

Quantum versus classical modeling of neutron scattering data

Gerald Kneller

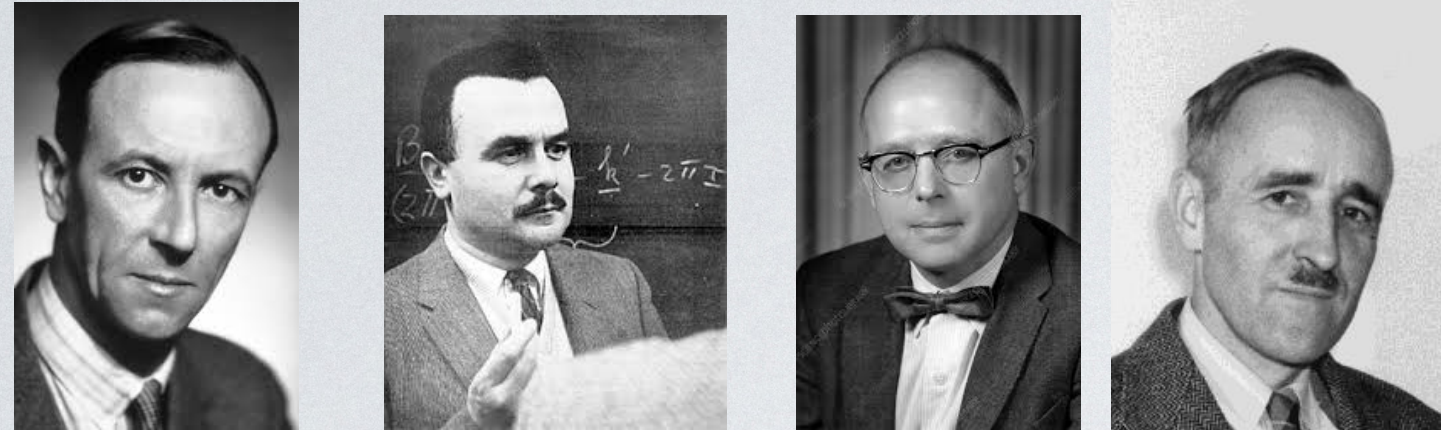
Centre de Biophysique Moléculaire CNRS and Université d'Orléans
Laboratoire des Biomolécules CNRS and Ecole Normale Supérieure Paris

*Presentation at the MDANSE 2024 school
Grenoble, 7 November 2024*



Thermal neutron scattering — probing the structural dynamics of condensed matter at the atomic scale

J. Chadwick B.N. Brockhouse C.G. Shull E. Wollan



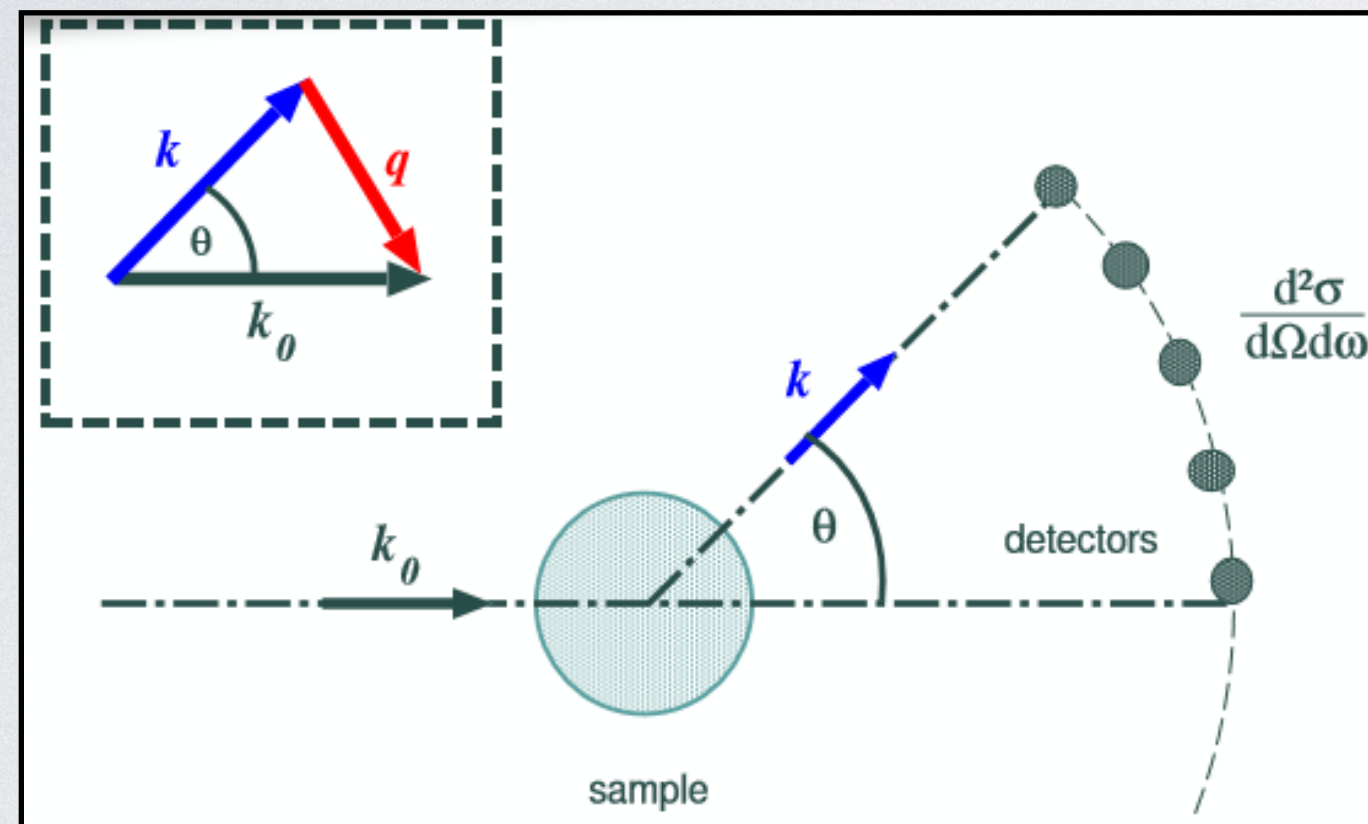
E. Fermi B. Lippmann J. Schwinger



G. Placzek G.C. Wick L. Van Hove A. Rahman



Scattering experiment



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

Differential scattering cross section

$$\hbar\mathbf{q} = \mathbf{p}_0 - \mathbf{p}$$

$$\hbar\omega = \frac{|\mathbf{p}_0|^2}{2m} - \frac{|\mathbf{p}|^2}{2m}$$

Momentum and Energy transfer

Scattering theory

Fermi pseudopotential

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_i b_i \delta(\mathbf{r} - \hat{\mathbf{R}}_i)$$

$$|b| \ll \lambda_n$$

Lippmann-Schwinger equation

$$|\Psi^{(+)}\rangle = |\Psi^{(0)}\rangle + \frac{\mathbf{1}}{E - \hat{\mathbf{H}}_n - \hat{\mathbf{H}}_t + i\epsilon} \hat{\mathbf{V}} |\Psi^{(+)}\rangle$$

Interpretation

Dynamic structure factor

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

Intermediate scattering function

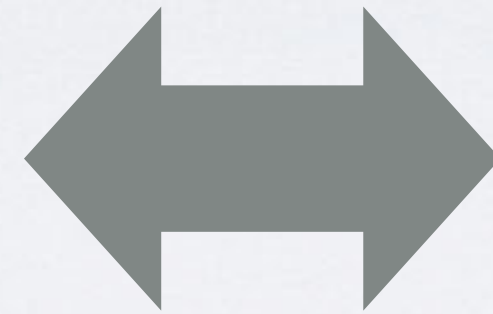
$$F(\mathbf{q}, t) = \frac{1}{N} \sum_{j,k} \Gamma_{jk} \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{R}}_j(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{R}}_k(t)} \right\rangle$$

$$\Gamma_{jk} = \overline{b_j^* b_k} + \delta_{jk} \overline{|b_j - \overline{b_j}|^2}$$

$F(\mathbf{q}, t)$ is a quantum time correlation function

Symmetries

$$\begin{aligned} F^*(\mathbf{q}, t) &= F(\mathbf{q}, -t), \\ F(\mathbf{q}, -t) &= F(-\mathbf{q}, t + i\beta\hbar) \end{aligned}$$



$$\begin{aligned} S^*(\mathbf{q}, \omega) &= S(\mathbf{q}, \omega), \\ S(\mathbf{q}, \omega) &= e^{\beta\hbar\omega} S(-\mathbf{q}, -\omega) \end{aligned}$$

Recoil moment

$$\int_{-\infty}^{+\infty} d\omega \, \omega S(\mathbf{q}, \omega) = -i \left. \frac{\partial F(\mathbf{q}, t)}{\partial t} \right|_{t=0} \propto \frac{\hbar |\mathbf{q}|^2}{2m}$$

vanishes in the classical limit, $\hbar \rightarrow 0$! Scattering atoms with infinite mass m .

Quantum and classical Van Hove function

PHYSICAL REVIEW

VOLUME 95, NUMBER 1

JULY 1, 1954

Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

LÉON VAN HOVE

Institute for Advanced Study, Princeton, New Jersey

(Received March 16, 1954)

1975 citations

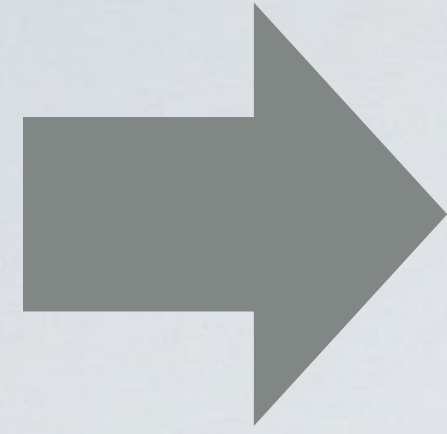
From (q,ω)-space to (r,t)-space

$$\begin{aligned} G(\mathbf{r}, t) &= \frac{1}{(2\pi)^3} \int \int d^3q dt e^{i(\omega t - \mathbf{q} \cdot \mathbf{r})} S(\mathbf{q}, \omega) \\ &= \frac{1}{N} \sum_{j,k} \Gamma_{jk} \int d^3r' \left\langle \delta \left(\mathbf{r} - \mathbf{r}' + \hat{\mathbf{R}}_j(0) \right) \delta \left(\mathbf{r}' - \hat{\mathbf{R}}_k(t) \right) \right\rangle \end{aligned}$$

$$\begin{aligned} G^*(\mathbf{r}, t) &= G(-\mathbf{r}, -t), \\ G(\mathbf{r}, -t) &= G(-\mathbf{r}, t - i\beta\hbar) \end{aligned}$$

Only for $\hbar \rightarrow 0$ $G(\mathbf{r}, t)$ becomes a time-dependent (real-valued) pair correlation function

$$G_{\text{cl}}(\mathbf{r}, t) = \frac{1}{N} \sum_{j,k} \Gamma_{jk} \langle \delta(\mathbf{r} - [\mathbf{R}_k(t) - \mathbf{R}_j(0)]) \rangle_{\text{cl}}$$



Van Hove, Léon
1958

Physica XXIV
Zernike issue
404-408

A REMARK ON THE TIME-DEPENDENT PAIR DISTRIBUTION

by LÉON VAN HOVE

Instituut voor theoretische fysica der Rijksuniversiteit, Utrecht, Nederland

30 citations

$$G(\mathbf{r}, t) = G_0(\mathbf{r}, t) + i\hbar G_1(\mathbf{r}, t)$$

$$n(\mathbf{r}, t) = \rho_0 - (2\pi a\hbar^2/m)\rho_0 \int_{-\infty}^t dt' G_1(\mathbf{r} - \mathbf{r}_{t'}, t - t').$$

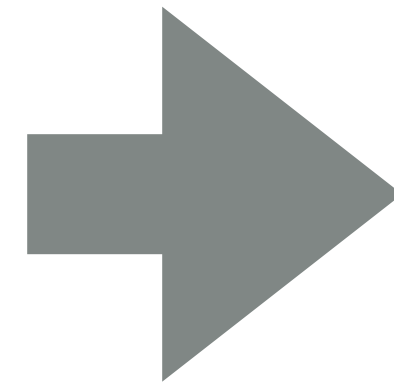
The imaginary (odd part in time) of $G(\mathbf{r}, t)$ describes the **density perturbation** of the sample due to the impact of the neutrons.

Impact-less description of neutron scattering

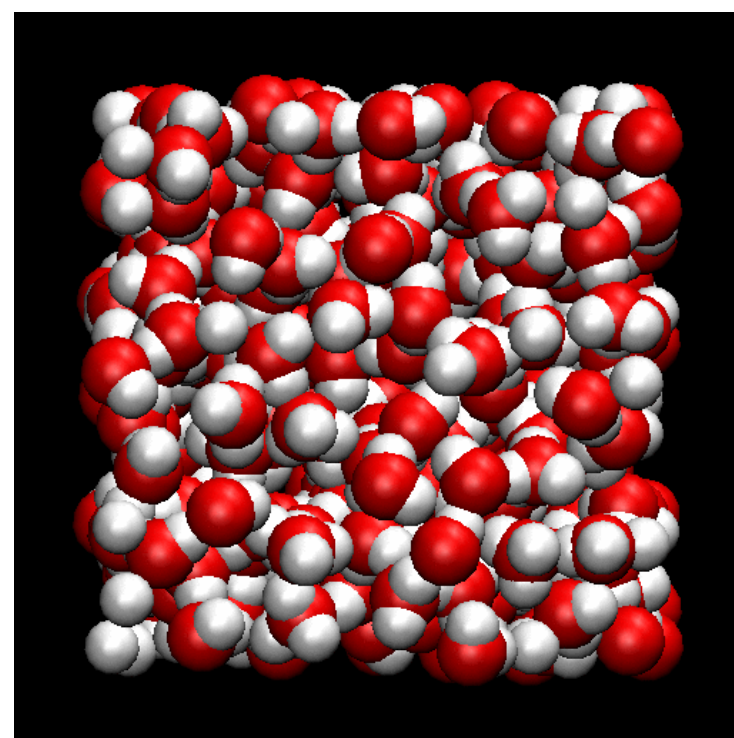
“Spatial motion models”

$$\partial_t G(\mathbf{r}, t) = D \Delta G(\mathbf{r}, t)$$

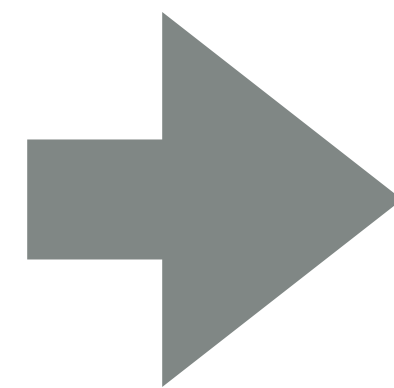
$$G(\mathbf{r}, t) = \frac{e^{-\frac{|\mathbf{r}|^2}{4Dt}}}{(2\sqrt{\pi Dt})^3}$$



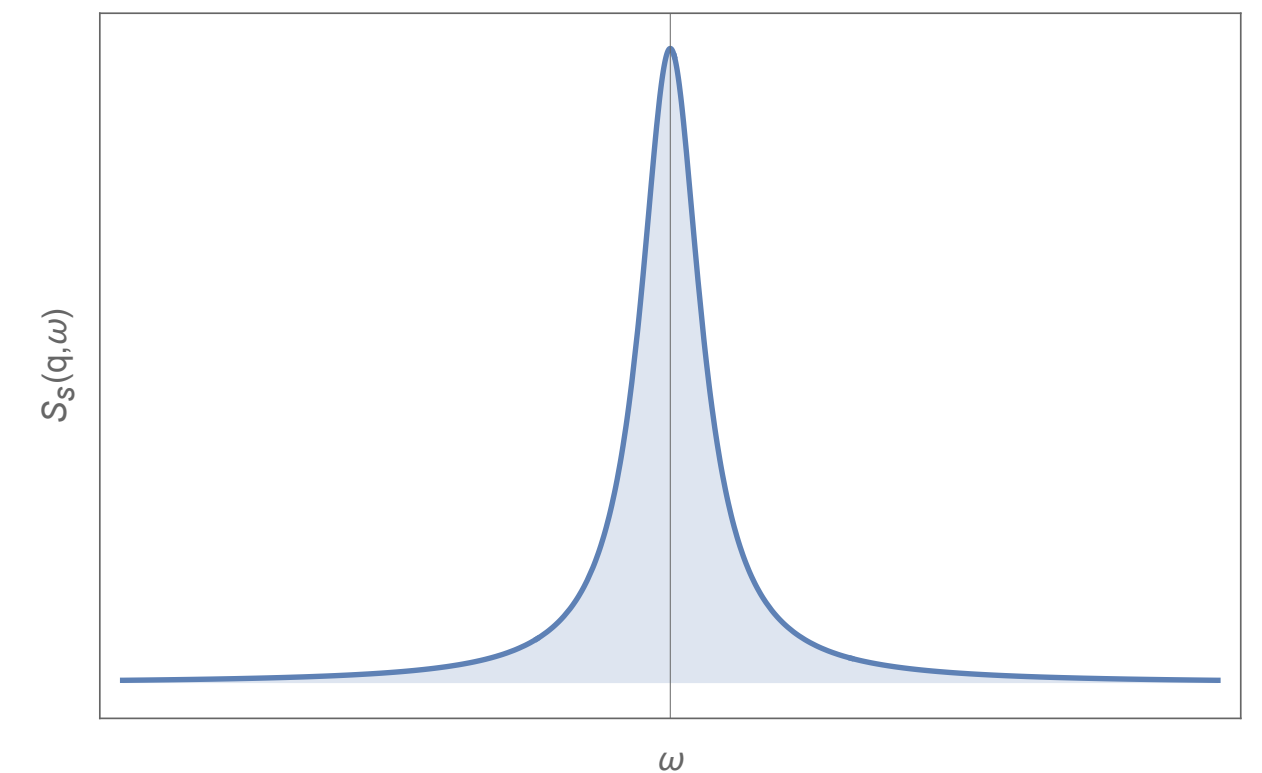
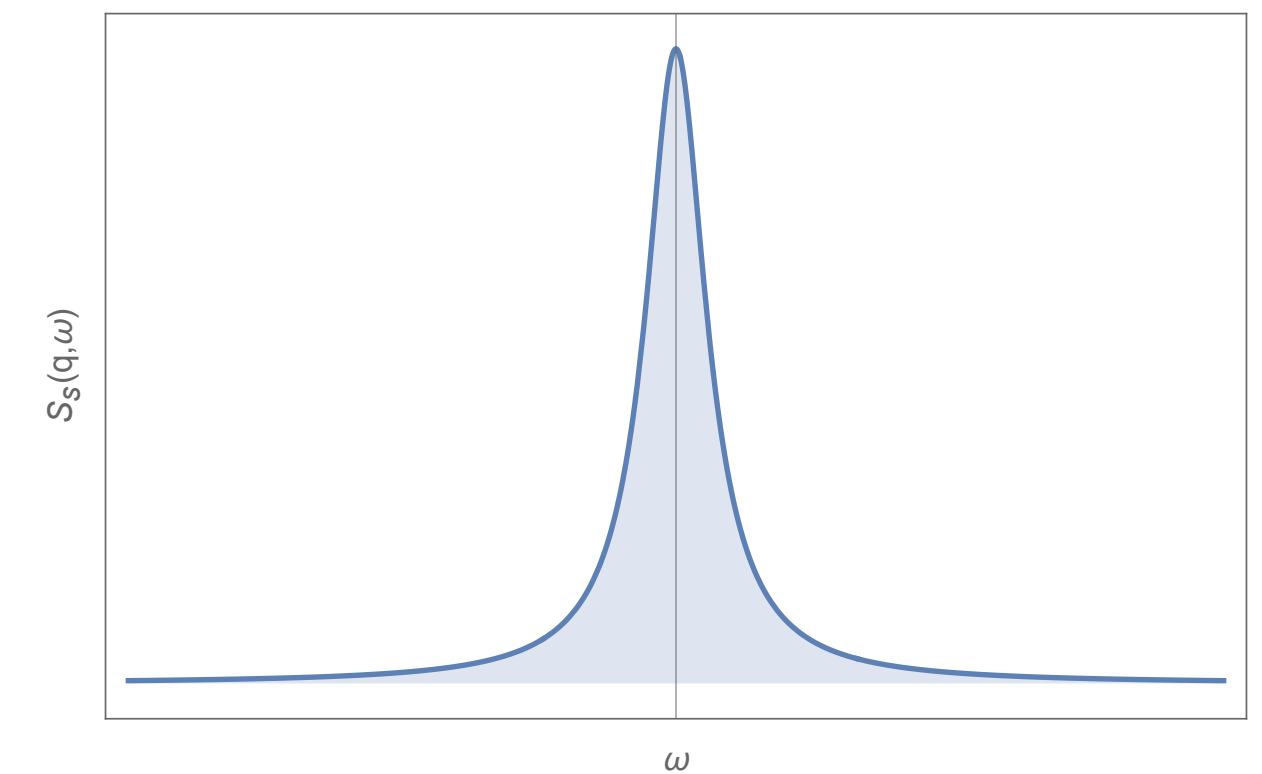
MD simulations / “trajectories”



$$F_{\text{cl}}(\mathbf{q}, t) \approx \frac{1}{N} \sum_{j,k} \Gamma_{jk} \frac{1}{T} \int_0^T d\tau e^{-i\mathbf{q} \cdot \mathbf{R}_j(\tau)} e^{i\mathbf{q} \cdot \mathbf{R}_k(\tau+t)}$$



$$S(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{D|\mathbf{q}|^2}{(D|\mathbf{q}|^2)^2 + \omega^2}$$



Spotting the “kick” of the neutron

PHYSICAL REVIEW

VOLUME 94, NUMBER 5

JUNE 1, 1954

The Scattering of Neutrons by Systems Containing Light Nuclei*

G. C. WICK

Carnegie Institute of Technology, Pittsburgh, Pennsylvania, and Institute for Advanced Study, Princeton, New Jersey

(Received January 21, 1954)



$$F_s(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_1(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_1(t)} \right\rangle = \boxed{\left\langle e^{it\hat{H}'(\mathbf{q})/\hbar} e^{-it\hat{H}/\hbar} \right\rangle}$$

“Positionless”
representation of $F(\mathbf{q}, t)$

$$\hat{H}'(\mathbf{q}) = \sum_k \frac{(\hat{p}_k + \hbar \mathbf{q} \delta_{1k})^2}{2m_k} + V(\hat{\mathbf{R}}_1, \dots, \hat{\mathbf{R}}_N)$$

“Kicked Hamiltonian”

Proof:

$$\begin{aligned} \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_1(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_1(t)} \right\rangle &= \frac{1}{Z} \text{tr} \left\{ e^{-\beta \hat{H}} e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_1} \underbrace{e^{it\hat{H}/\hbar} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_1} e^{-it\hat{H}/\hbar}}_{e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_1(t)}} \right\} \\ &= \frac{1}{Z} \text{tr} \left\{ e^{-\beta \hat{H}} \underbrace{e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_1} e^{it\hat{H}/\hbar} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_1}}_{e^{it\hat{H}'(\mathbf{q})/\hbar}} e^{-it\hat{H}/\hbar} \right\} \end{aligned}$$

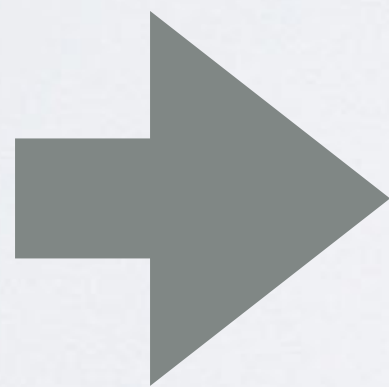
Quantum trajectory approach – Integrate the neutron kick into a trajectory-based description of neutron scattering

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

- Describe the neutron as an active probe in a trajectory-based scenario.
- Define the “physical classical limit” of the scattering functions.

Propagator form of the intermediate scattering function

$$F_s(\mathbf{q}, t) = \frac{1}{Z} \int \int \int dx dx' dx'' \underbrace{\langle x | e^{-\beta \hat{H}} | x' \rangle}_{K(x, x', -i\beta\hbar)} \underbrace{\langle x' | e^{it\hat{H}'(\mathbf{q})/\hbar} | x'' \rangle}_{K_q(x', x'', -t)} \underbrace{\langle x'' | e^{-it\hat{H}/\hbar} | x \rangle}_{K(x'', x, t)}$$

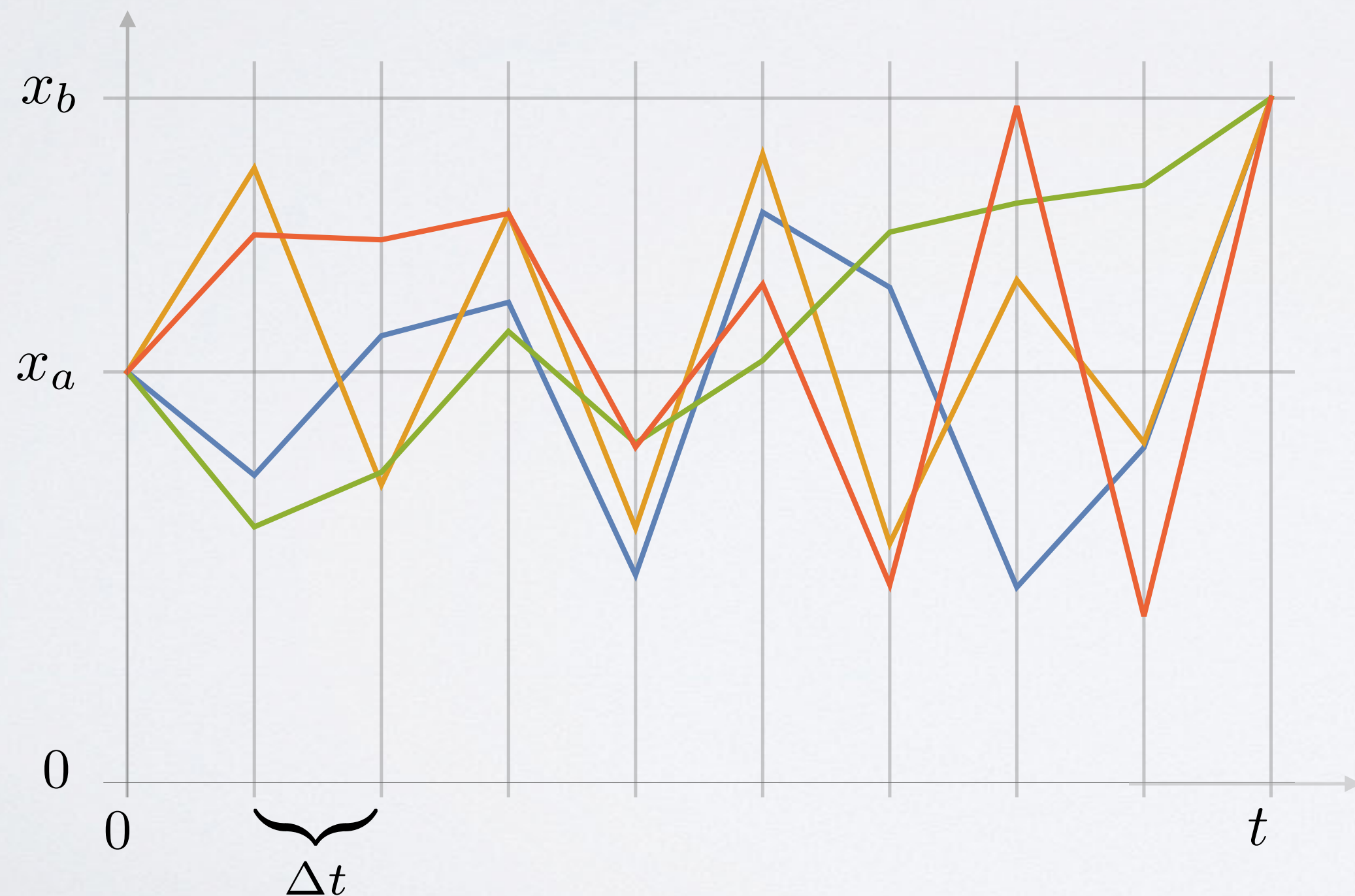


Retrieve trajectories through a **path integral representation** of the propagators

Real time propagator

Setting $\Delta t = t/n$

$$\begin{aligned} K(x_b, x_a, t) &= \langle x_b | e^{-it\hat{H}/\hbar} | x_a \rangle = \langle x_b | \left(e^{-i\frac{\Delta t}{\hbar} \hat{H}} \right)^n | x_a \rangle \\ &= \int \dots \int dx_1 \dots dx_n \langle x_b | \left(e^{-i\frac{\Delta t}{\hbar} \hat{H}} \right) | x_1 \rangle \langle x_1 | \left(e^{-i\frac{\Delta t}{\hbar} \hat{H}} \right) | x_2 \rangle \dots \\ &\quad \dots \langle x_n | \left(e^{-i\frac{\Delta t}{\hbar} \hat{H}} \right) | x_b \rangle \xrightarrow{n \rightarrow \infty} \int \mathcal{D}[x(\tau)] e^{iA[x(\tau)]/\hbar} \end{aligned}$$



Path action integral

$$A[x(\tau)] = \int_0^t d\tau \underbrace{\left(M\dot{x}(\tau)^2/2 - V(x(\tau)) \right)}_{L(\dot{x}(\tau), x(\tau))}$$

“Kicked” real time propagator

Phase factor form

$$K_q(x_b, x_a, t) = K(x_b, x_a, t) e^{iq(x_b - x_a)}$$

Path integral form

$$K(x_b, x_a, t) = \int \mathcal{D}[x(\tau)] e^{iA_q[x(\tau)]/\hbar}$$

“Kicked” path action integral

$$A_q[x(\tau)] = \int_0^t d\tau \underbrace{\left(M\dot{x}(\tau)^2/2 - V(x(\tau)) + \hbar q\dot{x}(\tau) \right)}_{L_q(\dot{x}(\tau), x(\tau))}$$

Coupling to the neutron

Imaginary time propagator

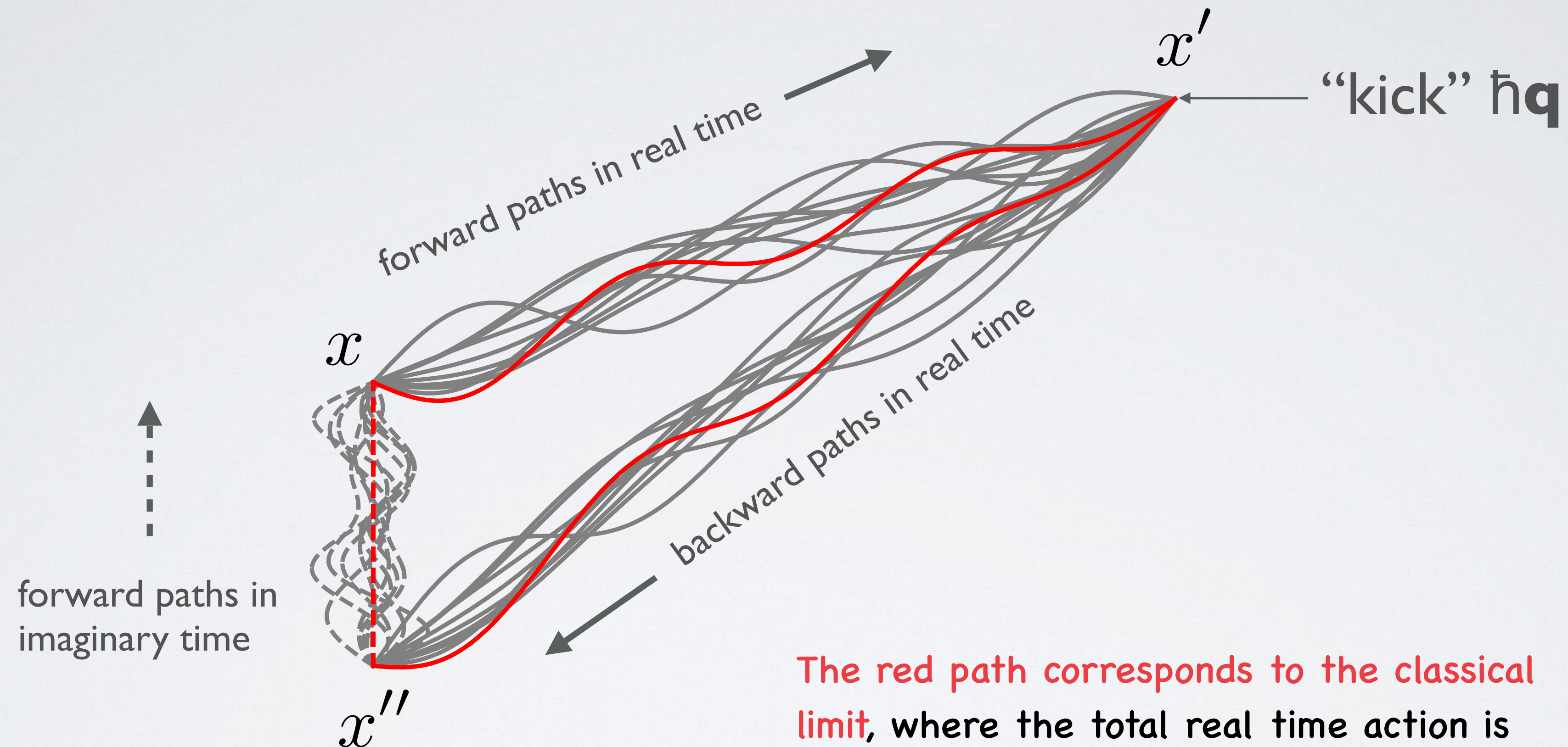
Setting $t_{th} = \beta\hbar$ and $\Delta t_{th} = t_{th}/n$

$$\begin{aligned} K(x_b, x_a, -i\beta\hbar) &= \langle x_b | e^{-\beta\hat{H}} | x_a \rangle = \langle x_b | \left(e^{-\frac{\Delta t_{th}}{\hbar} \hat{H}} \right)^n | x_a \rangle \\ &= \int \dots \int dx_1 \dots dx_n \langle x_b | \left(e^{-\frac{\Delta t_{th}}{\hbar} \hat{H}} \right) | x_1 \rangle \langle x_1 | \left(e^{-\frac{\Delta t_{th}}{\hbar} \hat{H}} \right) | x_2 \rangle \dots \\ &\quad \dots \langle x_n | \left(e^{-\frac{\Delta t_{th}}{\hbar} \hat{H}} \right) | x_b \rangle \xrightarrow{n \rightarrow \infty} \int \mathcal{D}[x(\tau)] e^{-\beta \bar{H}[x(\tau)]/\hbar} \end{aligned}$$

Average path energy

$$\bar{H}[x(\tau)] = \frac{1}{\beta\hbar} \int_0^t d\tau \underbrace{(M\dot{x}(\tau)^2/2 + V(x(\tau)))}_{H(\dot{x}(\tau), x(\tau))}$$

$$F_s(\mathbf{q}, t) = \frac{1}{Z} \int \int \int dx dx' dx'' K(x, x', -i\beta\hbar) K_q(x', x'', -t) K(x'', x, t)$$



The red path corresponds to the classical limit, where the total real time action is minimized and the high temperature/short time limit is used for the propagation in imaginary time. The “neutron kick” is taken into account.

