

Deep quantum perspective of quasielastic neutron scattering from proteins

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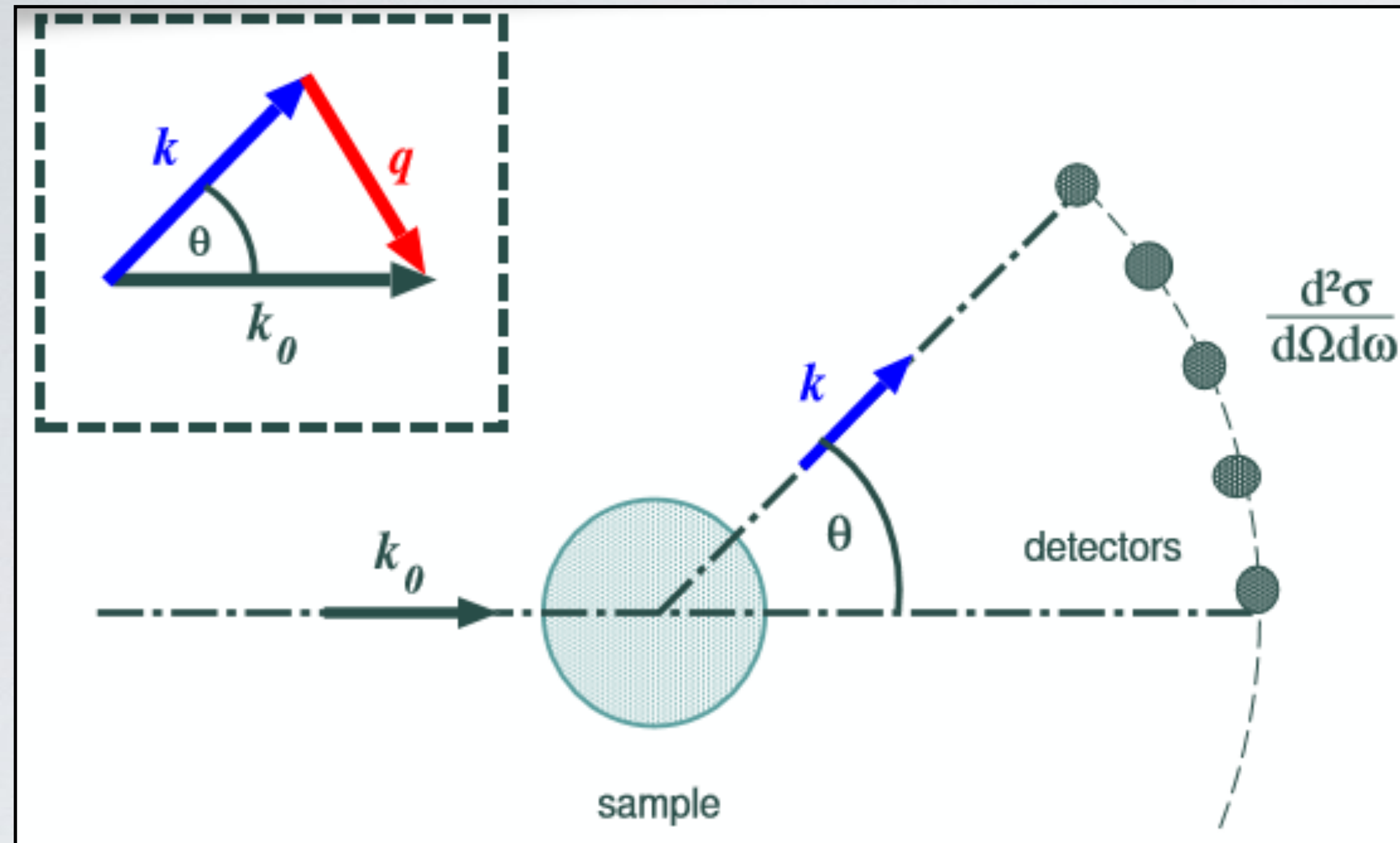


Outline

- Neutron scattering theory revisited
- Quantum and classical picture of (quasi-)elastic scattering
- Classical energy landscapes and non-exponential relaxation
- QENS from a tunneling particle in a quantum “energy landscape”
- Recoil in QENS

Neutron scattering theory revisited

Neutron Scattering experiment



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

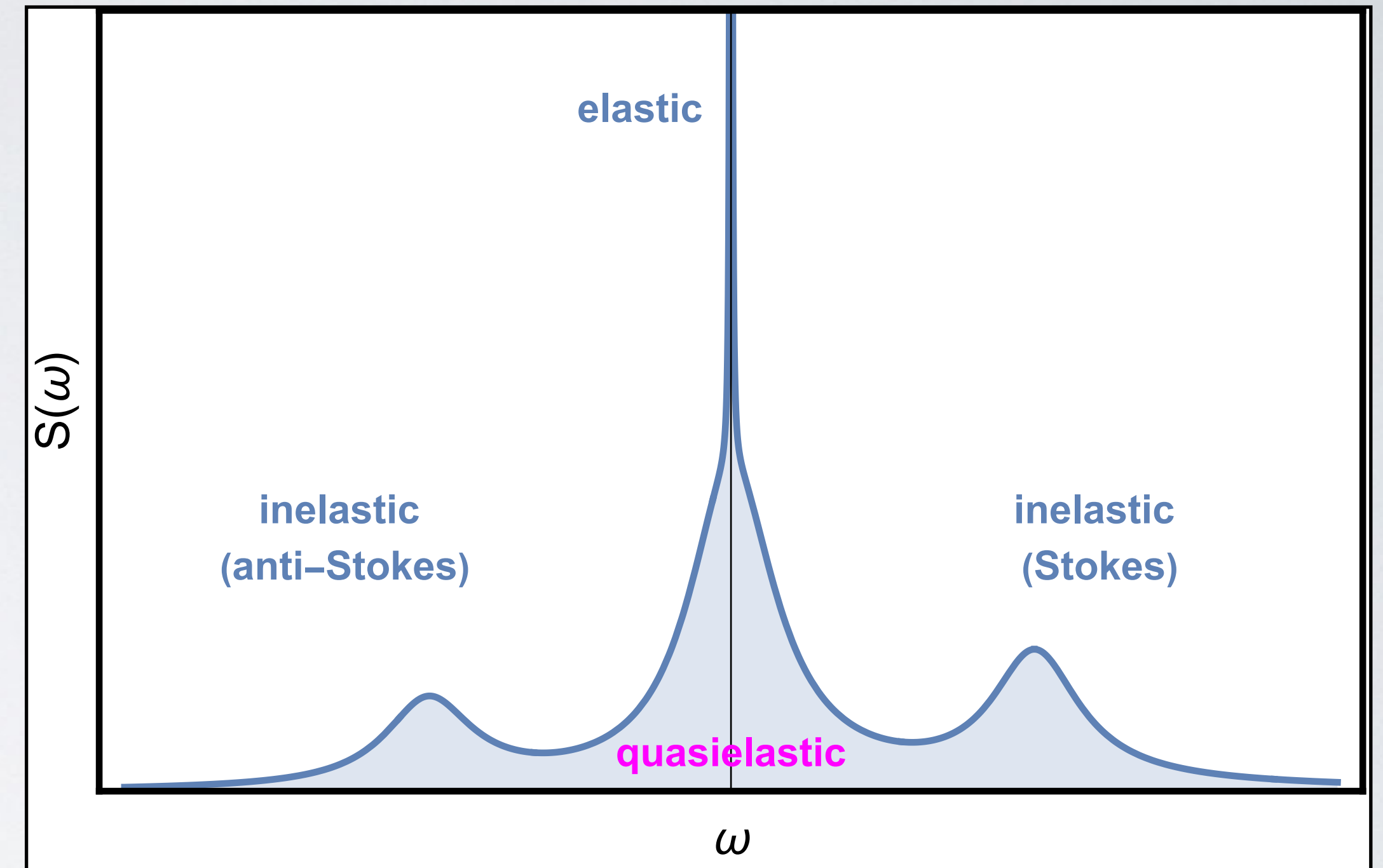
Differential scattering cross section

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

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

Momentum and Energy transfer

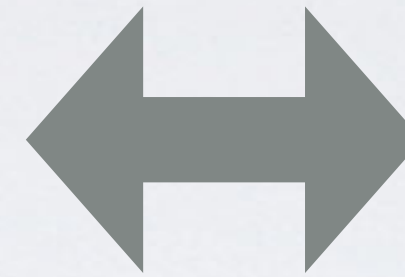
Sketch of a neutron scattering spectrum



- Elastic scattering from non-excitale modes
- Inelastic scattering from (de)excitations of vibrational modes
- Quasi-elastic scattering from (de)excitations of stochastic modes

Dynamic structure factor

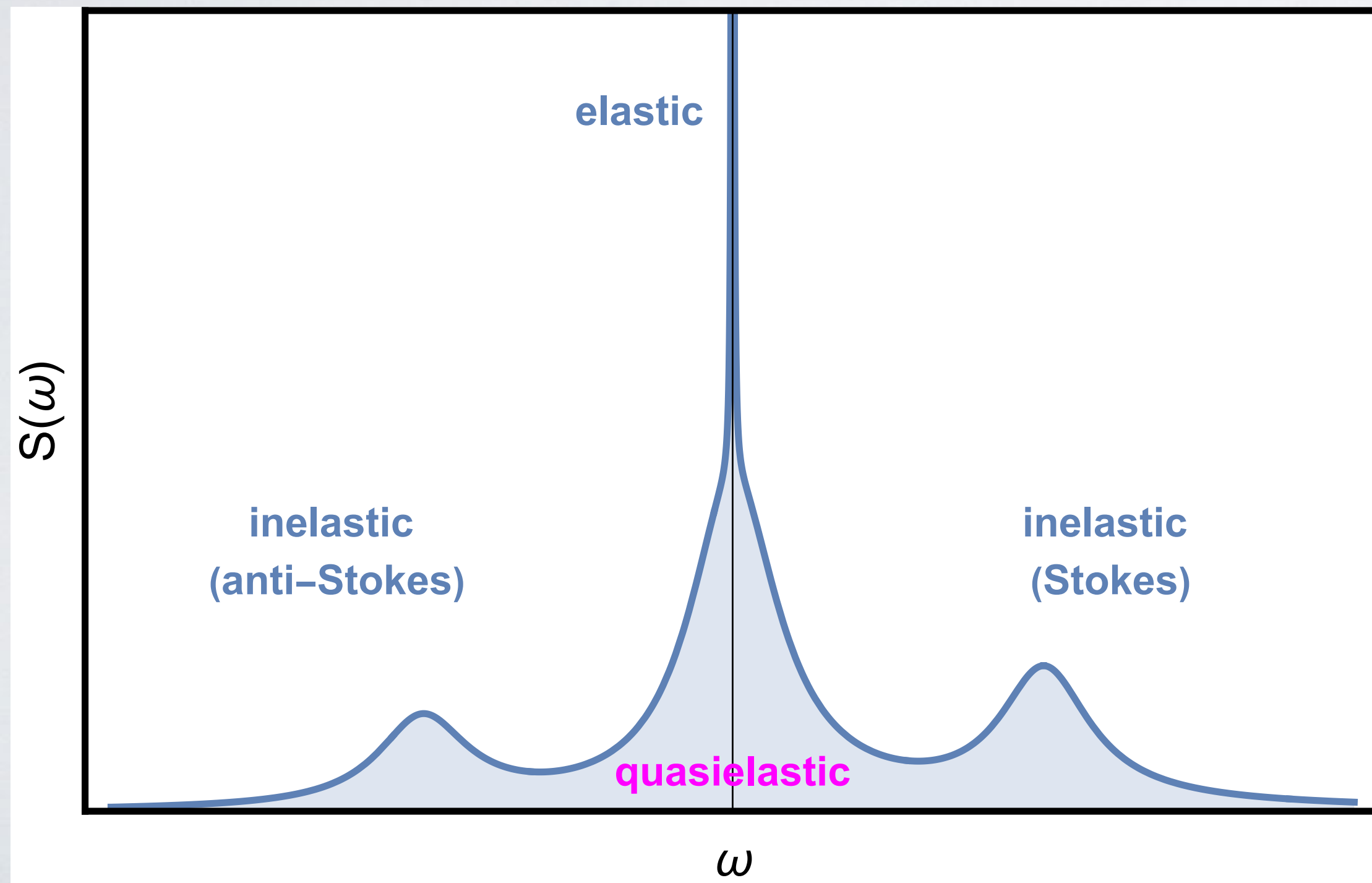
$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} F(\mathbf{q}, t)$$



Intermediate scattering function

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

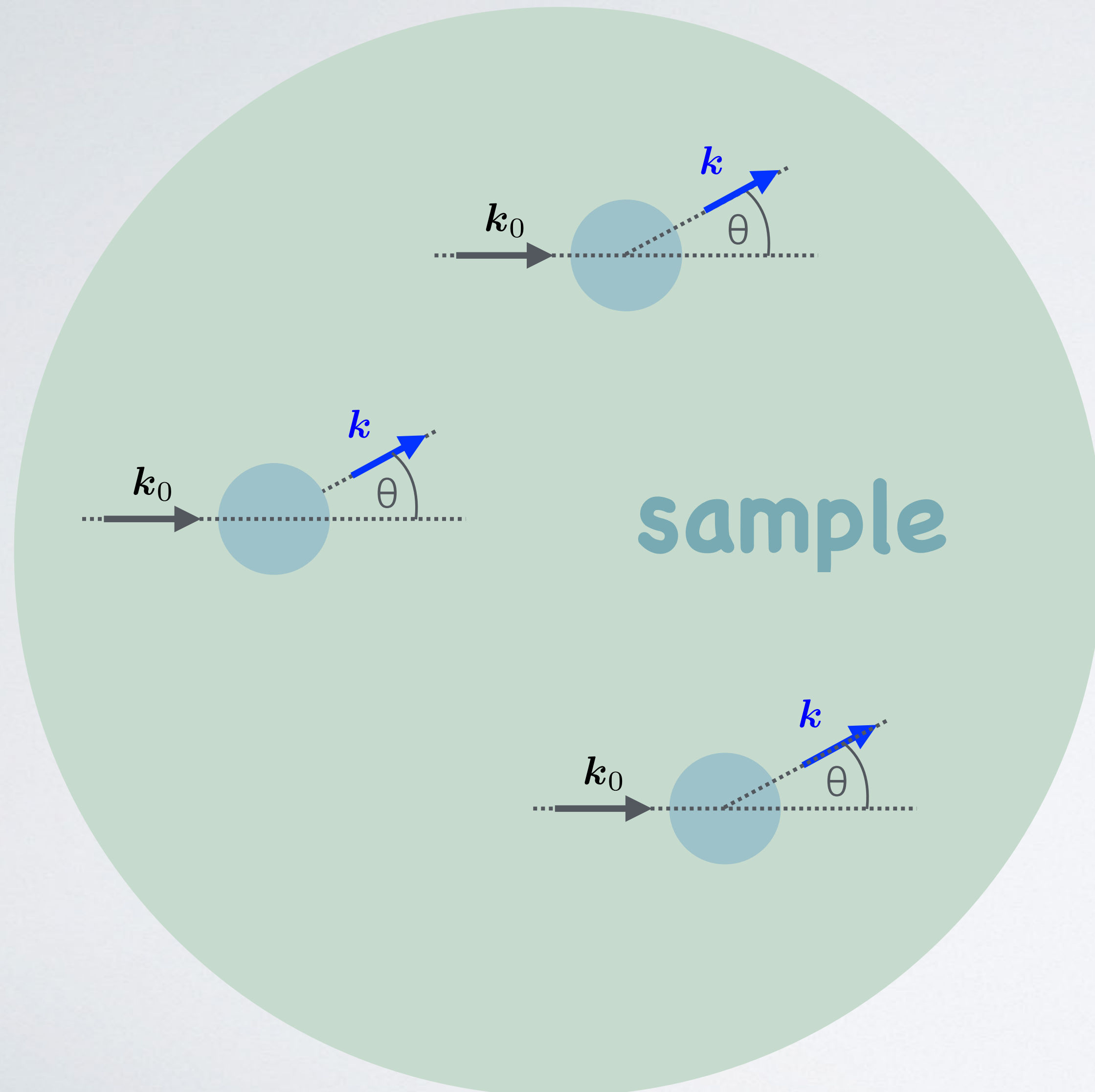
$$\Gamma_{jk} = \overline{b_j^*} \overline{b_k} + \delta_{jk} |\overline{b_j} - \overline{b_j}|^2$$



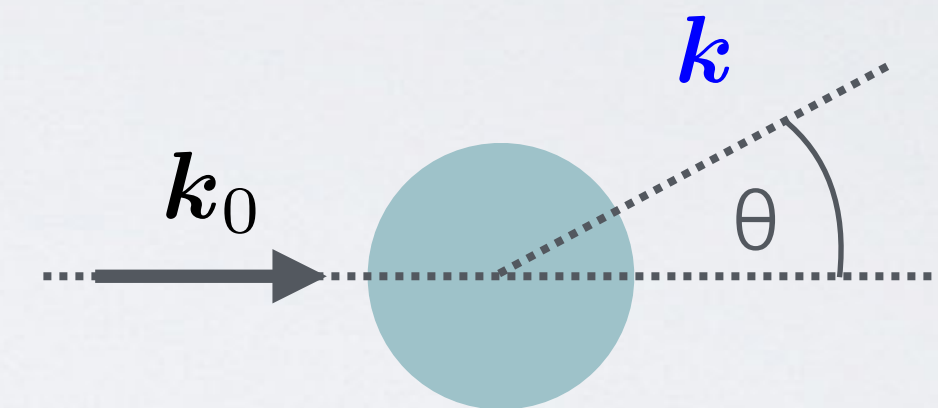
Partial intermediate scattering functions
are **quantum time correlation functions**

$$f_{jk}(\mathbf{q}, t) = \text{tr} \left\{ \hat{\rho}_{eq} e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j} \underbrace{e^{\frac{it}{\hbar} \hat{H}_s} e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} e^{-\frac{it}{\hbar} \hat{H}_s}}_{e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k(t)}} \right\}$$

