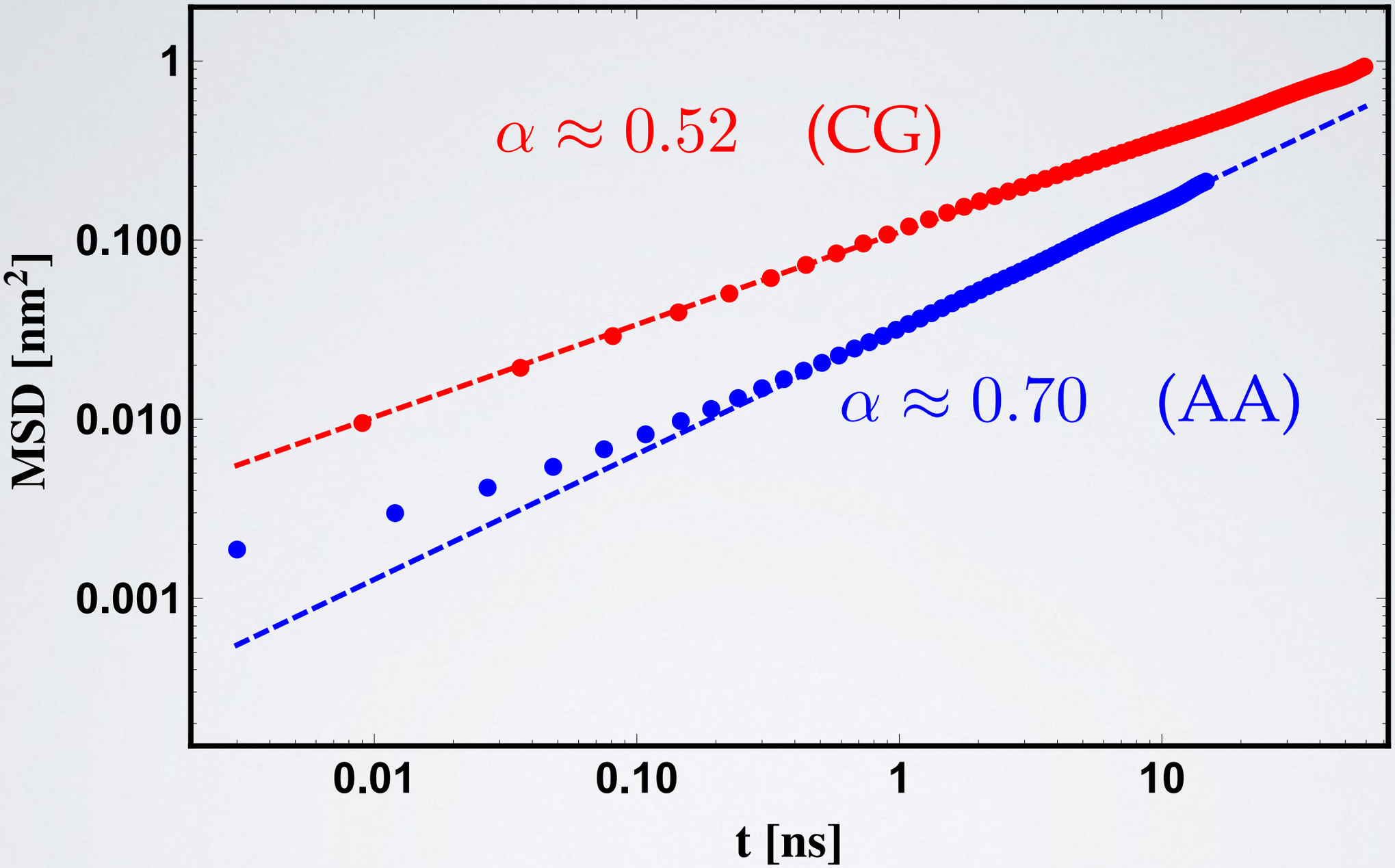




Precision in the lose-frequency regime matters!