Classical limit of the intermediate scattering function

Expressing the density matrix through the classical limit of the Wigner function and retaining only the classical path ($A \gg \hbar$) yields

$$\tilde{F}_{cl}(\mathbf{q}, t) = \frac{1}{Z_{cl}} \int \int d^3p d^3x e^{-\beta H(\mathbf{p}, \mathbf{x})} e^{-\beta \Delta V(\mathbf{p}, \mathbf{x}; \hbar \mathbf{q}, t)} \\ \times e^{i \Delta \Phi(\mathbf{p}, \mathbf{x}; \hbar \mathbf{q}, t) / \hbar} e^{i \mathbf{q} \cdot (\mathbf{x}'(\mathbf{p}, \mathbf{x}, t) - \mathbf{x})}$$

$$\Delta V(\mathbf{p}, \mathbf{x}; \hbar \mathbf{q}, t) = V((\mathbf{x} + \mathbf{x}'')/2) - V(\mathbf{x})$$

$$\Delta \Phi(\mathbf{p}, \mathbf{x}; \hbar \mathbf{q}, t) = A(\mathbf{x}, \mathbf{x}', t) - A(\mathbf{x}', \mathbf{x}'', t) + (\mathbf{p}_0 + \hbar \mathbf{q}) \cdot (\mathbf{x} - \mathbf{x}'')$$

where $\mathbf{x}' \equiv \mathbf{x}'(\mathbf{p}, \mathbf{x}, t)$ and $\mathbf{x}'' \equiv \mathbf{x}''(\mathbf{p}, \mathbf{x}; \hbar \mathbf{q}, t)$.

The standard classical limit reads

$$\lim_{\hbar \rightarrow 0} \tilde{F}_{cl}(\mathbf{q}, t) = \frac{1}{Z_{cl}} \int \int d^3p d^3x e^{-\beta H(\mathbf{p}, \mathbf{x})} e^{i \mathbf{q} \cdot (\mathbf{x}'(\mathbf{p}, \mathbf{x}, t) - \mathbf{x})}$$

- The intermediate scattering function $F(q,t)$ can be written as a path integral over closed paths, one of which is the classical path.
- The classical path minimizes the total action in real time and is ballistic in imaginary time (short time approximation).
- The “physical classical limit” of $F(q,t)$ corresponds to retaining only the total classical path, which preserves the scattering kinematics and the impact of the neutron on the scattering system.
- The recoil mass is the bare mass of the scattering atom.

Energy landscape-based description of neutron scattering

A wave-mechanical model of incoherent quasielastic scattering in complex systems

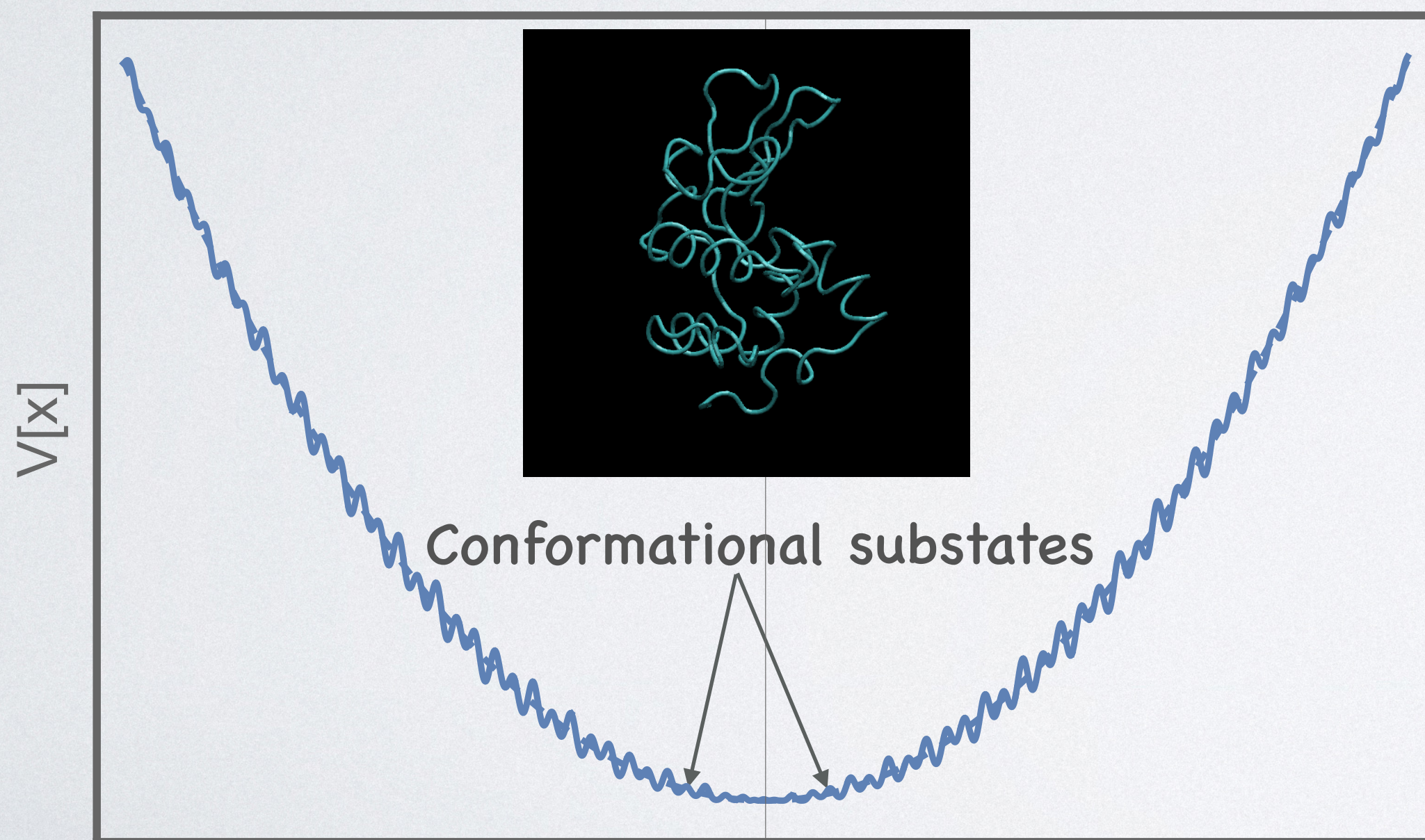
Hans Frauenfelder^{a,1}, Paul W. Fenimore^a, and Robert D. Young^b

^aTheoretical Biology and Biophysics Group, Los Alamos National Laboratory, Los Alamos, NM 87545; and ^bCenter for Biological Physics, Arizona State University, Tempe, AZ 85287-1504

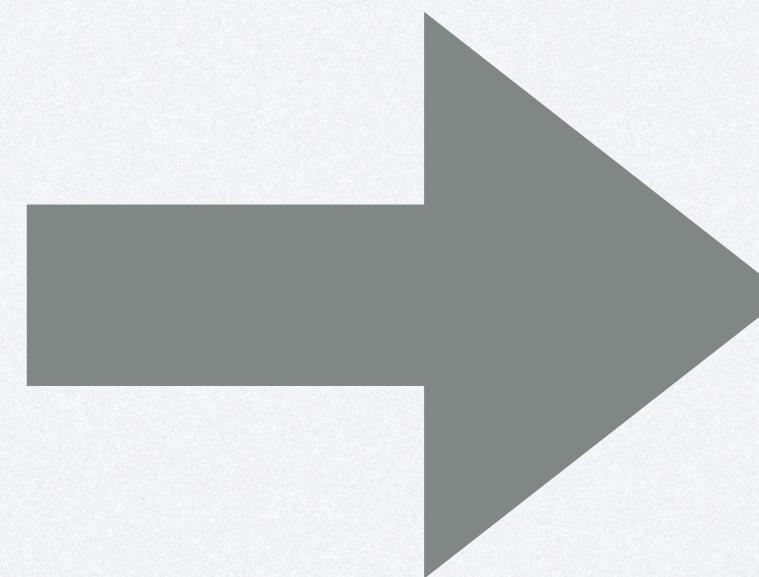
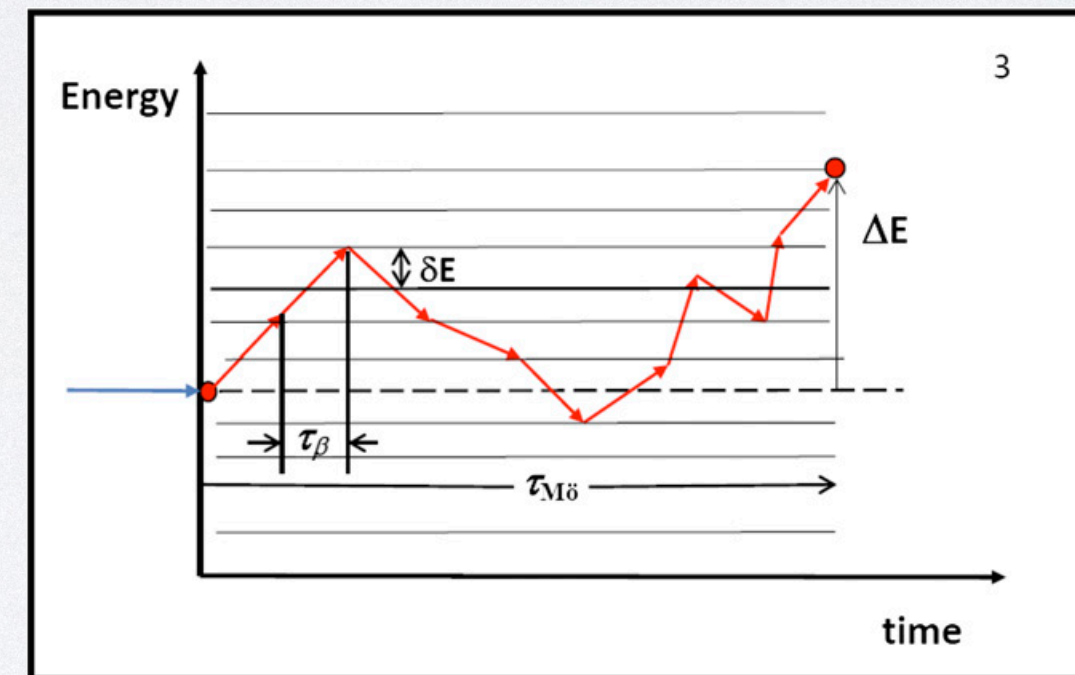
12764–12768 | PNAS | September 2, 2014 | vol. 111 | no. 35



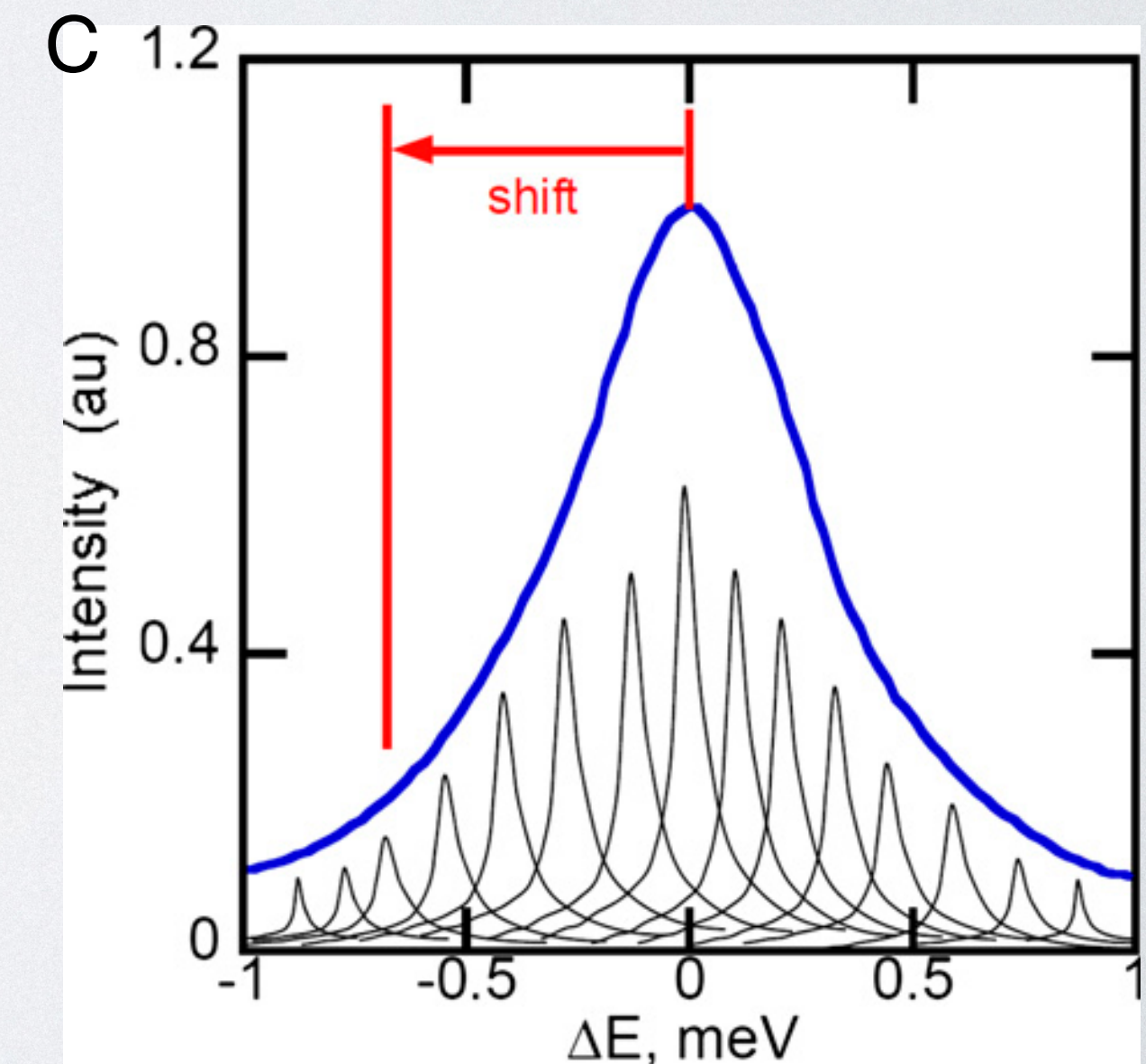
During its flight through the sample, the neutron wave packet records the net energy transition of the system from the initial energy level E to the final level $E + \Delta E$.

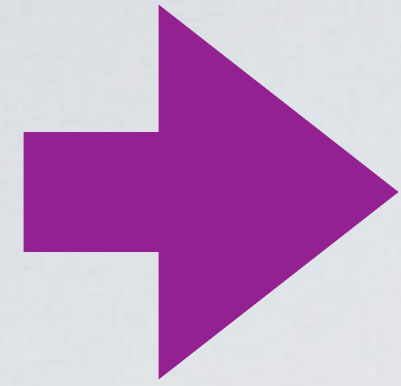


H. Frauenfelder et al, Science 254, 1598 (1991).

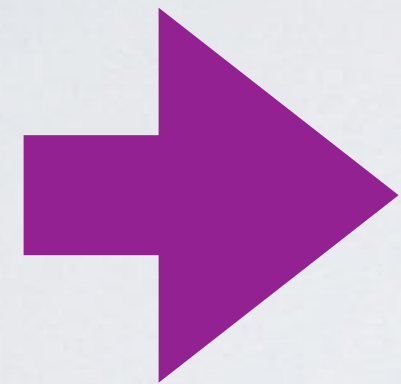


QENS spectrum composed of many « Mössbauer lines »





- The description is essentially qualitative
- The neutron is considered as a passive probe
- Momentum transfer is not considered



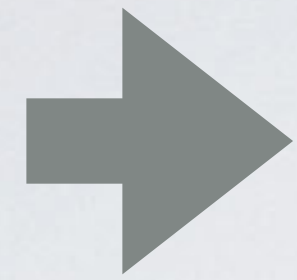
The role of momentum transfer during incoherent neutron scattering is explained by the energy landscape model

Hans Frauenfelder^{a,1}, Robert D. Young^b, and Paul W. Fenimore^{a,1}

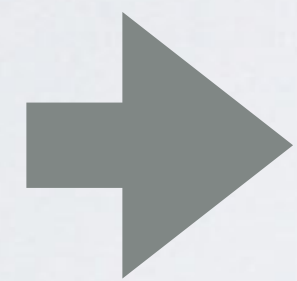
PNAS 114, 5130 (2017).

- The neutron is an active probe : “Local heating” of the sample due to the momentum transfer.
- But: Momentum and energy transfer are not connected through scattering kinematics.

Develop a theory of neutron scattering, which



is “spectroscopic”, in the sense that the neutron is an active probe, (de)exciting transitions in the scattering system



integrates the concept of energy landscapes, which is adapted for complex systems

Franck–Condon picture of incoherent neutron scattering

Gerald R. Kneller^{a,b,1}

PNAS, 115, pp. 9450 2018.

Use Wick's "kicked" Hamiltonian

$$F_s(\mathbf{q}, t) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} e^{i(E'_n - E_m)/\hbar} |a_{m \rightarrow n}(\mathbf{q})|^2$$

$$a_{m \rightarrow n}(\mathbf{q}) = \langle \phi'_n(\mathbf{q}) | \phi_m \rangle$$

$$\hat{H} |\phi_m\rangle = E_m |\phi_m\rangle$$

$$\hat{H}'(\mathbf{q}) |\phi'_n(\mathbf{q})\rangle = E'_n |\phi'_n(\mathbf{q})\rangle$$

↑
probabilities for a scattering-induced transition from the unperturbed energy level m to the perturbed energy level n.

Eigenfunctions and eigenvalues of the kicked Hamiltonian

$$\hat{H}'(\mathbf{q}) = \sum_k \frac{(\hat{p}_k + \hbar \mathbf{q} \delta_{1k})^2}{2m_k} + V(\hat{\mathbf{R}}_1, \dots, \hat{\mathbf{R}}_N)$$

$$E'_n = E_n$$

$$\tilde{\phi}'_n(\mathbf{P}) = \tilde{\phi}_n(\mathbf{P} + \hbar \mathbf{Q}_1)$$

$$\phi'_n(\mathbf{R}) = \phi_n(\mathbf{R}) e^{-i \mathbf{Q}_1 \cdot \mathbf{R}}$$

Momentum transfer to atom 1

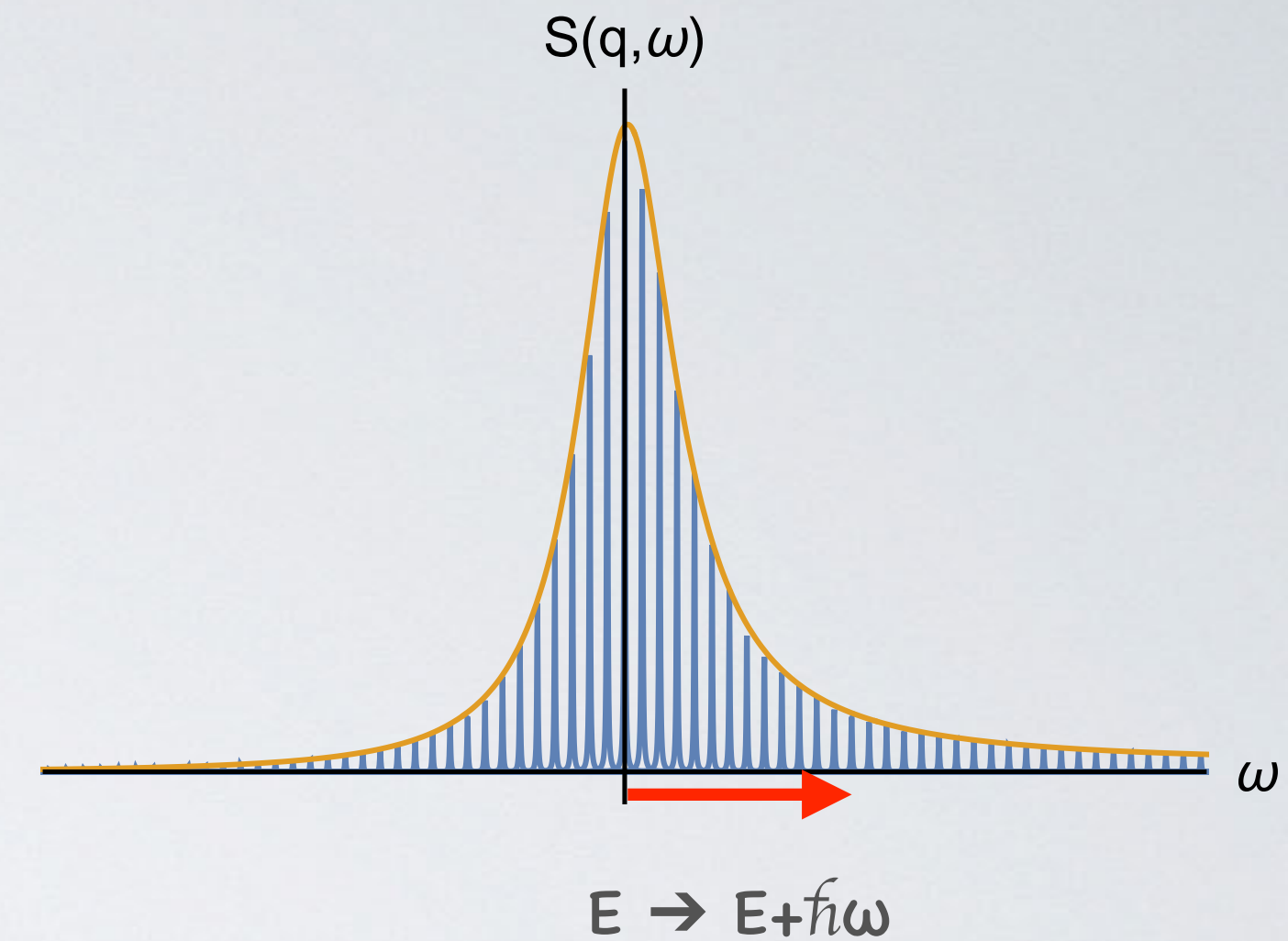
$$\mathbf{Q}_1^T = (\underbrace{q_x, q_y, q_z}_{\text{atom 1}}, \underbrace{0, 0, 0}_{\text{atom 2}}, \dots, \underbrace{0, 0, 0}_{\text{atom } N})$$

From the Brockhouse Nobel lecture (1994):

The neutron in being scattered “causes” **transitions between the quantum states** of the scattering system **but does not change the states.**

Scattering functions

$$F_s(\mathbf{q}, t) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} e^{it(E_n - E_m)/\hbar} |a_{m \rightarrow n}(\mathbf{q})|^2,$$
$$S_s(\mathbf{q}, \omega) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} |a_{m \rightarrow n}(\mathbf{q})|^2 \delta(\omega - [E_n - E_m]/\hbar).$$

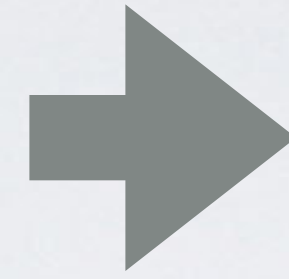


Franck-Condon form of the transition amplitudes

$$a_{m \rightarrow n}(\mathbf{q}) = \int d^{3N}p \tilde{\phi}_n^*(\mathbf{P} + \hbar\mathbf{Q}_1) \tilde{\phi}_m(\mathbf{P}) = \int d^{3N}p e^{i\mathbf{Q}_1 \cdot \mathbf{R}} \phi_n^*(\mathbf{R}) \phi_m(\mathbf{R})$$

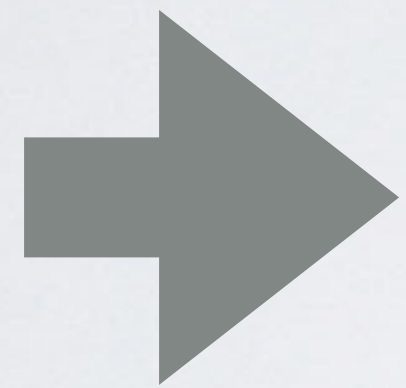
Symmetry properties of the transition probabilities

$$w_{m \rightarrow n}(\mathbf{q}) \equiv |a_{m \rightarrow n}(\mathbf{q})|^2$$



$$w_{m \rightarrow n}(\mathbf{q}) = w_{n \rightarrow m}(-\mathbf{q})$$

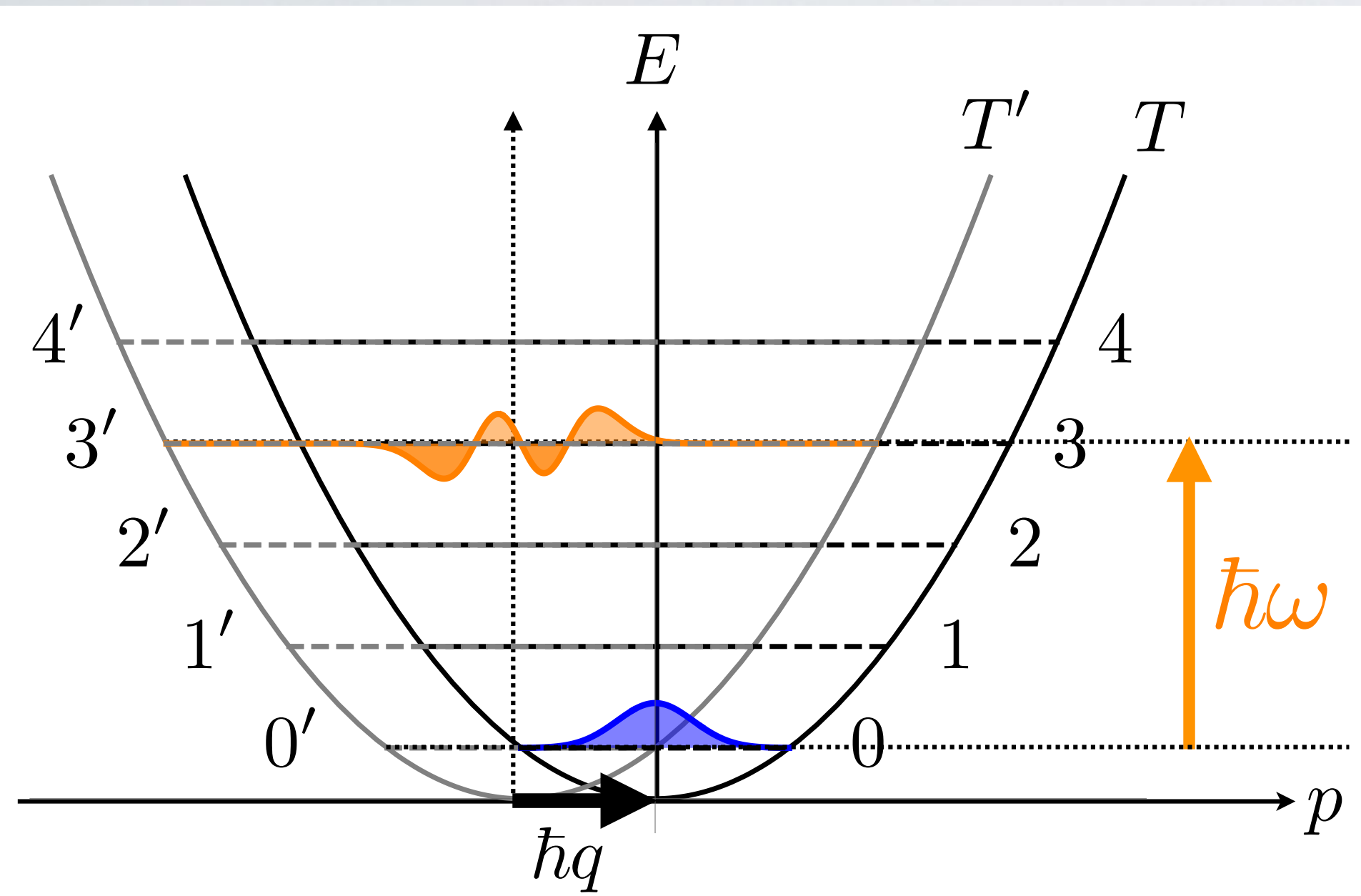
Detailed balance relation etc. fulfilled



$$F_s(\mathbf{q}, t) = F_s(-\mathbf{q}, -t + i\beta\hbar)$$
$$S_s(\mathbf{q}, \omega) = e^{\beta\hbar\omega} S_s(-\mathbf{q}, -\omega)$$