The coherence volume — what neutrons “see”



Each neutron is a **wave packet** and probes a **coherence volume**



- Linear dimension $\lesssim 10^{-5}$ cm
- Number of atoms in coherence volume $\lesssim 10^8$
- cf. number of atoms in 1 cm^3 of water $\approx 10^{23}$

J. Felber, R. Gähler, R. Golub, and K. Prechtel
Physica B: Condensed Matter, 252(1-2):34–43, 1998

F. Mezei
In *J. Phys. Colloques*, volume 45, C3-223-C3-228, 1984

The neutron kicks the scattering atom



G. C. Wick, "The scattering of neutrons by systems containing light nuclei", Physical Review, vol. 94, no. 5, pp. 1228–1242, 1954.

$$f_{jk}(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k(t)} \right\rangle$$

$$= \left\langle e^{i\mathbf{q} \cdot (\hat{\mathbf{r}}_k - \hat{\mathbf{r}}_j)} e^{\frac{it}{\hbar} \hat{H}'_s(\mathbf{q}, k)} e^{-\frac{it}{\hbar} \hat{H}_s} \right\rangle$$

Use that

$$e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}} g(\hat{\mathbf{p}}) e^{i\mathbf{q} \cdot \hat{\mathbf{r}}} = g(\hat{\mathbf{p}} + \hbar \mathbf{q})$$



Atom k receives a momentum kick $\hbar \mathbf{q}$.

$$\hat{H}'_s(\mathbf{q}, k) = \sum_{l=1}^N \frac{(\hat{\mathbf{p}}_l + \delta_{kl} \hbar \mathbf{q})^2}{2m_l} + U_s(\hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N),$$

$$\langle \hat{H}'_s(\mathbf{q}, k) - \hat{H}_s \rangle = \frac{\hbar^2 q^2}{2m_k} \quad (\text{average recoil energy})$$

$$f_{jk}(\mathbf{q}, t) = \text{tr} \left\{ \hat{\rho}_{eq} e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j} \underbrace{e^{\frac{it}{\hbar} \hat{H}_s} e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} e^{-\frac{it}{\hbar} \hat{H}_s}}_{e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k(t)}} \right\}$$

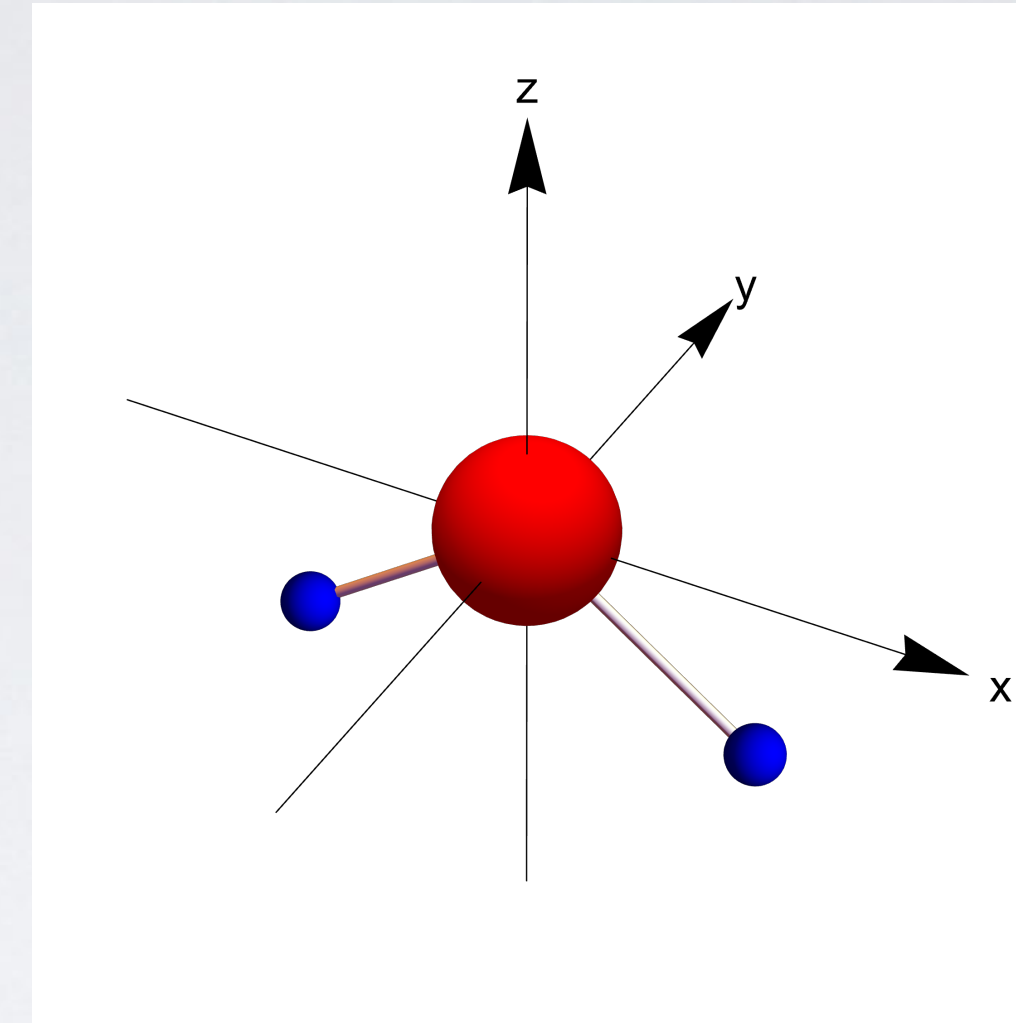
$$= \text{tr} \left\{ \hat{\rho}_{eq} e^{i\mathbf{q} \cdot (\hat{\mathbf{r}}_k - \hat{\mathbf{r}}_j)} \underbrace{e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_k} e^{\frac{it}{\hbar} \hat{H}_s} e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k}}_{e^{\frac{it}{\hbar} \hat{H}'_s(\mathbf{q}, k)}} e^{-\frac{it}{\hbar} \hat{H}_s} \right\}$$

Local and global heating the sample

Effective recoil energy

$$\Delta T(\mathbf{q}, k) = \frac{\hbar^2 q^2}{2m_{k,\text{eff}}}$$

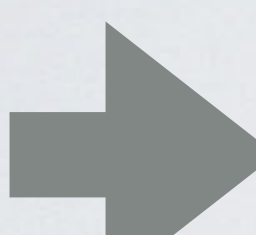
Effective masses for water



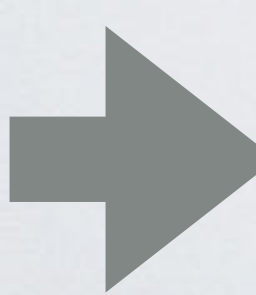
$$m_{H,\text{eff}} = 1.896 \text{ u}$$

$$m_{O,\text{eff}} = 17.08 \text{ u}$$

- R. G. Sachs and E. Teller, *Physical Review*, 60(1):18, 1941
- G. R. Kneller, *J Chem Phys*, 125(11):114107, 2006


$$H : \frac{\Delta T(q)}{\langle T \rangle} \approx 2.91 \times 10^{-2} [q]^2, \quad O : \frac{\Delta T(q)}{\langle T \rangle} \approx 3.23 \times 10^{-3} [q]^2 \quad (293 \text{ K})$$

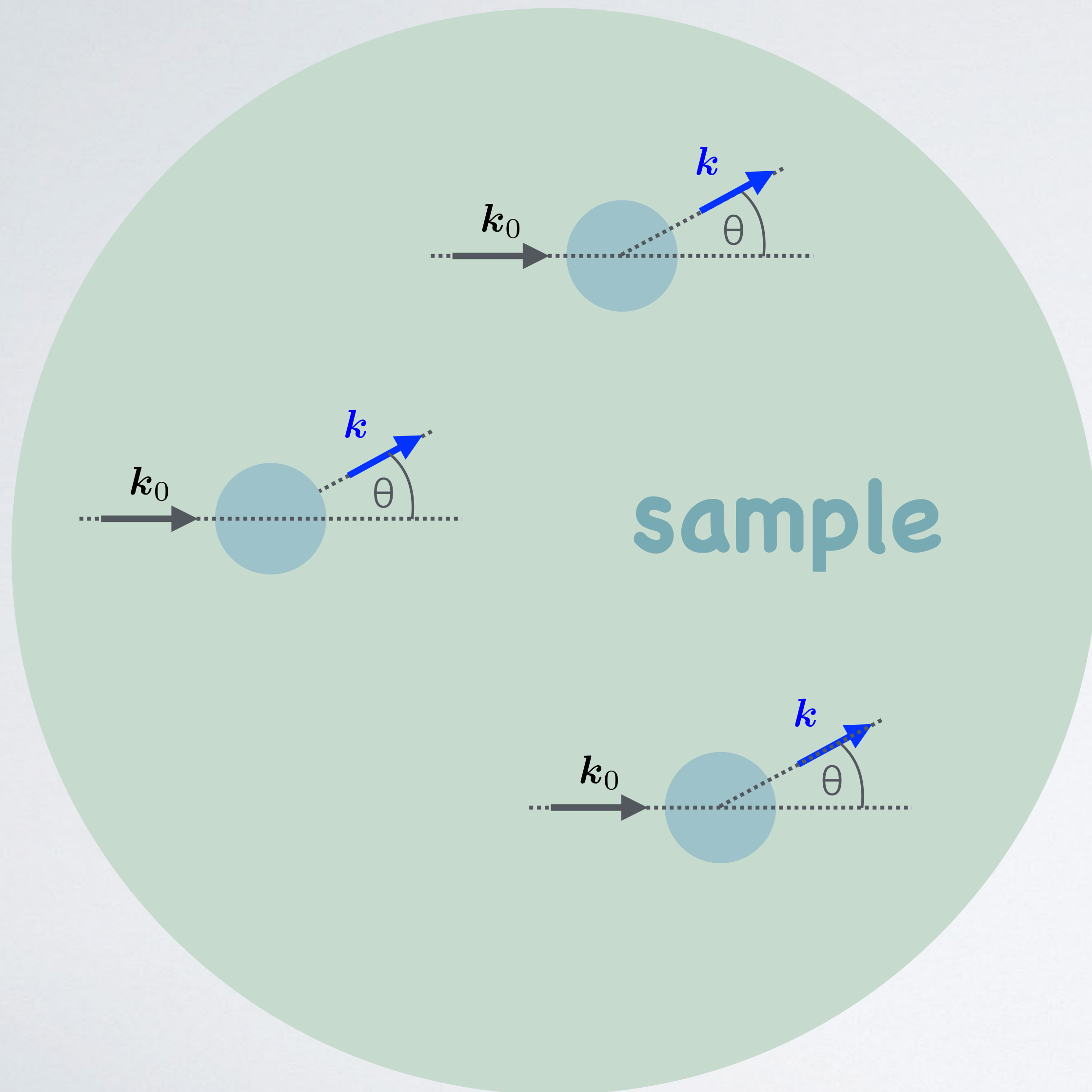
Local jump in “temperature” (kinetic energy) due to the neutron kick.


$$\frac{1}{\langle T \rangle} \frac{dT(q)}{dt} = 4.34 \times 10^{-11} \times [q]^2 / \text{s}$$

q in $\text{\AA}^{-1}$

Heating rate of a 1 cm^3 liquid-water sample exposed to a neutron flux of $\phi = 10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$.

Scattering from small open systems



- The **coherence volumes** in condensed matter are **small open systems** which are coupled to the **rest of the sample** which **acts as thermostat**.
- Thermostatting introduces irreversibility and relaxation processes.

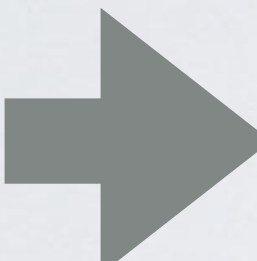
Spectroscopic formulation of the intermediate scattering function

G. R. Kneller, PNAS USA 115(38):9450–9455, 2018

$$\hat{H}'_s(\mathbf{q}, k) = \sum_{l=1}^N \frac{(\hat{\mathbf{p}}_l + \delta_{kl} \hbar \mathbf{q})^2}{2m_l} + U_s(\hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N)$$

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

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



$$\begin{aligned}\langle \mathbf{P} | \phi'_n(\mathbf{q}, k) \rangle &= \langle \mathbf{P} + \hbar \mathbf{Q}_k | \phi_n \rangle \\ \langle \mathbf{R} | \phi'_n(\mathbf{q}, k) \rangle &= \langle \mathbf{R} | \phi_n \rangle e^{-i \mathbf{Q}_k \cdot \mathbf{R}} \\ E'_n &= E_n\end{aligned}$$

Happily, because the nuclear and magnetic interactions between the neutron and atom are (in some sense) weak, the very good "first Born approximation" is applicable, and the neutrons are effectively "decoupled" from the dynamics of the scattering system which can be considered in isolation. **The neutron, in being scattered, "causes" transitions between the quantum states of the scattering system but does not change the states.**

From **Slow Neutron Spectroscopy and the Grand Atlas of the Physical World**
B. N. Brockhouse, *Rev. Mod. Phys.*, 67(4):735–751, octobre 1995

➔ The partial intermediate scattering functions can be entirely expressed in terms of transition amplitudes

$$f_{jk}(\mathbf{q}, t) = \sum_{m,n} \frac{e^{-\beta E_m}}{Z} e^{\frac{i}{\hbar}(E_n - E_m)t} a_{m \rightarrow n}^*(\mathbf{q}, j) a_{m \rightarrow n}(\mathbf{q}, k)$$

$$\sum_n \dots = \begin{cases} \sum_n \dots & \text{for discrete spectra,} \\ \int dE \rho(E) \dots & \text{for continuous spectra.} \end{cases}$$

Amplitudes for the scattering-induced transition $|\phi_m\rangle \rightarrow |\phi_n\rangle$ if atom k is hit:

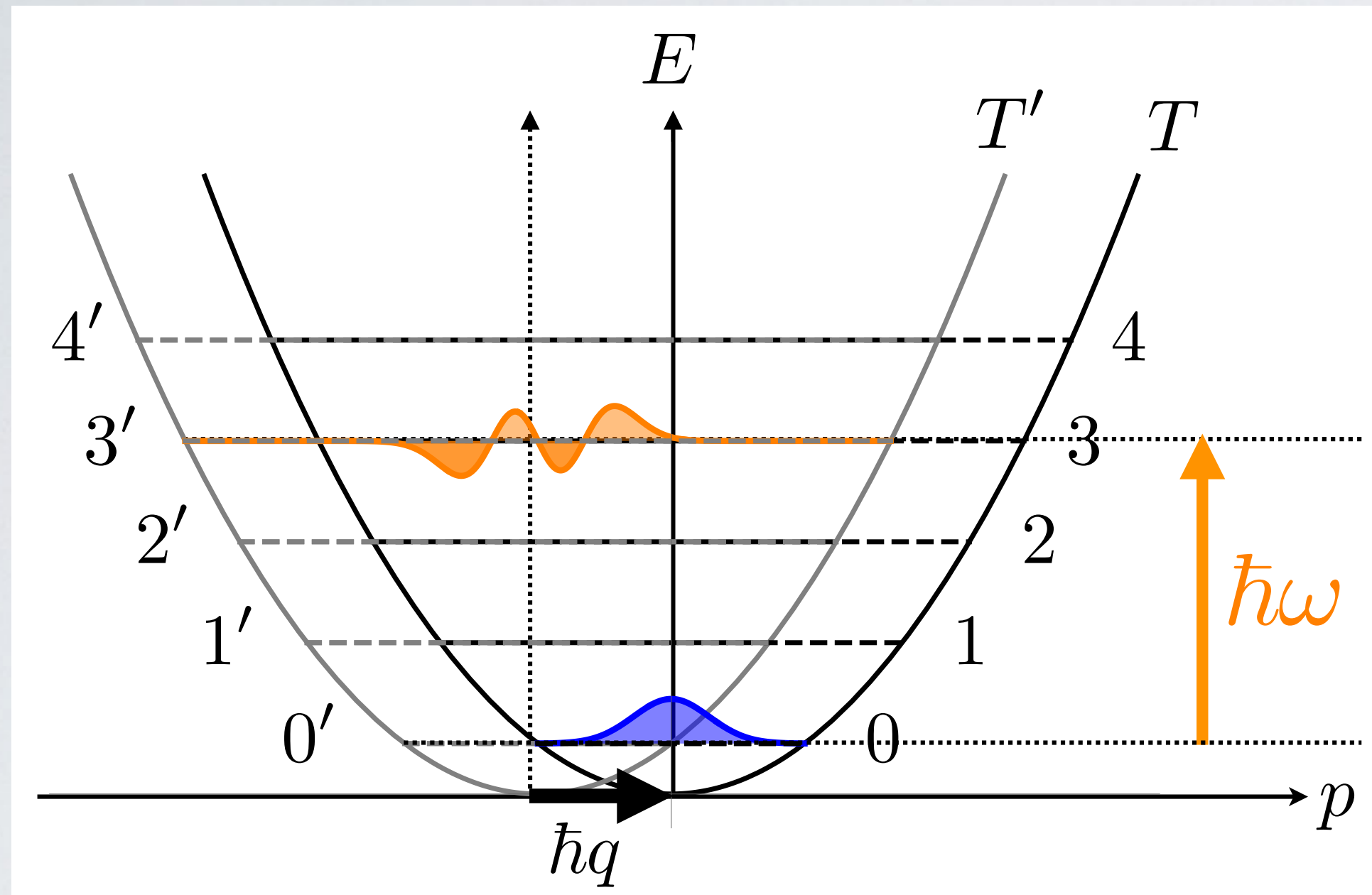
$$\begin{aligned} a_{m \rightarrow n}(\mathbf{q}, k) &= \int d^3N P \tilde{\phi}_n^*(\mathbf{P} + \hbar \mathbf{Q}_k) \tilde{\phi}_m(\mathbf{P}) \\ &= \int d^3N R e^{i \mathbf{Q}_k \cdot \mathbf{R}} \phi_n^*(\mathbf{R}) \phi_m(\mathbf{R}) \end{aligned}$$

$$\hat{H}|\phi_m\rangle = E_m|\phi_m\rangle, \quad \phi_m(\mathbf{R}) \equiv \langle \mathbf{R} | \phi_m \rangle, \quad \tilde{\phi}_m(\mathbf{P}) \equiv \langle \mathbf{P} | \phi_m \rangle$$

$$\mathbf{Q}_k = (\underbrace{0, 0, 0}_1, \dots, \underbrace{0, 0, 0}_{k-1}, \underbrace{q_x, q_y, q_z}_k, \underbrace{0, 0, 0}_{k+1}, \dots, \underbrace{0, 0, 0}_N)^T$$