Both FFT and AR estimations give very similar results

Mean square displacement (log-log)



α	MSD	WDFT	MEE
AA	0.700 ± 0.003	0.426 ± 0.007	0.406 ± 0.018
CG	0.516 ± 0.002	0.452 ± 0.003	0.466 ± 0.012

D_α	MSD	WDFT	MEE
AA	0.0160 ± 0.0001	0.0225 ± 0.0003	0.0205 ± 0.0007
CG	0.0555 ± 0.0003	0.0466 ± 0.0004	0.0394 ± 0.0012

TABLE I: Fit parameters α and D_α [$\mathrm{nm}^2/\mathrm{ps}^\alpha$], obtained by fits of a) Expression (1) to the MSD, b) Expression (5) to $g(\omega)$ from a windowed discrete Fourier transform, c) Expression (5) to $g(\omega)$ from maximum entropy estimation. Here AA stands for ”all atom” and CG to ”coarse-grained.

Relation with QENS

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

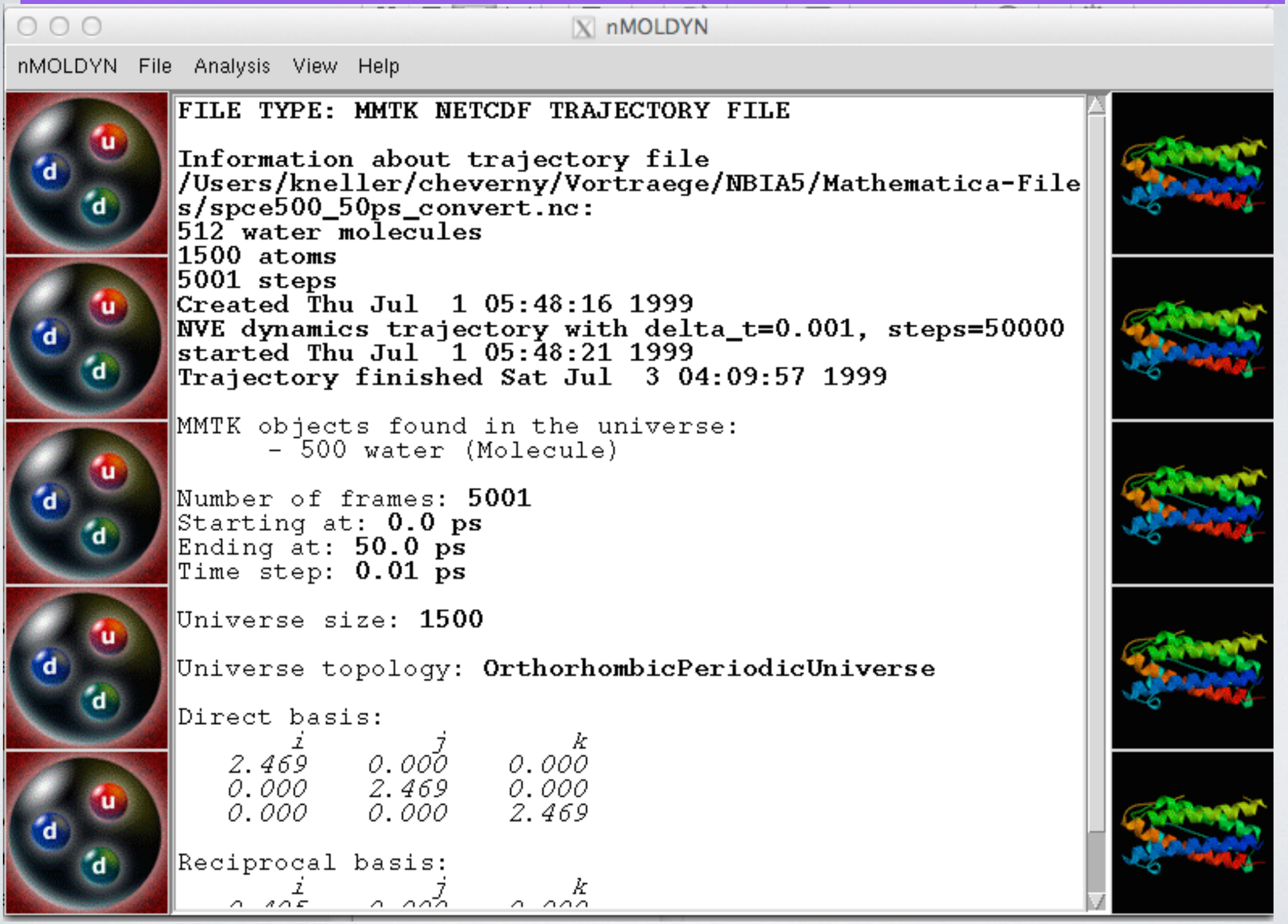
where $g(\omega) \overset{\omega\to 0}{\sim} \omega^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) \Gamma(1+\alpha) D_\alpha$

The asymptotic small frequency regime can be estimated through

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

where τ_v is in the picosecond regime.