An analytical example - the harmonic oscillator

Wave functions for the $0 \rightarrow 3'$ transition



T **V**

$$E = \frac{p^2}{2m} + \frac{1}{2}m\Omega^2 x^2$$

Transition probabilities

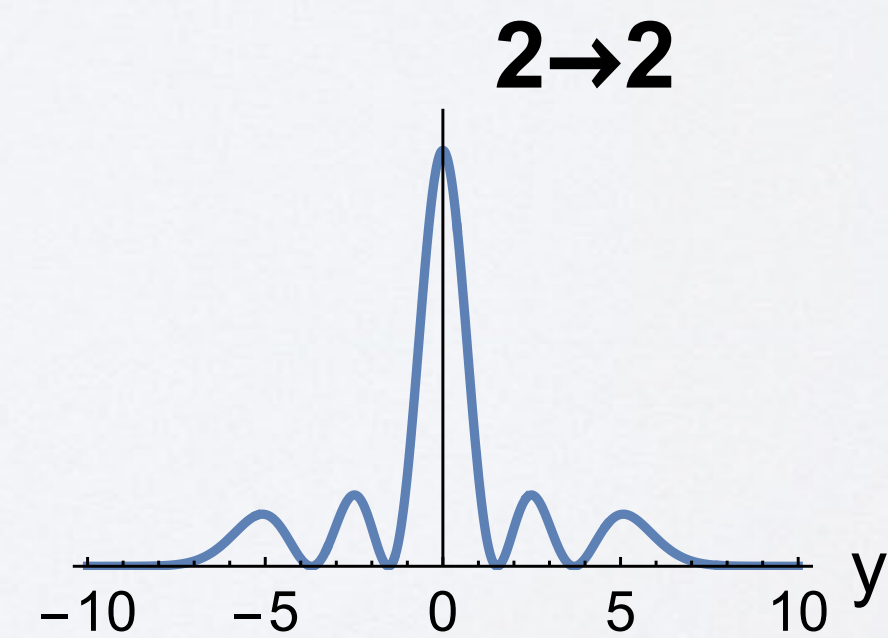
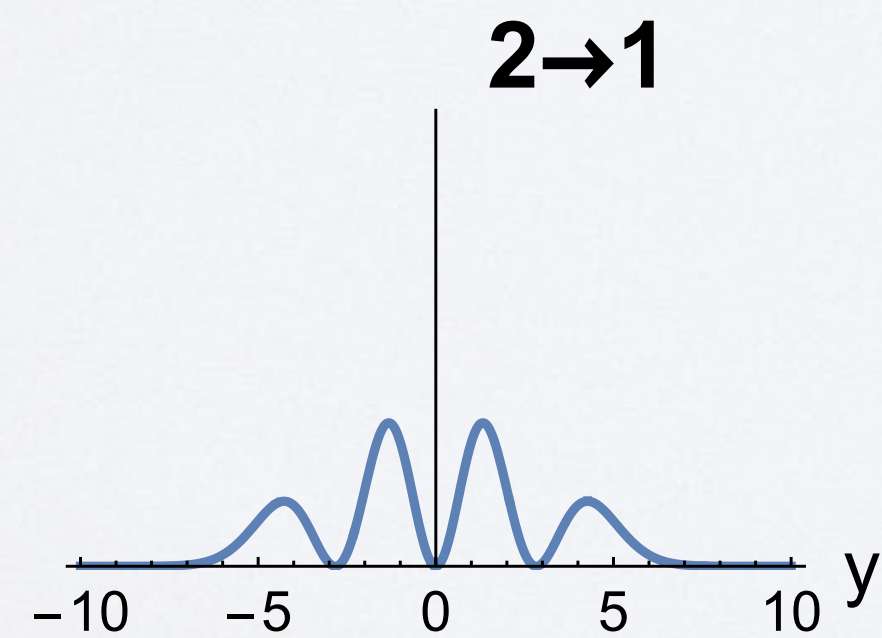
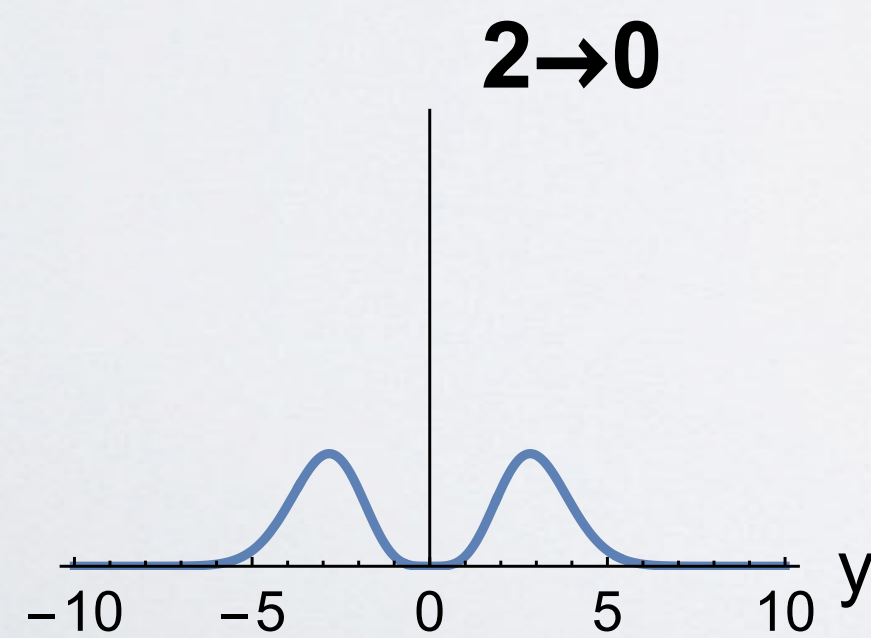
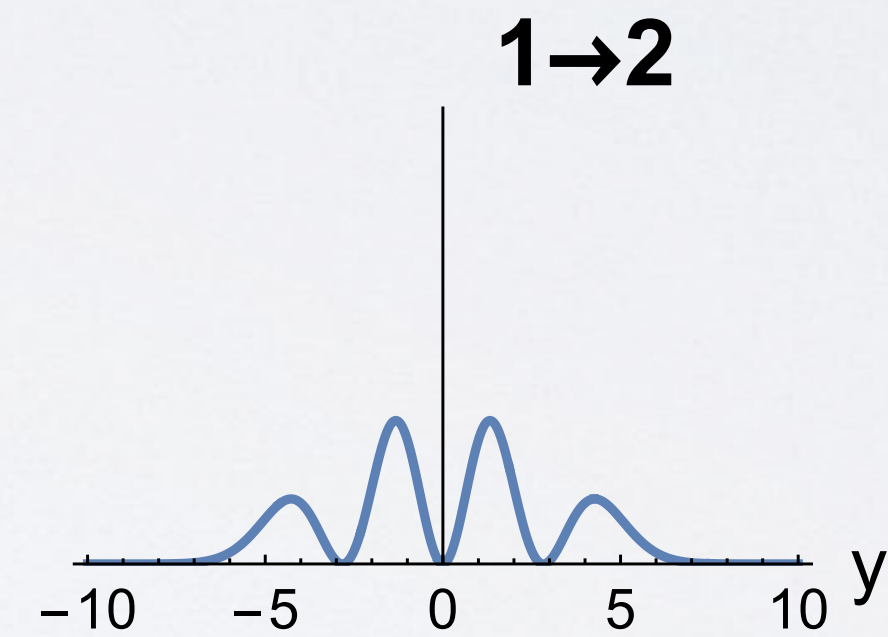
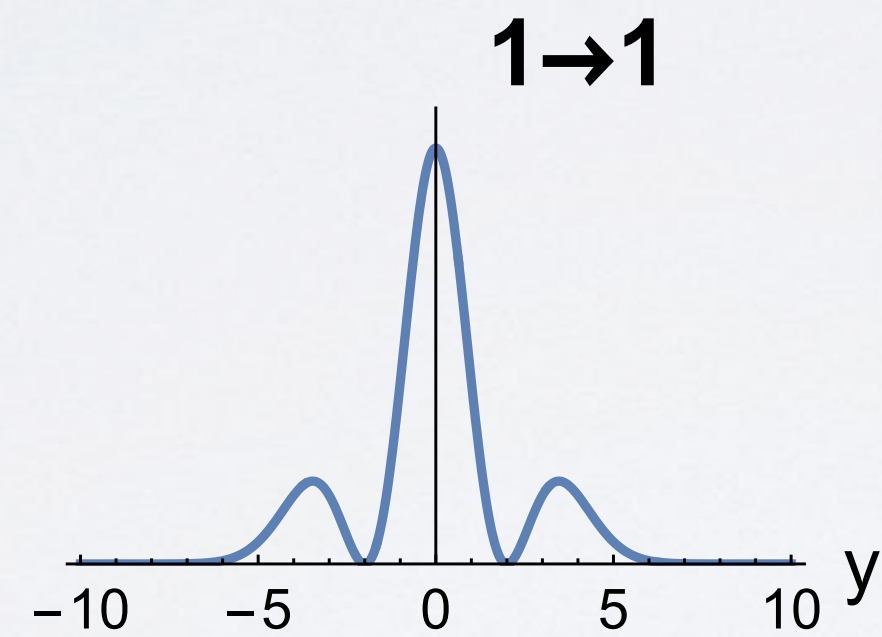
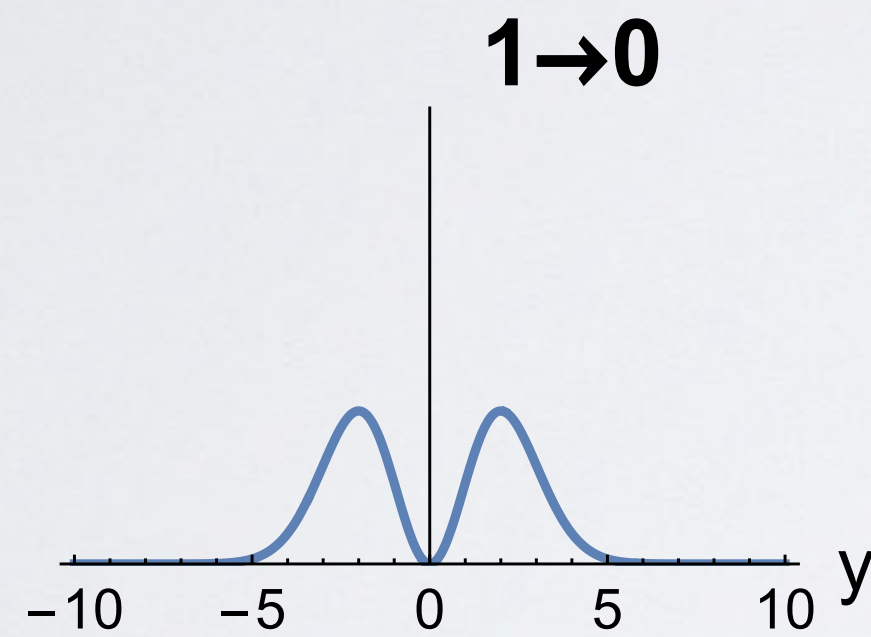
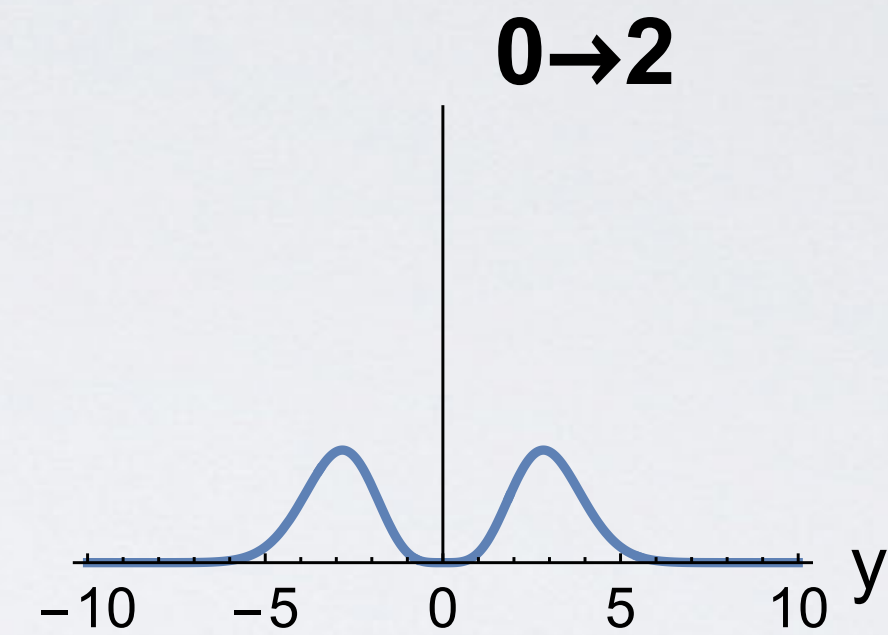
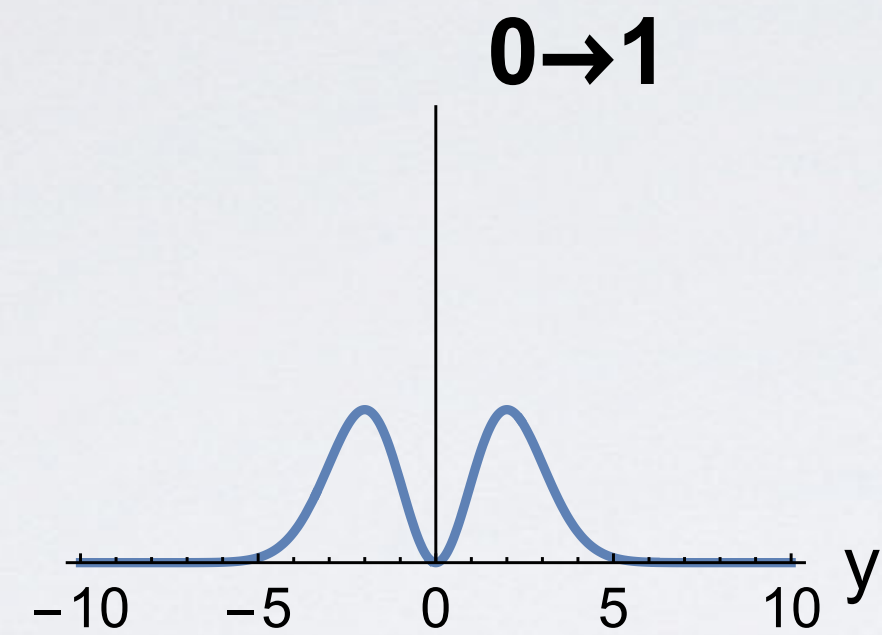
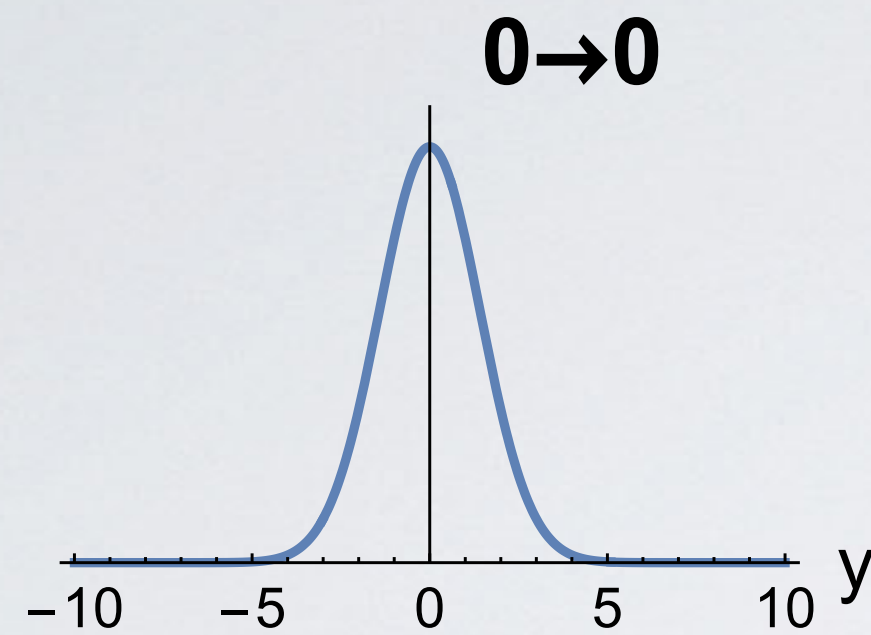
$$w_{m \rightarrow n}(q) = e^{-\frac{y^2}{4}} (-1)^{m+n} L_m^{(n-m)} \left(\frac{y^2}{4} \right) L_n^{(m-n)} \left(\frac{y^2}{4} \right)$$

$$y(q) = \sqrt{\frac{2\hbar}{M\Omega}} q$$

Textbook result (c.f. Lovesey)

$$F_s(q, t) = e^{i\frac{y(q)^2}{4}} \left(\sin(\Omega t) + i(1 - \cos(\Omega t)) \coth\left(\frac{\beta\Omega\hbar}{2}\right) \right)$$

Some transition probabilities as a function of momentum transfer

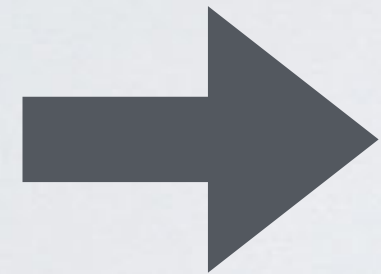


$$y(q) = \sqrt{\frac{2\hbar}{M\Omega}} q$$

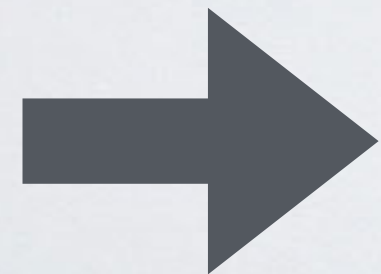
Back to recoil: The effective mass

$F(\mathbf{q}, t)$ is the moment-generating function of $S(\mathbf{q}, \omega)$

$$F(\mathbf{q}, t) = \int_{-\infty}^{+\infty} d\omega e^{i\omega t} S(\mathbf{q}, \omega)$$



$$\langle \omega^k \rangle_S \equiv \int_{-\infty}^{+\infty} d\omega \omega^k S(\mathbf{q}, \omega) = (-i)^k \partial_t^k F(\mathbf{q}, t) \big|_{t=0}$$



$$\langle \omega \rangle_S = \frac{\hbar q^2}{2M}$$

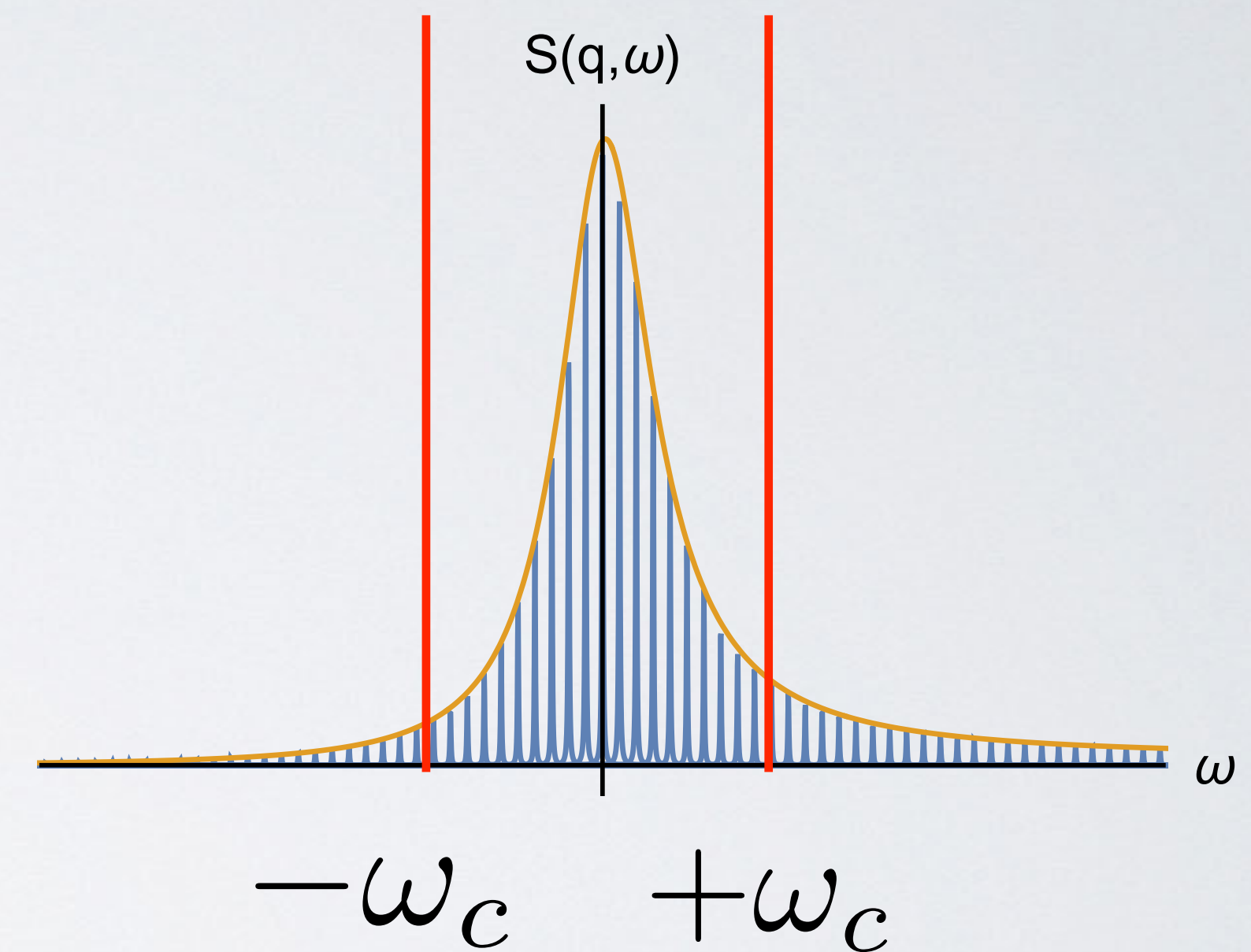
Recoil moment

Incomplete recoil moment – effective mass

$$\bar{S}(q, \omega) \equiv \frac{1}{4\pi} \int d\Omega_q S(q\mathbf{n}_q, \omega) \quad \text{Angular average}$$

$$\frac{\hbar q^2}{2M_{\text{eff}}(q, \omega_c)} \equiv \int_{-\omega_c}^{+\omega_c} d\omega \, \omega \bar{S}(q, \omega)$$

$$M \leq M_{\text{eff}}(q, \omega_c) < \infty$$



Sachs-Teller mass for small "rigid" molecules

JULY 1, 1941

PHYSICAL REVIEW

VOLUME 60

The Scattering of Slow Neutrons by Molecular Gases

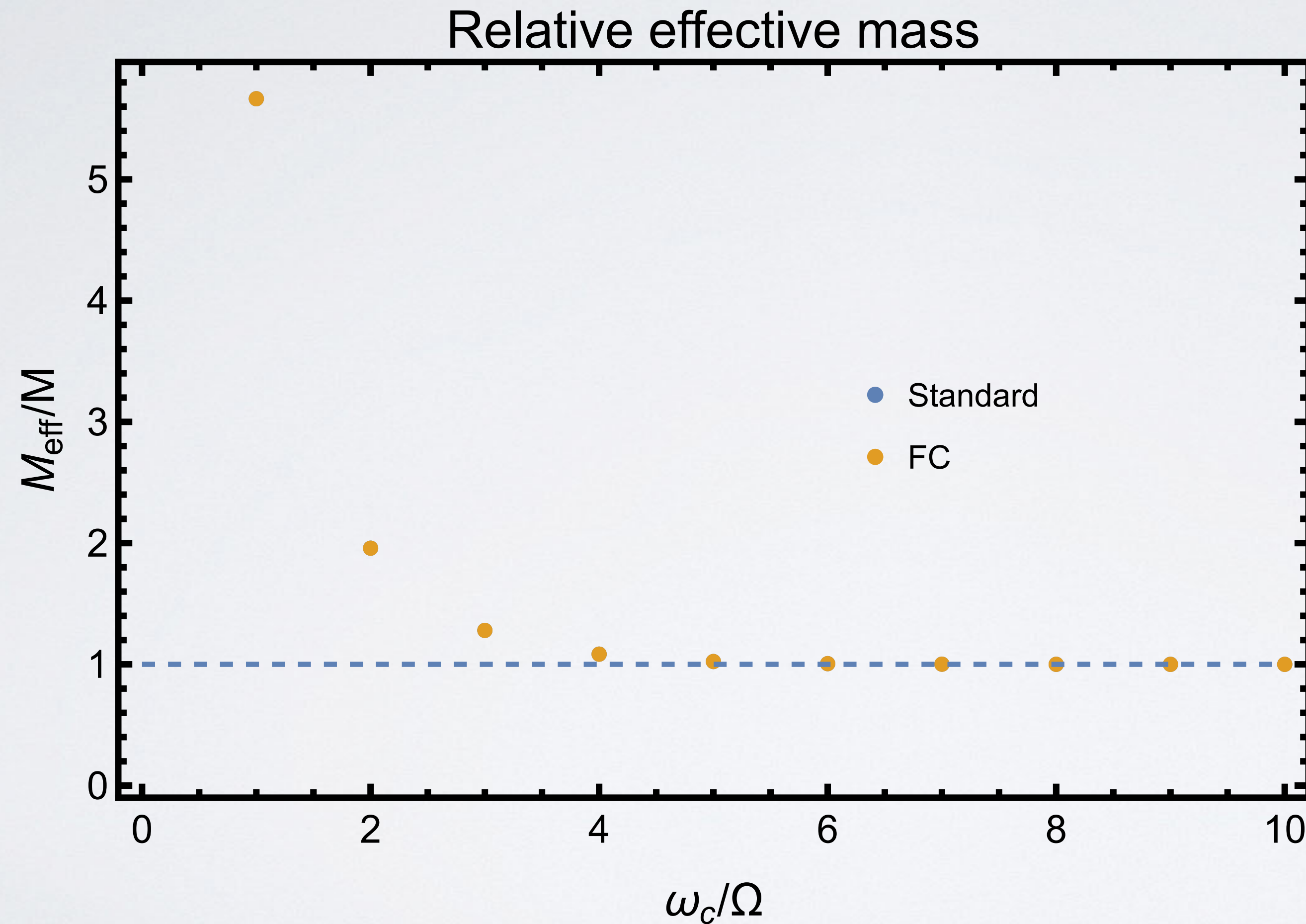
R. G. SACHS* AND E. TELLER

The George Washington University, Washington, D. C.

(Received April 18, 1941)

It has been shown by Fermi that the cross section for the scattering of slow neutrons by protons is four times greater for protons strongly bound to an infinite mass than it is for free protons initially at rest. A simple generalization of this factor of four can be given for the scattering of neutrons by molecular gases if the neutron energy is great as compared to the energy differences of the rotational levels of the scattering molecule but small compared to the quanta of molecular vibration. In this case, the proton may be replaced by a freely moving hypothetical mass point whose mass is a tensor depending on the mass and structure of the molecule. On this basis the total cross section for the scattering of slow neutrons by H_2 and by CH_4 , NH_3 and H_2O at low temperatures has been calculated as a function of the ratio of the neutron energy to the thermal energy of the scattering gas. The possibility of applying the theory to a determination of the neutron-proton scattering cross section is discussed.