Illustration - single harmonic oscillator

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



$$E = \underbrace{\frac{p^2}{2m}}_{T(p)} + \underbrace{\frac{1}{2}m\Omega^2 x^2}_{V(x)}$$

$$E_n = \left(n + \frac{1}{2}\right) \hbar\Omega$$

Transition probabilities

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

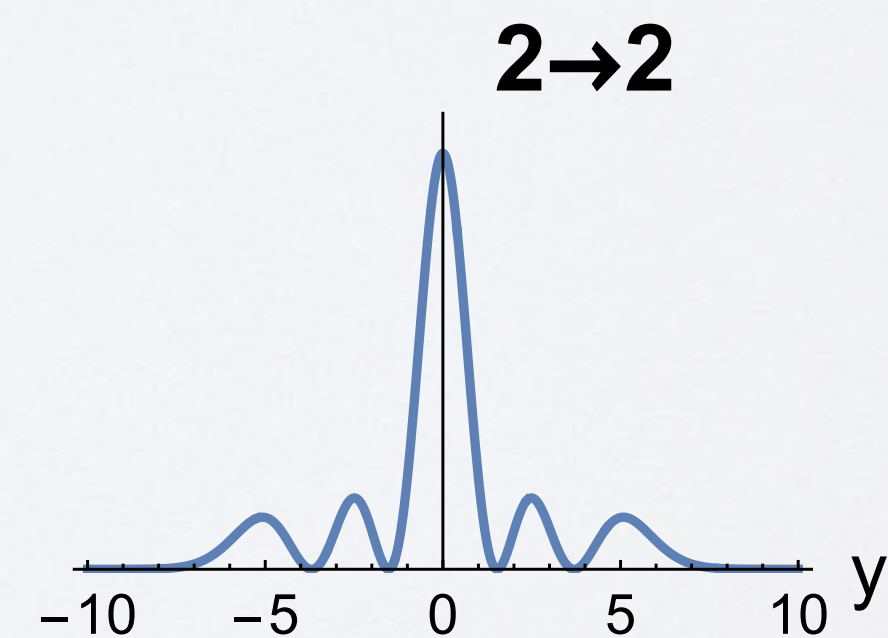
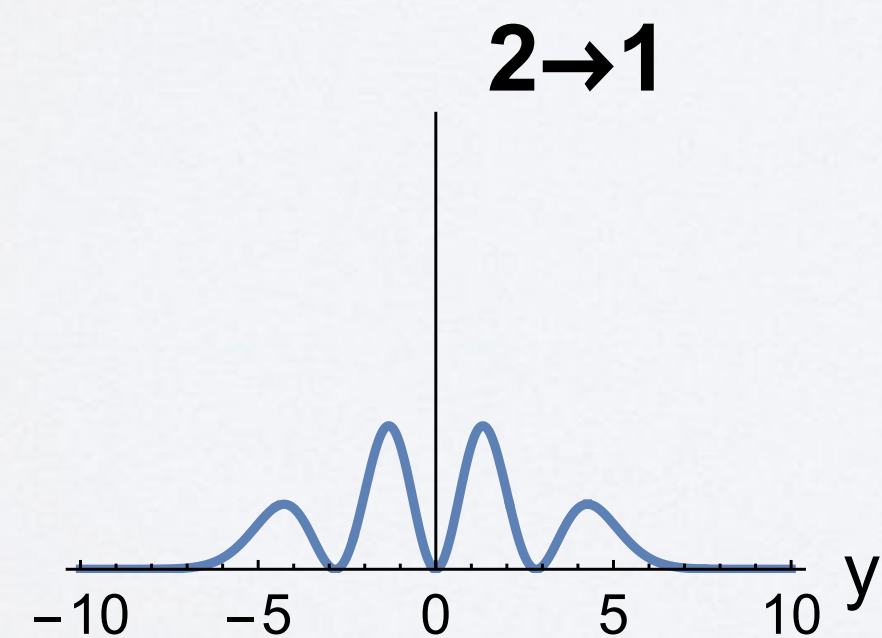
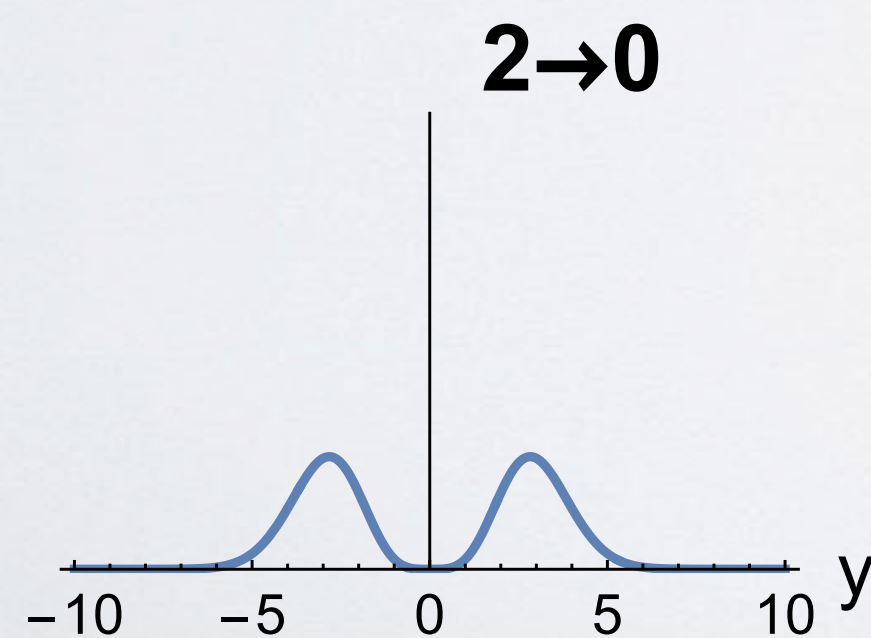
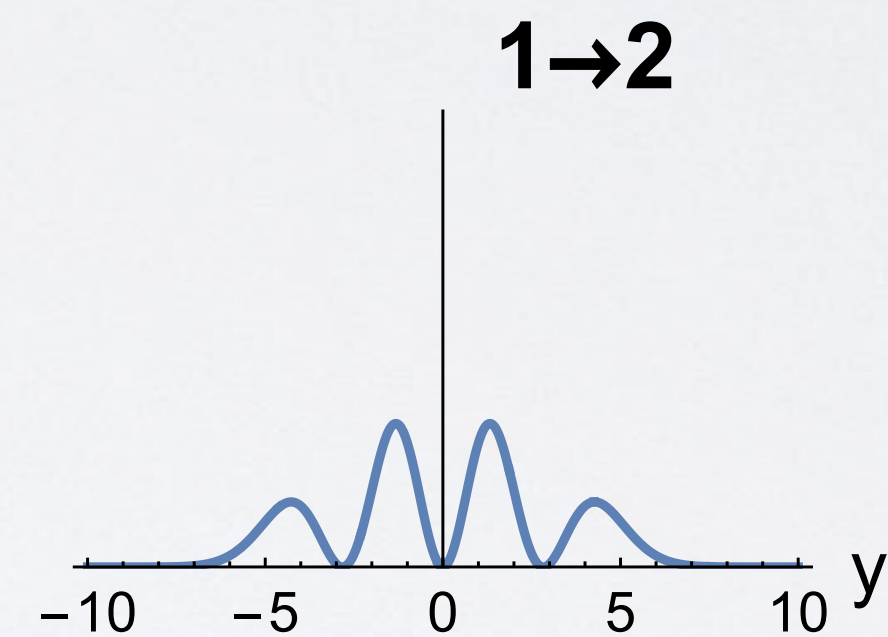
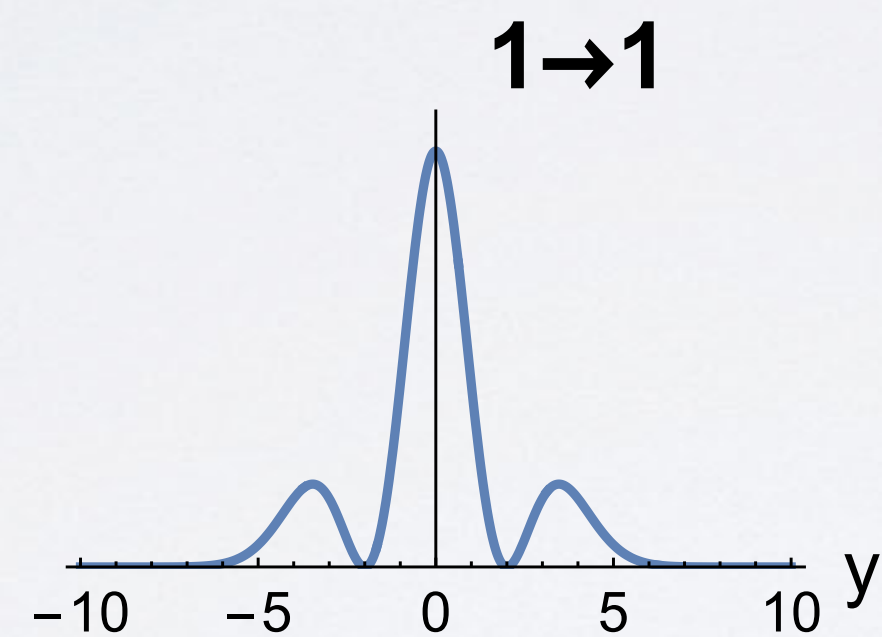
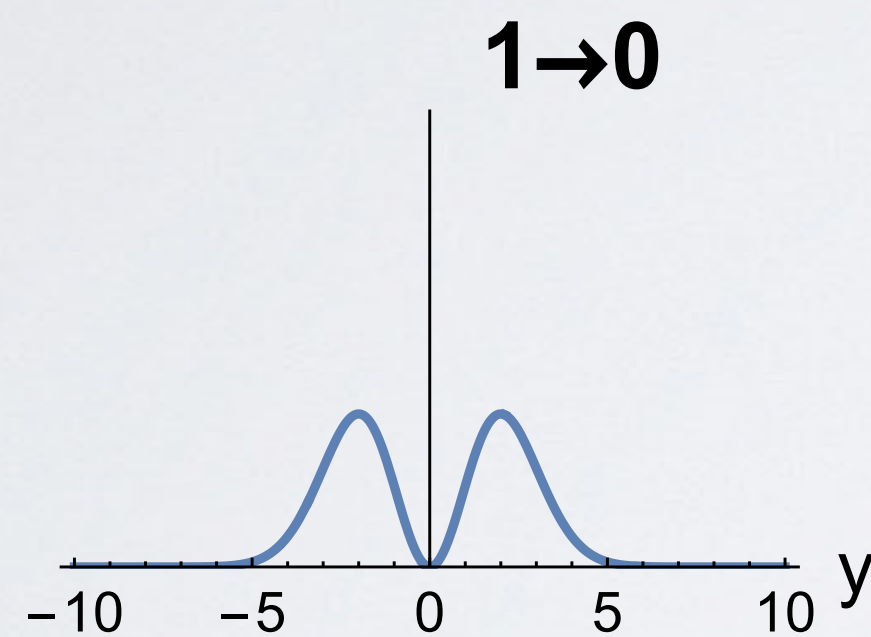
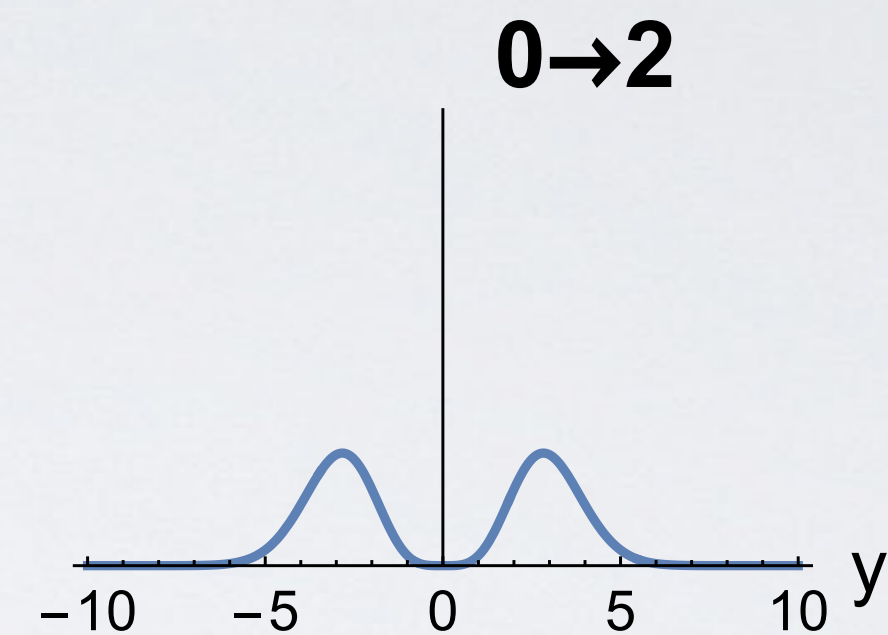
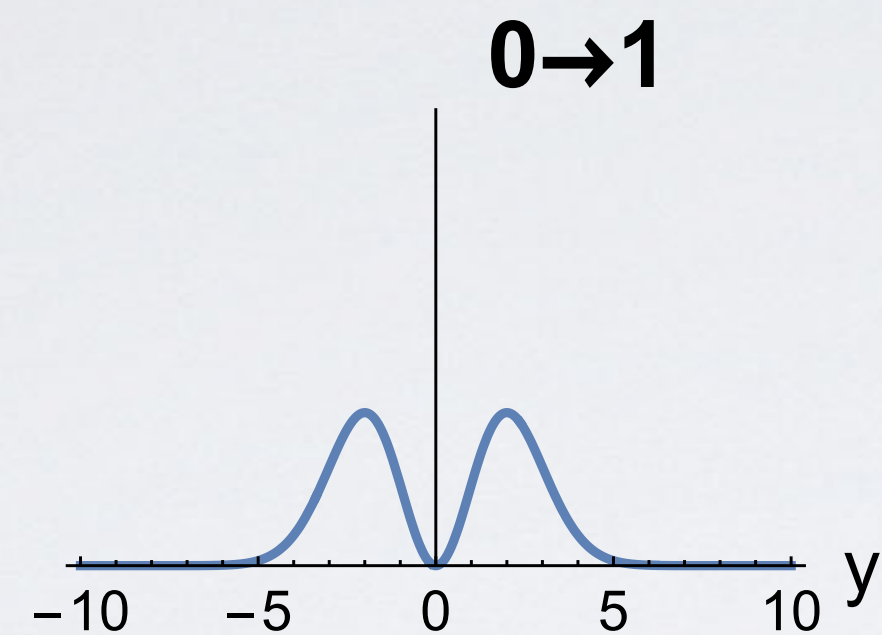
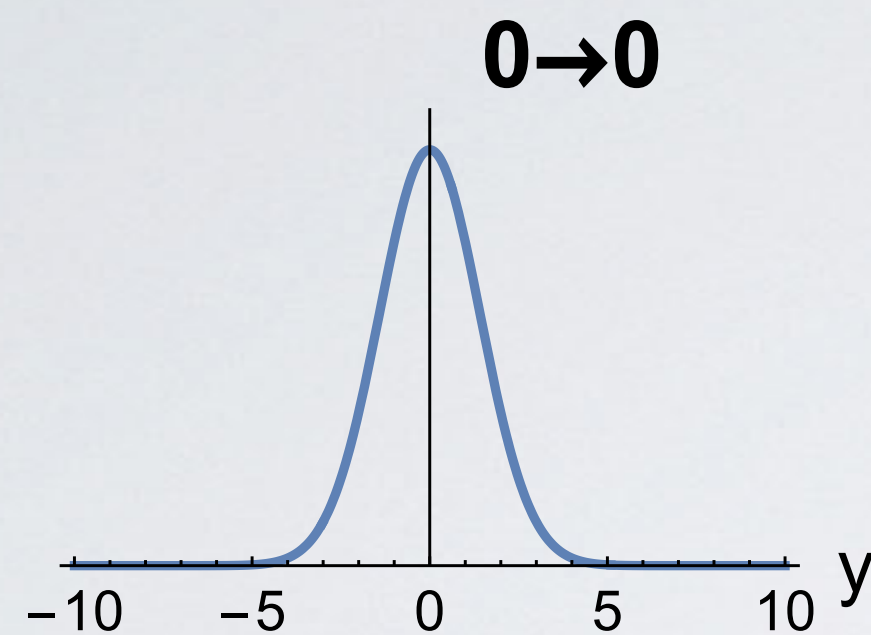
$$y(q) = \sqrt{\frac{2\hbar}{M\Omega}} q$$

$$F(q, t) = \sum_{m,n} \frac{e^{-\beta E_m}}{Z} e^{\frac{i}{\hbar}(E_n - E_m)t} |a_{m \rightarrow n}(q)|^2$$