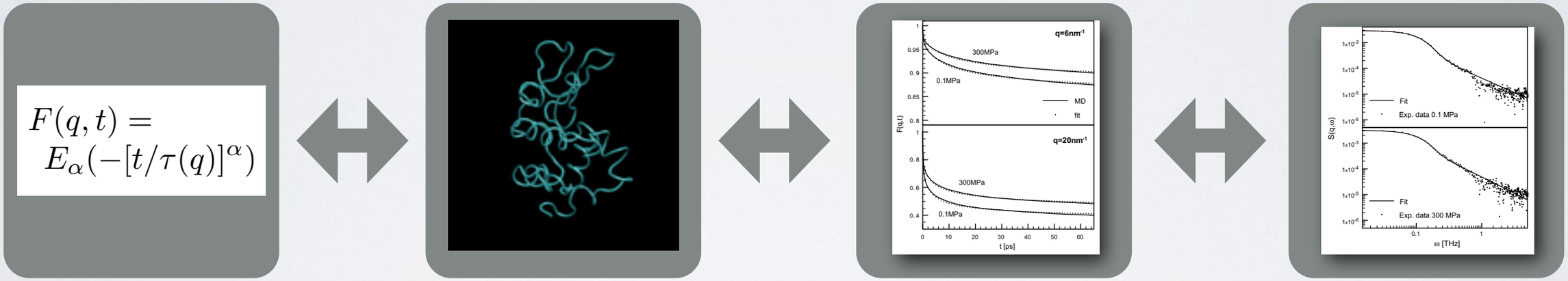
nMoldyn


nMOLDYN
nMOLDYN File Analysis View Help
FILE TYPE: MMTK NETCDF TRAJECTORY FILE
Information about trajectory file
/Users/kneller/cheverny/Vortraege/NBIA5/Mathematica-File
s/spce500_50ps_convert.nc:
512 water molecules
1500 atoms
5001 steps
Created Thu Jul 1 05:48:16 1999
NVE dynamics trajectory with delta_t=0.001, steps=50000
started Thu Jul 1 05:48:21 1999
Trajectory finished Sat Jul 3 04:09:57 1999
MMTK objects found in the universe:
- 500 water (Molecule)
Number of frames: 5001
Starting at: 0.0 ps
Ending at: 50.0 ps
Time step: 0.01 ps
Universe size: 1500
Universe topology: OrthorhombicPeriodicUniverse
Direct basis:
i j k
2.469 0.000 0.000
0.000 2.469 0.000
0.000 0.000 2.469
Reciprocal basis:
i j k

Ideal and «real» *in silico* experiments...

Integrating molecular simulation in "virtual" experiments probing the structure and dynamics of condensed matter