Effective mass of an harmonic oscillator



$$V(x) = \frac{1}{2} M \Omega^2 x^2$$

$$\frac{\hbar q^2}{2M} = \Omega$$

$$\frac{\hbar \Omega}{k_B T} = 1$$

ARTICLE

Received 6 Jun 2012 | Accepted 4 Sep 2012 | Published 9 Oct 2012

DOI: 10.1038/ncomms2117

Quantum oscillations of nitrogen atoms in uranium nitride

A.A. Aczel¹, G.E. Granroth¹, G.J. MacDougall¹, W.J.L. Buyers², D.L. Abernathy¹,
G.D. Samolyuk³, G.M. Stocks³ & S.E. Nagler^{1,4}

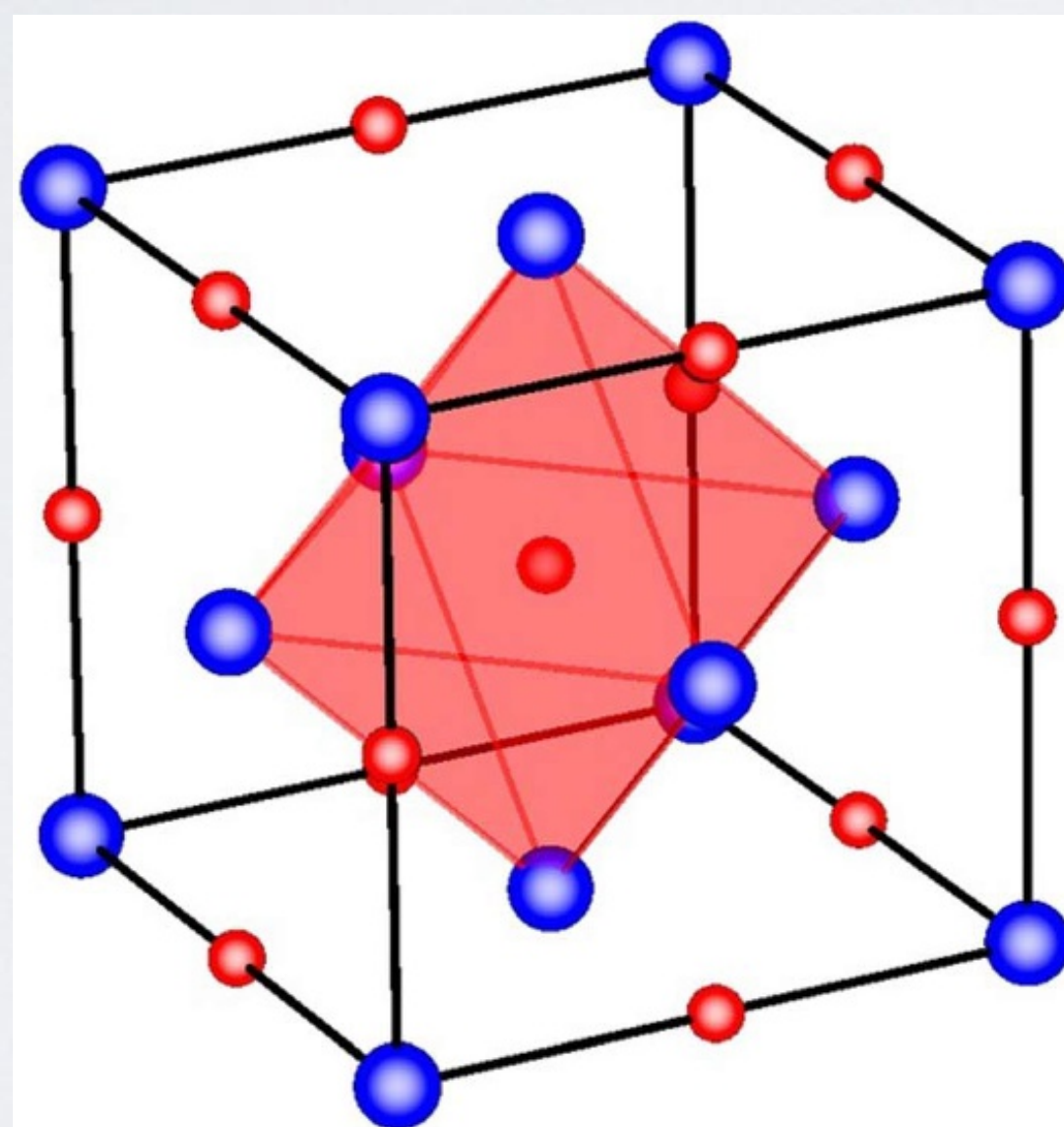
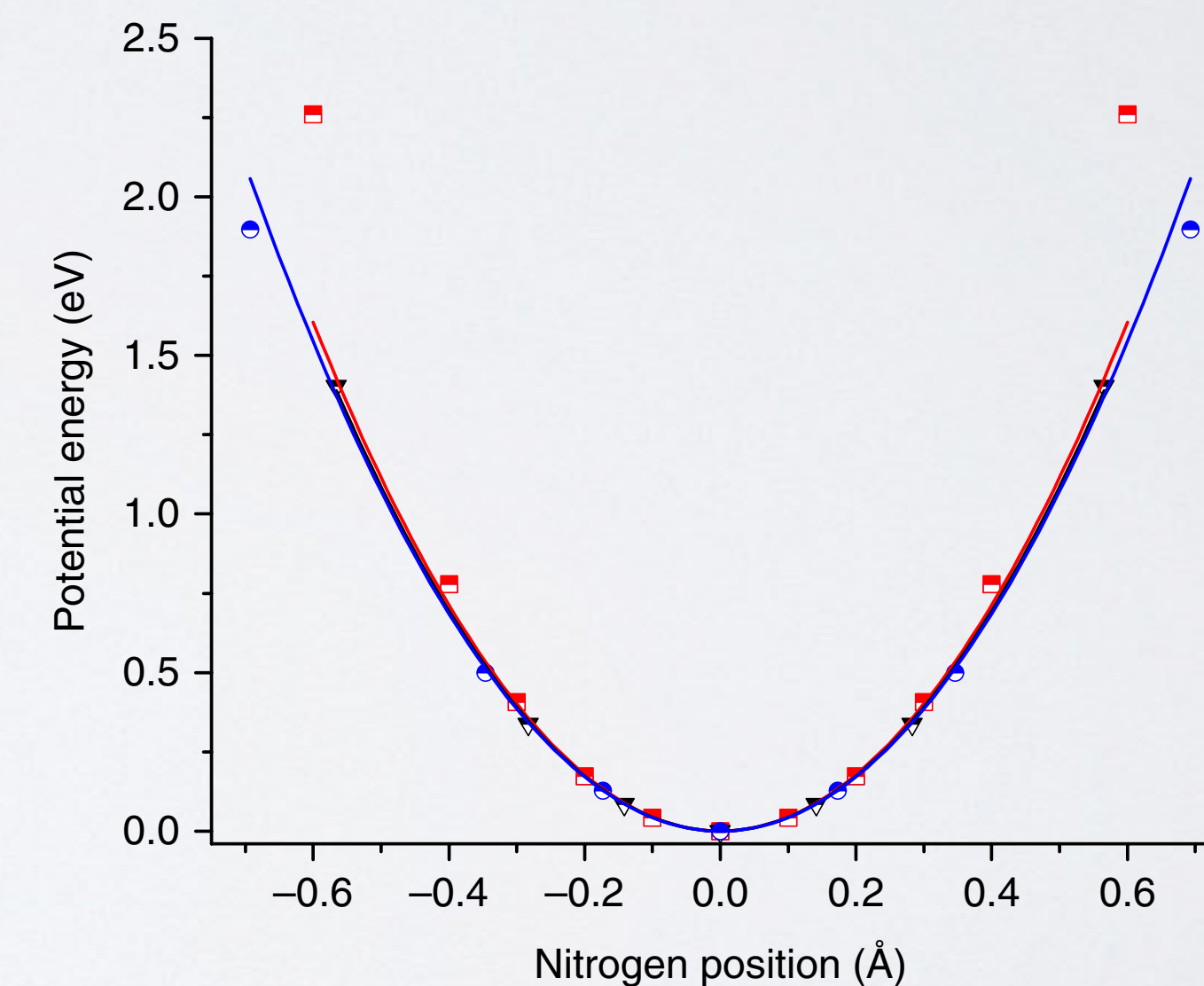
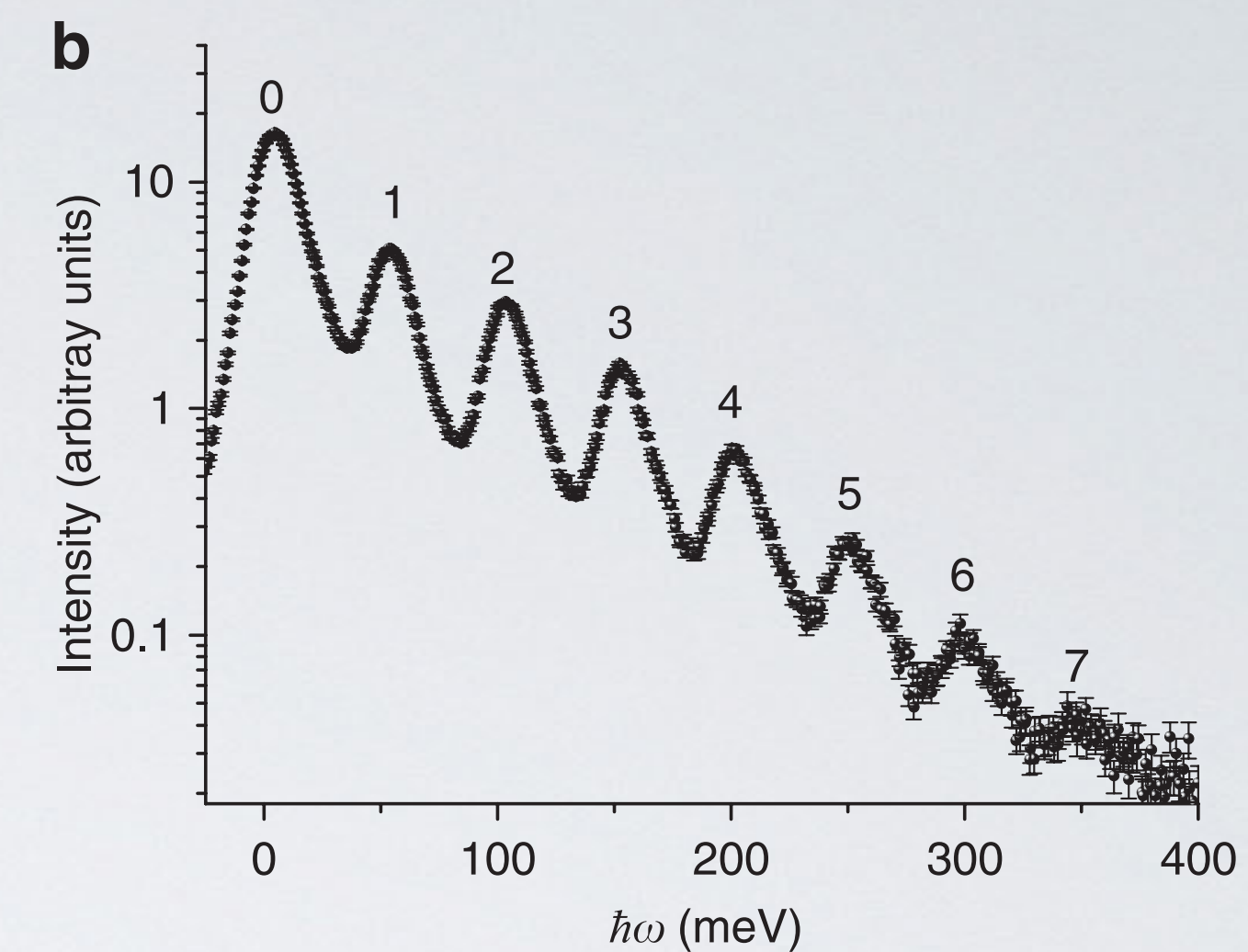
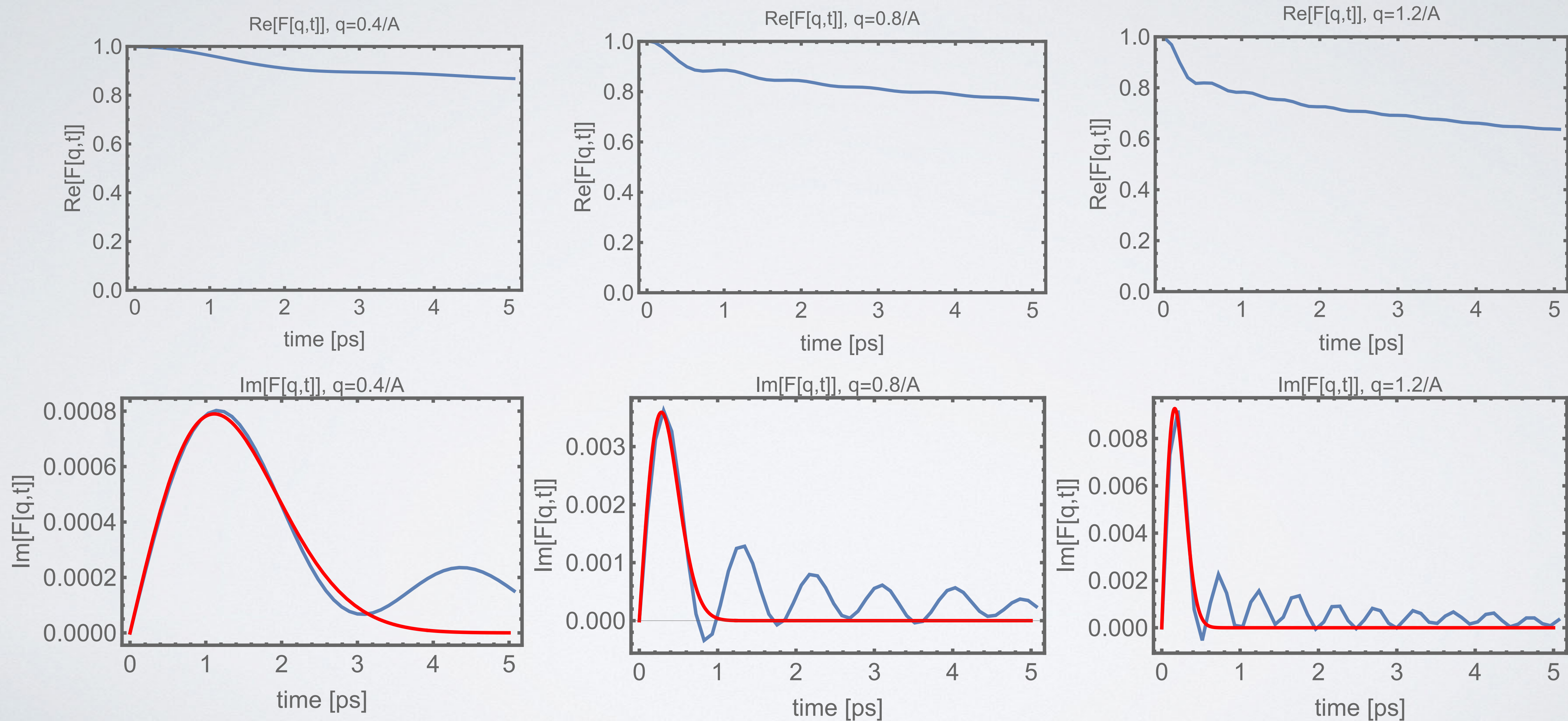


Figure 1 | Rocksalt crystal structure of uranium nitride. Each N atom (small red spheres) is centred in a regular octahedron of U atoms (large blue spheres).

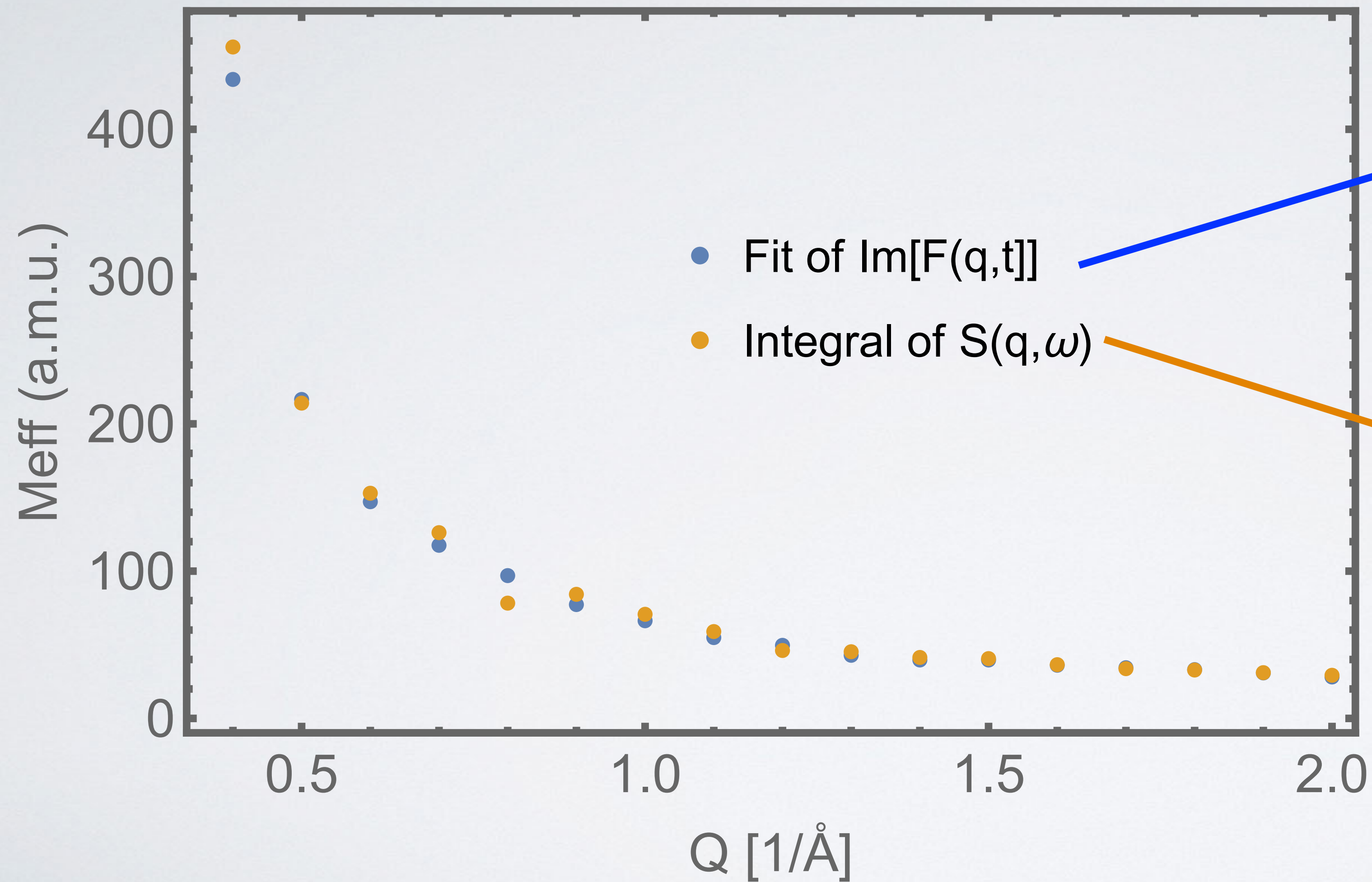


$F(q,t)$ from real QENS spectra: myoglobin in solution (IN6, ILL)

Data from: A. M. Stadler *et al*, Biophysical Journal, vol. 102, pp. 351–359, Jan. 2012.



Effective mass $\approx$ side chain mass: $\overline{M_{\text{eff}}} \approx 92 \text{ a.m.u.}$



$$\text{Im}\{F(q, t)\} \approx e^{-at^2} \sin(t\Omega)$$

$$\Omega = \frac{\hbar q^2}{2M_{\text{eff}}(q)}$$

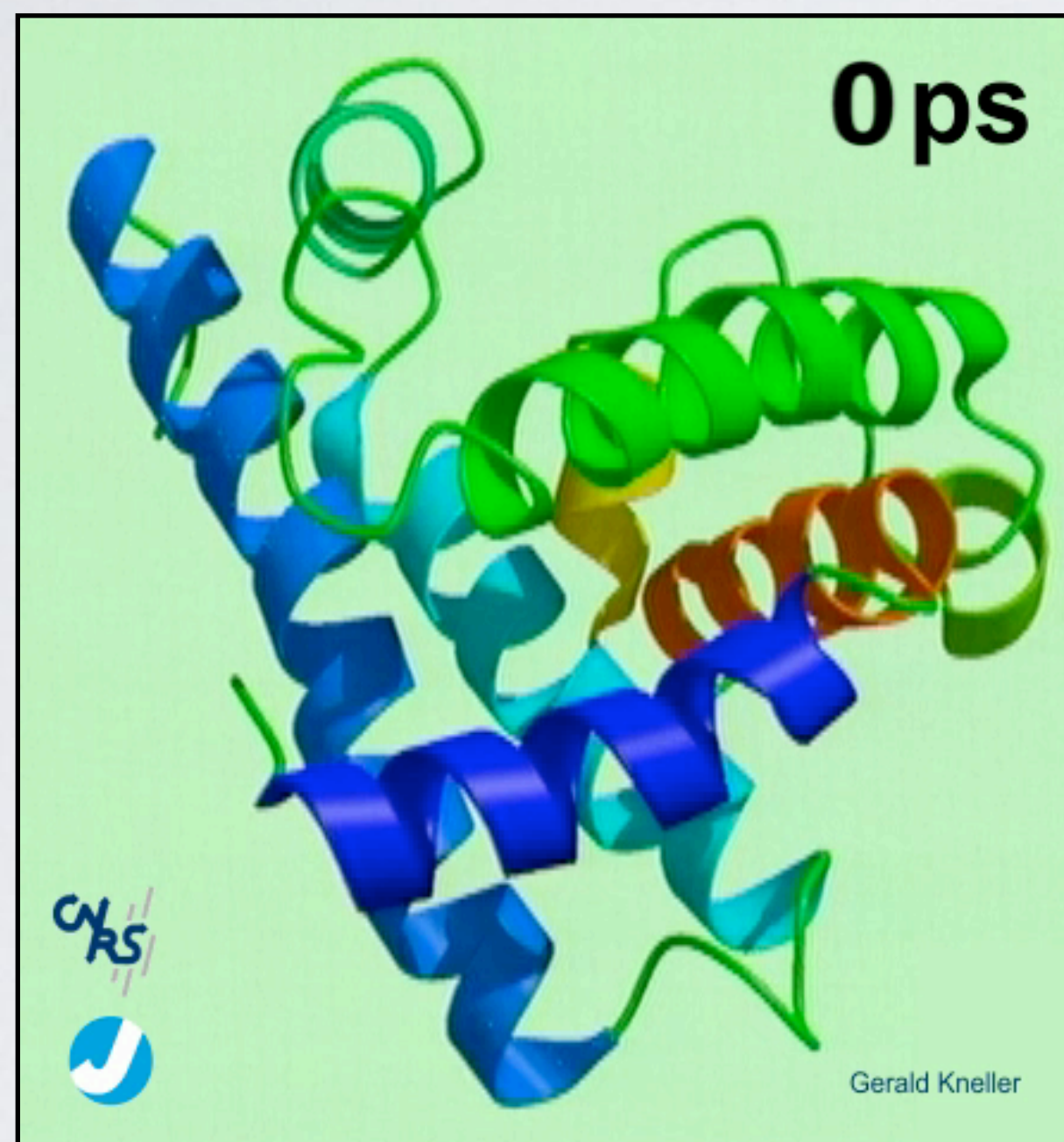
$$\frac{\hbar q^2}{2M_{\text{eff}}(q, \omega_c)} \equiv \int_{-\omega_c}^{+\omega_c} d\omega \, \omega \overline{S}(q, \omega)$$

$$\omega_c \approx 20 \text{ meV}$$

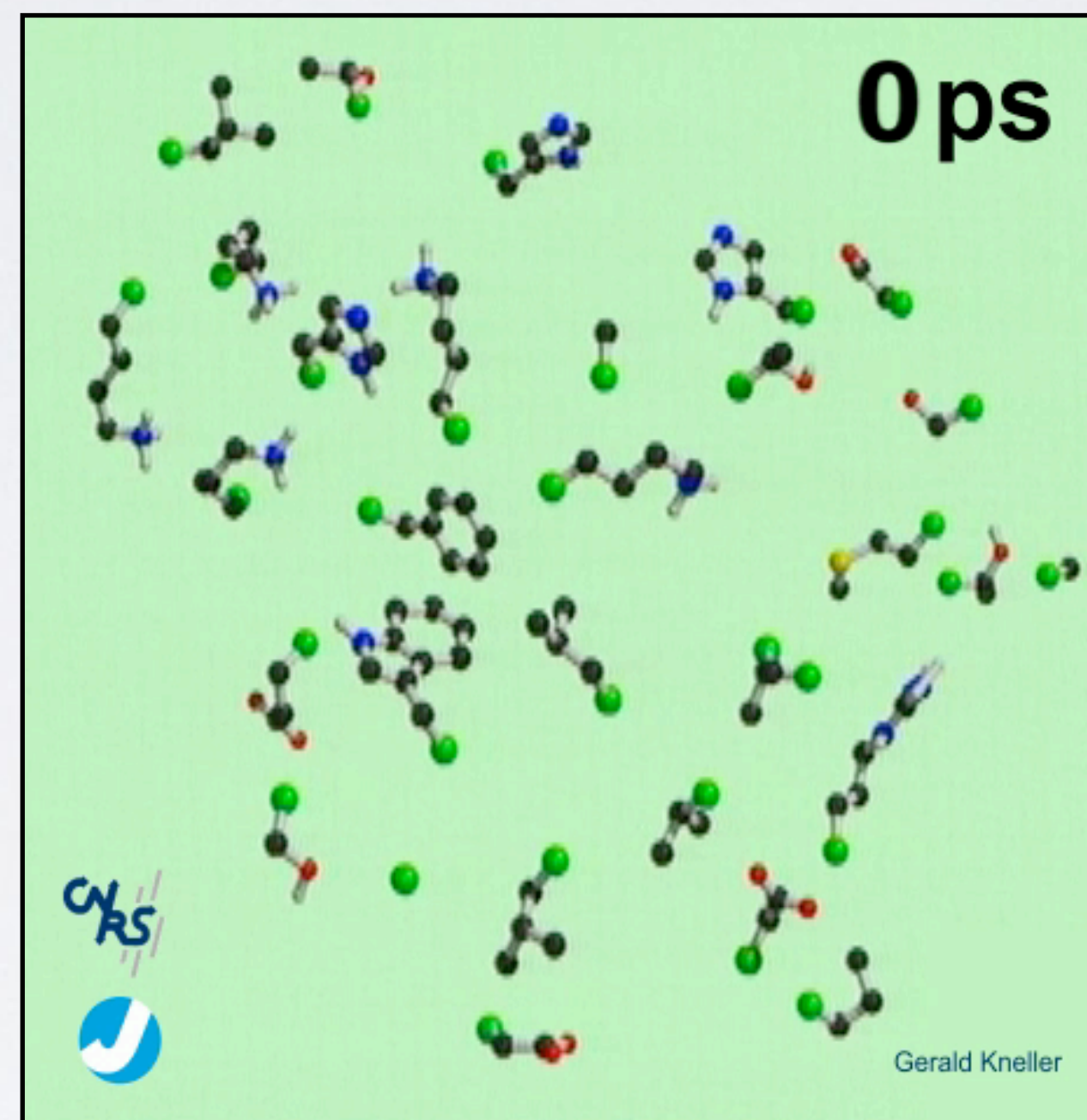
Back to liquid-like side chain motions in myoglobin

G. R. Kneller and J. C. Smith, "Liquid-like Side-Chain Dynamics in Myoglobin," J Mol Biol, vol. 242, no. 3, pp. 181–185, 1994.

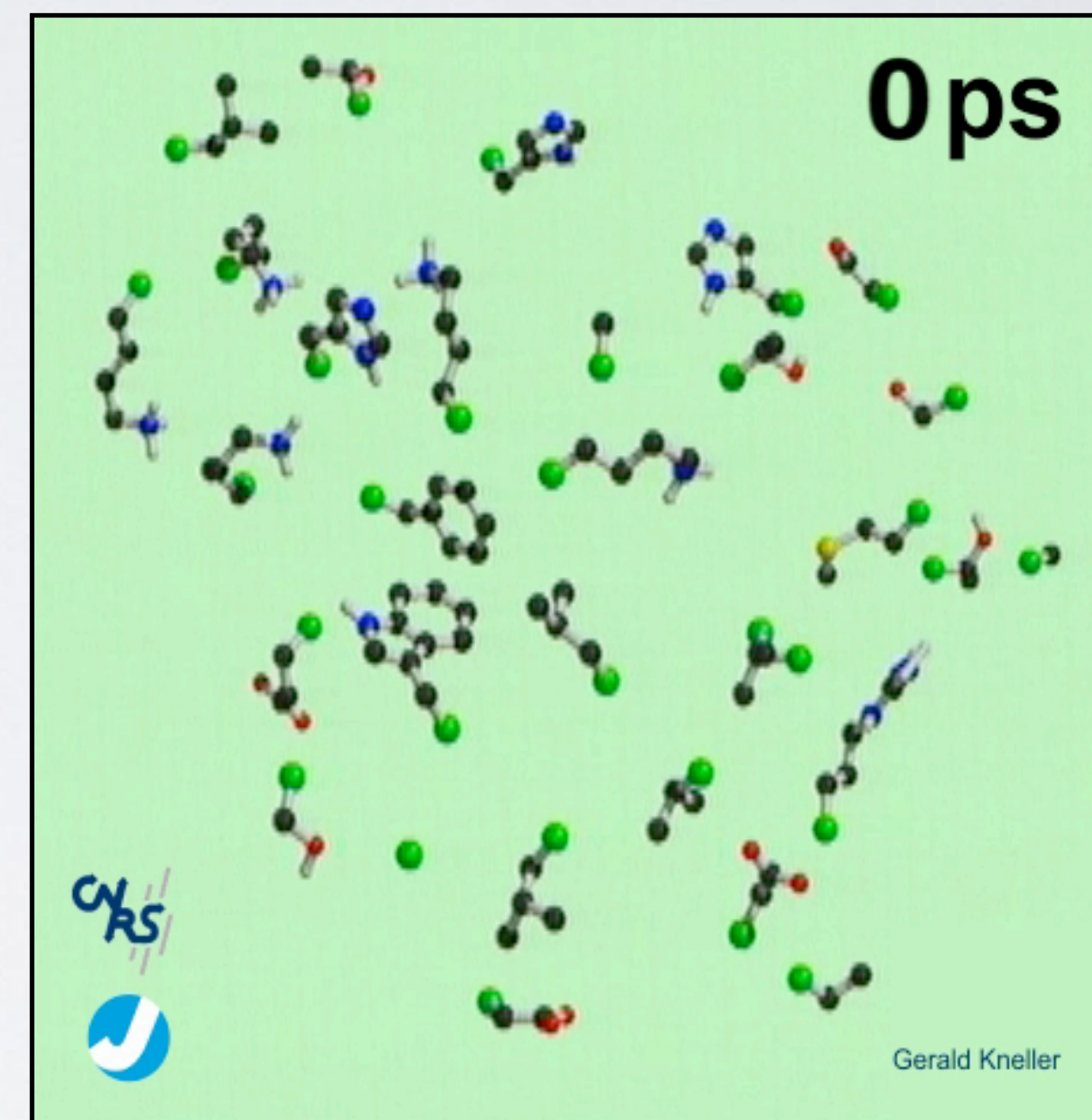
Backbone



The "side-chain liquid"



Flexible



Rigid : seen by QENS on IN6

COMMUNICATION

Liquid-like Side-chain Dynamics in Myoglobin

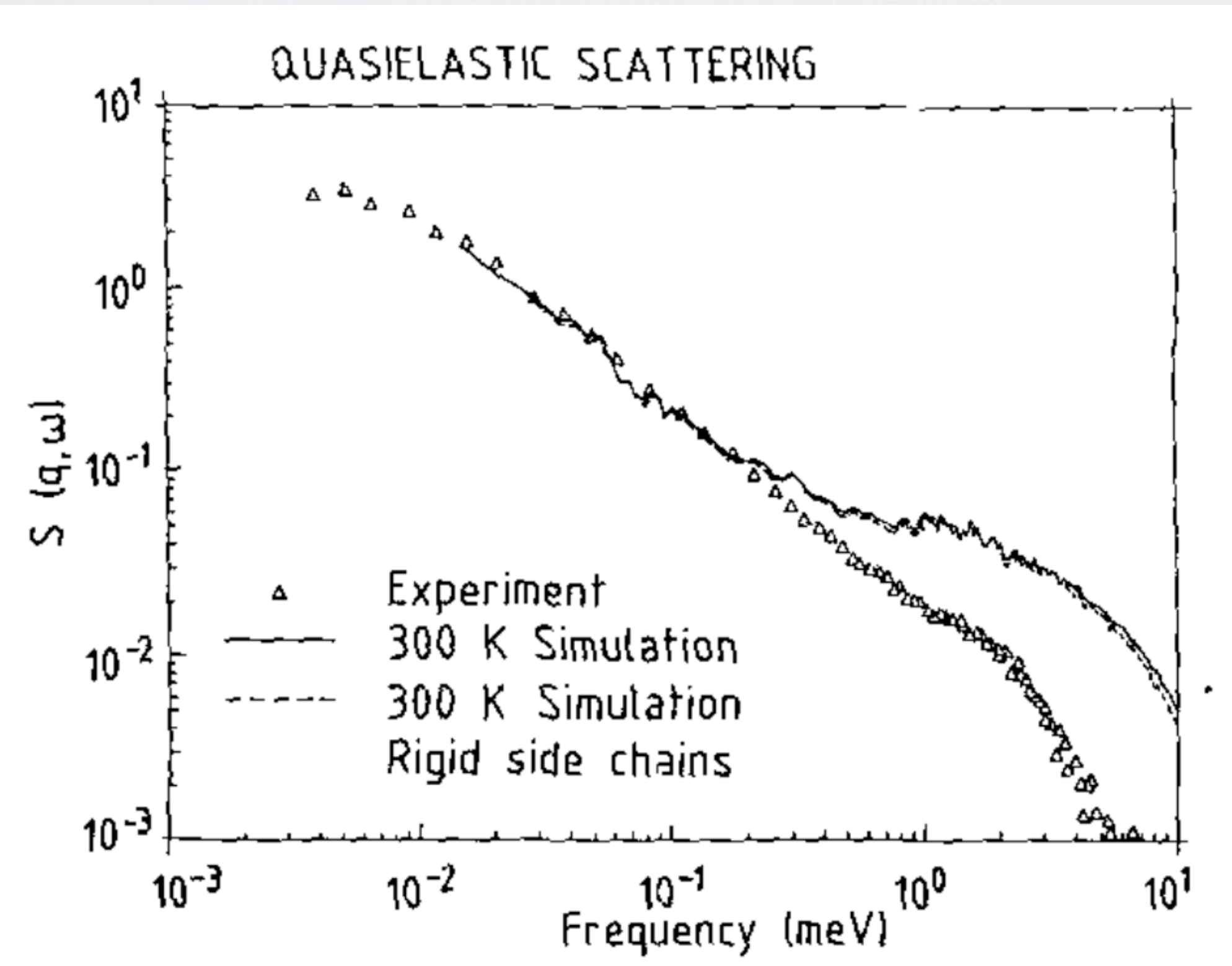
Gerald R. Kneller^{1,2} and Jeremy C. Smith²

¹*IBM France*

68–76 Quai de la Rapée F-75012 Paris, France

²*SBPM DBCM*

Commissariat à l'Energie Atomique, CE Saclay F-91191 Gif-sur-Yvette, France



Conclusions and perspectives

- Recoil effects are not only a subject for deep inelastic scattering (neutron Compton scattering), but are even visible in QENS experiments.
- The imaginary part of $F(q,t)$ contains valuable information, even if it is very small compared to the real part.
- Exploit the fact that the q -dependence of the effective mass contains information about the forces acting on the scattering atom.