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

Textbook result (c.f. Lovesey)

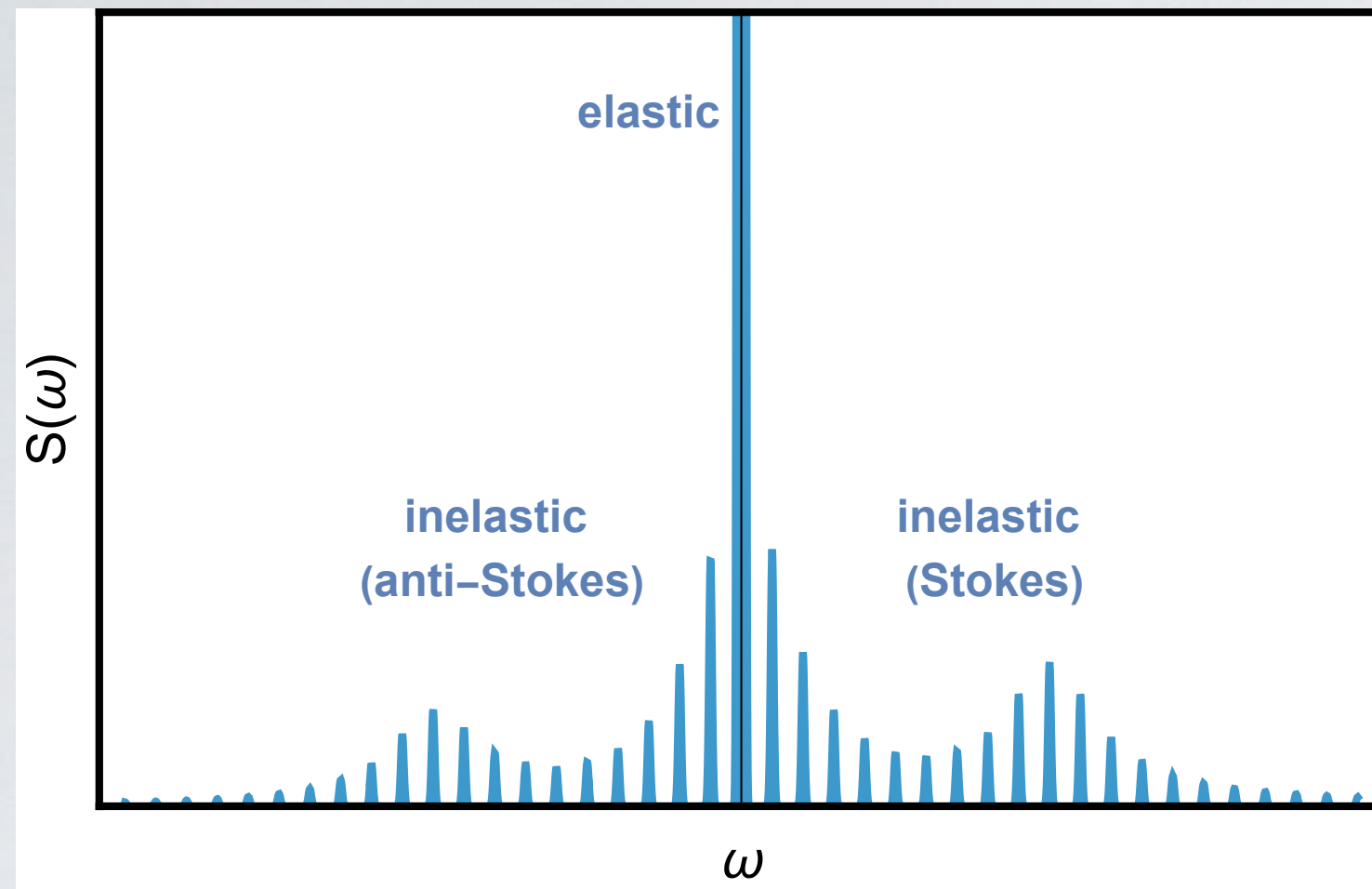
Some transition probabilities as a function of momentum transfer



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

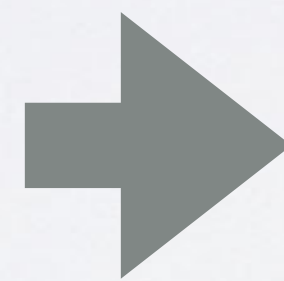
Quantum and classical picture of (quasi-)elastic scattering

Elastic scattering for a discrete energy spectrum



$$f_{jk}^{(\text{el})}(\mathbf{q}) = \sum_m \frac{e^{-\beta E_m}}{Z} |a_{m \rightarrow m}(\mathbf{q}, j)|^2$$

$$a_{m \rightarrow m}(\mathbf{q}, k) = \int d^3N R e^{i\mathbf{Q}_k \cdot \mathbf{R}} |\phi_m(\mathbf{R})|^2 \equiv \langle \phi_m | e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} | \phi_m \rangle$$



$$f_{jk}^{(\text{el})}(\mathbf{q}) = \sum_m \frac{e^{-\beta E_m}}{Z} \langle \phi_m | e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j} | \phi_m \rangle \langle \phi_m | e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} | \phi_m \rangle$$

The elastic intensity has **not** the factorised form as in classical statistical physics:

$$f_{jk}^{(\text{el})}(\mathbf{q}) \neq \langle e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_j} \rangle^* \langle e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} \rangle \quad \text{with} \quad \langle \dots \rangle = \sum_m \frac{e^{-\beta E_m}}{Z} \langle \phi_m | \dots | \phi_m \rangle$$

Elastic scattering in the picture of **classical** statistical physics

$$f_{jk}(\mathbf{q}, t) = \langle e^{-i\mathbf{q} \cdot \mathbf{r}_j(0)} e^{i\mathbf{q} \cdot \mathbf{r}_k(t)} \rangle = \int \int d^3N_{\mathbf{R}_0} d^3N_{\mathbf{R}_t} e^{-i\mathbf{Q}_j \cdot \mathbf{R}_0} e^{i\mathbf{Q}_k \cdot \mathbf{R}_t} \underbrace{p(\mathbf{R}_t, t | \mathbf{R}_0, 0)}_{\text{transition } \mathbf{R}_0 \rightarrow \mathbf{R}_t} p_{\text{eq}}(\mathbf{R}_0)$$

$\propto e^{-\beta V(\mathbf{R}_0)}$

Smoluchowski equation

$$\partial_t p(\mathbf{R}, t | \mathbf{R}_0, 0) = \nabla \cdot \mathbf{D} \cdot \{ \nabla + \beta \nabla V(\mathbf{R}) \} p(\mathbf{R}, t | \mathbf{R}_0, 0)$$

$$p(\mathbf{R}_t, t | \mathbf{R}_0, 0) \stackrel{t \rightarrow \infty}{\sim} p_{\text{eq}}(\mathbf{R}_t)$$

**7. Über Brownsche Molekularbewegung
unter Einwirkung äußerer Kräfte und deren
Zusammenhang mit der verallgemeinerten
Diffusionsgleichung;
von M. v. Smoluchowski.**

M. V. Smoluchowski, Annalen der Physik, 353(24):1103–1112, 1916

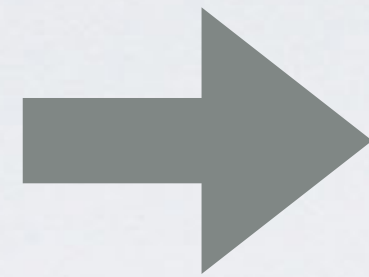
➔

$$f_{jk}(\mathbf{q}, t) \stackrel{t \rightarrow \infty}{=} \int \int d^3N_{\mathbf{R}_0} d^3N_{\mathbf{R}_t} e^{-i\mathbf{Q}_j \cdot \mathbf{R}_0} e^{i\mathbf{Q}_k \cdot \mathbf{R}_t} p_{\text{eq}}(\mathbf{R}_t) p_{\text{eq}}(\mathbf{R}_0) = \langle e^{i\mathbf{q} \cdot \mathbf{r}_j(0)} \rangle^* \langle e^{i\mathbf{q} \cdot \mathbf{r}_k(0)} \rangle$$

Debye-Waller factors of quantum oscillators

Definition of the DW factor

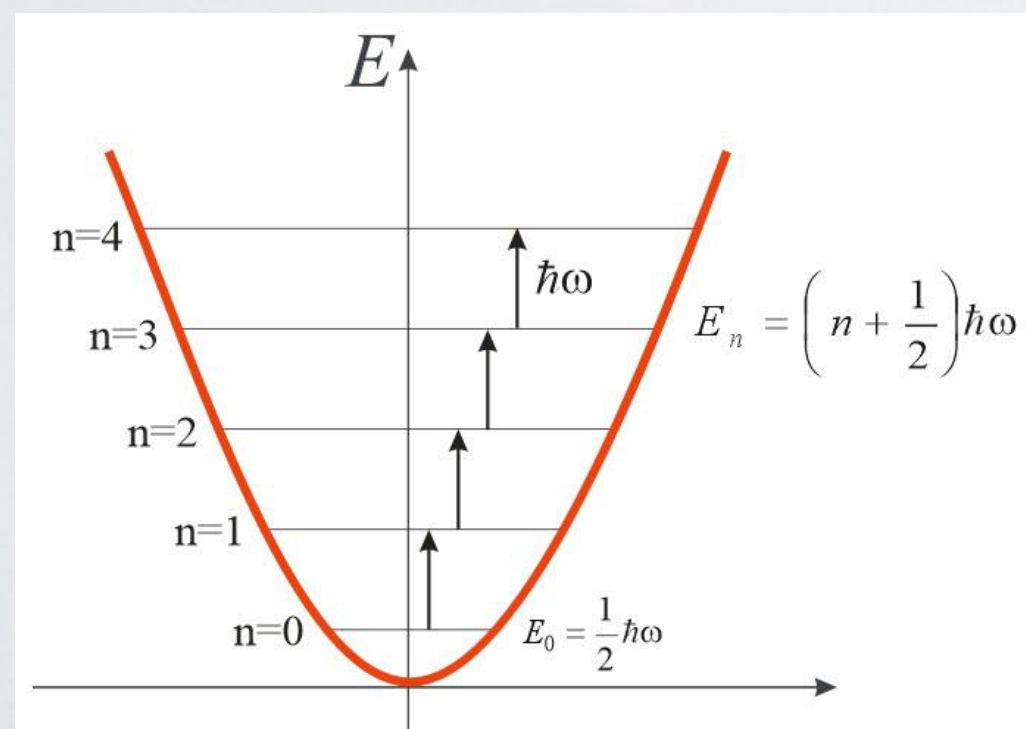
$$F_{\text{el}}(q) = e^{-2W(q) + O(q^4)}$$



$$2W(q) = q^2 \sum_m \frac{e^{-\beta E_m}}{Z} \left\{ \langle \phi_m | \hat{x}^2 | \phi_m \rangle - \langle \phi_m | \hat{x} | \phi_m \rangle^2 \right\}$$

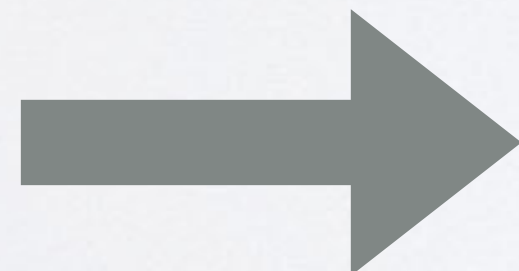
Harmonic potential

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



$$\langle \hat{x}^2 \rangle_m = \frac{\hbar}{2M\Omega} (2m + 1)$$

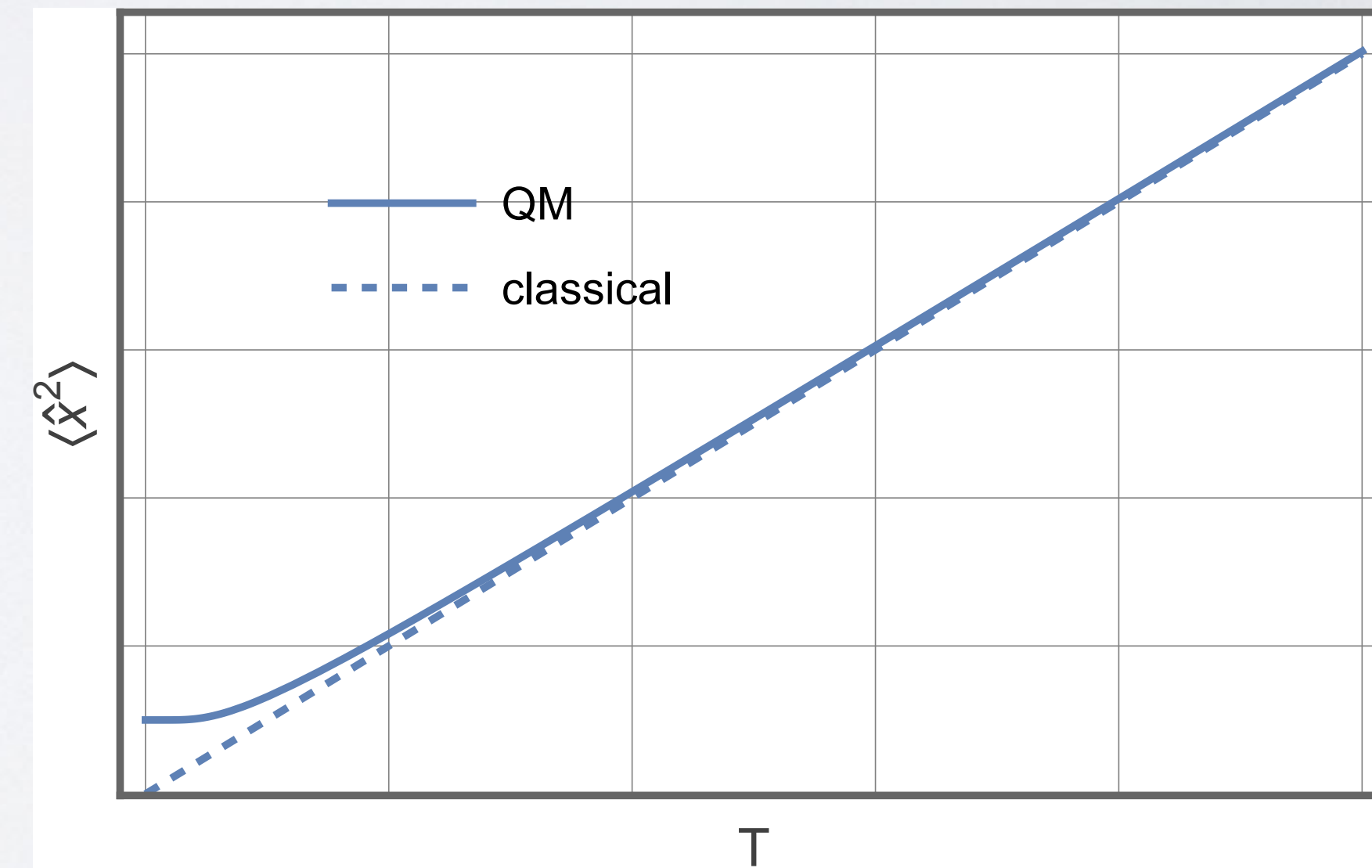
$$\langle \hat{x} \rangle_m = 0$$



$$\langle \hat{x}^2 \rangle = \frac{\hbar \coth\left(\frac{\beta \Omega \hbar}{2}\right)}{2M\Omega}$$

$$\xrightarrow{\hbar \rightarrow 0} \frac{1}{\beta M \Omega^2} = \frac{k_B T}{K}$$