Model	Simulation	Ideal experiment	Real experiment



Model development

Detailed analysis

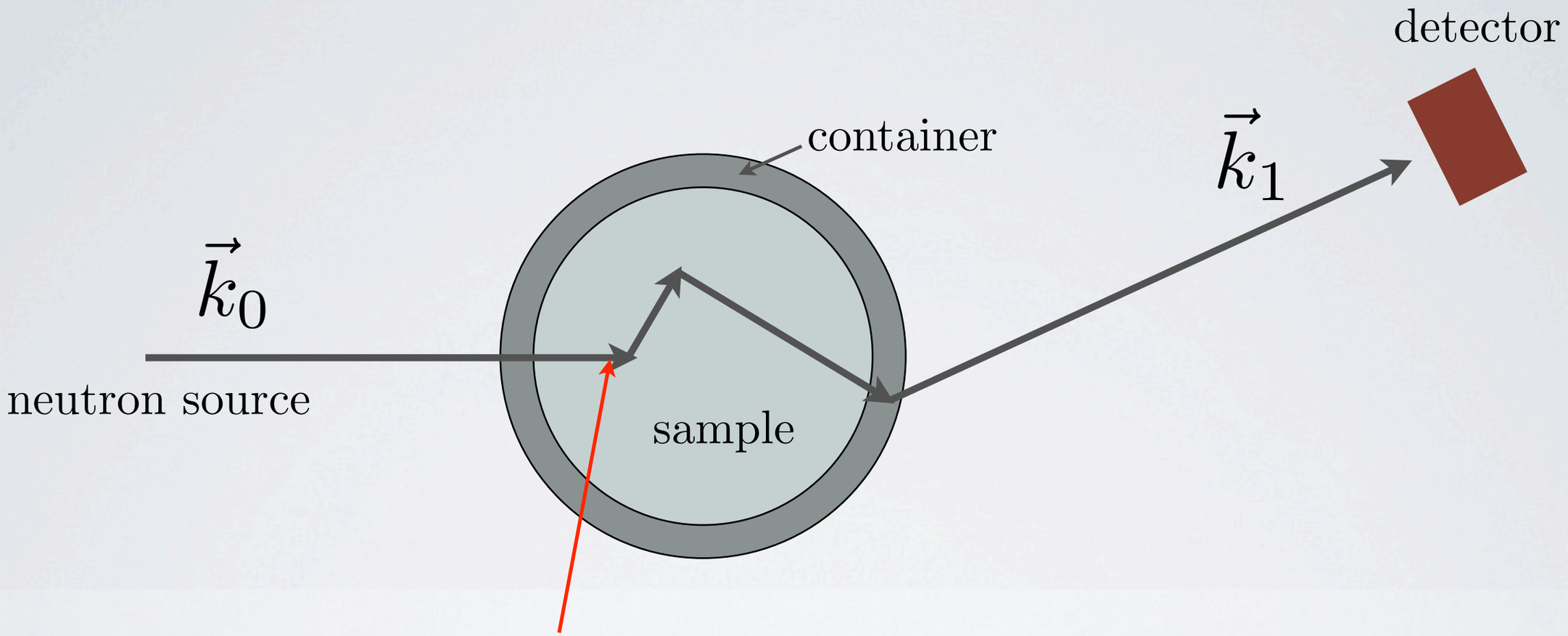
Environment

"Classical" nMoldyn

nMoldyn + McStas

Multiple scattering: example for an undesirable effect

In the MDANSE version of nMoldyn, such effects can be simulated with the McStas instrument simulator



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

Differential scatterung cross section for ideal experiment

References

nMoldyn

1. G.R. Kneller, V. Keiner, M. Kneller, and M. Schiller, Comp. Phys. Commun. 91, 191 (1995).
2. T. Rog, K. Murzyn, K. Hinsen, and G.R. Kneller, J Comp. Chem. 24, 657 (2003).
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Other

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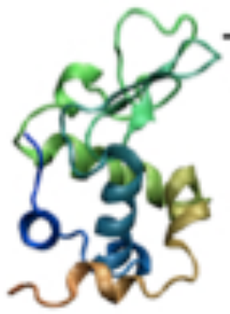

Theoretical Biophysics, Molecular Simulation, and Numerically Intensive Computation

Software

Aller au niveau supérieur

Numerical methods are of little use without ready-to-use and tested implementations. Our policy is to make all methods developped in the group freely available to the scientific community.

MMTK — Par Konrad Hinsen — Dernière modification 13/02/2007 18:28

The Molecular Modelling Toolkit is a library which contains a wide range of algorithms that are used in molecular simulations and modelling. It is particularly useful for data analysis and visualization, but also contains standard techniques such as energy minimization and Molecular Dynamics. All our recently developped techniques for biomolecules have been implemented in MMTK.

nMOLDYN — Par Gerald Kneller — Dernière modification 14/02/2007 09:28

nMOLDYN is an interactive analysis program for Molecular Dynamics simulations. It is especially designed for the computation and decomposition of neutron scattering spectra, but also computes other quantities.

DomainFinder — Par Konrad Hinsen — Dernière modification 13/02/2007 18:29

DomainFinder is an interactive program to analyze collective motions in large proteins, either by comparing two experimental structure, or by applying an efficient normal mode technique to a single structure. Proteins up to a few thousand residues can be treated on a desktop computer in a few minutes.

ScrewFit — Par Paolo Calligari — Dernière modification 16/02/2007 18:22

ScrewFit is a program for the characterization of protein secondary structures. It provides an efficient description of structural

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