NEMD “q-Kick Response” method for the evaluation of the Dynamic Liquid Structure Factor

W. A. B. Evans and C. J. Ojeda,

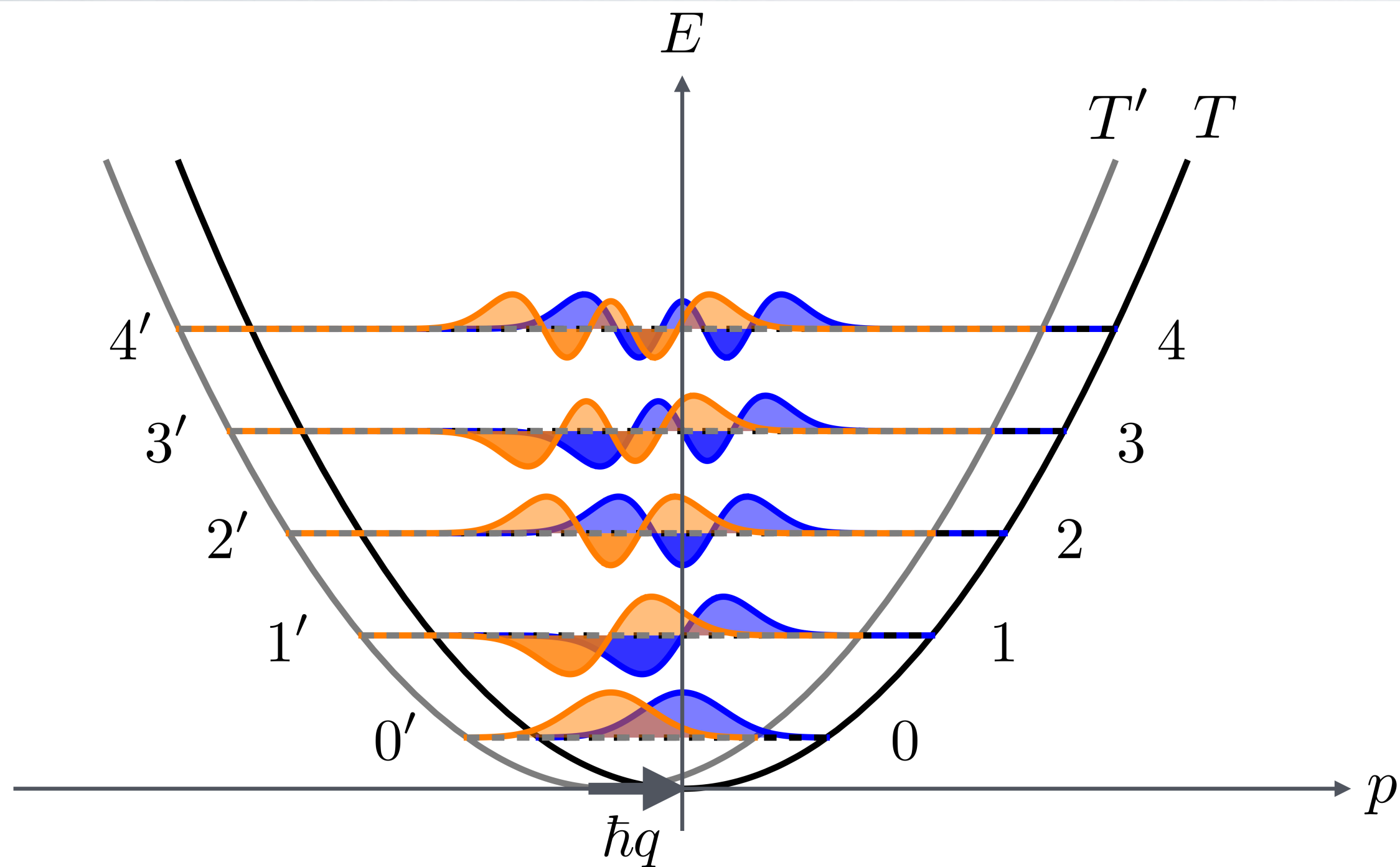
Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, UK.

Abstract

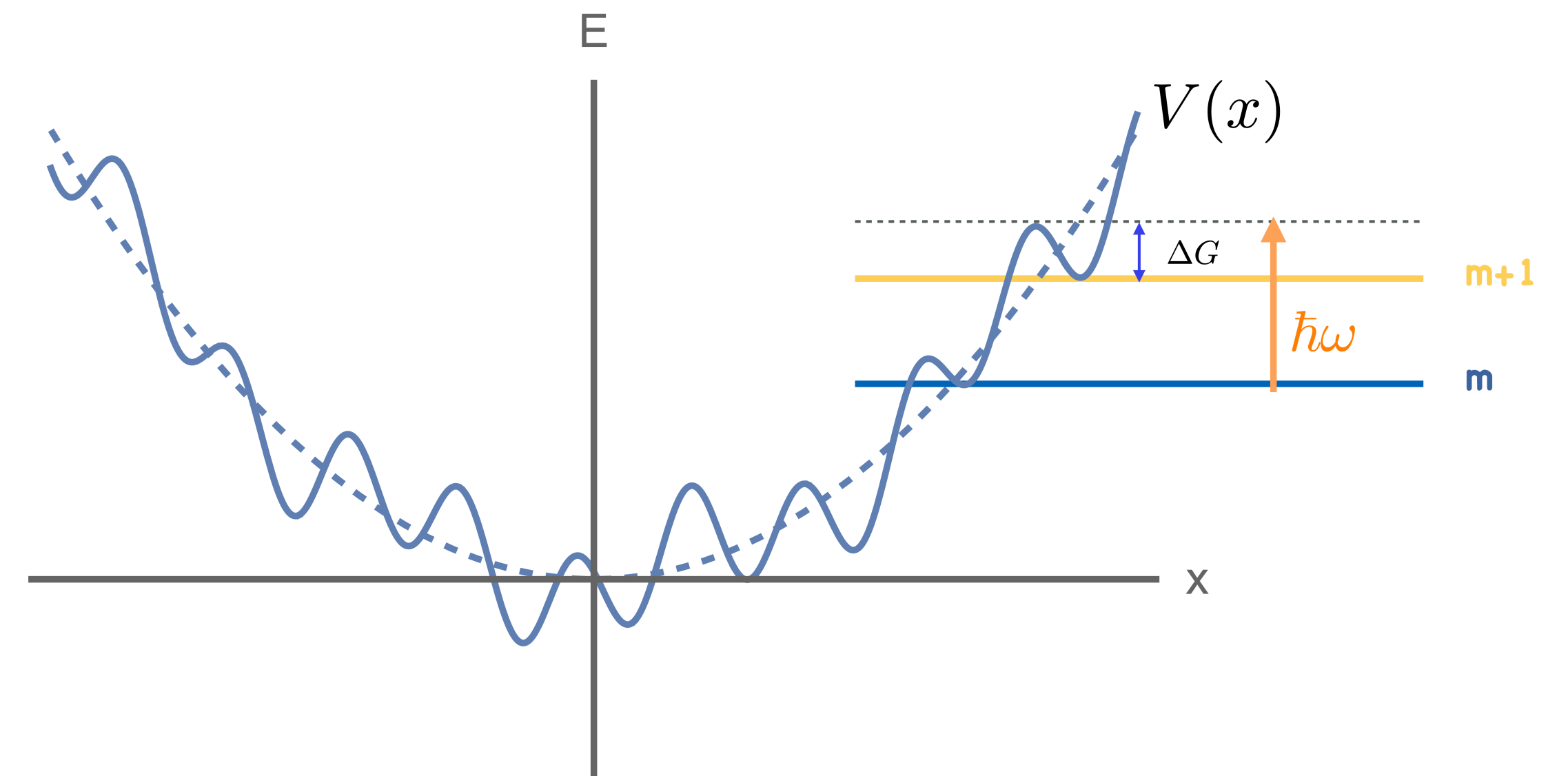
A new non-equilibrium molecular dynamics (NEMD) technique to obtain the Van-Hove dynamic liquid structure factor, $S(q, \omega)$, is presented. The technique depends on evaluating the system's density response to a *density-coupling*, time-impulsive and space-sinusoidal field of wave vector, q , by the perturbation-and-difference method. Results pertaining to a Lennard-Jones fluid model of liquid Argon are presented as an illustration.

Semiclassical energy landscapes

Quantum “energy landscape”



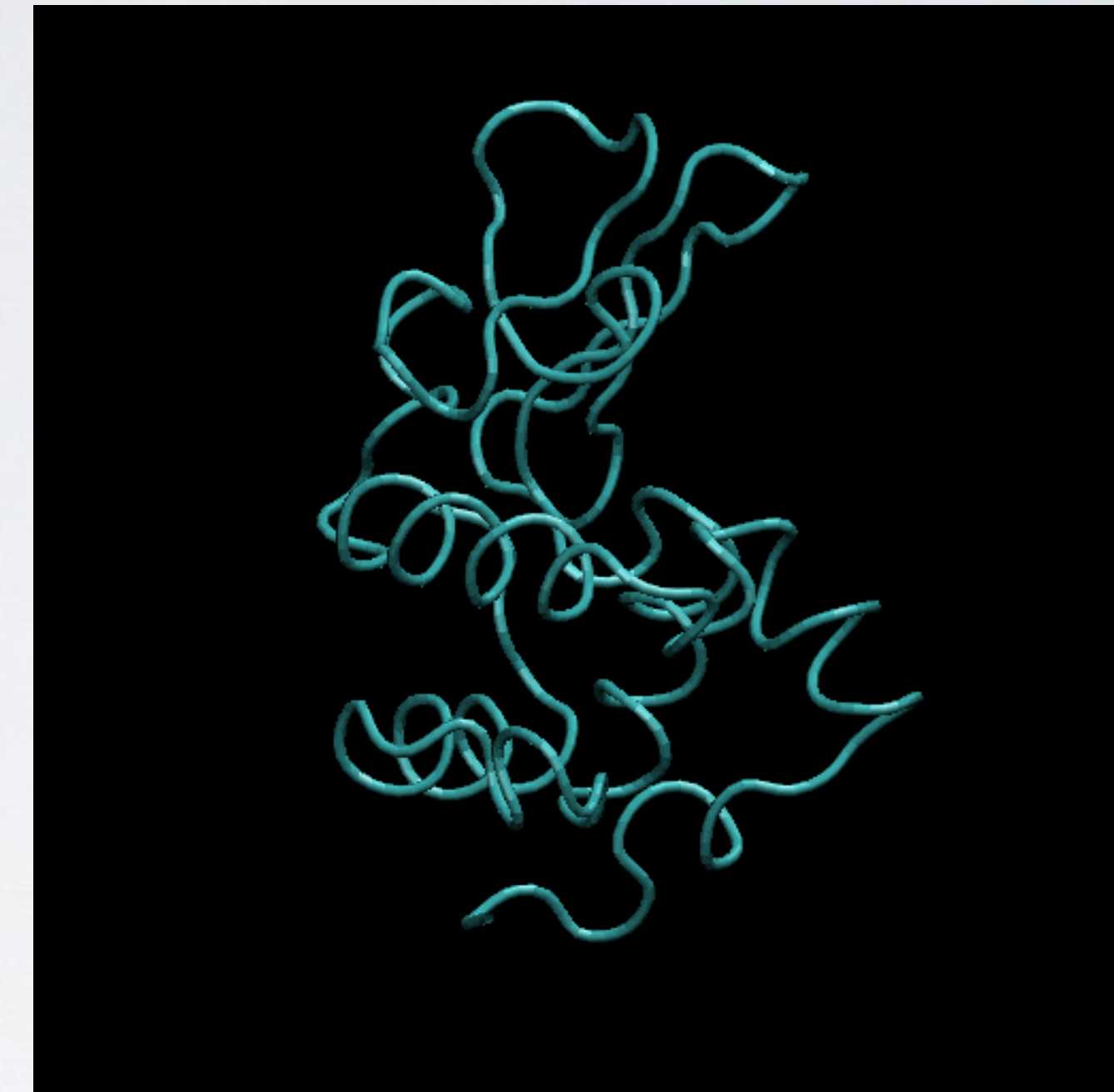
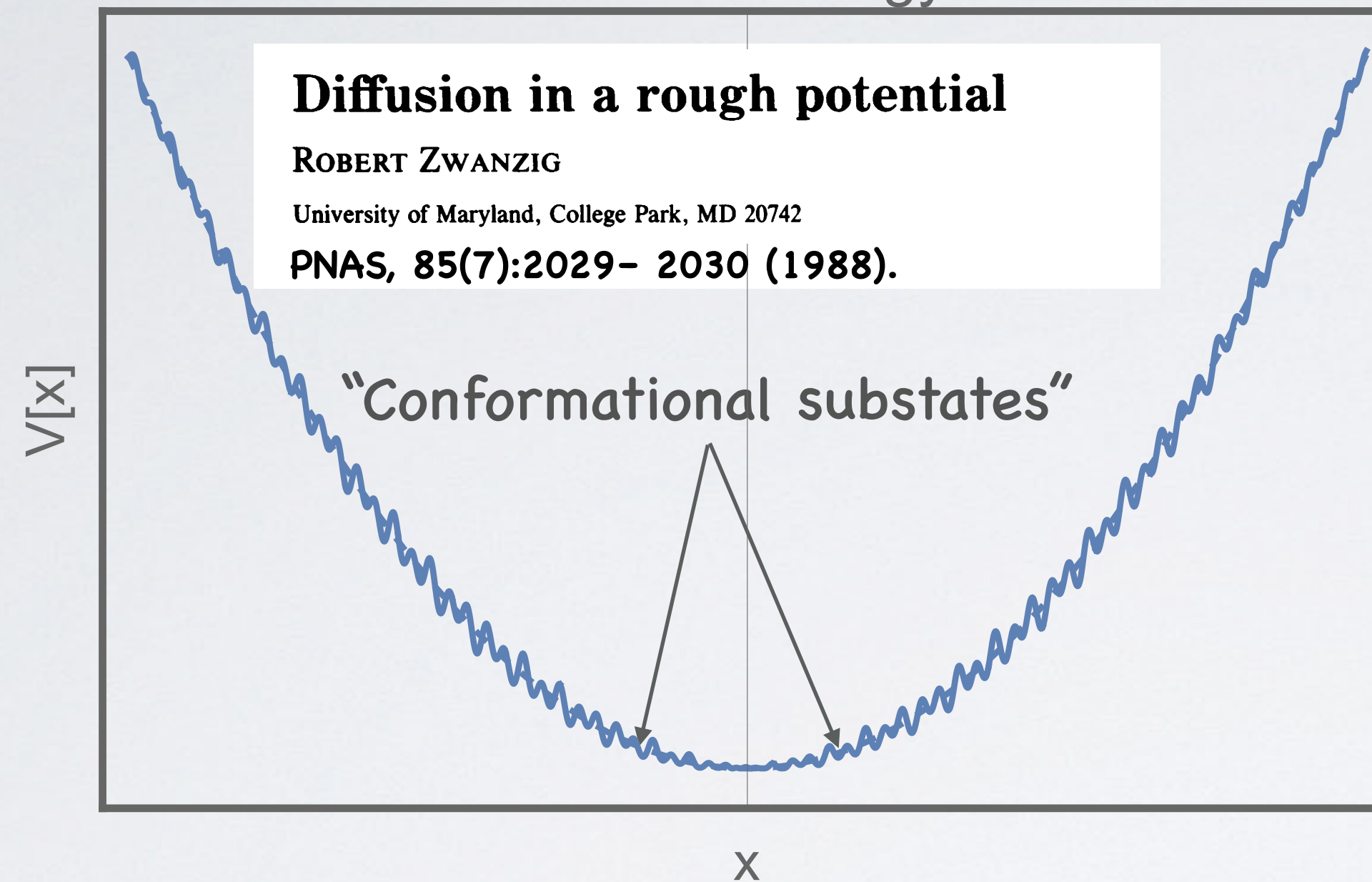
Classical energy landscape



Semiclassical picture for a continuum of energy levels

Diffusion — jumps between almost equal neighboring energy minima

Continuum of energy levels



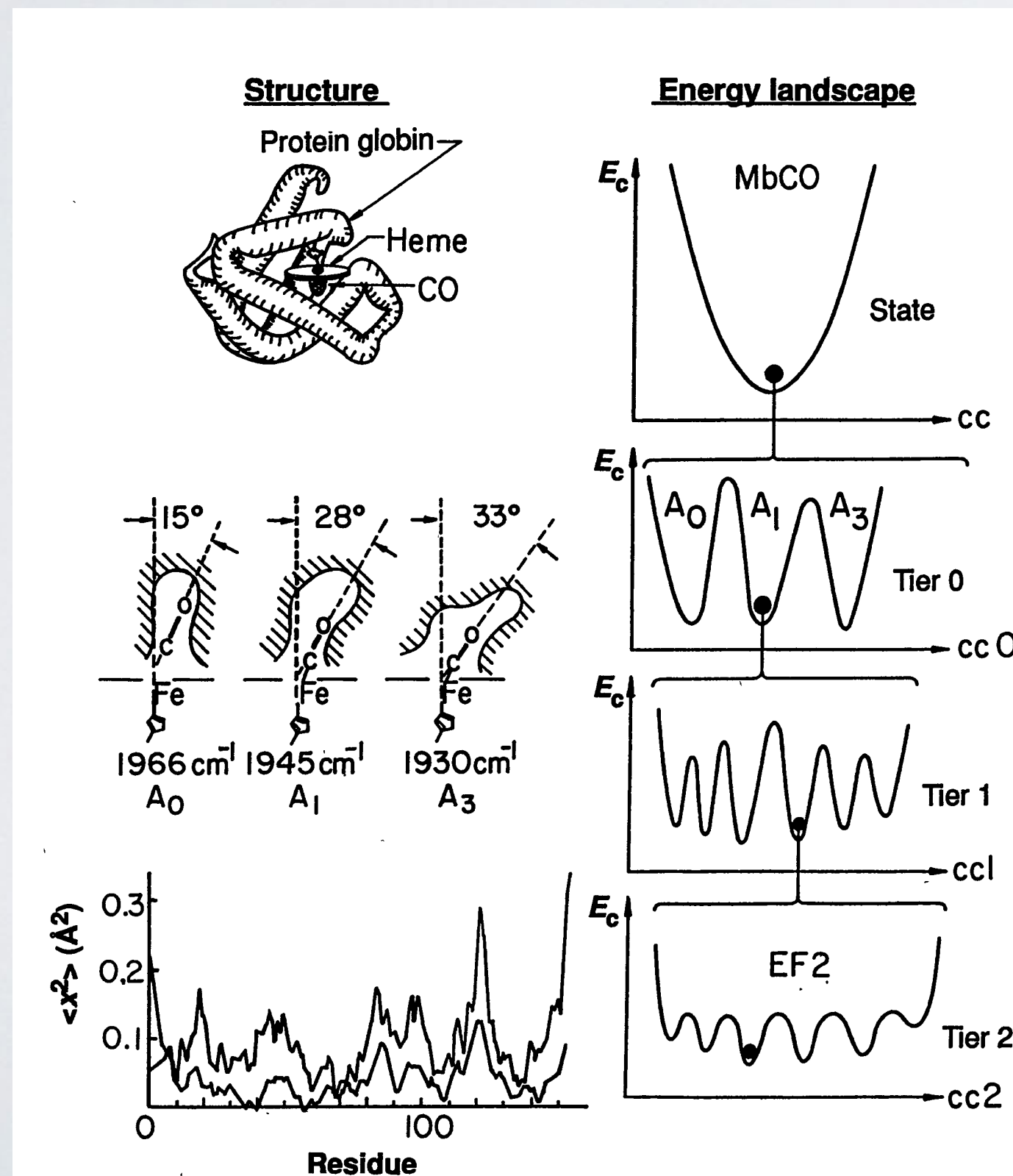
$$W_{cl}(E', E, \mathbf{q}) \approx W_{cl}(E, E', -\mathbf{q})$$
$$E' \approx E + \frac{\hbar^2 |\mathbf{q}|^2}{2M}$$

$$F(\mathbf{q}, t + i\beta\hbar/2) \approx F_{cl}(\mathbf{q}, t)$$

The Energy Landscapes and Motions of Proteins

HANS FRAUENFELDER, STEPHEN G. SLIGAR, PETER G. WOLYNES

Conformational substates



SCIENCE, VOL. 254

Non-exponential rebinding kinetics of CO



$$N(t) = \int dH g(H) \exp[-k(H)t]$$

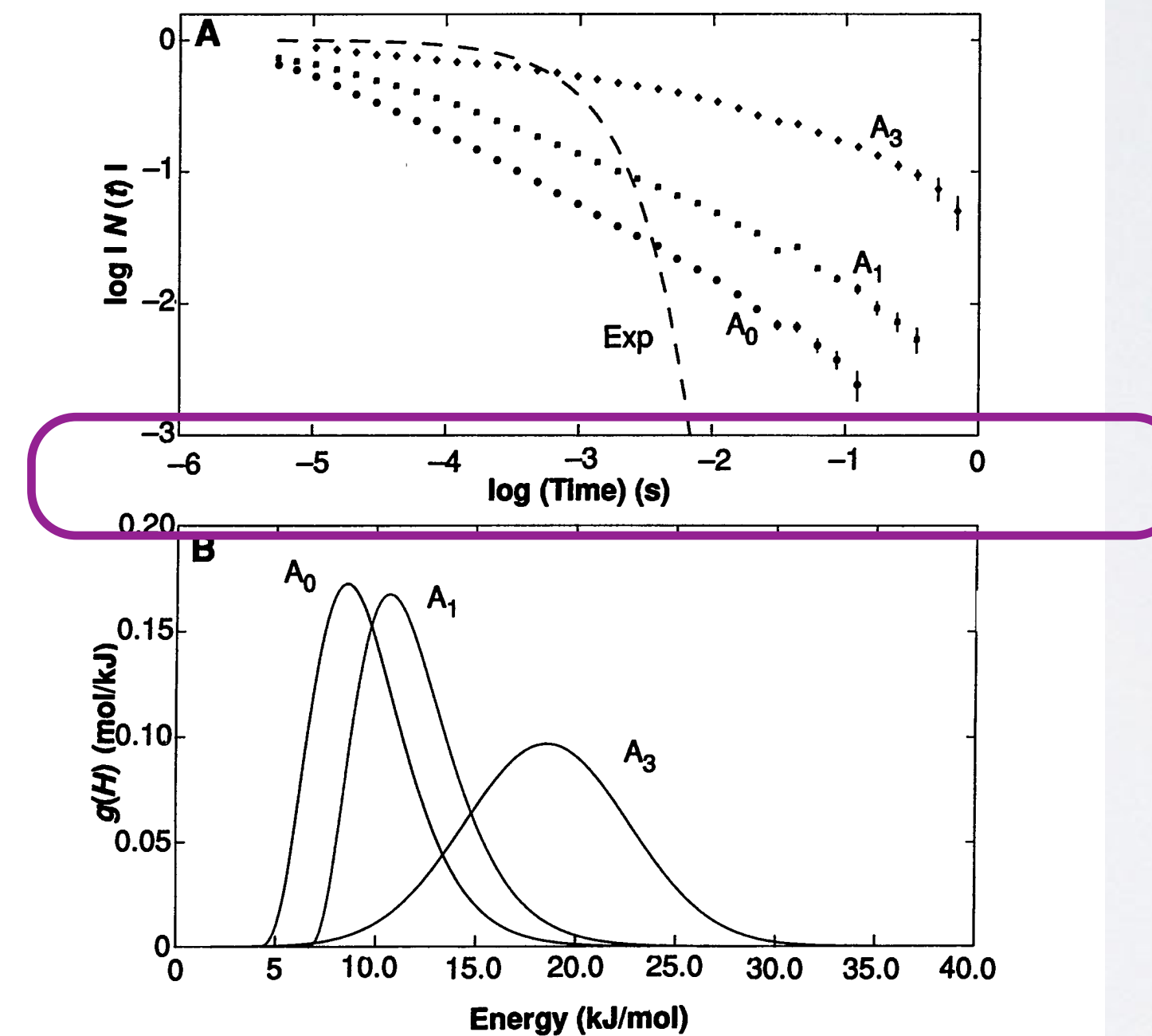


Fig. 2. Rebinding of CO to Mb after photodissociation, measured separately for the substates of tier 0 at pH 5.7. (A) $N(t)$ is the fraction of proteins that have not rebound a CO at the time t after photodissociation. All three substates (A₀, A₁, and A₃) rebound nonexponentially in time. (B) The activation enthalpy spectra, defined through Eq. 1.

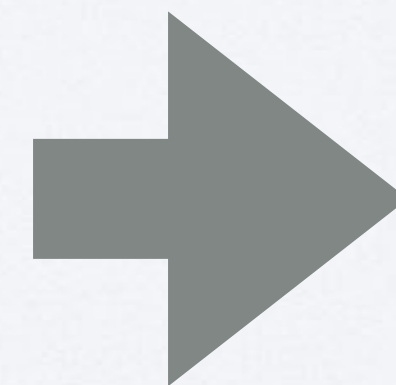
Protein dynamics displays self-similarity

Relaxation and time correlation functions have a multi-exponential form:

$$\phi(t) = \int_0^\infty d\lambda p(\lambda) e^{-\lambda t}$$

For complex systems these functions decay for long times slowly with a power law and exhibit thus self-similarity:

$$\phi(t) \stackrel{t \rightarrow \infty}{\sim} (t/\tau)^{-\alpha}$$



$$\phi(\mu t) \stackrel{t \rightarrow \infty}{\sim} \mu^{-\alpha} \phi(t)$$

Self-similar relaxation dynamics seen in CO-rebinding kinetics of Mb

46

Biophysical Journal Volume 68 January 1995 46-53

A Fractional Calculus Approach to Self-Similar Protein Dynamics

Walter G. Glöckle and Theo F. Nonnenmacher

Department of Mathematical Physics, University of Ulm, D-89069 Ulm, Germany

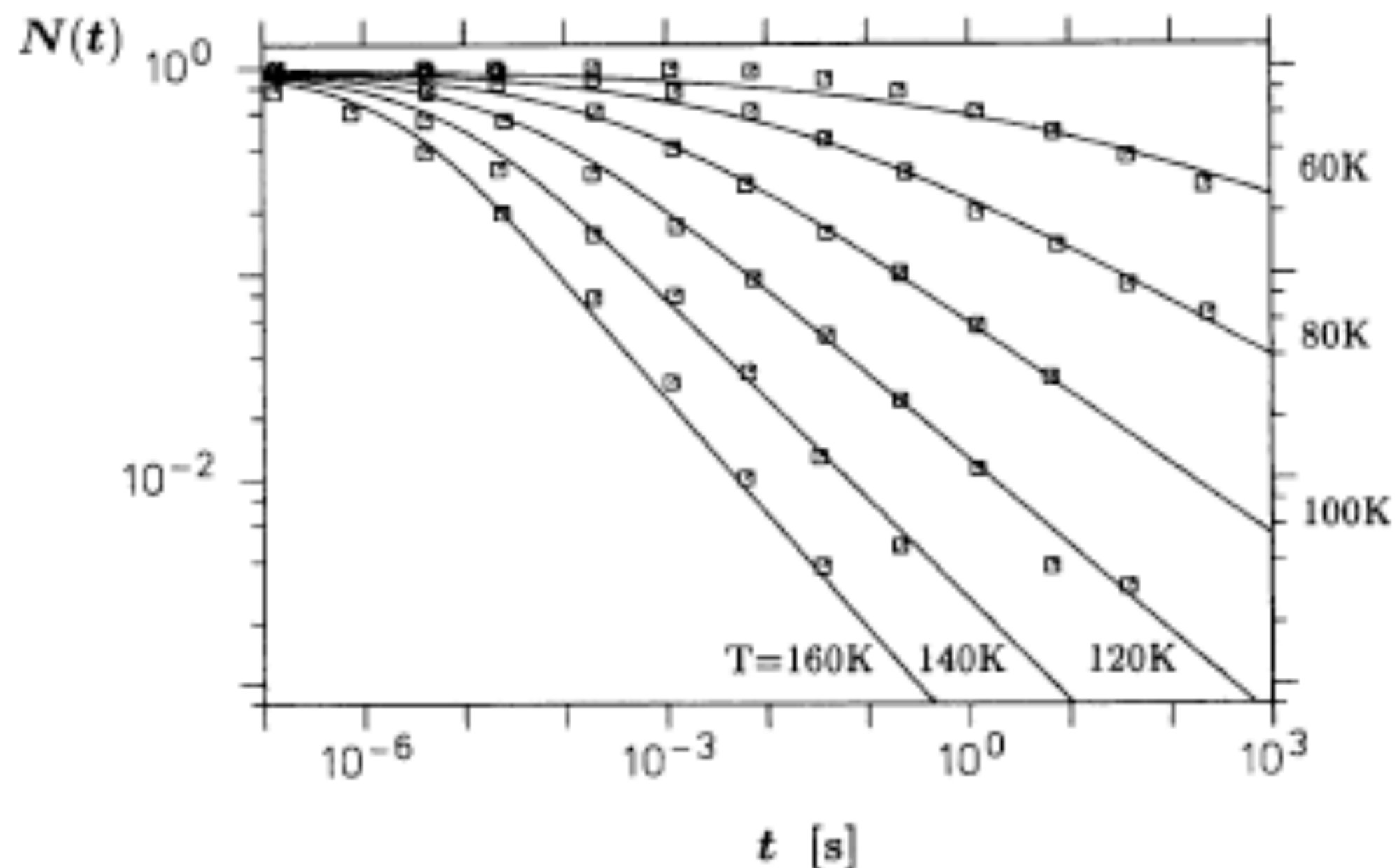


FIGURE 2 Three-parameter model Eq. 32 for rebinding of CO to Mb after photo dissociation. The parameters are $\tau_m = 8.4 \times 10^{-10}$ s, $\alpha = 3.5 \times 10^{-3} K^{-1}$ and $k = 130$, the data points are from Austin et al. (1975).

$$N(t) = N(0)E_{\alpha}(-(t/\tau)^{\alpha})$$

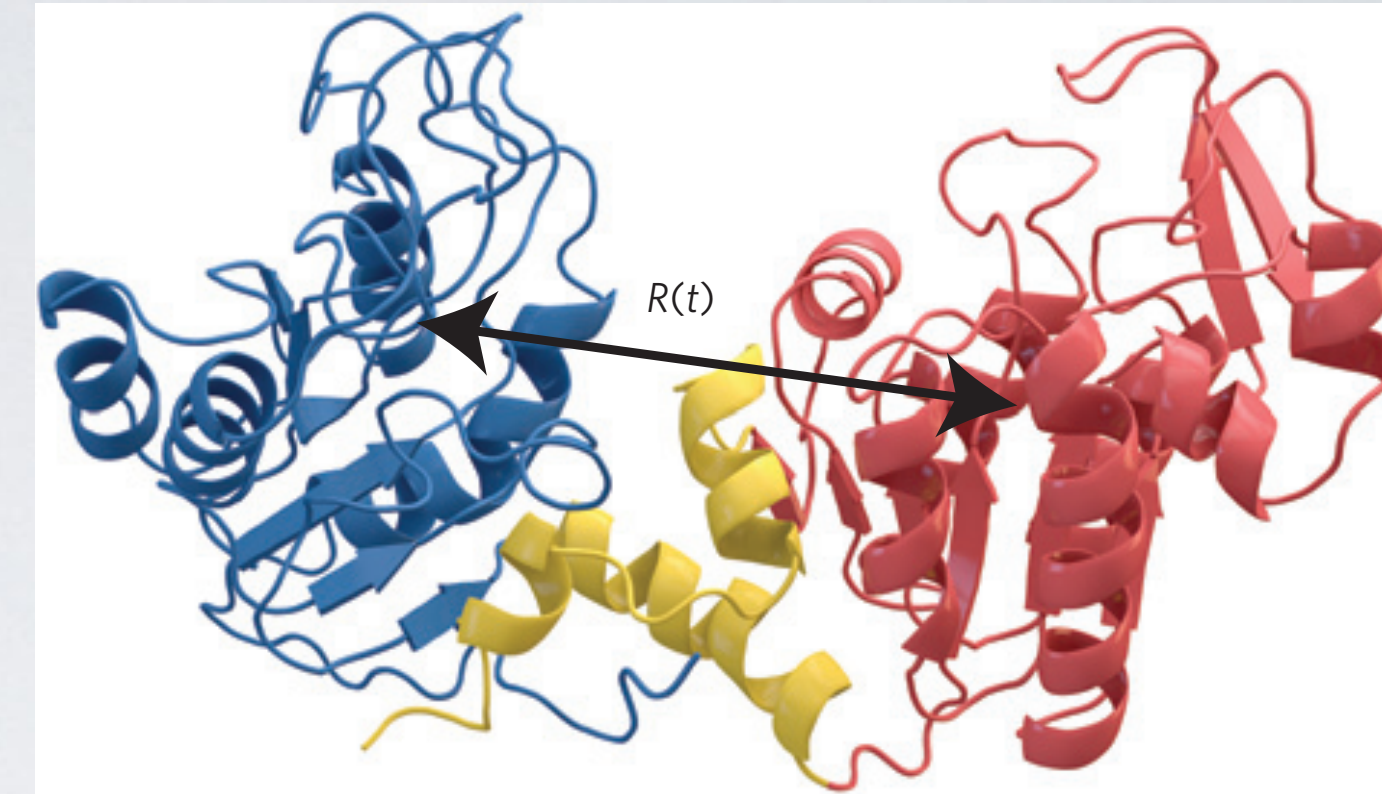
Mittag-Leffler function

$$E_{\alpha}(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(1 + \alpha n)}$$

$$E_{\alpha}(-(t/\tau)^{\alpha}) \stackrel{t \rightarrow \infty}{\sim} \frac{(t/\tau)^{-\alpha}}{\Gamma(1 - \alpha)}$$