$$\langle \hat{x} \rangle = 0$$

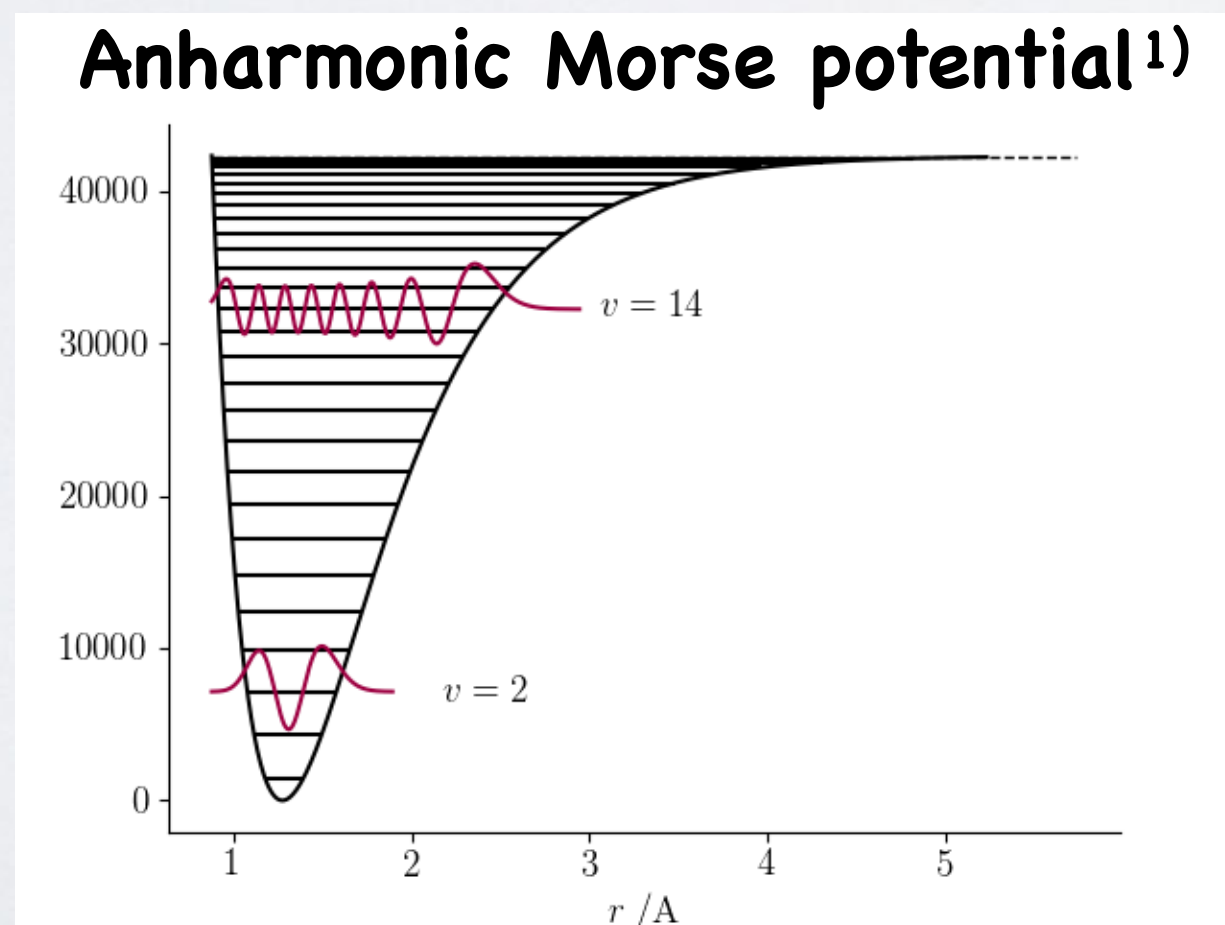


Quantum versus classical Debye-Waller factor

Quantum mechanics:
$$2W(q) = q^2 \left\{ \underbrace{\sum_m \frac{e^{-\beta E_m}}{Z} \langle \phi_m | \hat{x}^2 | \phi_m \rangle}_{\langle \hat{x}^2 \rangle} - \underbrace{\sum_m \frac{e^{-\beta E_m}}{Z} \langle \phi_m | \hat{x} | \phi_m \rangle^2}_{=\langle \hat{x} \rangle^2 \text{ iff } \langle \phi_m | \hat{x} | \phi_m \rangle = \text{const.}} \right\}$$

Classical stat. physics:
$$2W(q) = q^2 \{ \langle x^2 \rangle - \langle x \rangle^2 \} = q^2 \langle (x - \langle x \rangle)^2 \rangle$$

For anharmonic potentials, where $\langle \phi_m | \hat{x} | \phi_m \rangle$ is not constant, differences between the temperature dependences of the quantum and classical Debye-Waller factors are also to be expected for high temperatures.

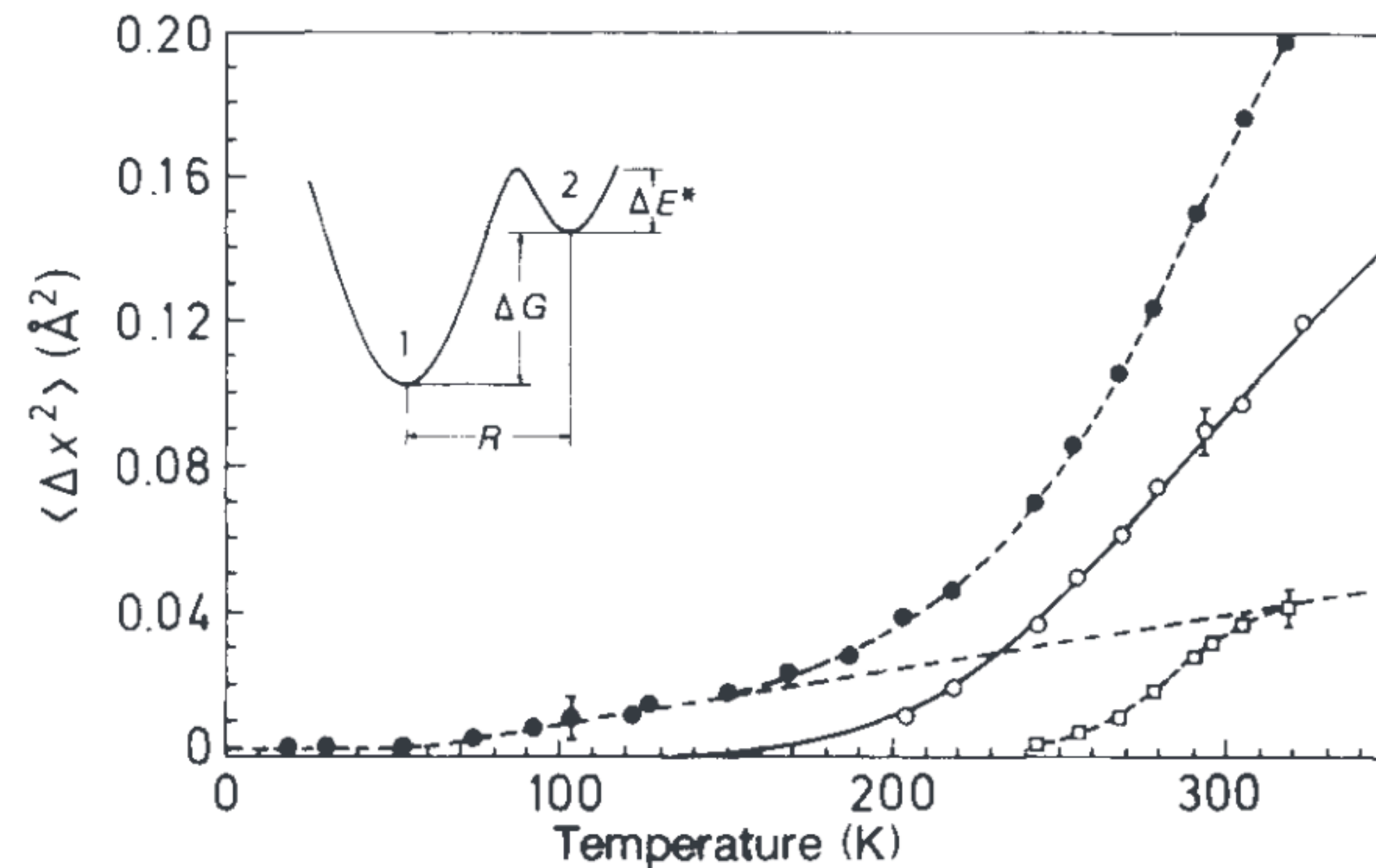
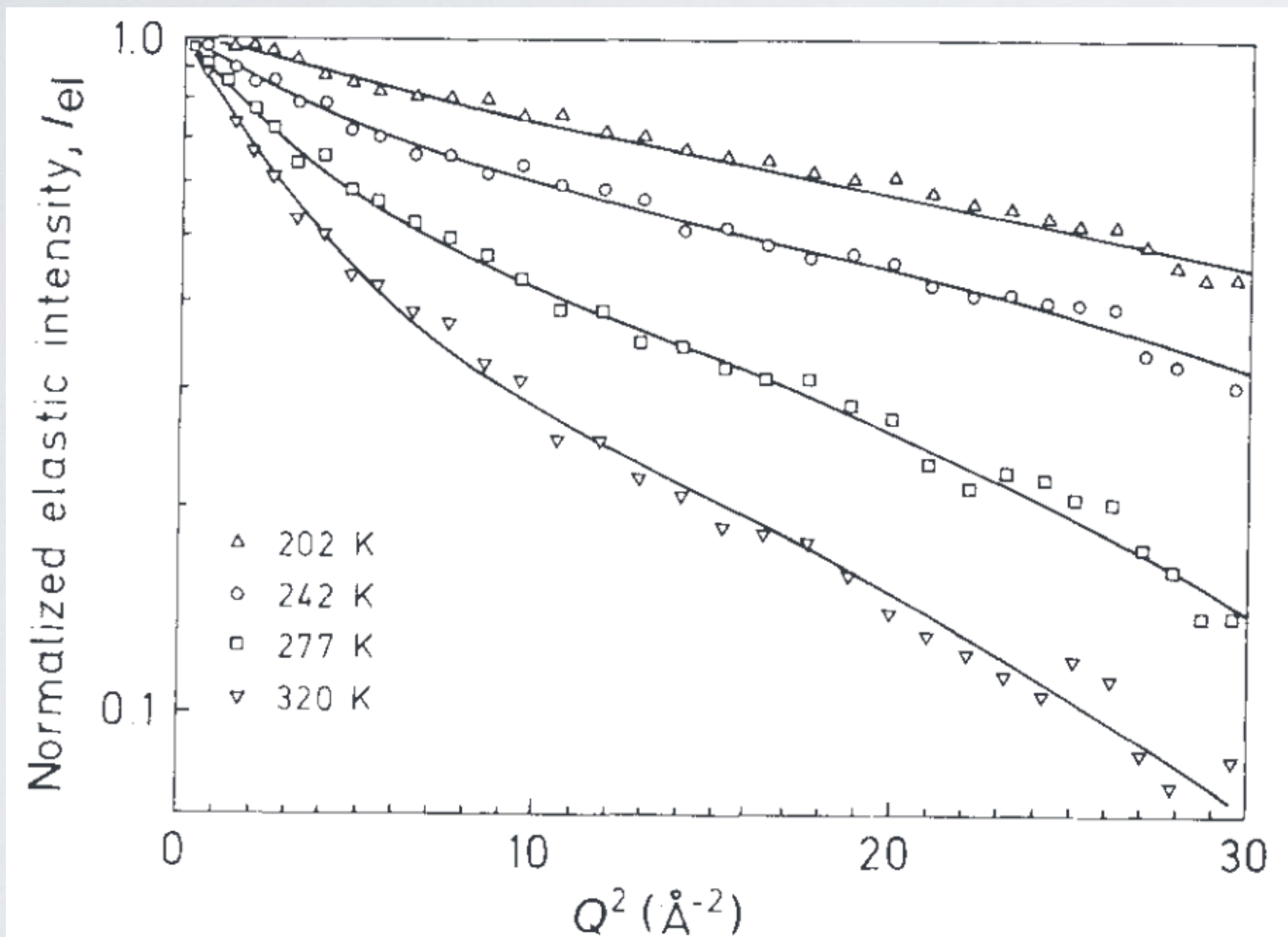


1) <https://scipython.com/blog/the-morse-oscillator/>

Elastic scattering and the dynamical transition in proteins

$$\log(F(q, \infty))$$

$$\langle \Delta x^2 \rangle = -\frac{1}{2} \frac{\partial \log(F(q, \infty))}{\partial q^2} \bigg|_{q=0}$$



Dynamical transition of myoglobin revealed by inelastic neutron scattering

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‡ Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

Nature, 337(6209):754–756, Feb 1989

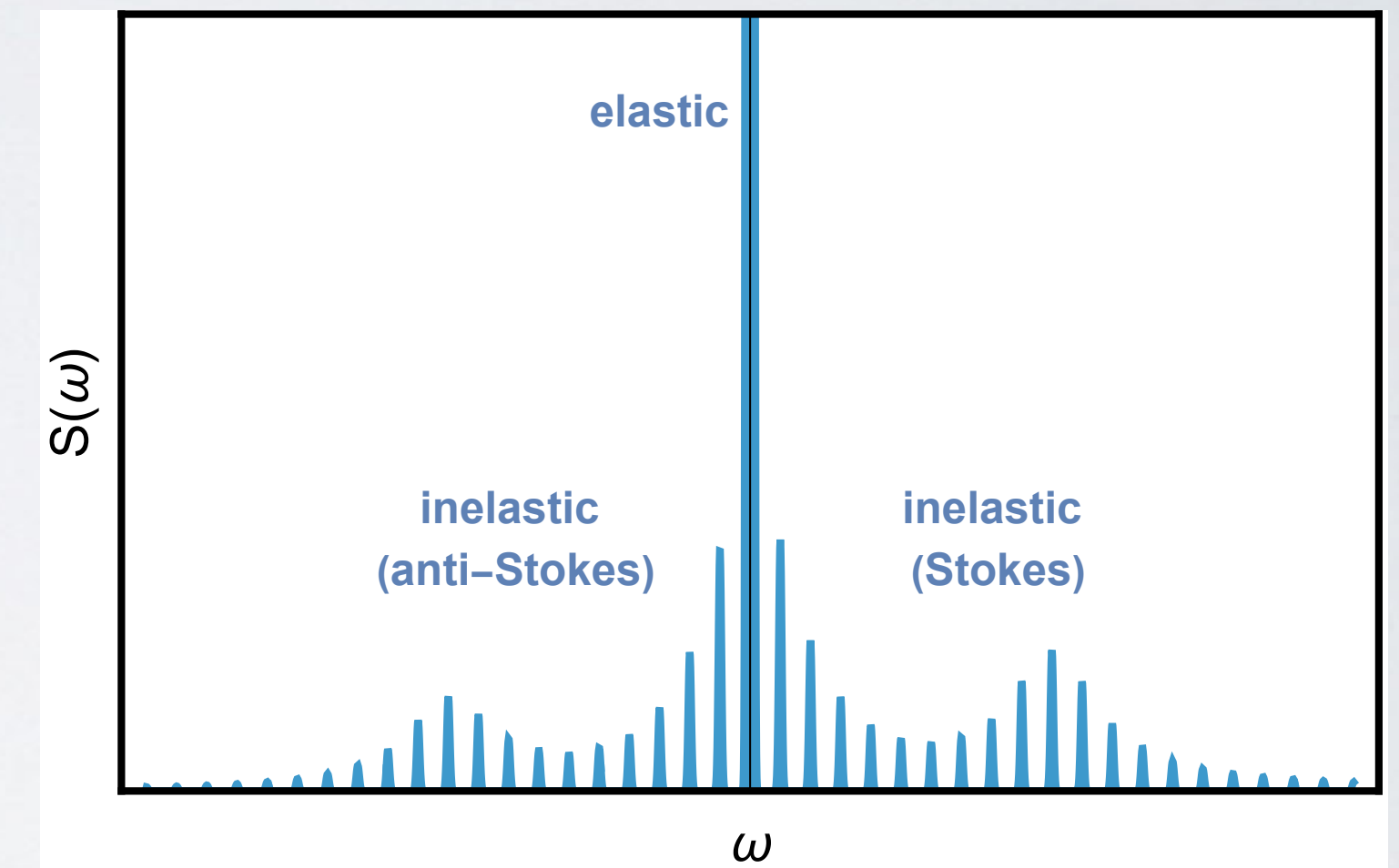
(Quasi-)Elastic scattering for continuous energy spectra

For a discrete energy spectrum the intermediate scattering function **oscillates** about this elastic amplitude and the dynamic structure factor is a **line spectrum**:

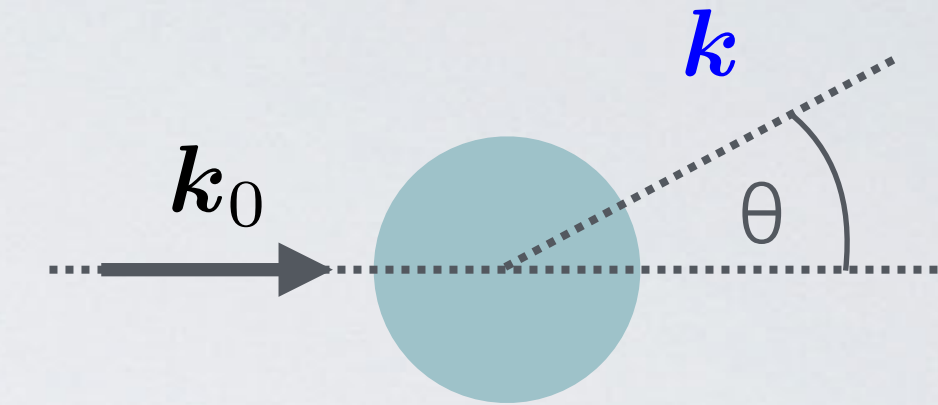
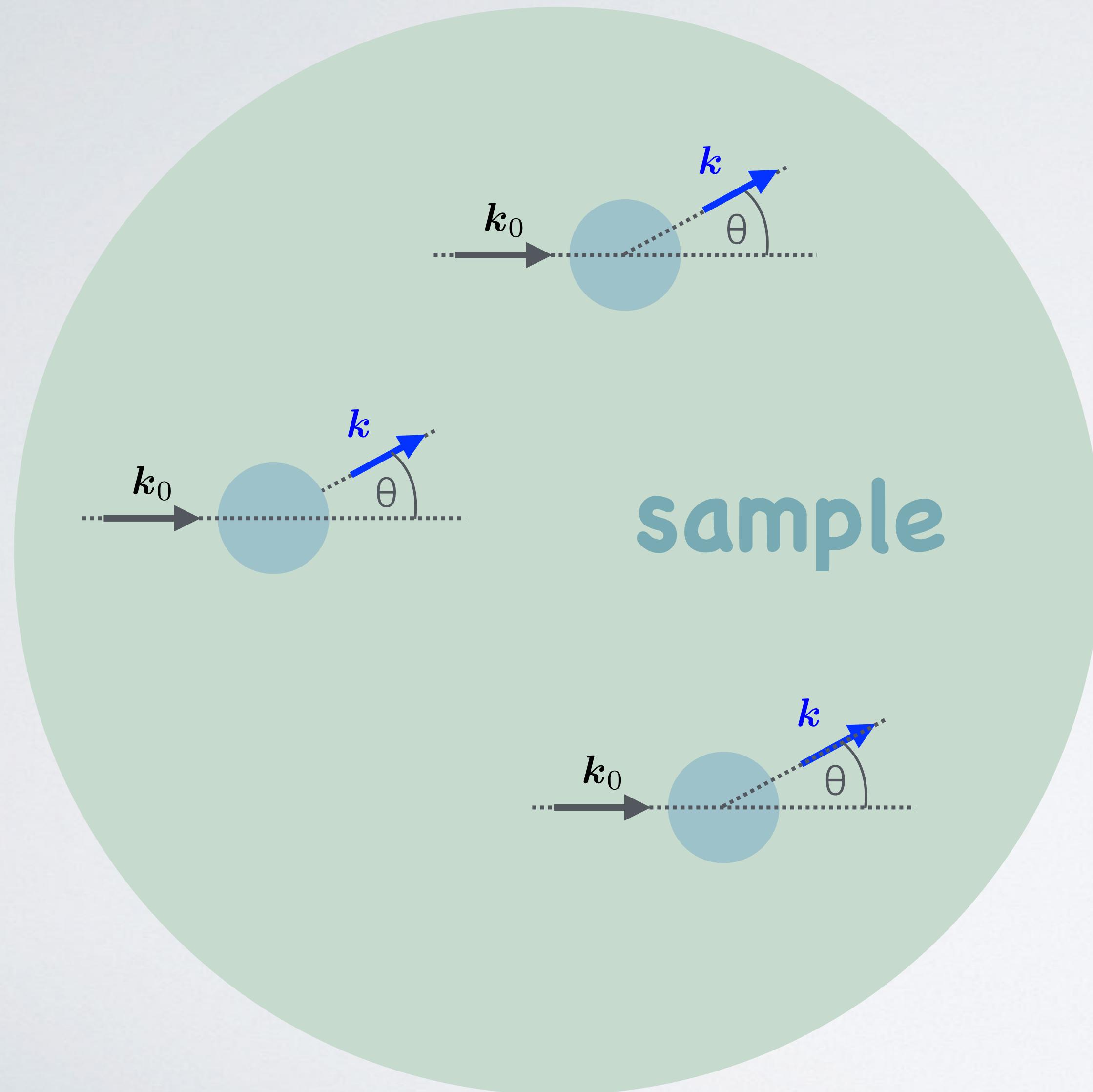
$$f_{jk}(\mathbf{q}, t) = f_{jk}^{(\text{el})}(\mathbf{q}) + \sum_{m \neq n} \frac{e^{-\beta E_m}}{Z} e^{\frac{i}{\hbar}(E_n - E_m)t} a_{m \rightarrow n}^*(\mathbf{q}, j) a_{m \rightarrow n}(\mathbf{q}, k)$$

No ergodicity !

$$s_{jk}(\mathbf{q}, \omega) = f_{jk}^{(\text{el})}(\mathbf{q}) \delta(\omega) + \sum_{m \neq n} \frac{e^{-\beta E_m}}{Z} \delta\left(\omega - \frac{E_n - E_m}{\hbar}\right) a_{m \rightarrow n}^*(\mathbf{q}, j) a_{m \rightarrow n}(\mathbf{q}, k)$$



Justification for a continuous spectrum of energies



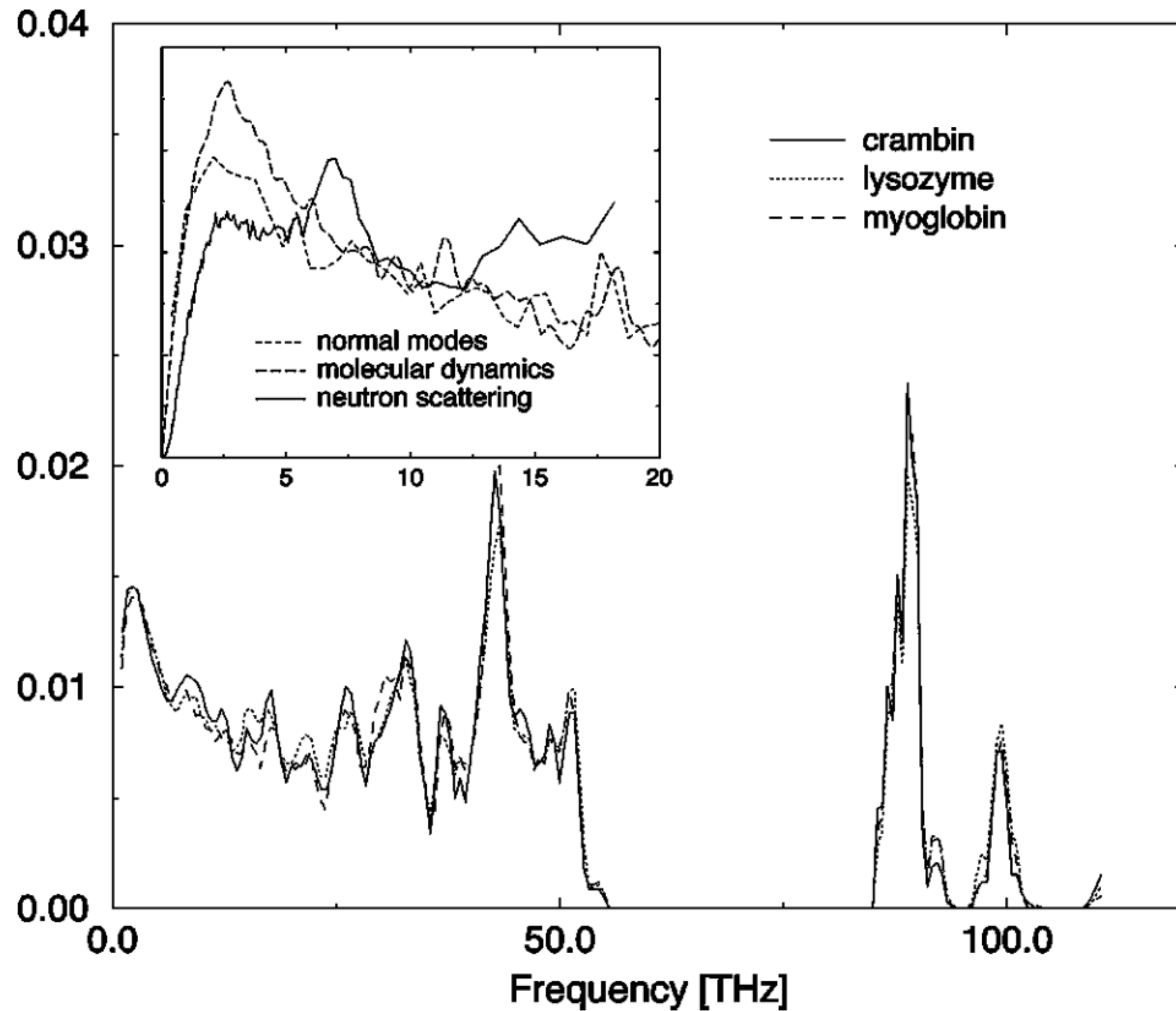
- Each coherence volume is a small open system which is thermostatted by the sample.
- the neutrons see $\approx 10^{15}$ almost identical copies of the same system with a slightly different energy spectrum.

If the energy differences $E_{m+1} - E_m$ in the coherence volumes are comparable to the statistical variation δE_m of its energy levels from one copy to another, the energy spectrum seen as a whole is continuous.

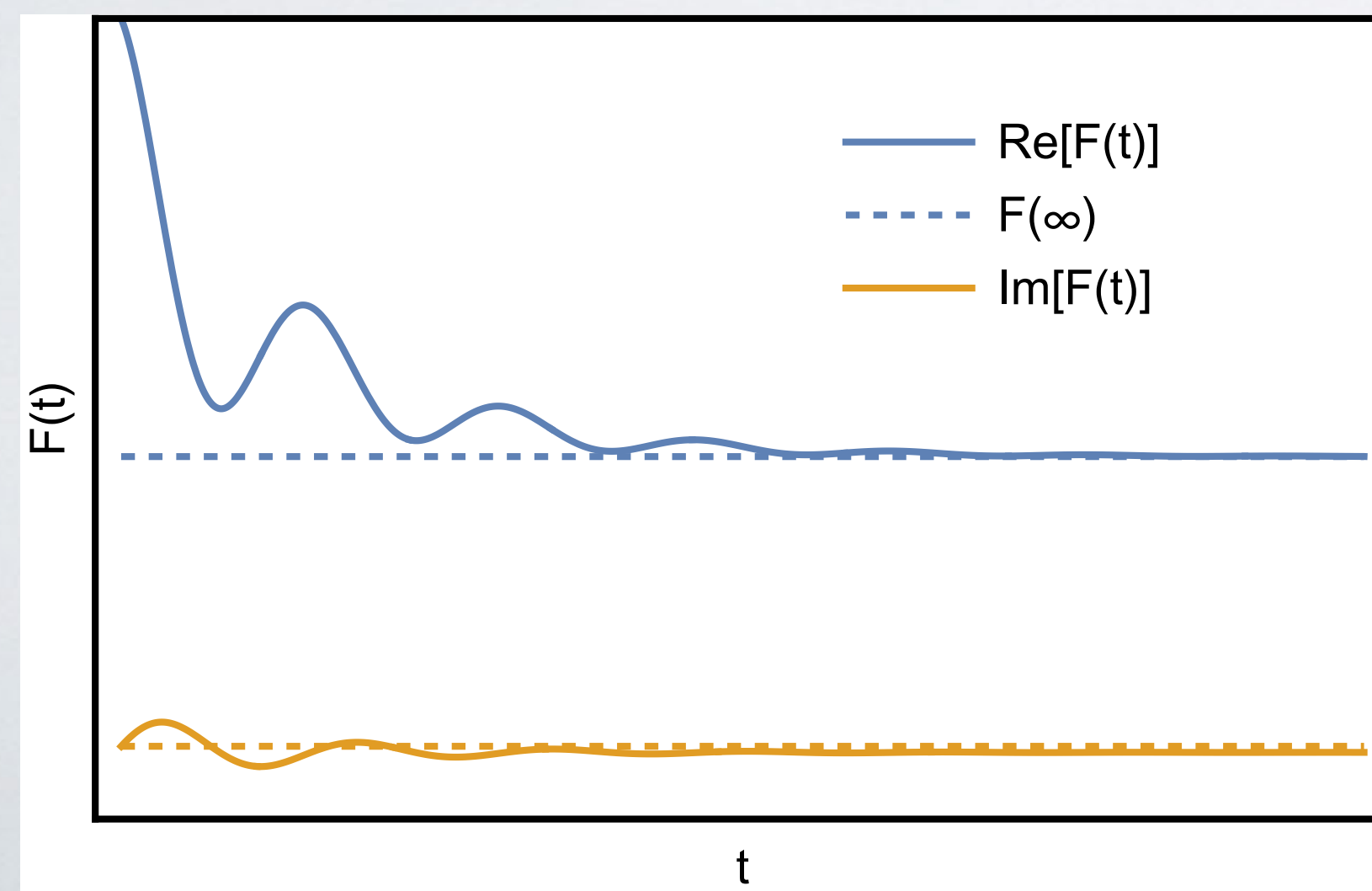
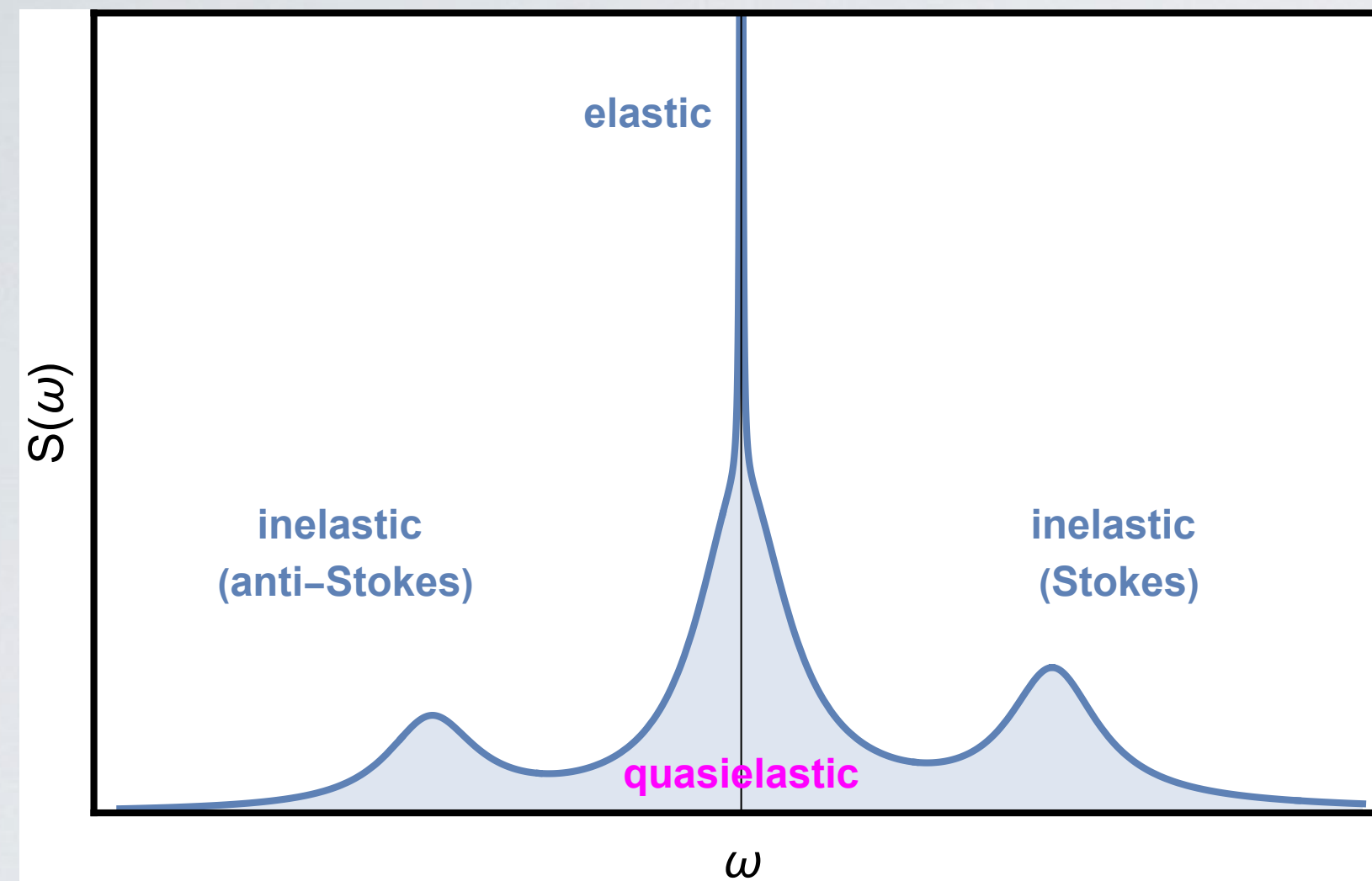
Quasi-continuous vibrational spectra of proteins

K. Hinsen and G. R. Kneller

J Chem Phys, 111(24):10766–10769, 1999



For a continuous energy spectrum (quasi-)elastic scattering is described by correlations for $t \rightarrow \infty$:

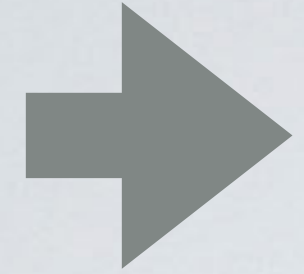


$$f_{jk}(\mathbf{q}, t) \stackrel{t \rightarrow \infty}{\sim} \underbrace{\int \int dE dE' \rho(E) \rho(E') \frac{e^{-\beta E}}{Z} e^{\frac{i}{\hbar}(E' - E)t}}_{E' \approx E} a_{E \rightarrow E'}^*(\mathbf{q}, j) a_{E \rightarrow E'}(\mathbf{q}, k)$$

$$f_{jk}(\mathbf{q}, \infty) = \int dE \rho(E)^2 \frac{e^{-\beta E}}{Z} \langle \phi_E | e^{-i\mathbf{q} \cdot \hat{\mathbf{r}}_j} | \phi_E \rangle \langle \phi_E | e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} | \phi_E \rangle = f_{jk}^{(\text{el})}(\mathbf{q})$$

This is again not of the classical form

$$f_{jk}(\mathbf{q}, \infty) \neq \underbrace{\left(\int dE \rho(E) \frac{e^{-\beta E}}{Z} \langle \phi_E | e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_j} | \phi_E \rangle \right)^*}_{\langle e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_j} \rangle^*} \underbrace{\left(\int dE' \rho(E') \frac{e^{-\beta E'}}{Z} \langle \phi_{E'} | e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} | \phi_{E'} \rangle \right)}_{\langle e^{i\mathbf{q} \cdot \hat{\mathbf{r}}_k} \rangle}$$



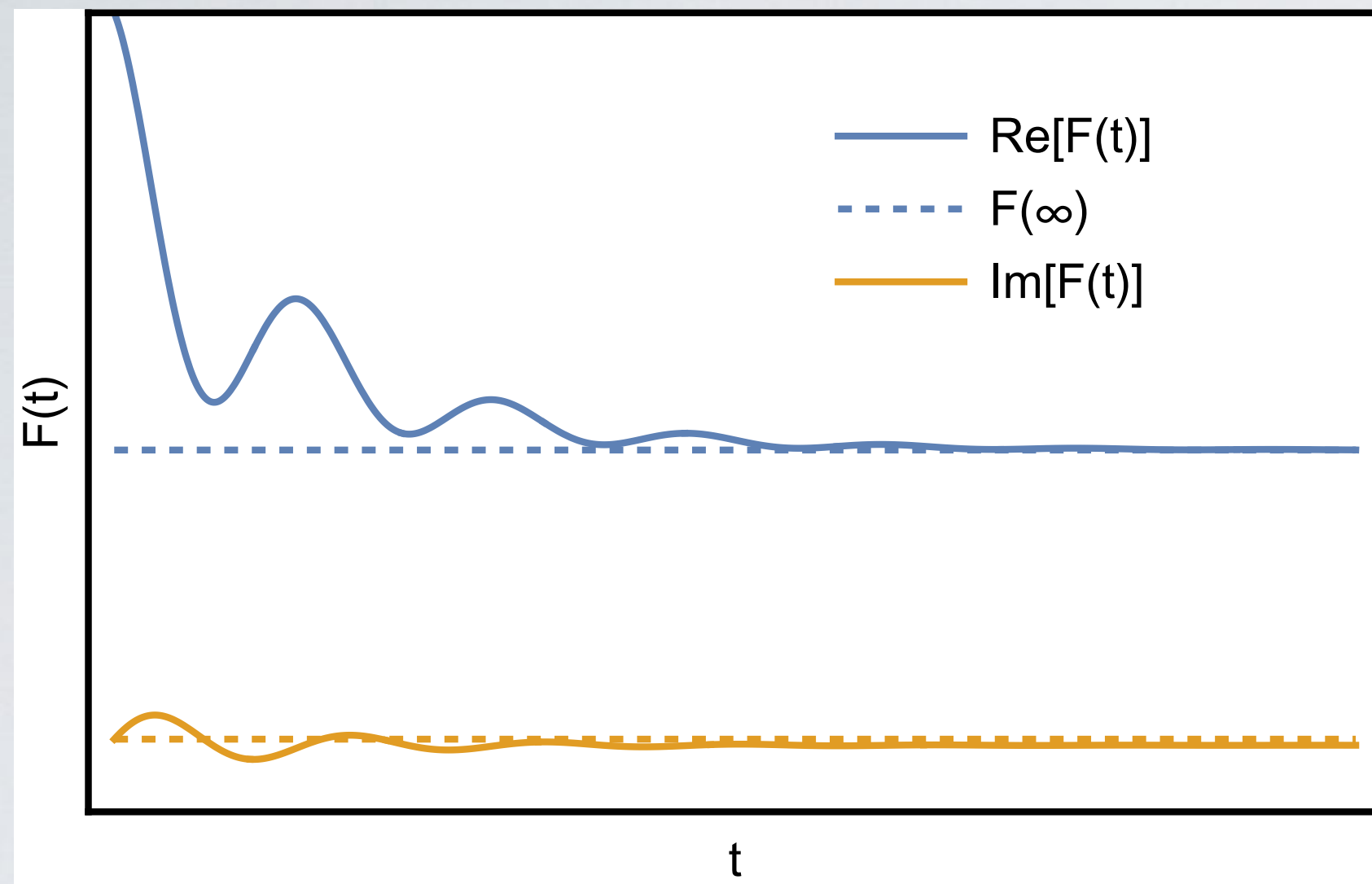
The partial intermediate scattering functions $\langle e^{-i\mathbf{q}\cdot\hat{\mathbf{r}}_j(0)} e^{i\mathbf{q}\cdot\hat{\mathbf{r}}_k(t)} \rangle$ are normal time correlation functions which do **not** fulfil the relation

$$\langle e^{-i\mathbf{q}\cdot\hat{\mathbf{r}}_j(0)} e^{i\mathbf{q}\cdot\hat{\mathbf{r}}_k(t)} \rangle \stackrel{t \rightarrow \infty}{\sim} \langle e^{-i\mathbf{q}\cdot\hat{\mathbf{r}}_j} \rangle \langle e^{i\mathbf{q}\cdot\hat{\mathbf{r}}_k} \rangle$$

expected from classical statistical physics.

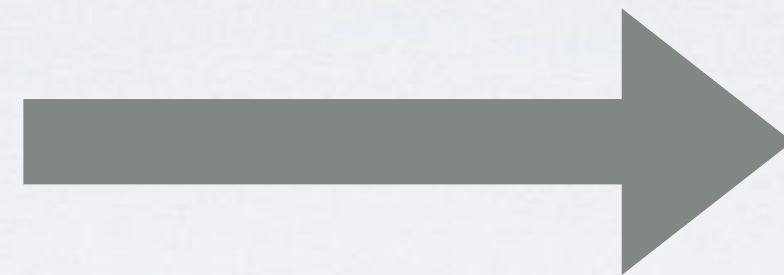
Regularized dynamic structure factor

Intermediate scattering function

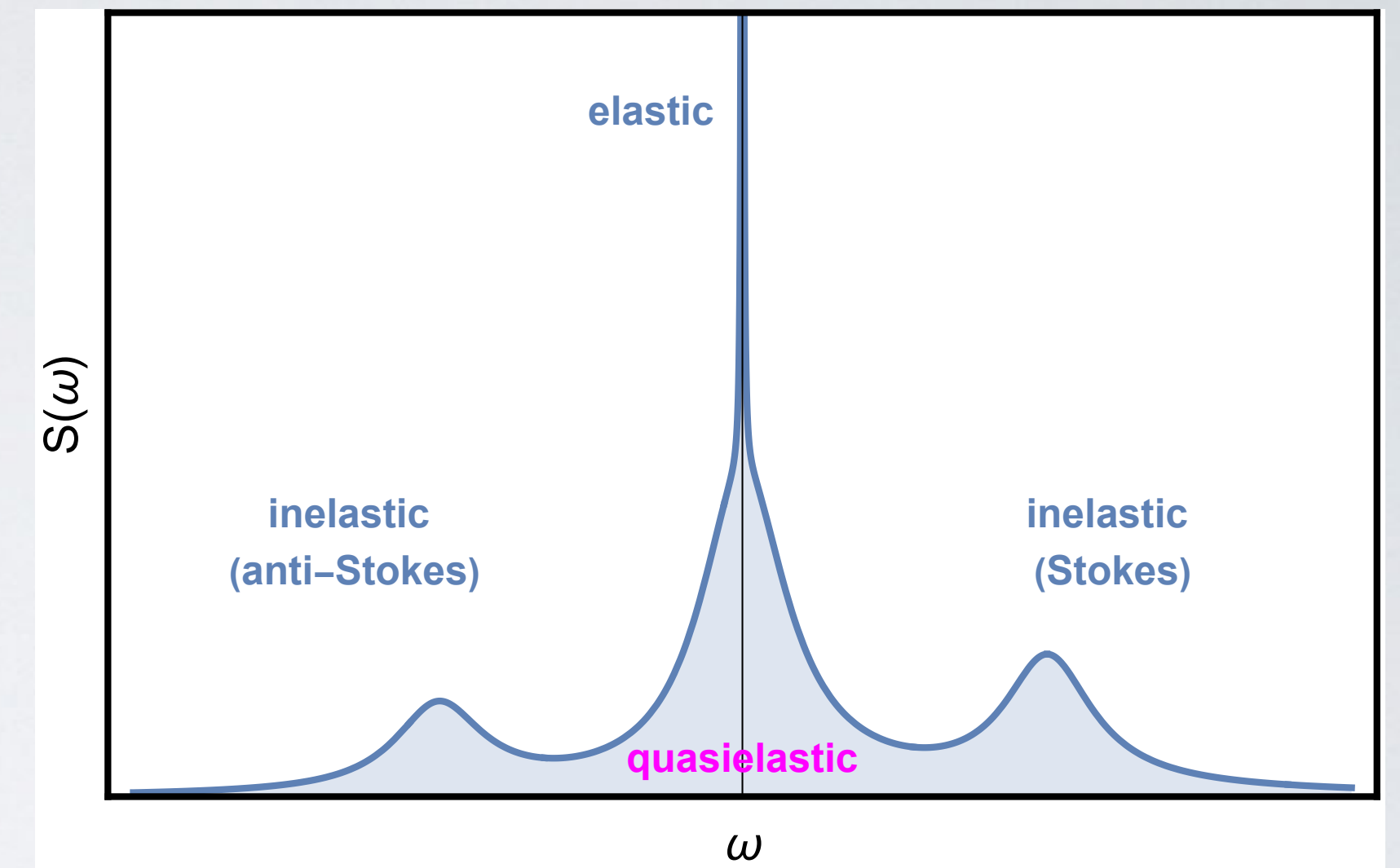


Regularised FT

$$S(\omega) = \lim_{\epsilon \rightarrow 0+} \frac{1}{\pi} \text{Re}[\hat{F}(i\omega + \epsilon)]$$



Dynamic structure factor



$$F(t) = F(\infty) + (F(0) - F(\infty)) \phi(t)$$

Fourier-Laplace transform:

$$\hat{F}(i\omega + \epsilon) = \int_0^\infty dt e^{-i\omega t} \boxed{e^{-\epsilon t} F(t)}$$

$$S(\omega) = F(\infty) \underbrace{\left\{ \lim_{\epsilon \rightarrow 0+} \frac{1}{\pi} \frac{\epsilon}{\omega^2 + \epsilon^2} \right\}}_{\delta(\omega)} + (F(0) - F(\infty)) \underbrace{\left\{ \lim_{\epsilon \rightarrow 0+} \frac{1}{\pi} \text{Re} [\hat{\phi}(i\omega + \epsilon)] \right\}}_{\tilde{\phi}(\omega)}$$

Overlap of the two components for $\omega \approx \epsilon$!

QENS from asymptotic analysis of $F(q,t)$

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

Von *J. Karamata* in Belgrad.

SUR UN MODE DE CROISSANCE RÉGULIÈRE.
THÉORÈMES FONDAMENTAUX;

PAR M. J. KARAMATA

(Beograd).

$$h(t) \stackrel{t \rightarrow \infty}{\sim} L(t)t^\rho \longleftrightarrow \boxed{\hat{h}(s) \equiv \int_0^\infty dt e^{-st} h(t)} \stackrel{s \rightarrow 0}{\sim} L\left(\frac{1}{s}\right) \frac{\Gamma(1+\rho)}{s^{1+\rho}} \quad (\rho > -1)$$

$$\frac{L(\lambda t)}{L(t)} \stackrel{t \rightarrow \infty}{\sim} 1 \quad (\lambda > 0)$$

Karamata's theorem

**Slowly growing/
varying function**

$$F(t) = F(\infty) + (F(0) - F(\infty)) \phi(t)$$

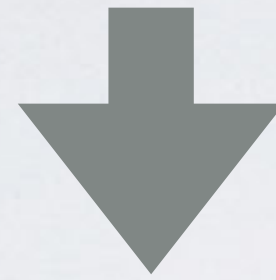
$$\hat{F}(s) \stackrel{s \rightarrow 0}{\sim} \frac{1}{s} F\left(\frac{1}{s}\right) = F(\infty) \frac{1}{s} + (F(0) - F(\infty)) \frac{1}{s} \phi\left(\frac{1}{s}\right)$$

**Apply Karamata's
theorem with $\rho=0$**

Inferring $S(\omega)$ for $\omega \rightarrow 0$ from $F(t)$ for $t \rightarrow \infty$

G. R. Kneller, PNAS USA 115(38):9450–9455, 2018

$$F(t) = F(\infty) + (F(0) - F(\infty)) \phi(t)$$

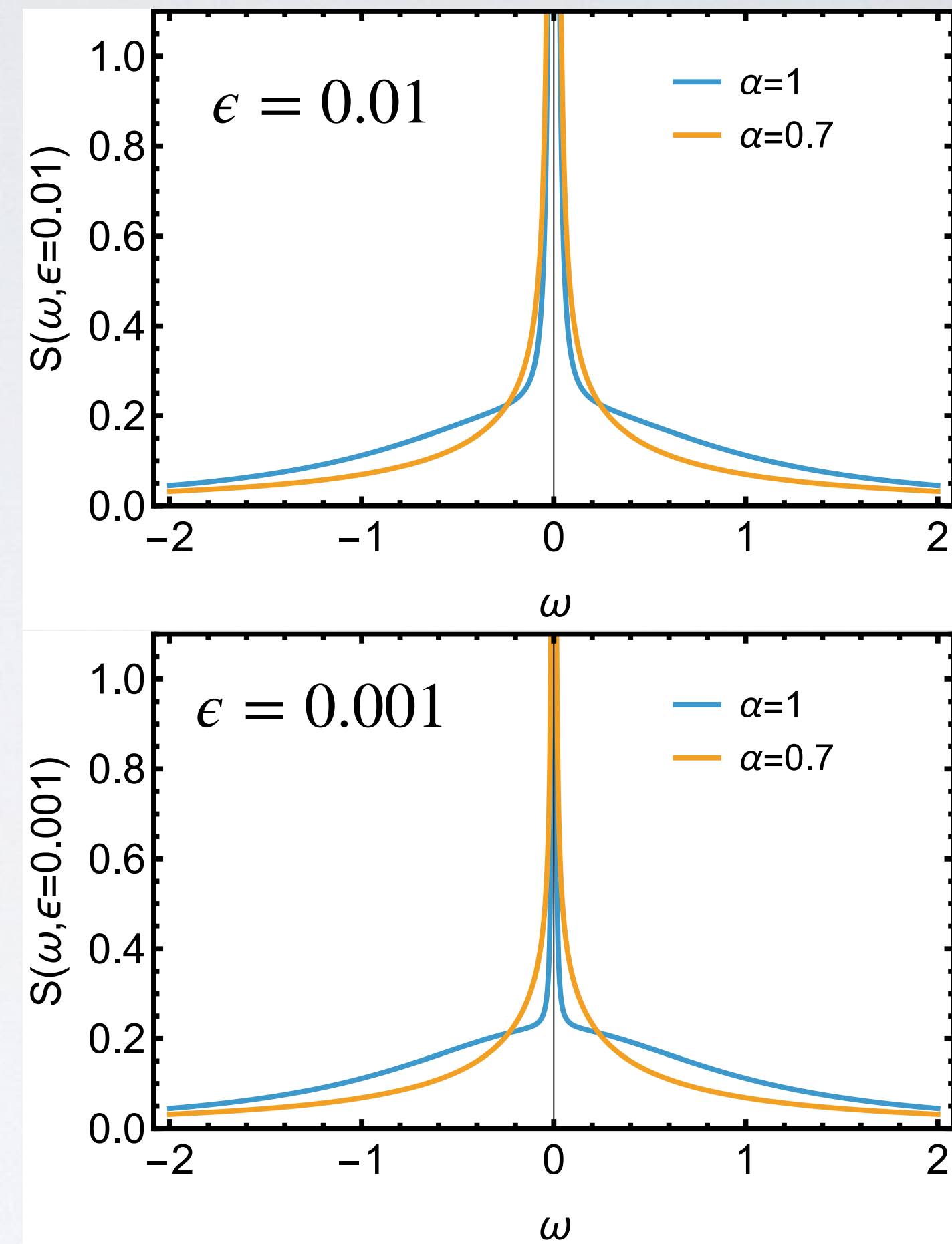


$$S_s(\omega) \stackrel{\omega \rightarrow 0}{\sim} \lim_{\epsilon \rightarrow 0+} \frac{1}{\pi} \Re \left\{ \frac{F_s(1/(i\omega + \epsilon))}{i\omega + \epsilon} \right\}$$