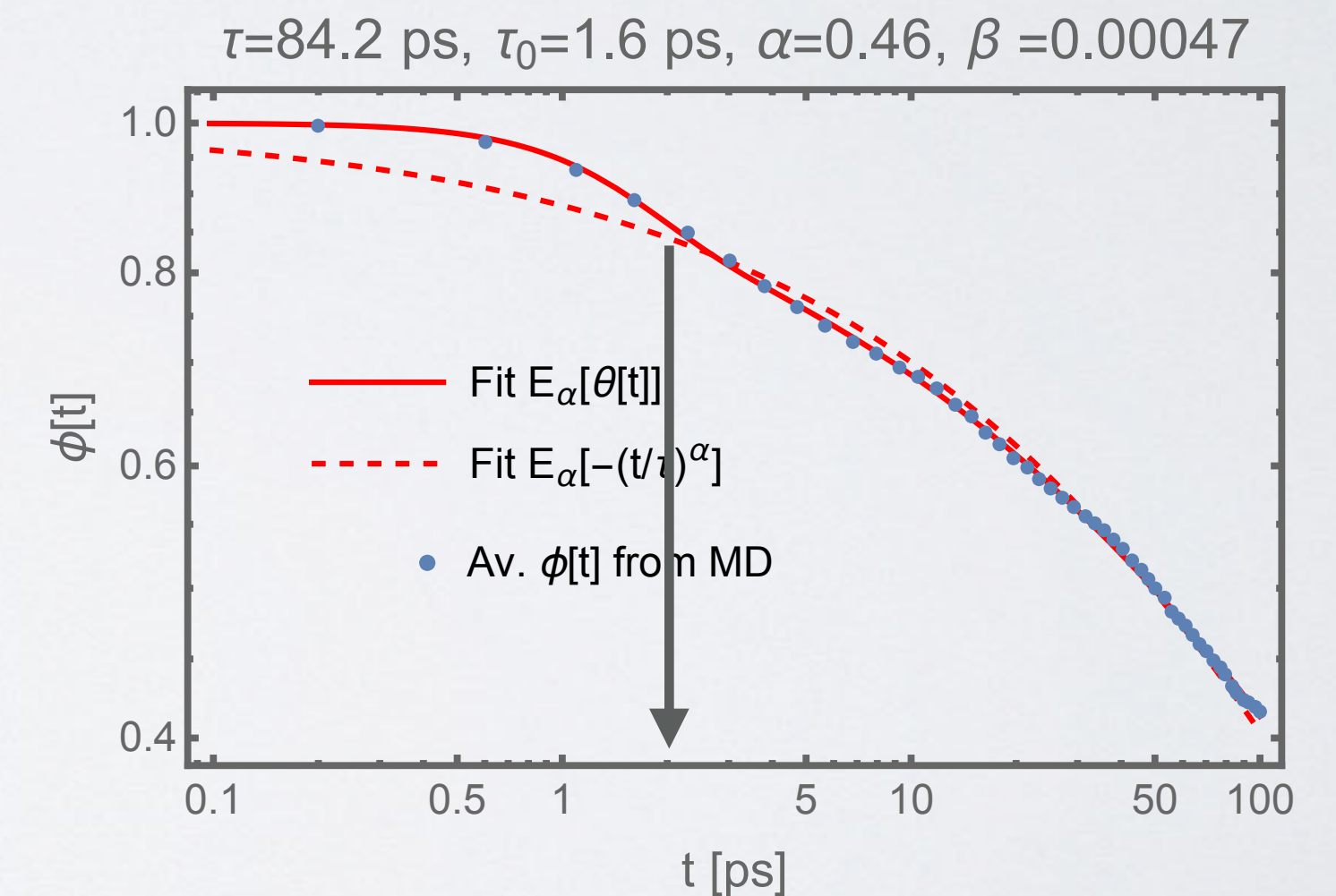
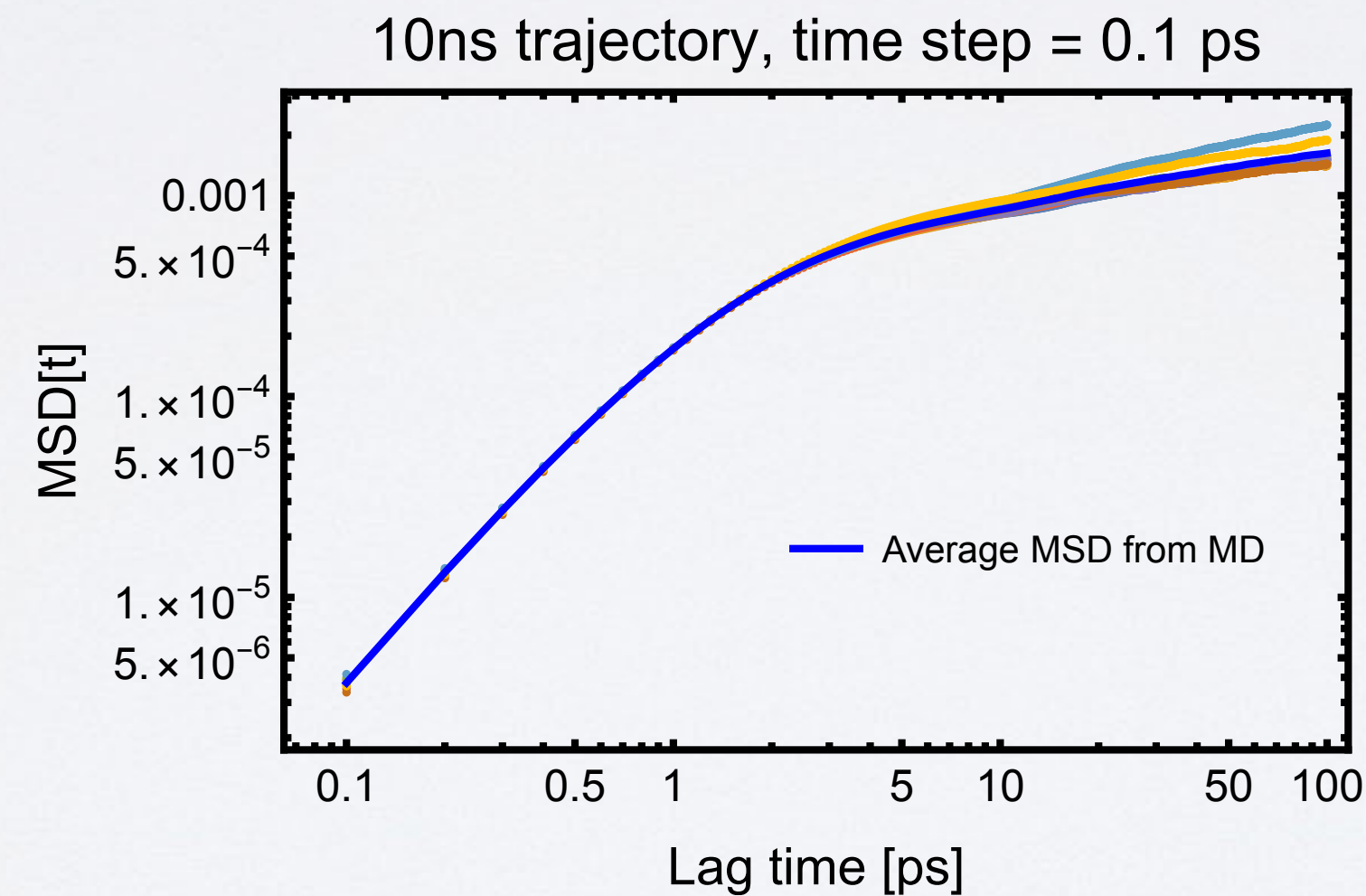
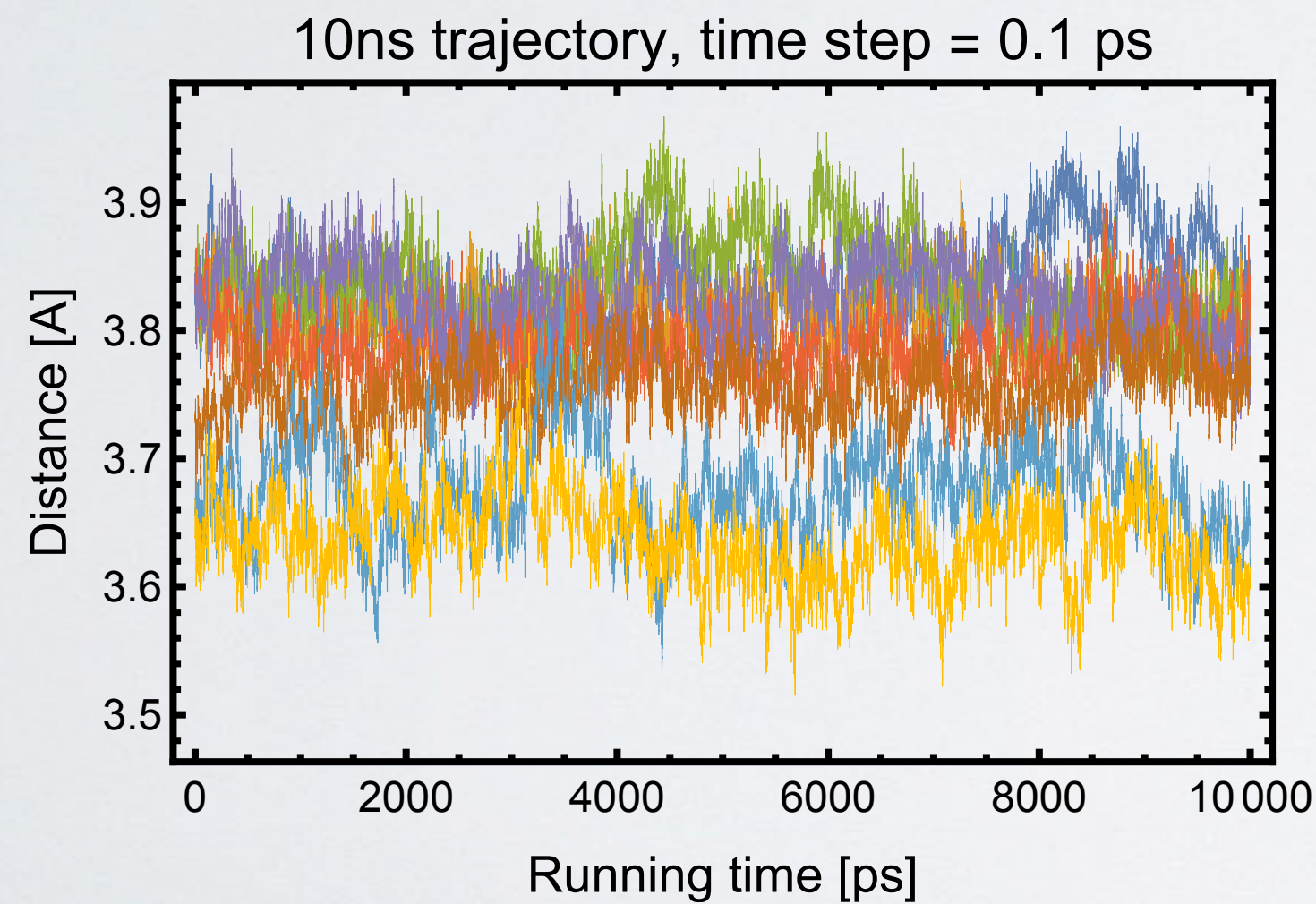
The dynamics of single protein molecules is non-equilibrium and self-similar over thirteen decades in time

Xiaohu Hu^{1,2}, Liang Hong³, Micholas Dean Smith¹, Thomas Neusius⁴, Xiaolin Cheng¹
and Jeremy C. Smith^{1,5*}



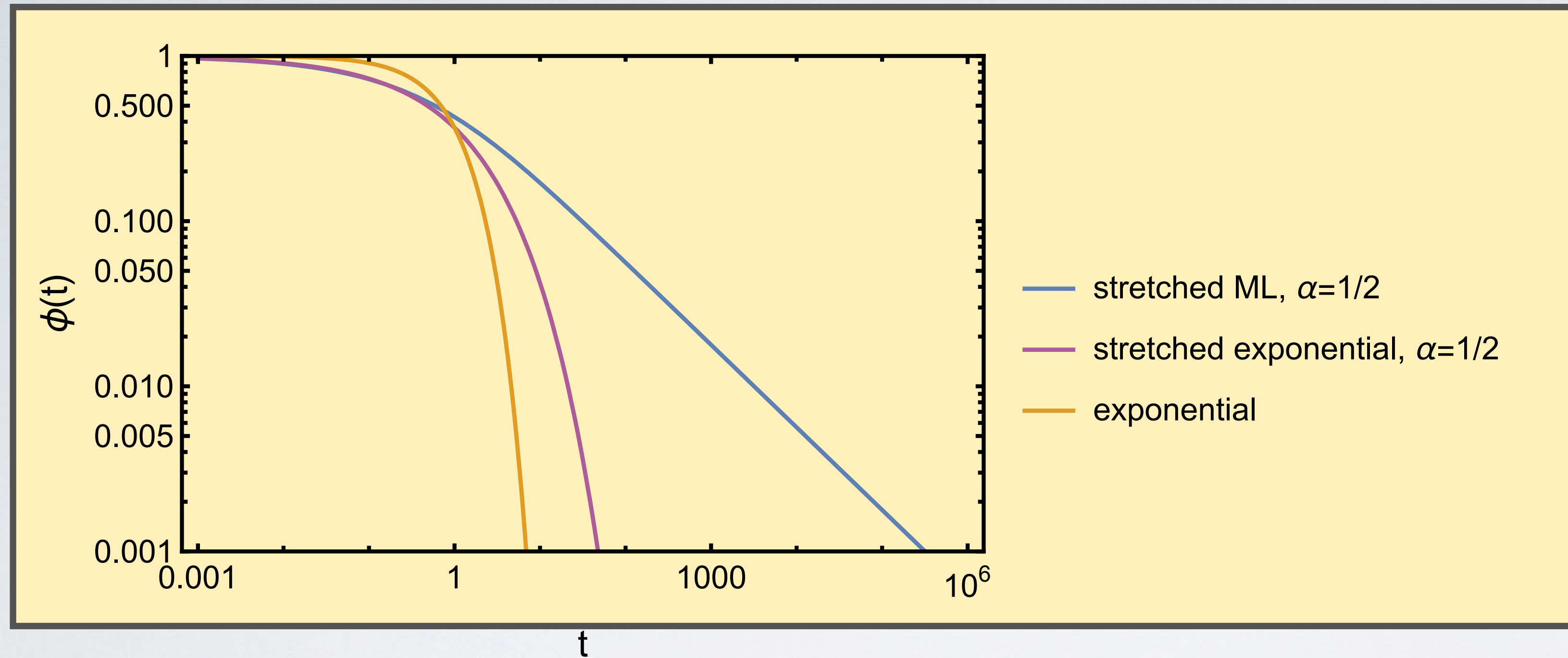
$$MSD(t) = \langle (\mathbf{R}(t) - \mathbf{R}(0))^2 \rangle$$

$$\phi(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle \mathbf{R}(0) \cdot \mathbf{R}(0) \rangle}$$



Transition in the ps regime!

Mathematical properties of the stretched Mittag-Leffler function



$$\frac{d\phi_{\text{ML}}(t)}{dt} + \tau^{-\alpha} \left[{}_0\partial_t^{1-\alpha} \right] \phi_{\text{ML}}(t) = 0$$

Fractional differential equation

$${}_0\partial_t^{1-\rho} \phi_{\text{ML}}(t) \equiv \frac{d}{dt} \int_0^t dt' \frac{(t-t')^{\rho-1}}{\Gamma(\rho)} \phi_{\text{ML}}(t')$$

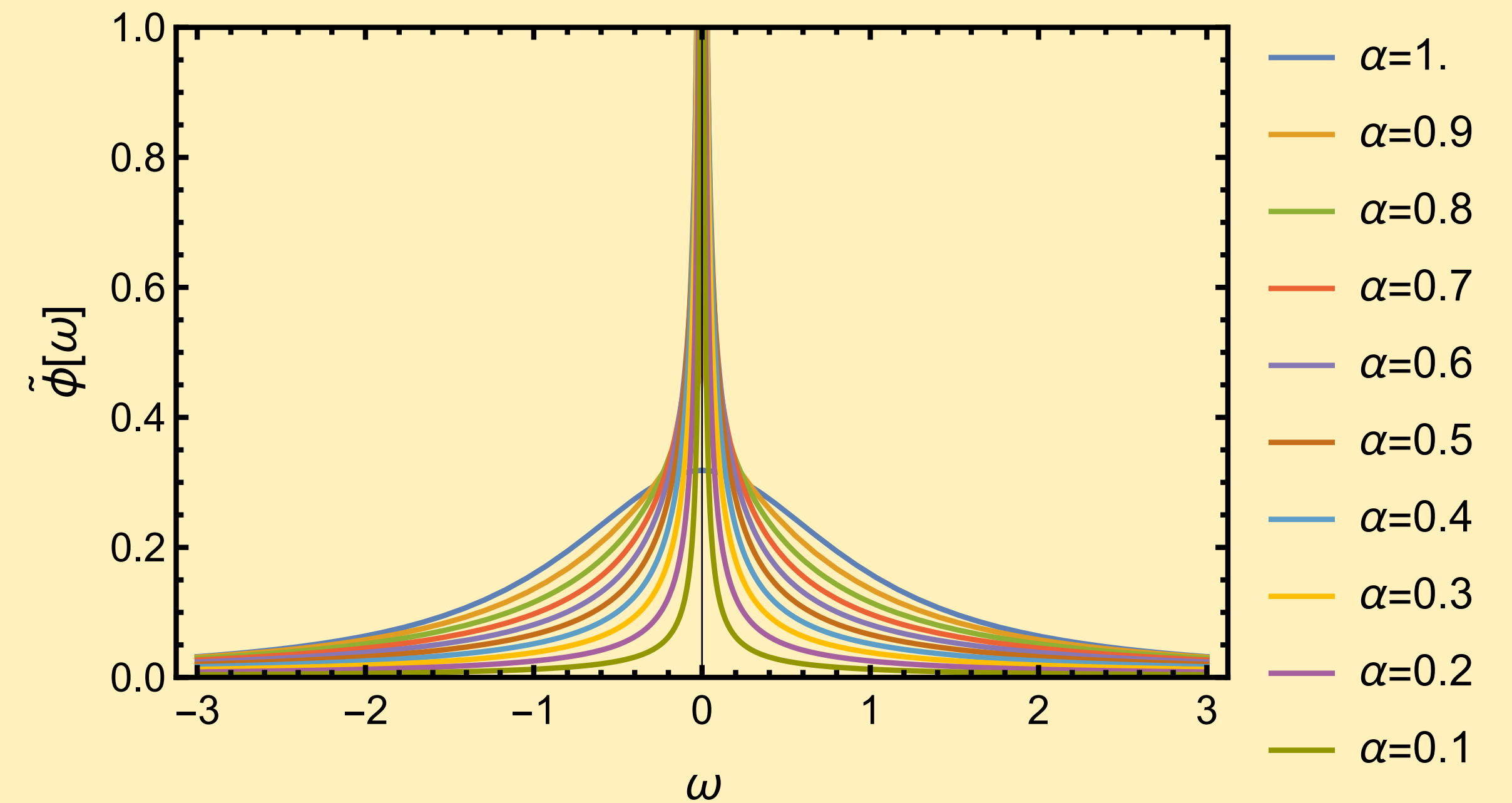
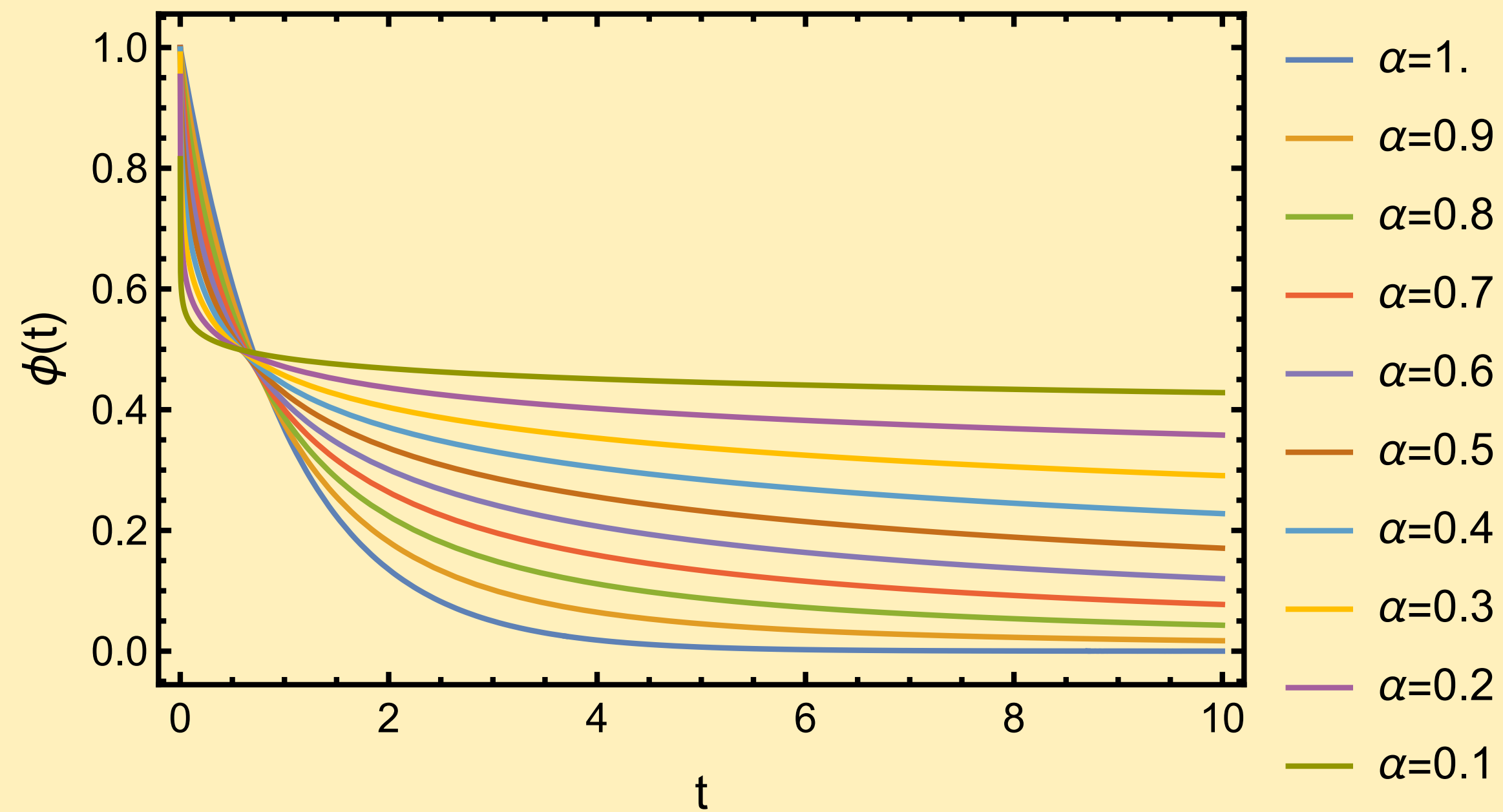
Fractional derivative = memory effects

G. R. Kneller and M. Saouessi. Acta Physica Polonica B, 53(2):A-2, 2022.

Stretched ML function and Fourier spectrum

$$\phi(t) = E_{\alpha}(-t^{\alpha})$$

$$\tilde{\phi}(\omega) = \frac{\sin\left(\frac{\pi\alpha}{2}\right)}{\pi\omega\left(\omega^{-\alpha} + \omega^{\alpha} + 2\cos\left(\frac{\pi\alpha}{2}\right)\right)}$$



Relating relaxation rates to the “roughness” of the energy landscape

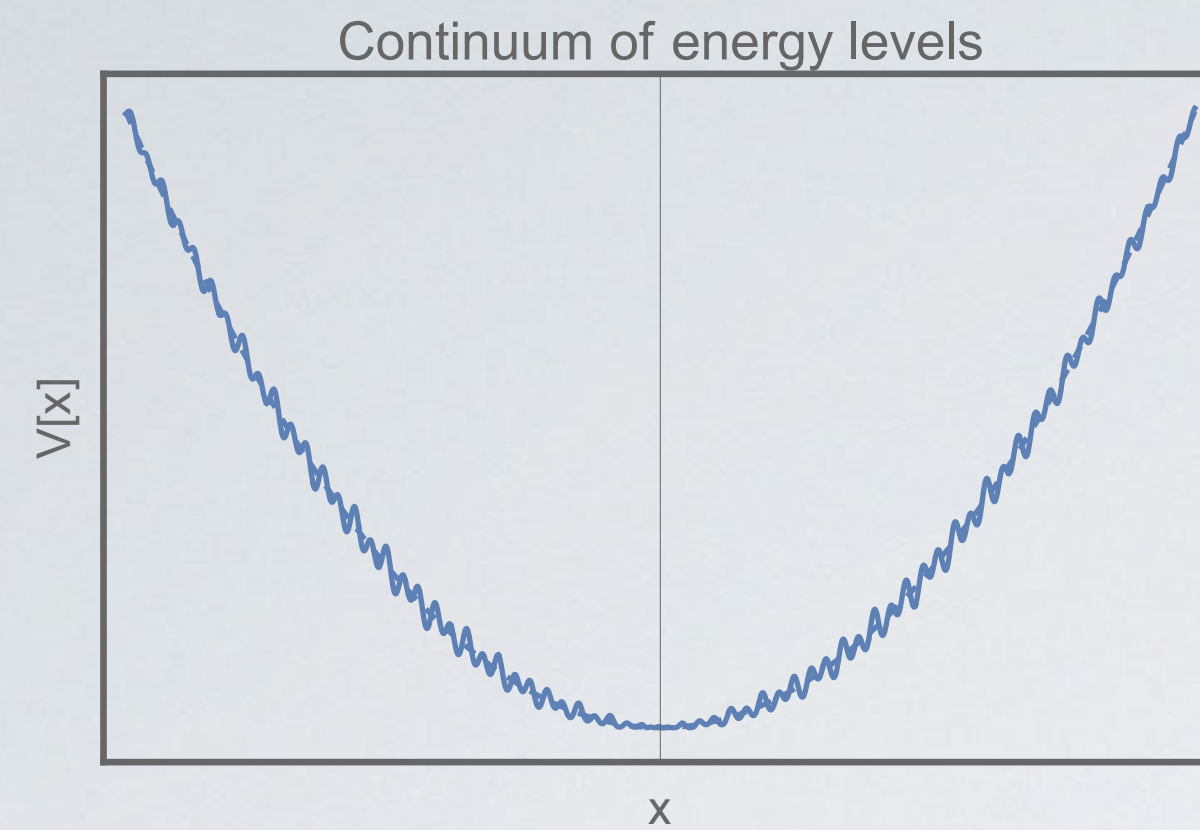
The distribution barrier heights corresponds to a distribution of rates for kinetic process and conformational relaxation.

$$\lambda = f(\epsilon), \quad \epsilon = \frac{\Delta E}{k_B T} \quad \Rightarrow \quad p(\lambda) \rightarrow \tilde{p}(\epsilon)$$

To relate barrier heights and relaxation rates, one needs a model.

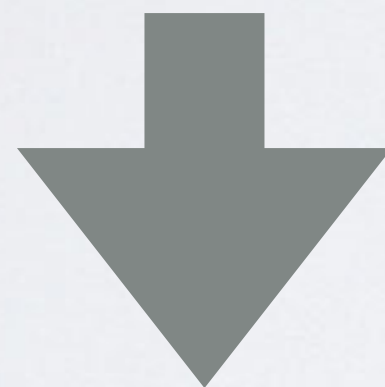
$$\lambda = \lambda_0 e^{-\epsilon} \quad \text{Arrhenius}$$

$$\lambda = \lambda_0 e^{-\epsilon^2} \quad \text{R. Zwanzig, PNAS 85,1988.}$$



For diffusion in a
harmonic potential

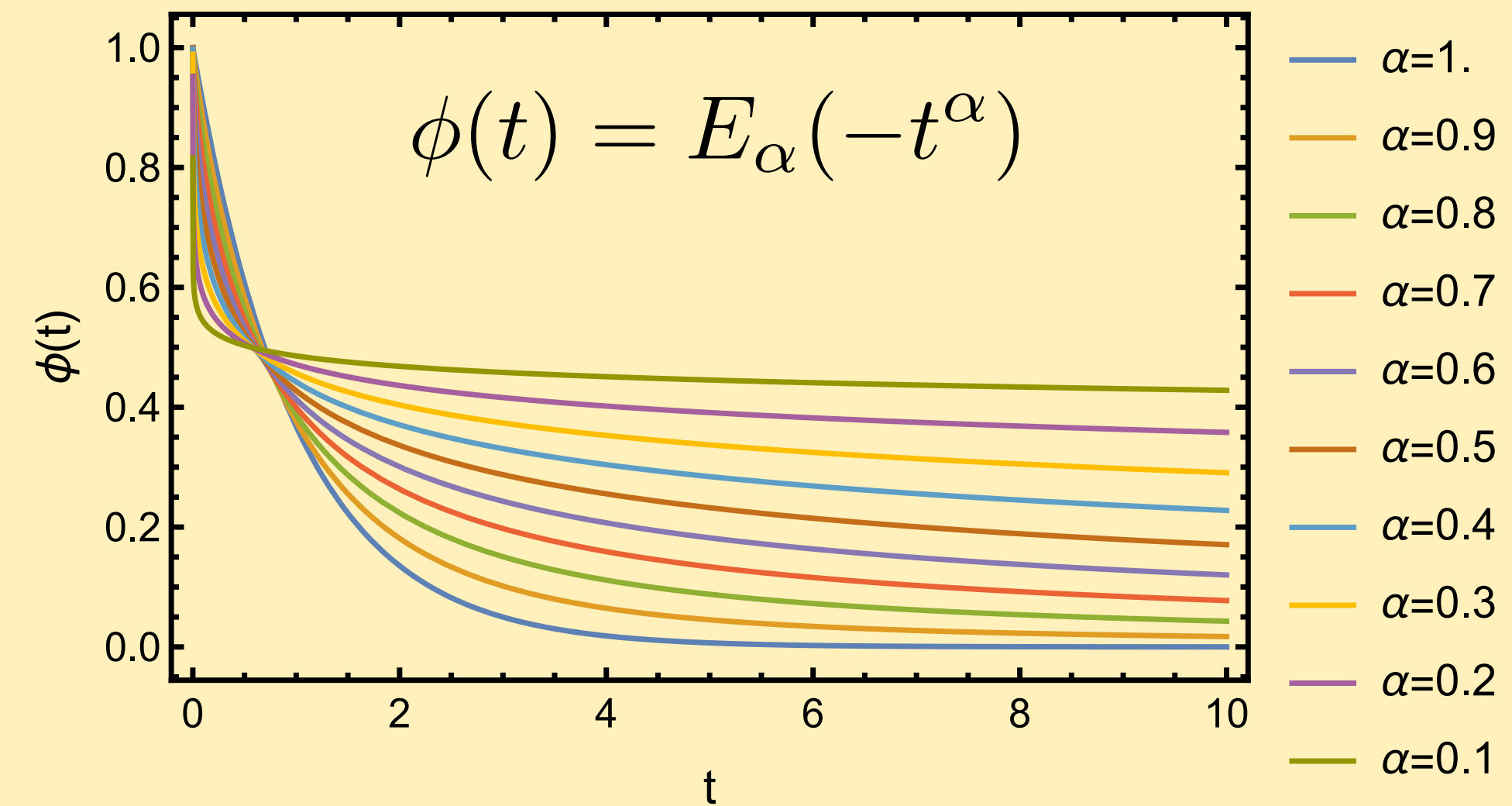
$$D_0 = \langle x^2 \rangle \lambda_0$$



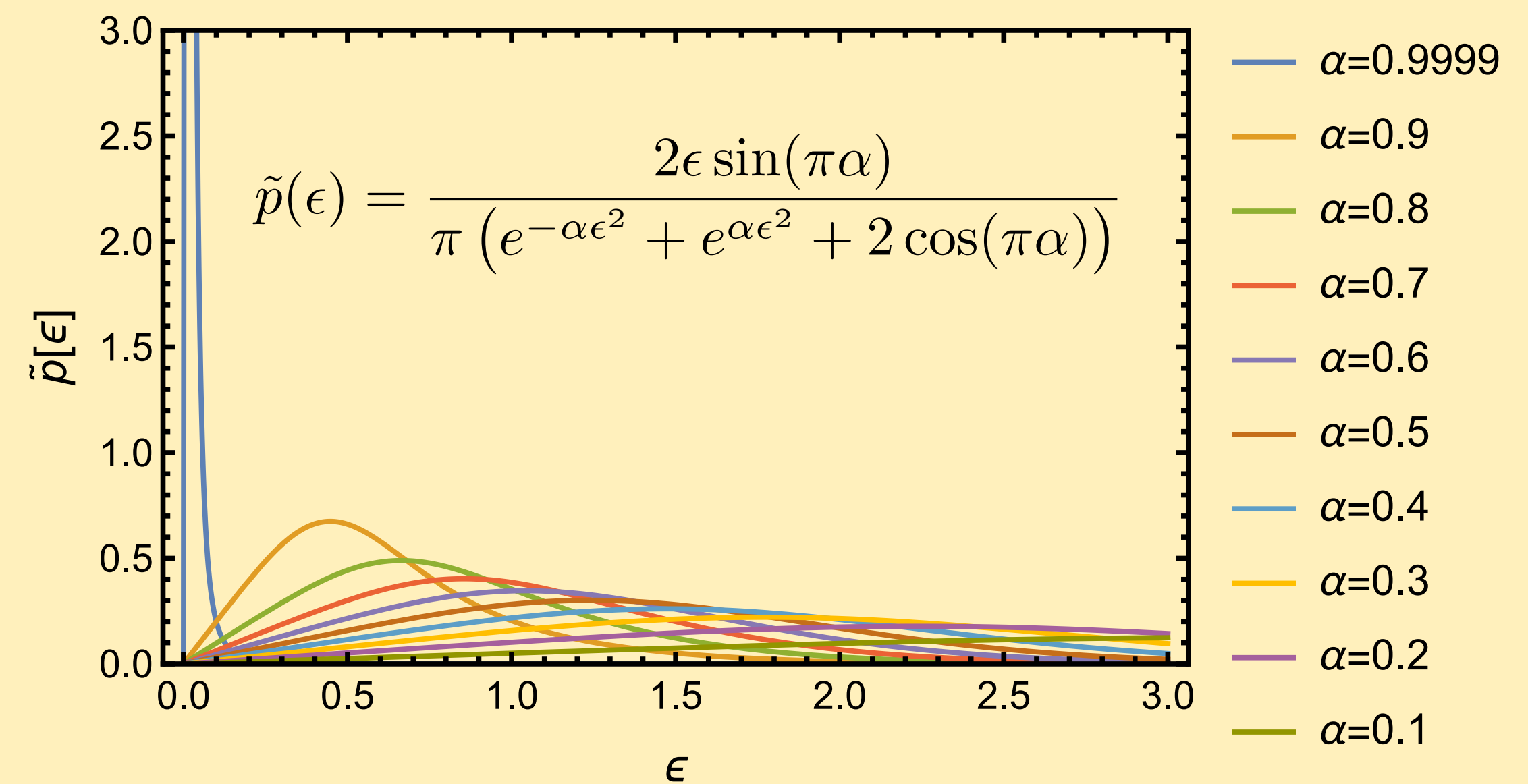
$$\lambda = \lambda_0 e^{-\epsilon^2}$$

Saouessi, Peters &
Kneller, JCP150, 2019.

Relaxation function



Energy barrier distribution



Application to neutron scattering

Dynamical variable:

$$a(\mathbf{q}, t) \equiv e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_a(t)}$$

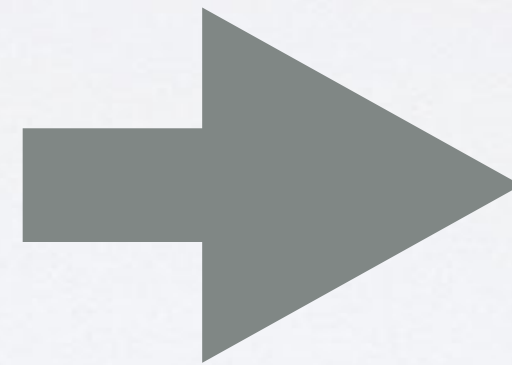
$$\xi(\mathbf{q}, t) \equiv a(\mathbf{q}, t) - \langle a(\mathbf{q}, t) \rangle$$

Relaxation dynamics

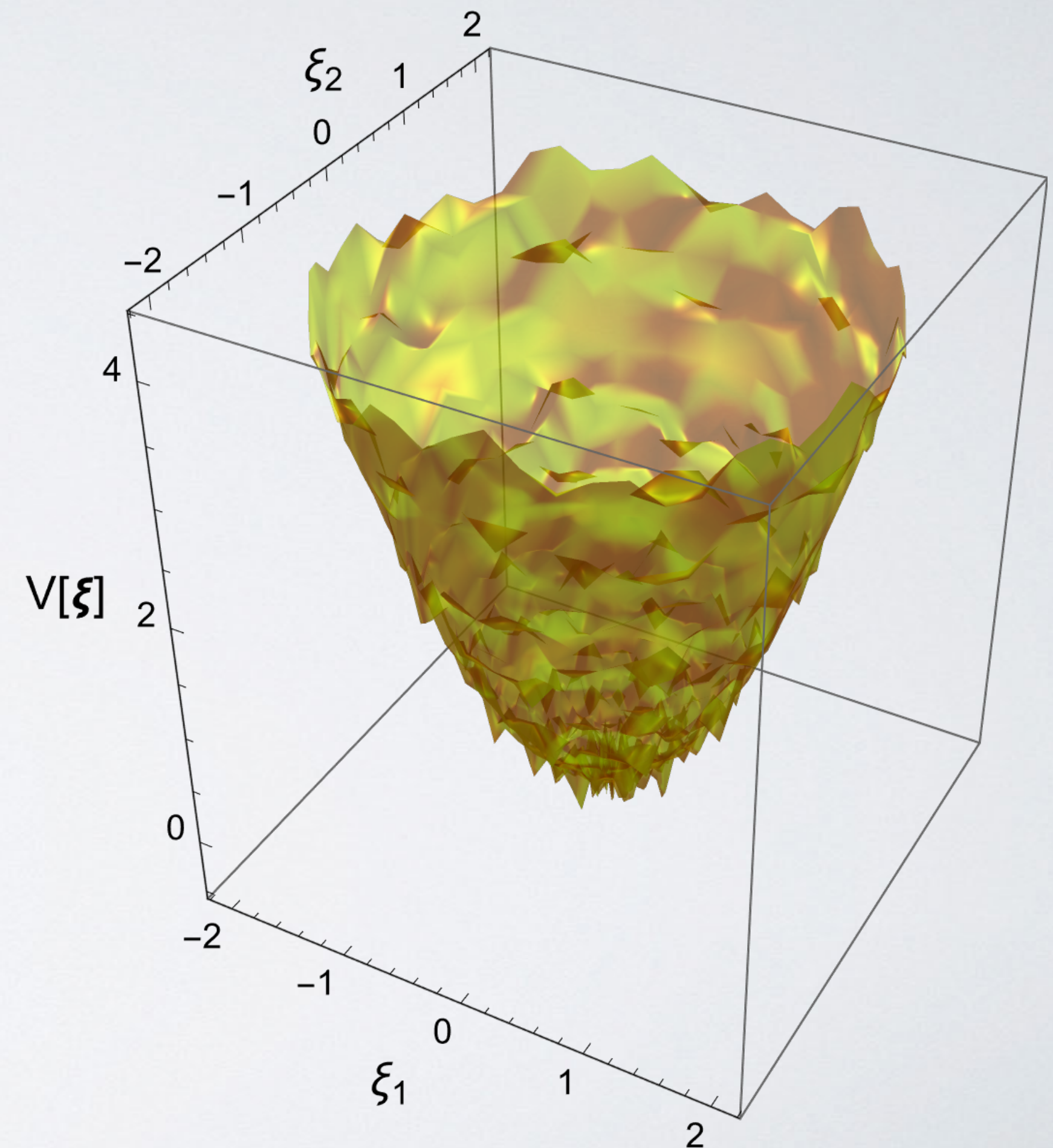
$$\phi(\mathbf{q}, t) = \langle \xi^\dagger(\mathbf{q}, 0) \xi(\mathbf{q}, t) \rangle$$

Anomalous diffusion in a 2-d
harmonic potential

$$\xi \equiv \begin{pmatrix} \Re\{\xi\} \\ \Im\{\xi\} \end{pmatrix} \equiv \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}$$



$$V(\xi) = \frac{K_\xi}{2} |\xi|^2 + \delta V(\xi)$$



Correlation function with a stochastic model

$$\langle \xi^*(0) \xi(t) \rangle = \int \int d^2 \xi d^2 \xi_t \, \xi_0 \cdot \xi_t \underbrace{P(\xi_t, t | \xi_0, 0)}_{\text{dynamics: } \xi_0 \rightarrow \xi_t} \underbrace{P_{eq}(\xi_0)}_{\text{equilibrium}}$$

Fokker-Planck equation for
the transition probability



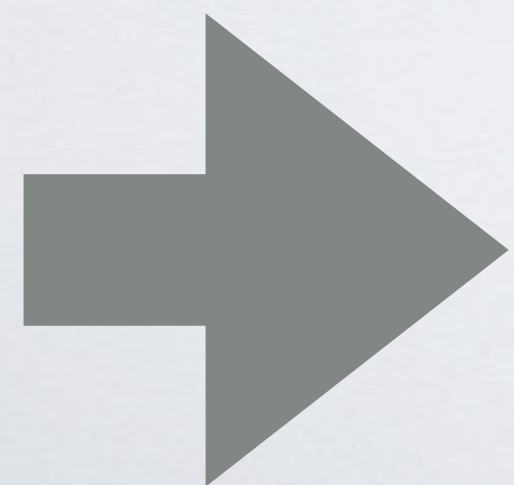
Anomalous diffusion in a “rough” 2-d harmonic potential:

Fractional Ornstein-Uhlenbeck process / diffusion with memory

$$\partial_t P = {}_0\partial_t^{1-\alpha} \left\{ \eta_\xi^{(\alpha)} \frac{\partial}{\partial \xi} \cdot \{ \xi P \} + D_\xi^{(\alpha)} \frac{\partial}{\partial \xi} \cdot \frac{\partial P}{\partial \xi} \right\}$$

$${}_0\partial_t^{1-\alpha} f(t) \equiv \frac{d}{dt} \int_0^t dt' \frac{(t-t')^{\alpha-1}}{\Gamma(\alpha)} f(t')$$

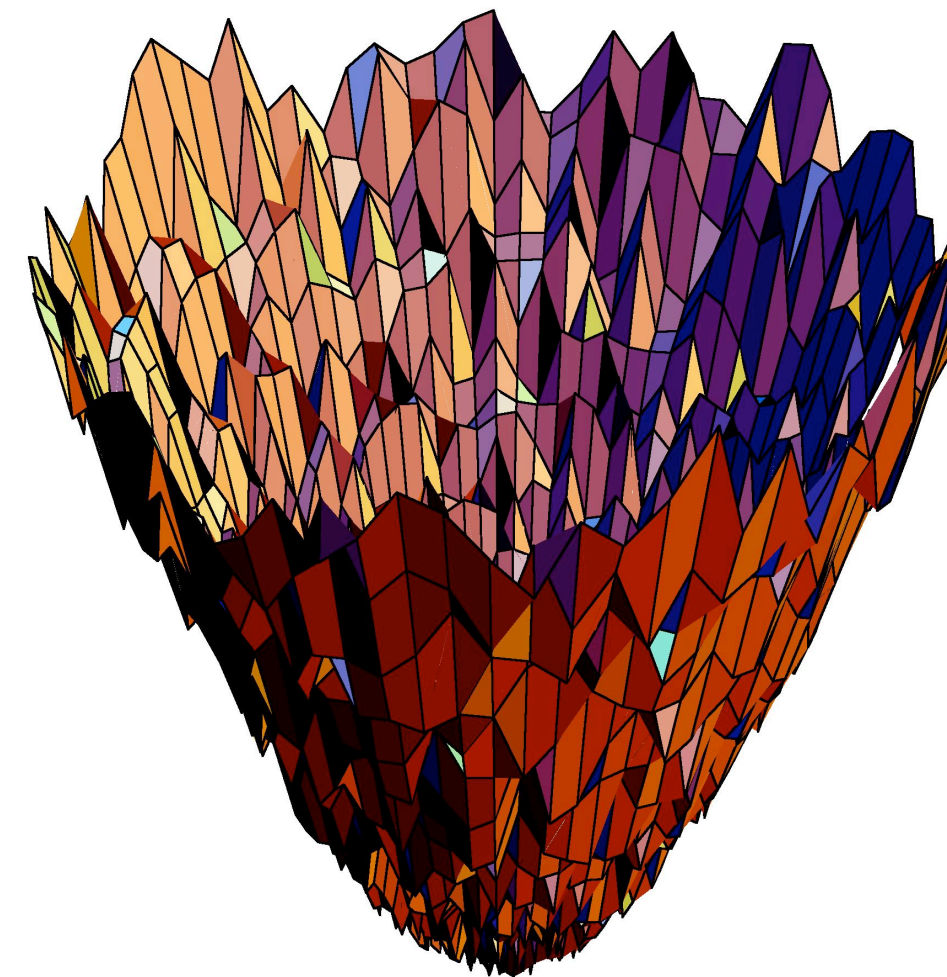
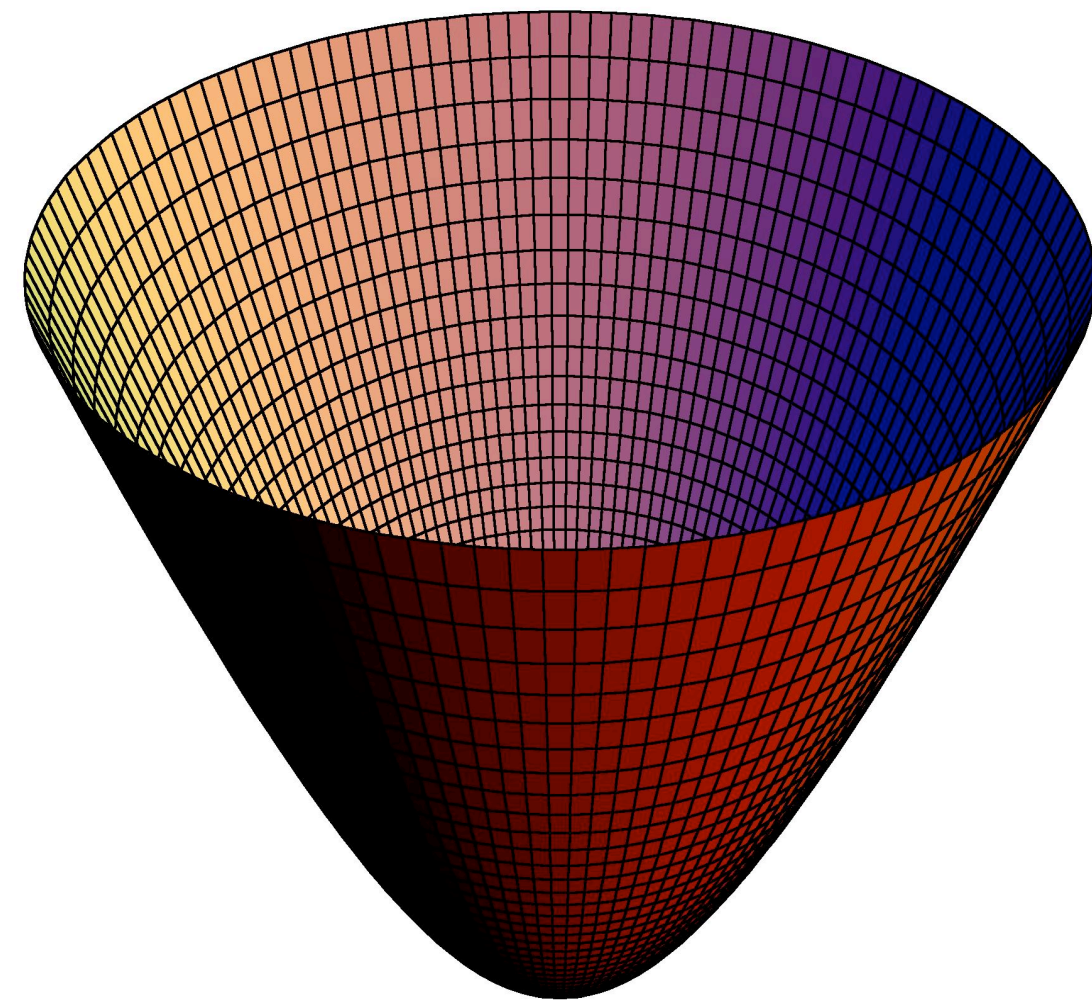
$$D_\xi^{(\alpha)} = \eta_\xi^{(\alpha)} k_B T / K_\xi = \eta_\xi^{(\alpha)} \langle |\xi|^2 \rangle_{cl}$$



$$\phi(t) \equiv \langle \xi(0) \cdot \xi(t) \rangle / \langle |\xi|^2 \rangle = E_\alpha \left(-\eta_\xi^{(\alpha)} |t|^\alpha \right) \stackrel{\alpha \rightarrow 1}{\Rightarrow} e^{-\eta_\xi |t|}$$

$$\alpha = 1$$

$$0 < \alpha < 1$$



[1] G. E. Uhlenbeck and L. S. Ornstein,
Phys. Rev. **36**, pp. 823–841, 1930.

[2] R. Metzler and J. Klafter,
Phys. Rep., vol. 339, pp. 1–77, 2000.

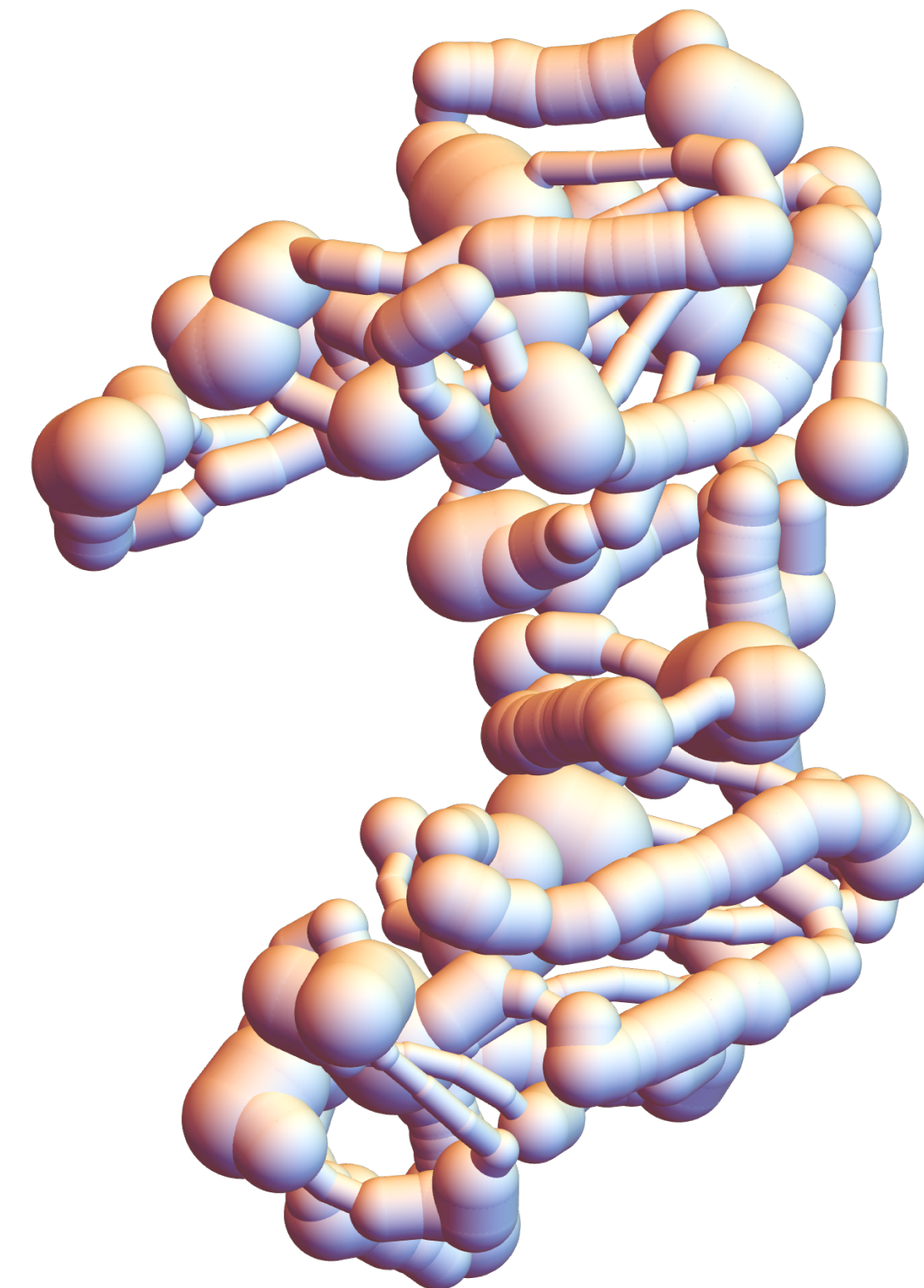


Influence of ATP on the internal dynamics seen by QENS

Secondary structure



ScrewFrame tube model



Basic data treatment

Subtract the solvent

$$S(q, \omega) = S(q, \omega)_{\text{protein solution}} - (1 - \phi) \cdot S(q, \omega)_{\text{buffer}}$$

Volume fraction

$$\phi = \bar{v} \cdot c \approx 4 \%$$

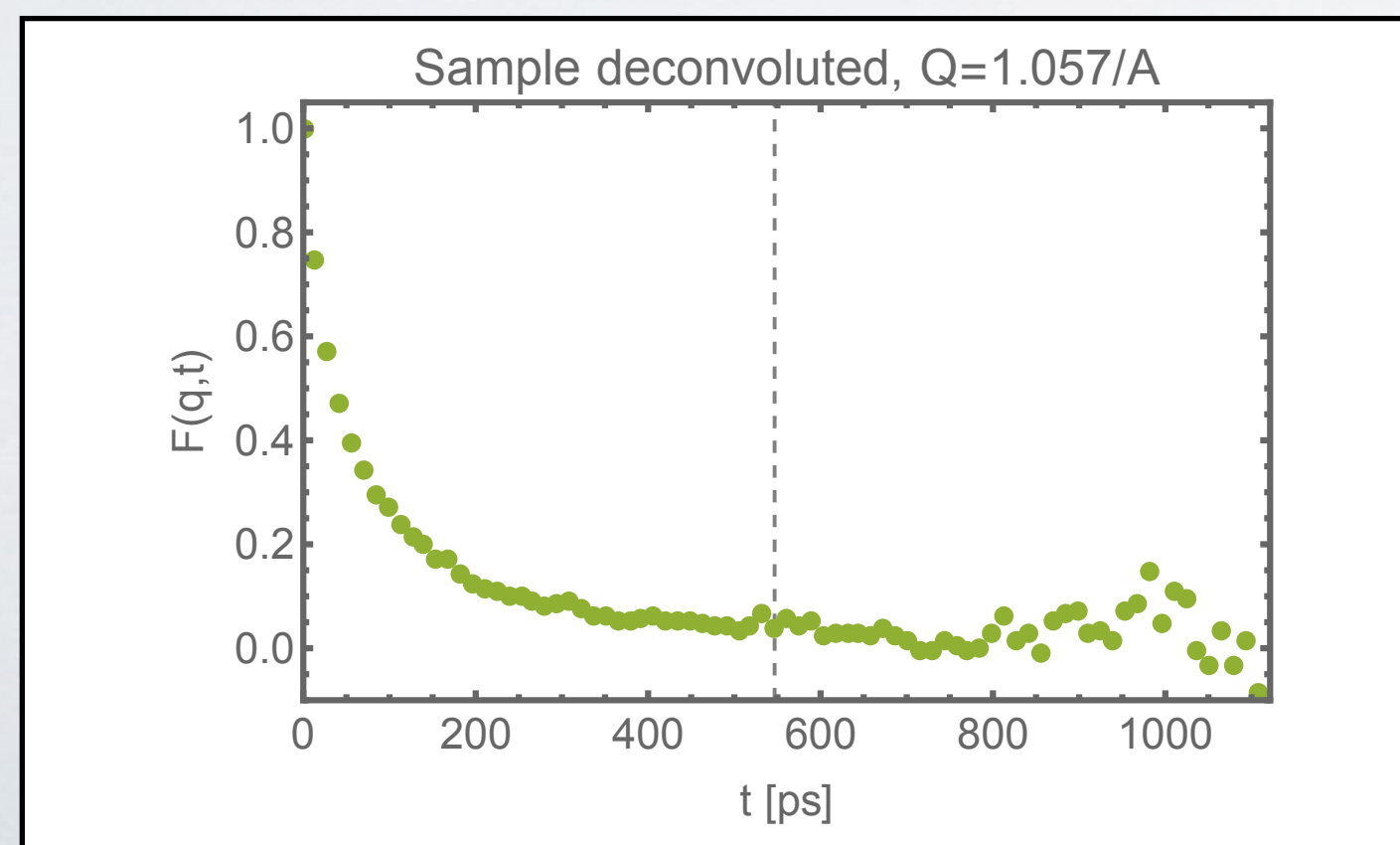
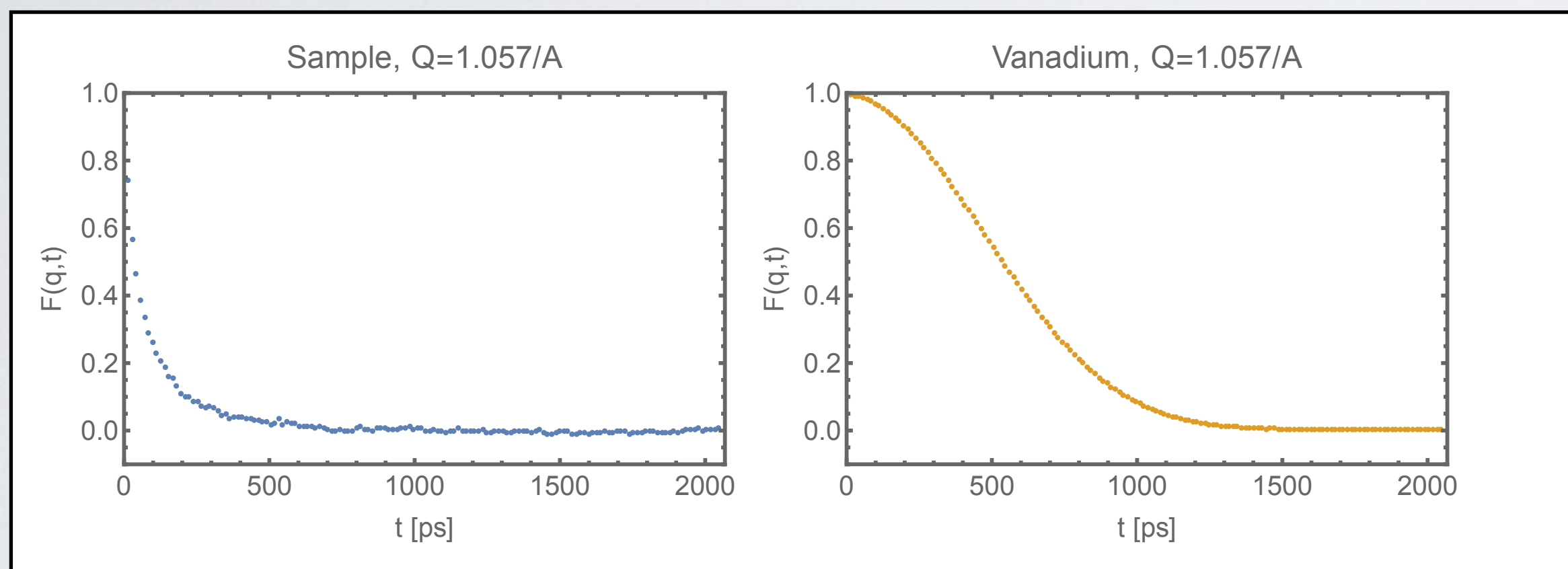
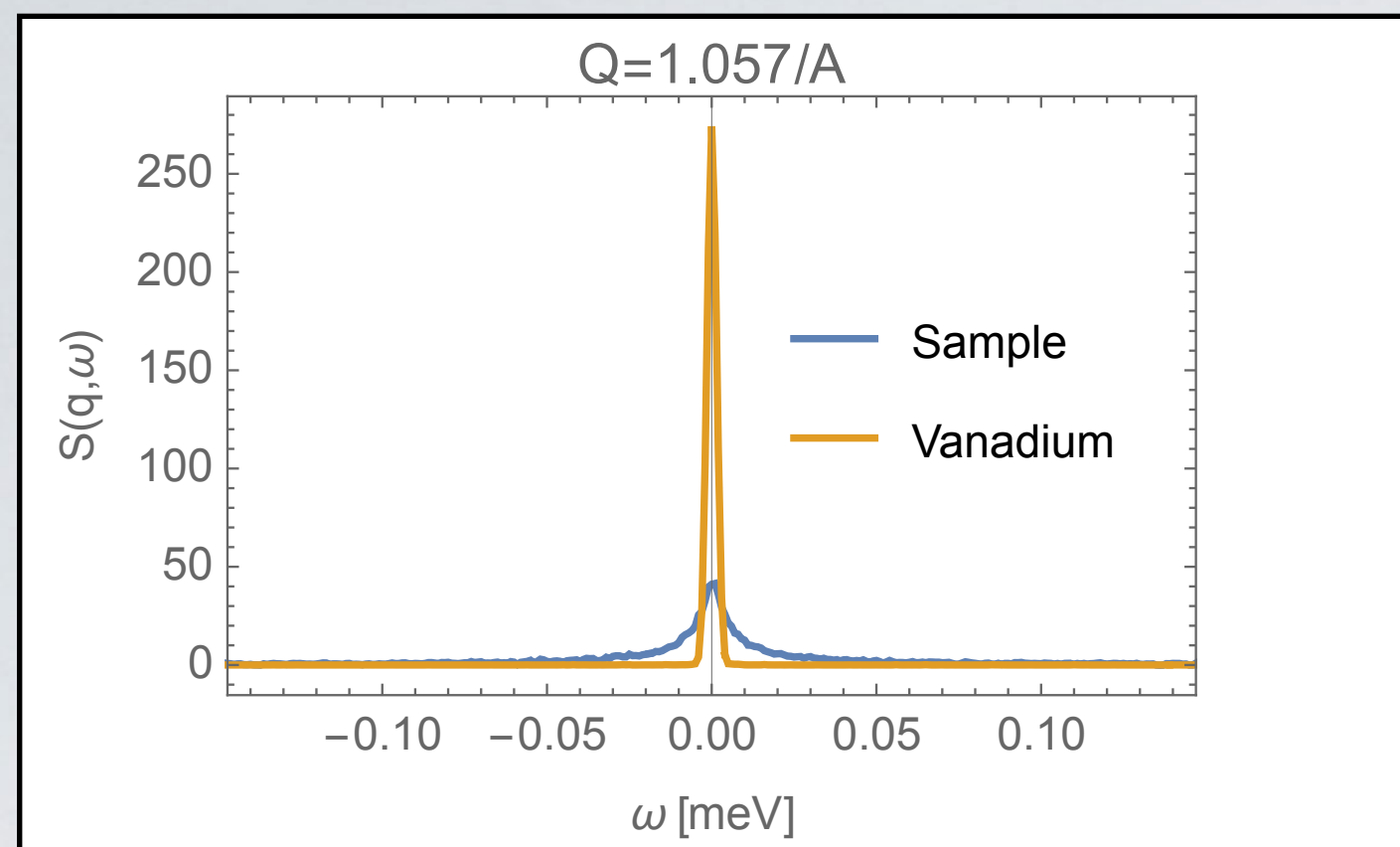
Symmetrize and normalize the QENS spectra

$$S^{(+)}(q, \omega) \approx \frac{\exp(-\beta \hbar \omega / 2) S_{cl}(q, \omega)}{\int_{-\infty}^{+\infty} d\omega \exp(-\beta \hbar \omega / 2) S_{cl}(q, \omega)} \iff F^{(+)}(q, t) = \frac{F(q, t + i\beta \hbar / 2)}{F(q, +i\beta \hbar / 2)}$$

Semiclassical approximation

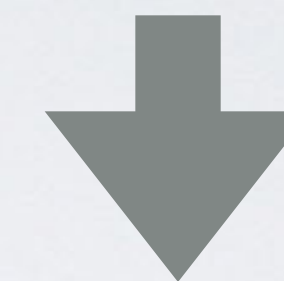
$$F^{(+)}(q, t) \approx F_{cl}(q, t)$$

P. Schofield, Phys. Rev. Lett. 4, 239 (1960)



Instrument deconvolution

$$S_m^{(+)}(q, \omega) = \int_{-\infty}^{+\infty} d\omega' \tilde{R}(q, \omega - \omega') S^{(+)}(q, \omega') + \tilde{N}(q, \omega)$$



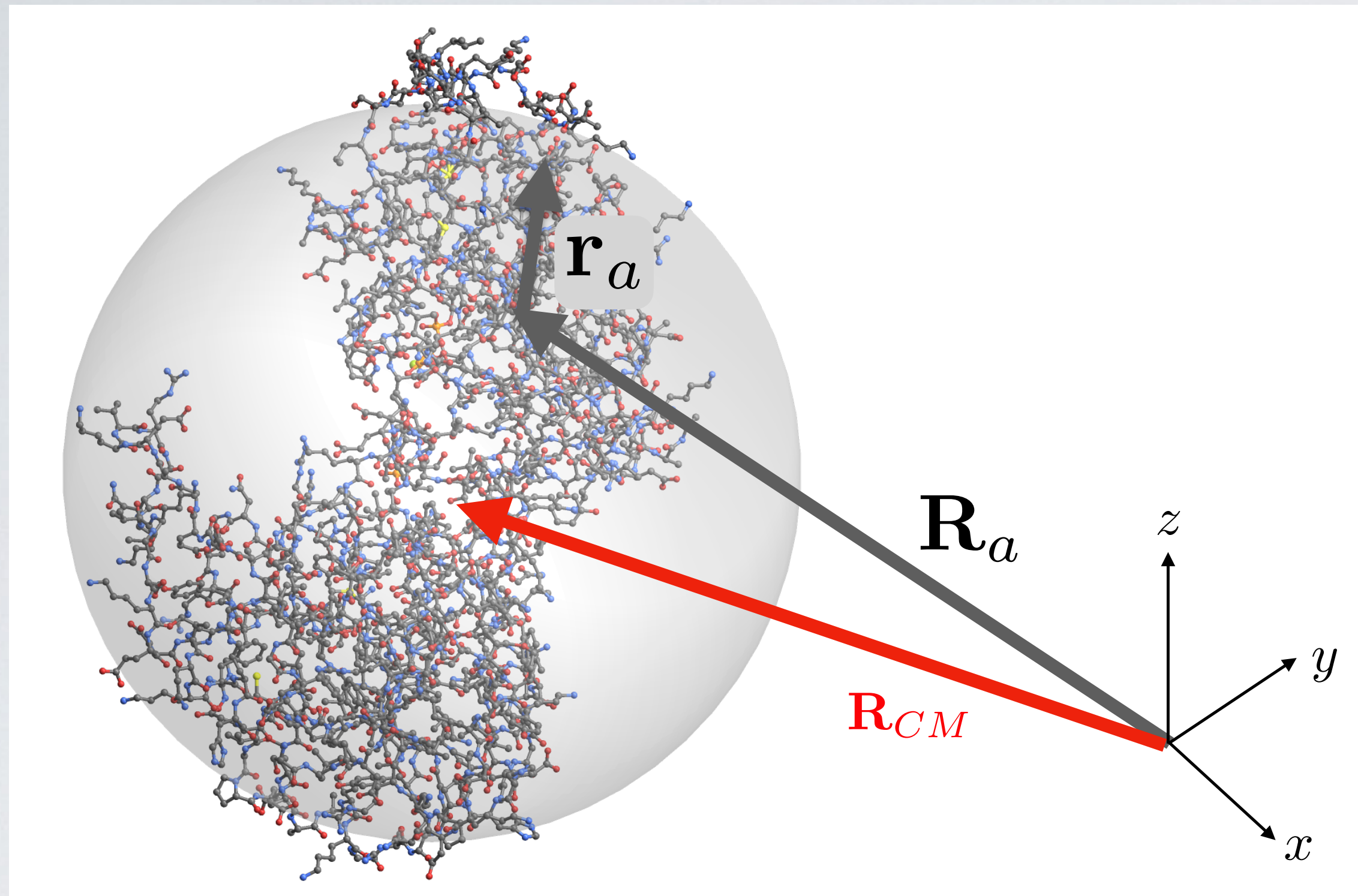
Discrete Fourier transform

$$F_m^{(+)}(q, t) = F^{(+)}(q, t) R(q, t) + N(q, t)$$



Instrument deconvolution in the time domain

$$F^{(+)}(q, t) = \frac{F_m^{(+)}(q, t)}{R(q, t)} - \frac{N(q, t)}{R(q, t)}$$



Independent Dynamical variables:

$$a_{\mathbf{q}} \equiv e^{i\mathbf{q} \cdot \mathbf{r}_a} \quad \text{Intra-domain dynamics}$$

$$A_{\mathbf{q}} \equiv e^{i\mathbf{q} \cdot \mathbf{R}_a} \quad \text{Inter-domain dynamics}$$

$$\overline{F}^{(+)}(q, t) \approx \overline{\langle A_{\mathbf{q}}^* A_{\mathbf{q}}(t) \rangle_{cl}} \overline{\langle a_{\mathbf{q}}^* a_{\mathbf{q}}(t) \rangle_{cl}}$$

$$\xi = \begin{cases} a_{\mathbf{q}} - \langle a_{\mathbf{q}} \rangle & \text{for intra-domain motions,} \\ A_{\mathbf{q}} - \langle A_{\mathbf{q}} \rangle & \text{for inter-domain motions,} \end{cases}$$

Fractional O.U. process

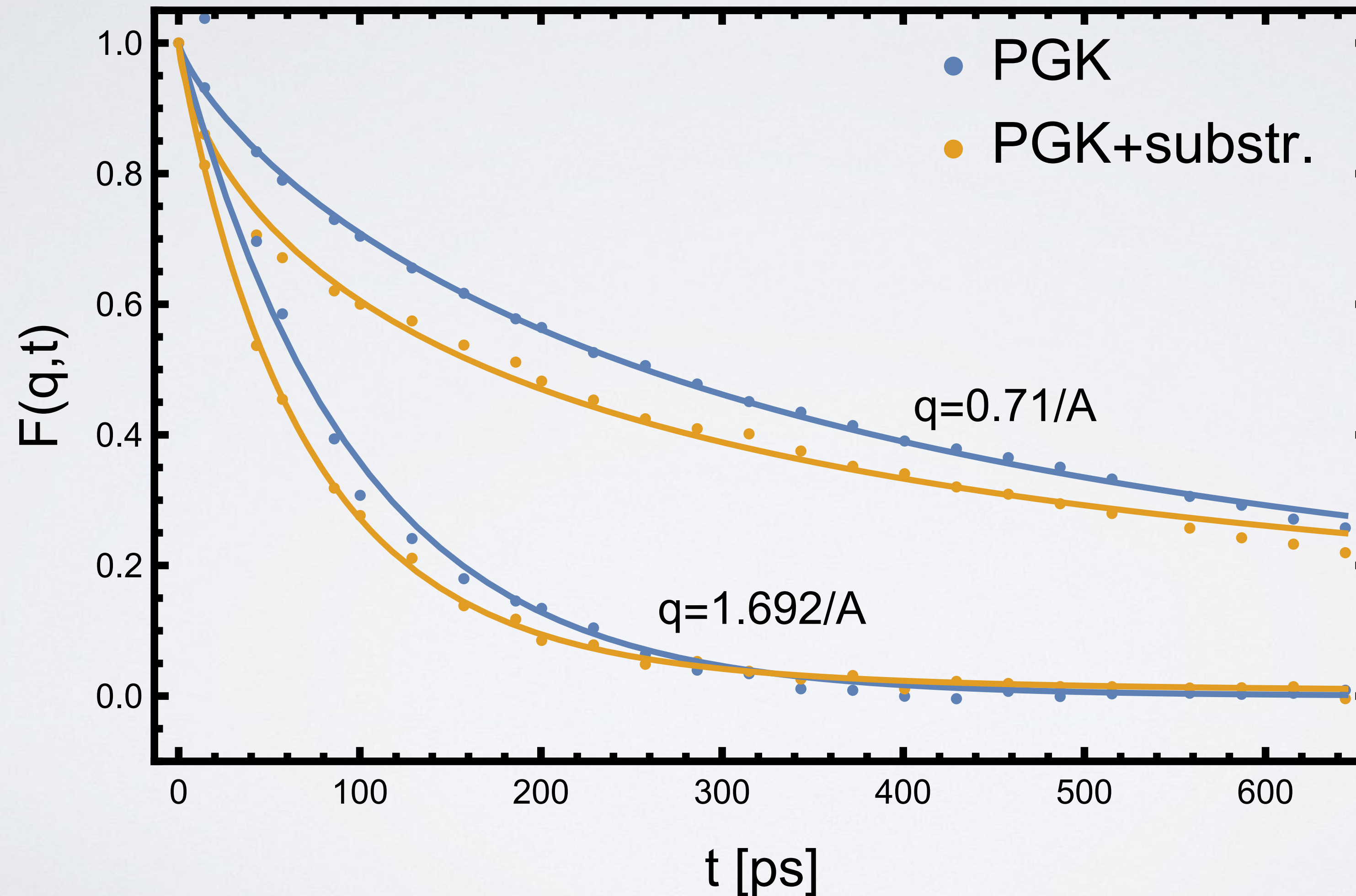
Normal O.U. process

Four parameter fit

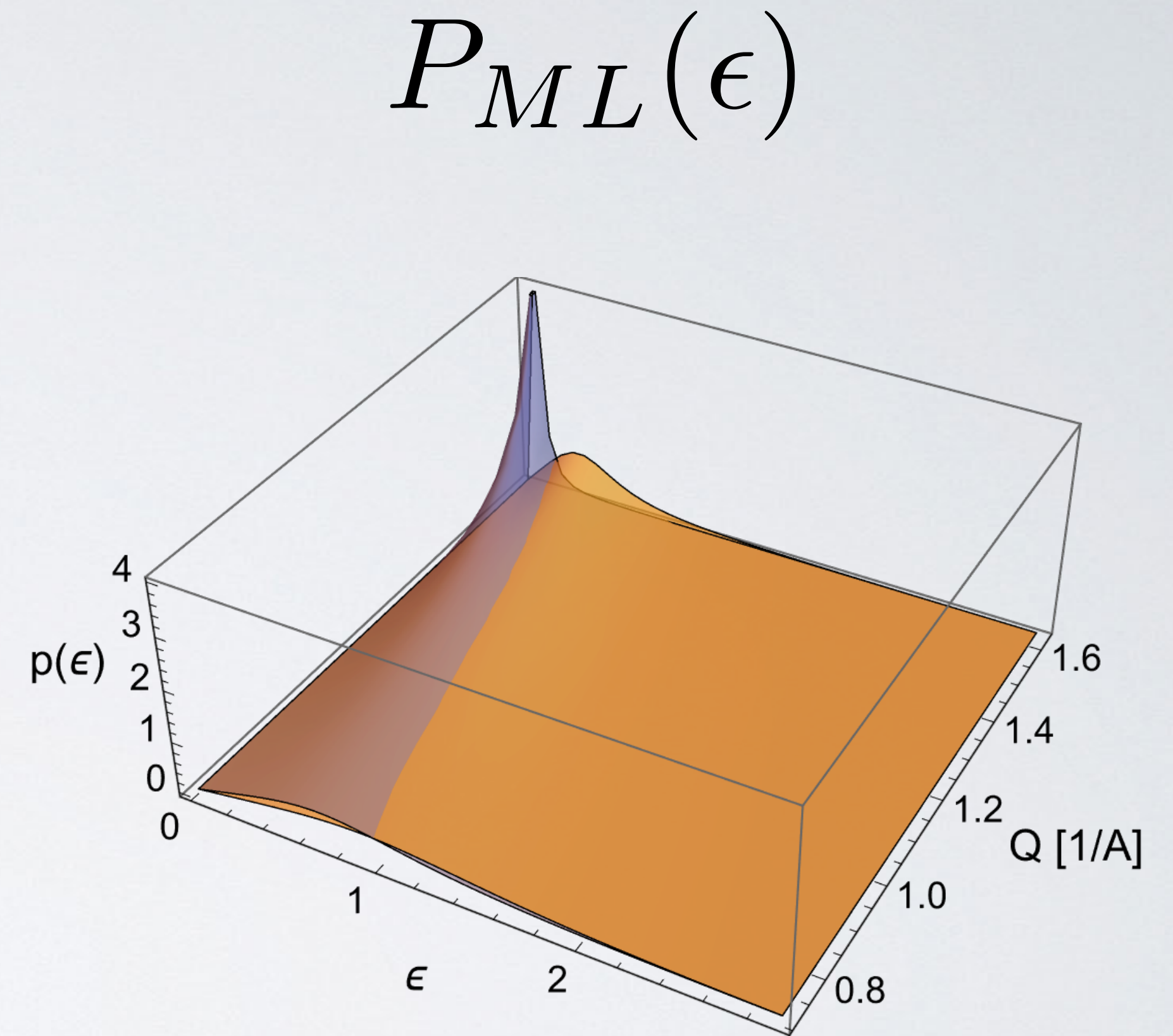
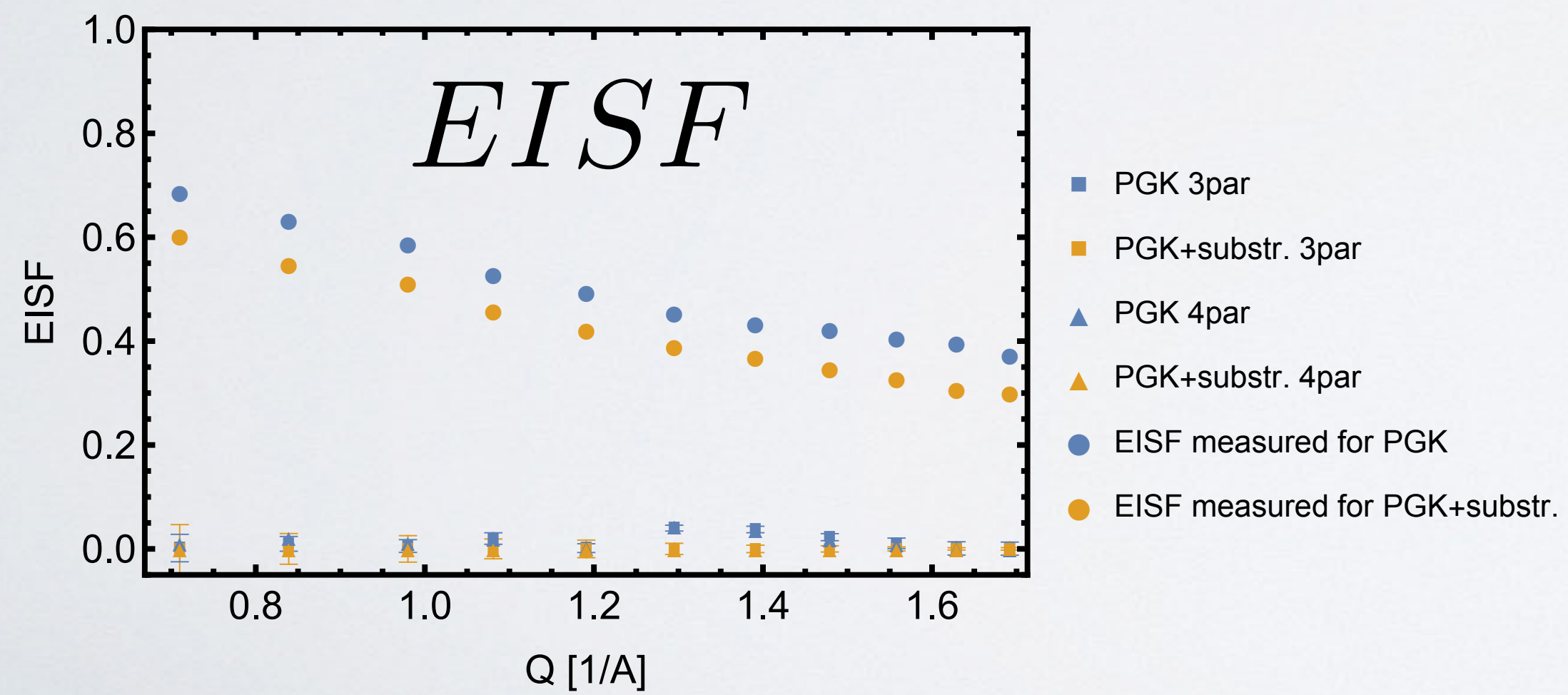
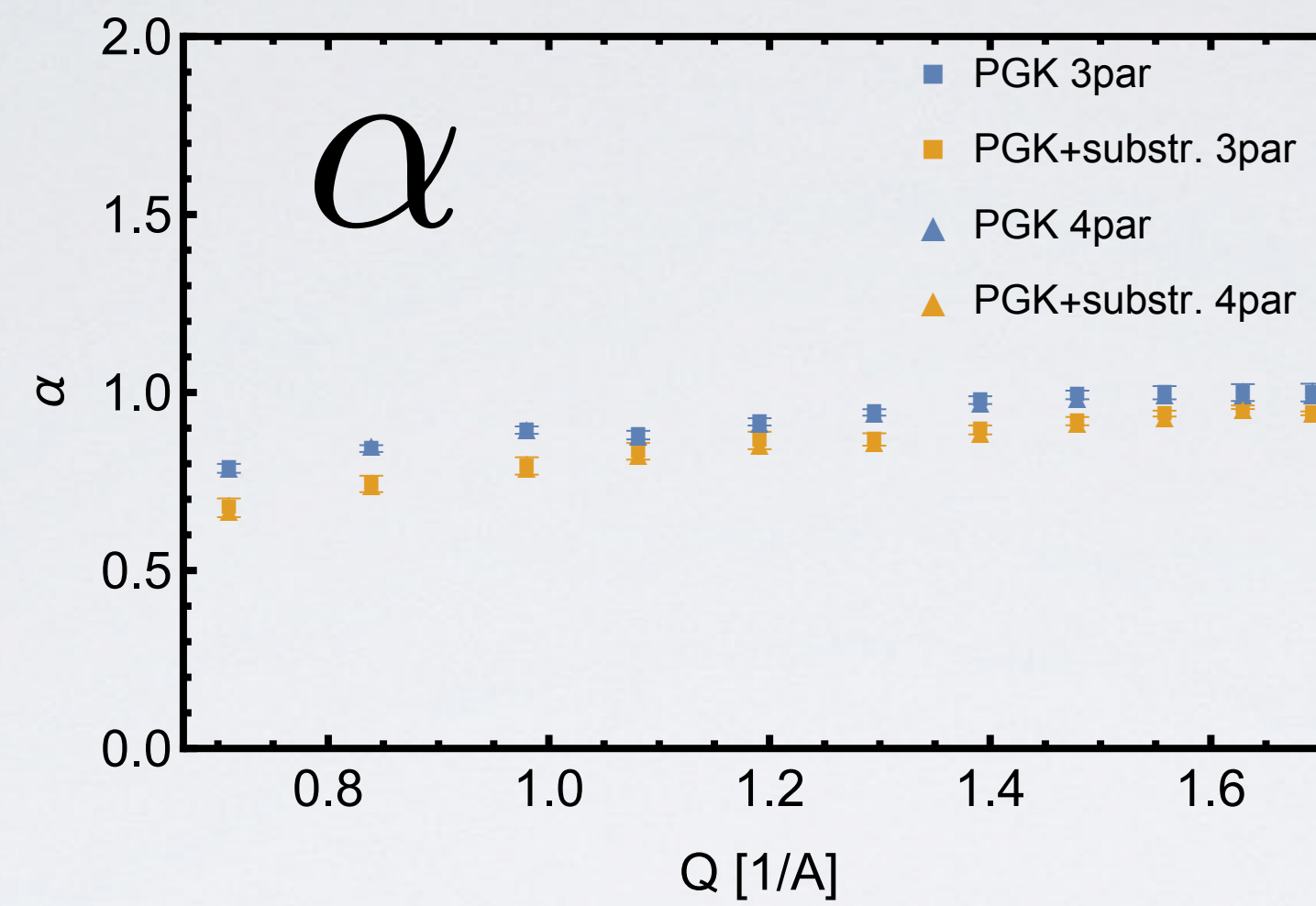
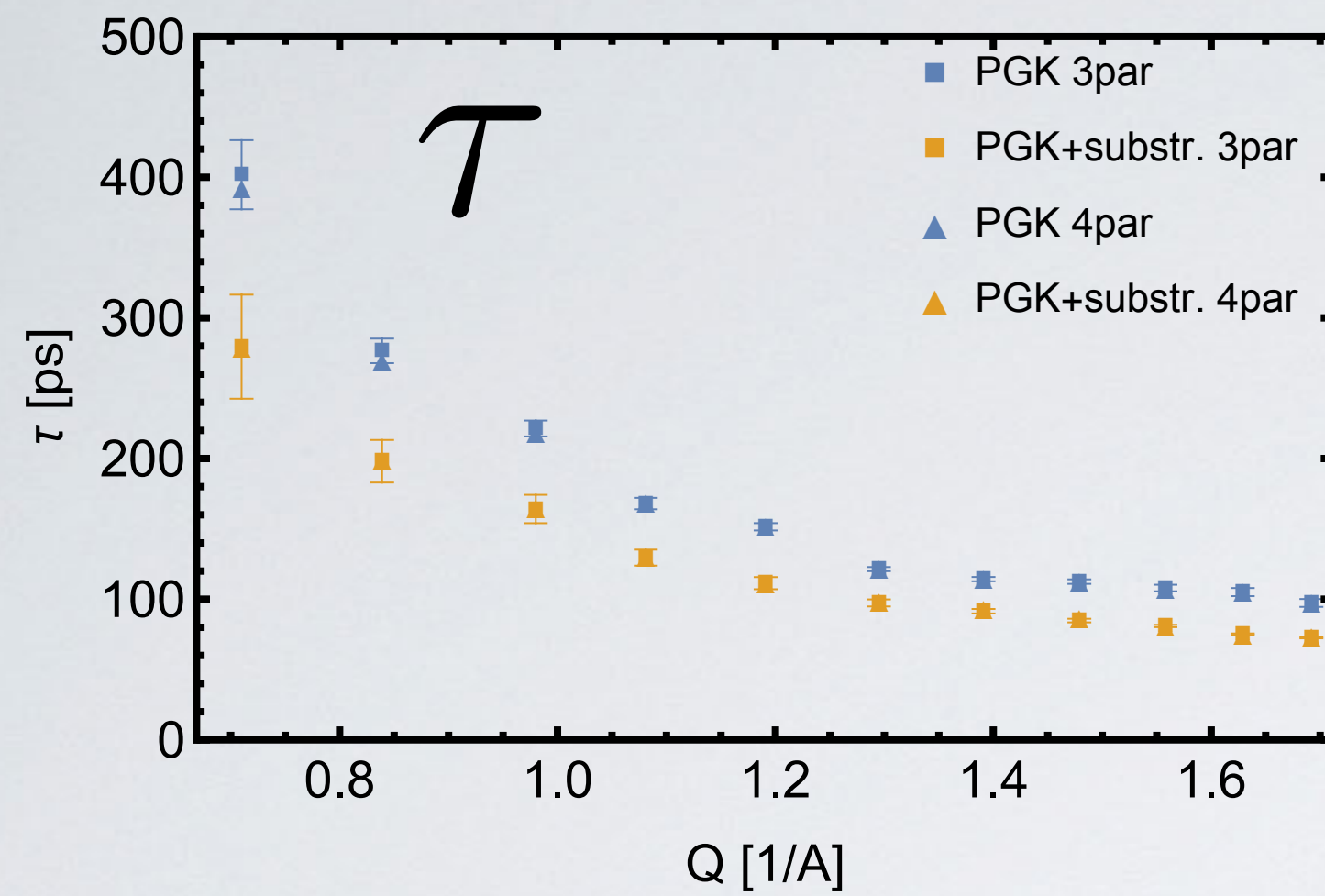
$$F(q, t) = e^{-D(q)q^2 t} (EISF(q) + (1 - EISF(q)) E_\alpha(-[t/\tau]^\alpha))$$

$$\alpha \equiv \alpha(q)$$

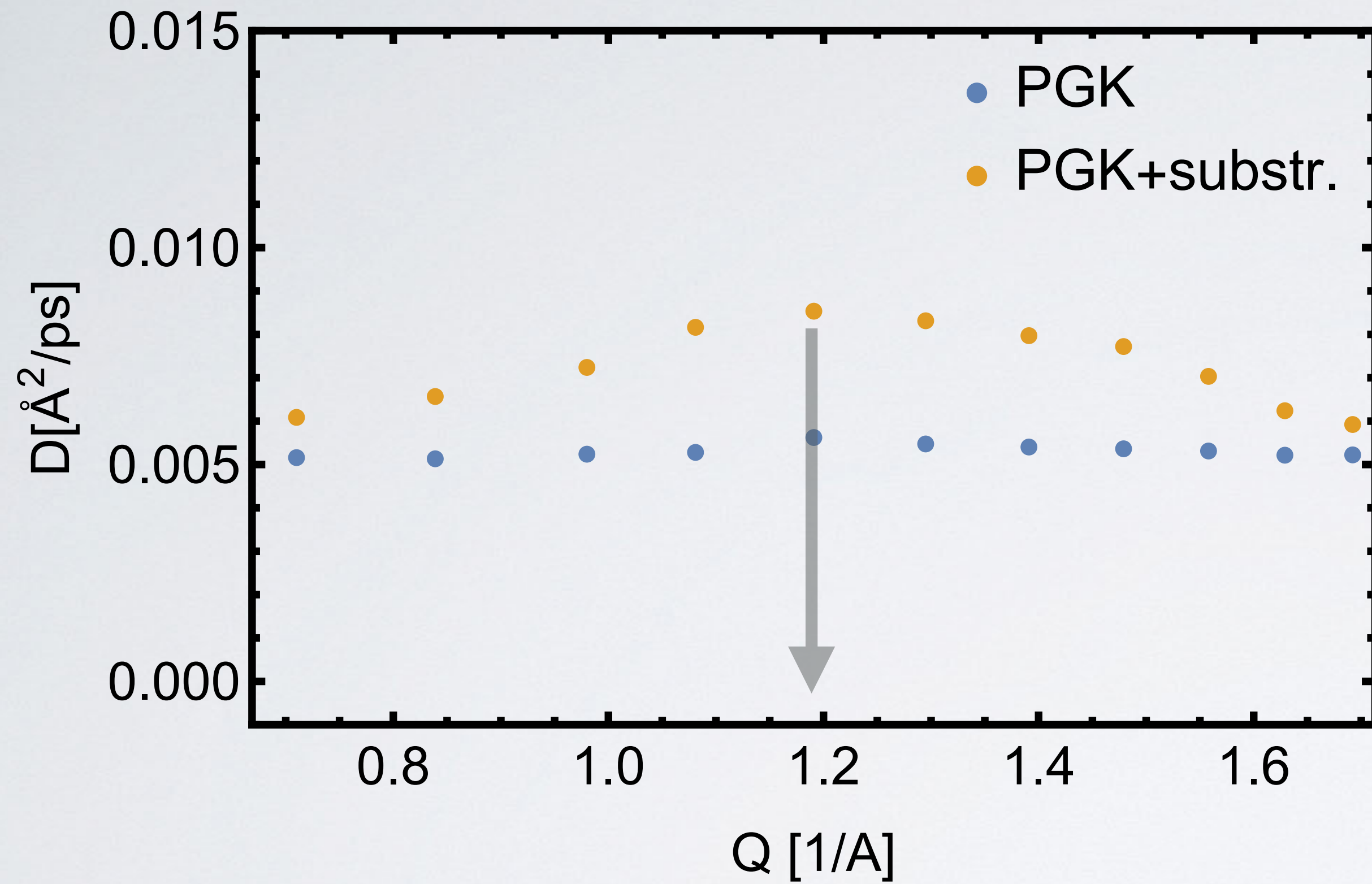
$$\tau \equiv \tau(q)$$



Intra-domain dynamics



Inter-domain dynamics



$$D_0 = \frac{k_B T}{6\pi\eta R_H} \approx 5.1 \times 10^{-3} \text{\AA}^2/\text{ps}.$$

Interpretation

In presence of the substrates

- The domains in PGK are stiffened
 1. The α -parameter becomes smaller, indicating a wider distribution of energy barriers.
 2. The motions become smaller, too, indicating faster motions.
- The interdomained dynamics is enhanced

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