- The asymptotic form of $F(t)$ for $t \rightarrow \infty$ determines asymptotic form of $S(\omega)$ for $\omega \rightarrow 0$.
- For power law relaxation

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

the elastic and quasi-elastic line are fused.



$$E_\alpha(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(1 + \alpha n)} \quad \text{Mittag-Leffler function}$$

Quasi-elastic “contamination” of the elastic line

$$\frac{S(0)}{S_{\text{el}}(0)} \stackrel{\epsilon \rightarrow 0}{\sim} 1 + e^{-1/\epsilon} \frac{F(0) - F(\infty)}{F(\infty)} \quad \text{Exponential relaxation}$$

$$\frac{S(0)}{S_{\text{el}}(0)} \stackrel{\epsilon \rightarrow 0}{\sim} 1 + \frac{\epsilon^\alpha}{\Gamma(1 - \alpha)} \frac{F(0) - F(\infty)}{F(\infty)} \quad \text{Power law relaxation}$$

Classical energy landscapes and non-exponential relaxation

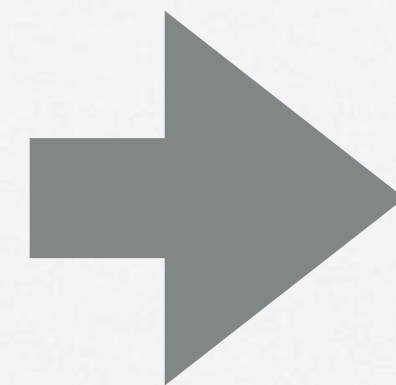
Complex systems display multiscale self-similar relaxation

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:

$$\phi(t) \stackrel{t \rightarrow \infty}{\sim} (t/\tau)^{-\alpha} \quad (0 < \alpha < 1)$$



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

Self-similar relaxation dynamics seen in CO-rebinding kinetics

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

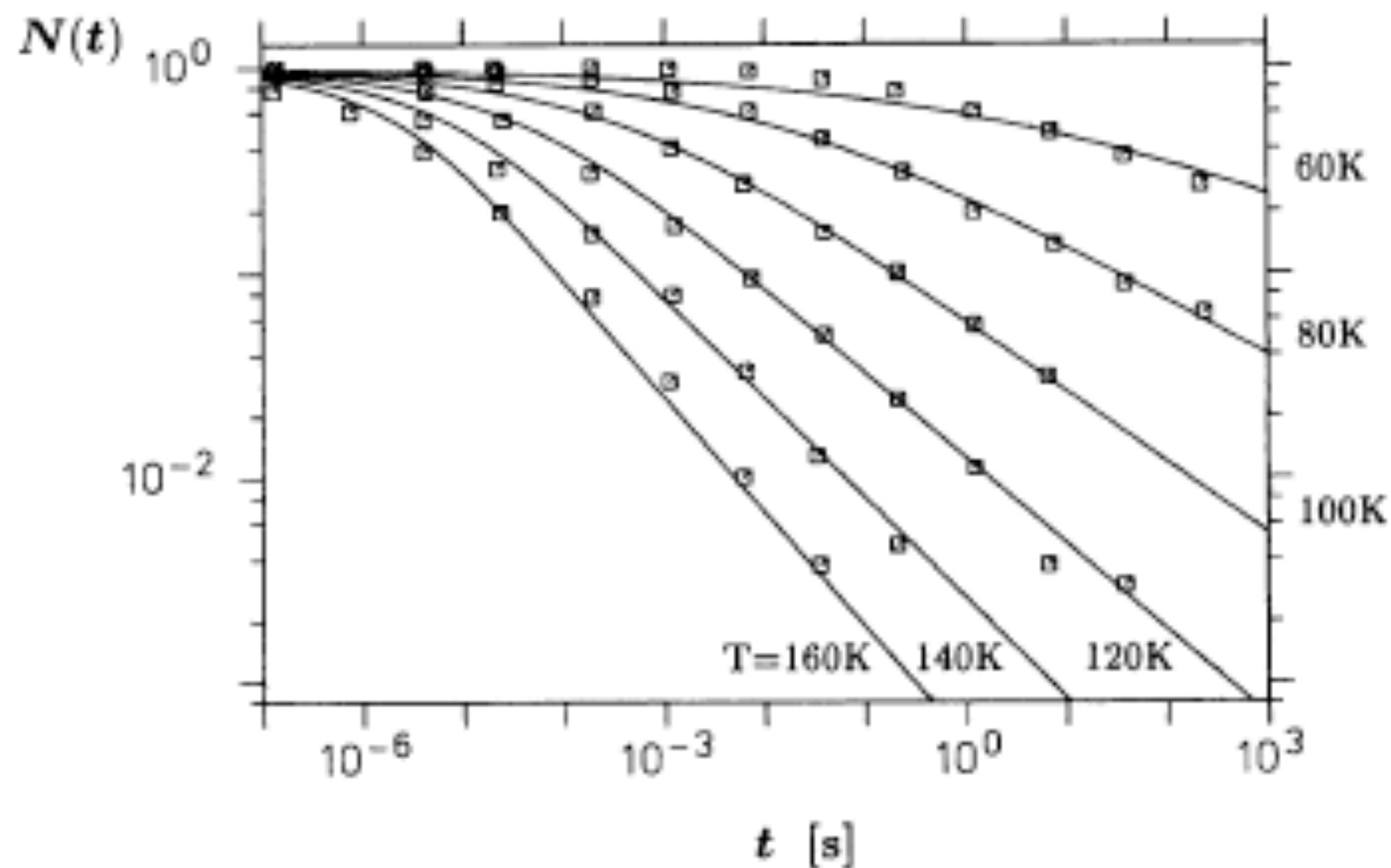


FIGURE 2 Three-parameter model Eq. 32 for rebinding of CO to Mb after photo dissociation. The parameters are $\tau_m = 8.4 \times 10^{-10}$ s, $\alpha = 3.5 \times 10^{-3} K^{-1}$ and $k = 130$, the data points are from Austin et al. (1975).

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

Mittag-Leffler function

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

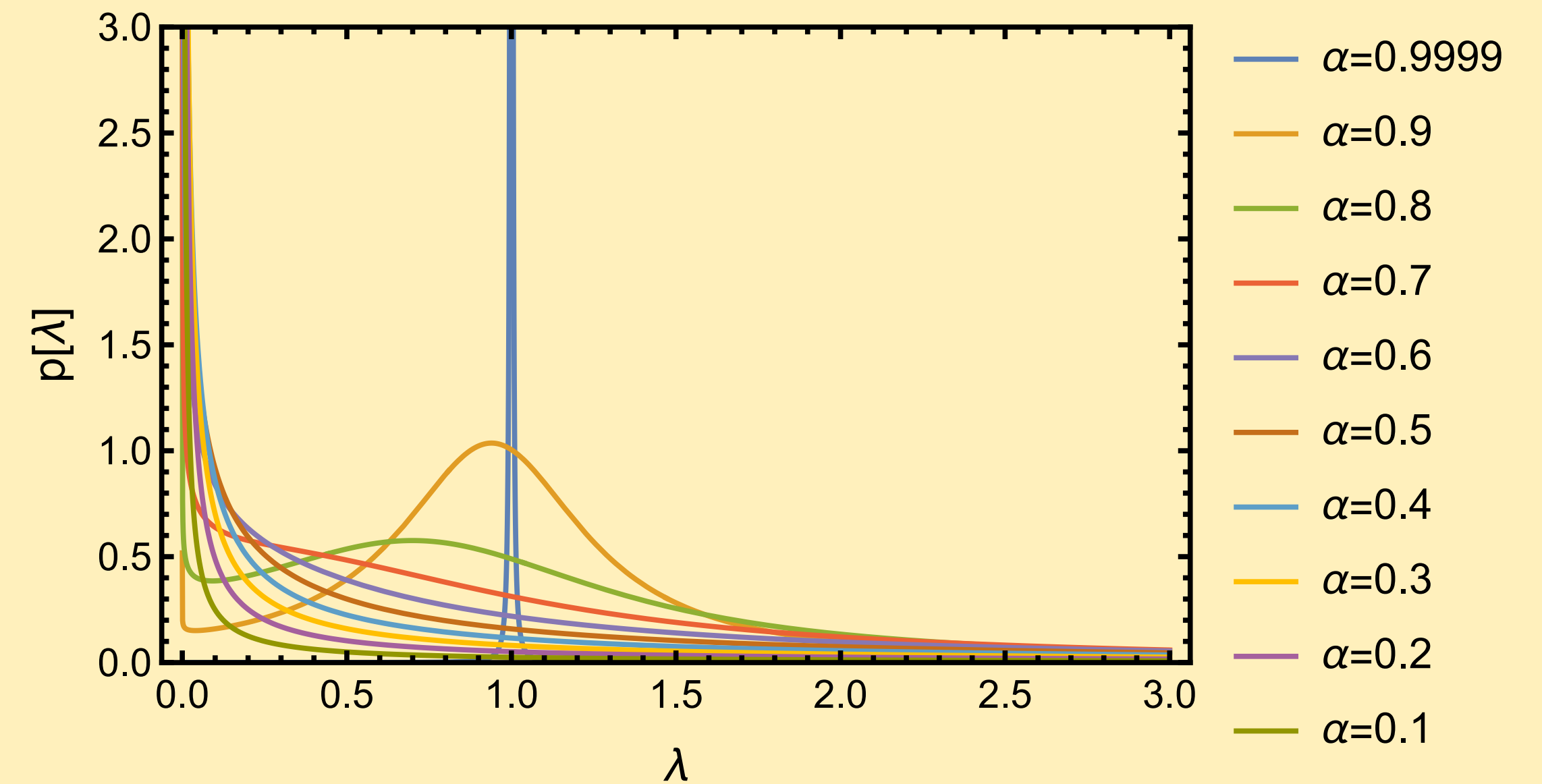
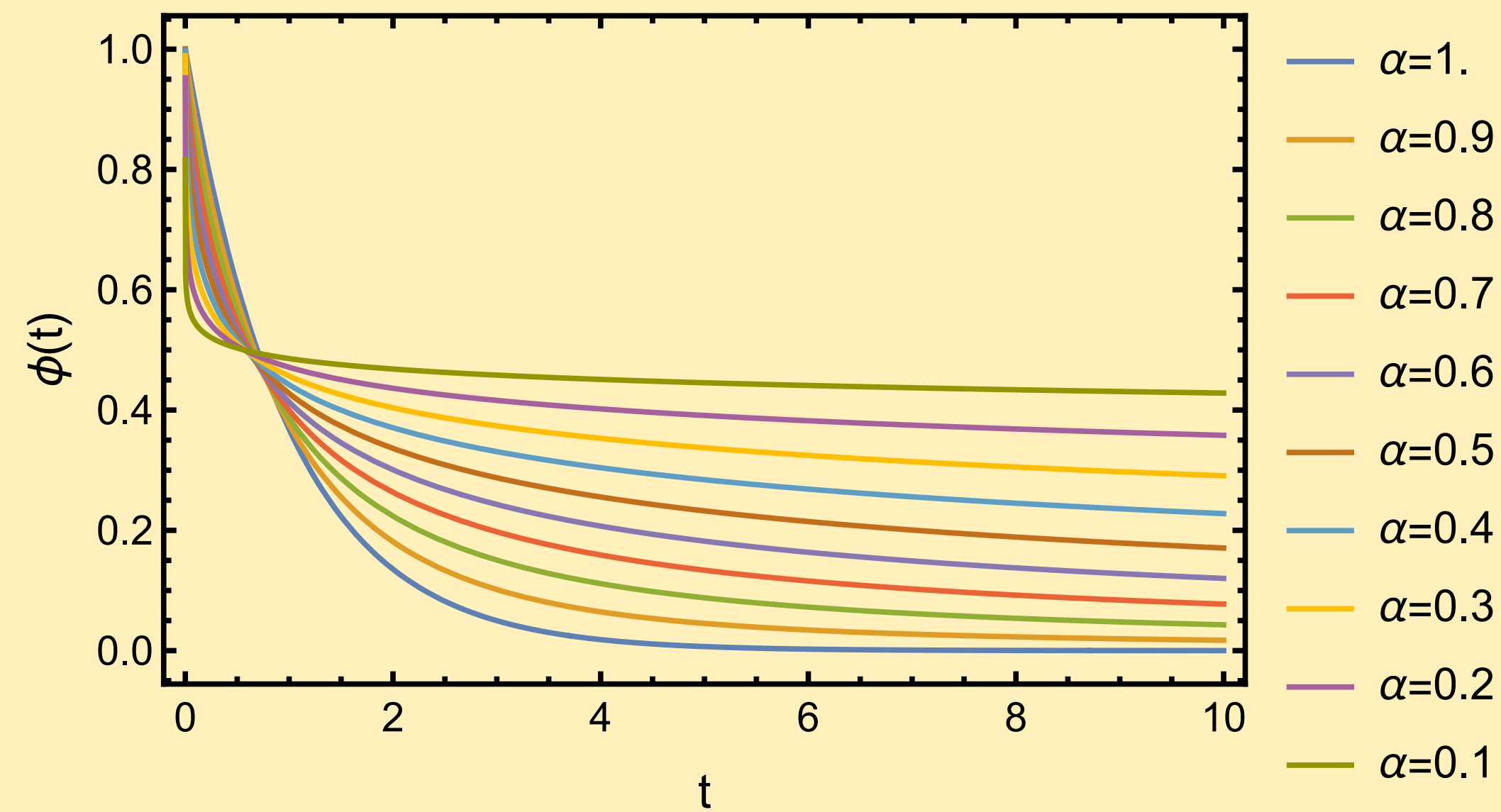
$$E_{\alpha}(-(t/\tau)^{\alpha}) \stackrel{t \rightarrow \infty}{\sim} \frac{(t/\tau)^{-\alpha}}{\Gamma(1 - \alpha)}$$

“Stretched” ML function and relaxation rate spectrum

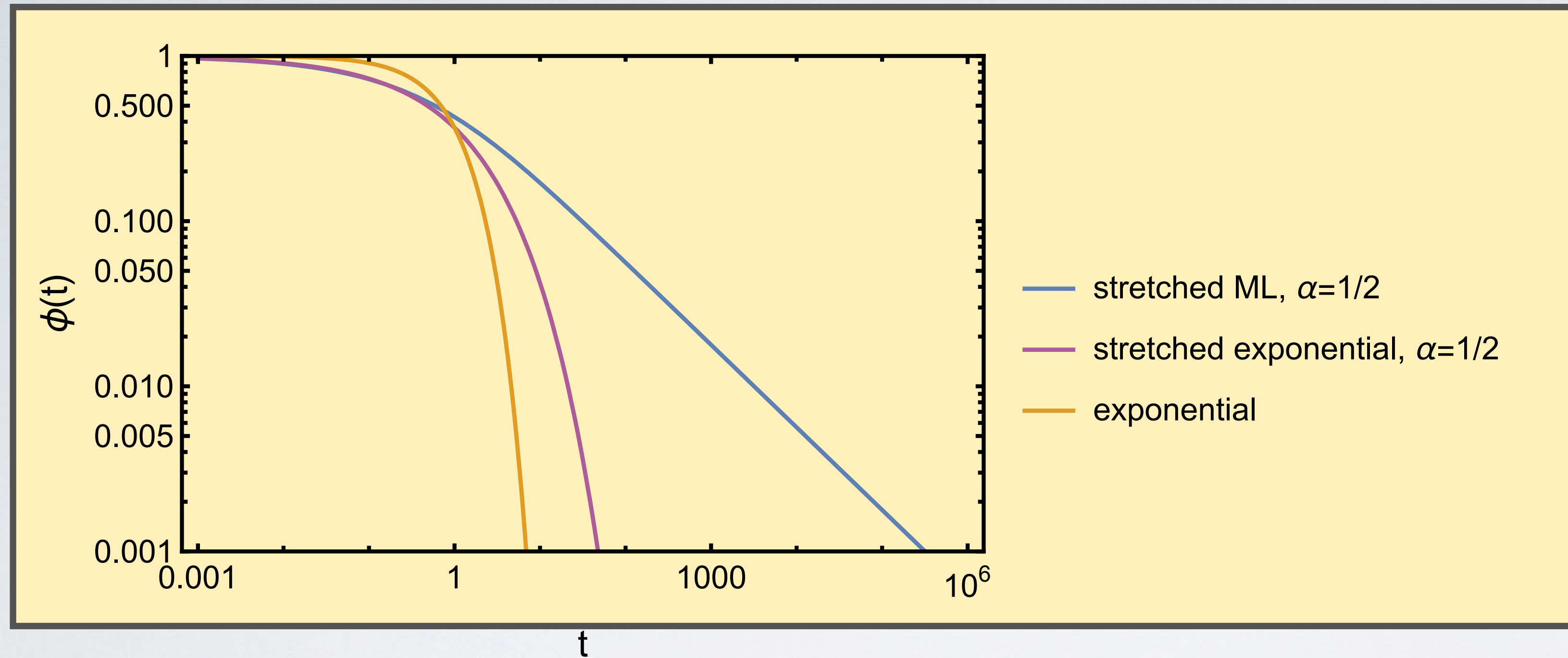
$$\phi(t) = \int_0^\infty d\lambda p(\lambda) e^{-\lambda t}$$

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

$$p(\lambda) = \frac{\sin(\pi\alpha)}{\pi\lambda(\lambda^{-\alpha} + \lambda^\alpha + 2\cos(\pi\alpha))}$$



Mittag-Leffler relaxation 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

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

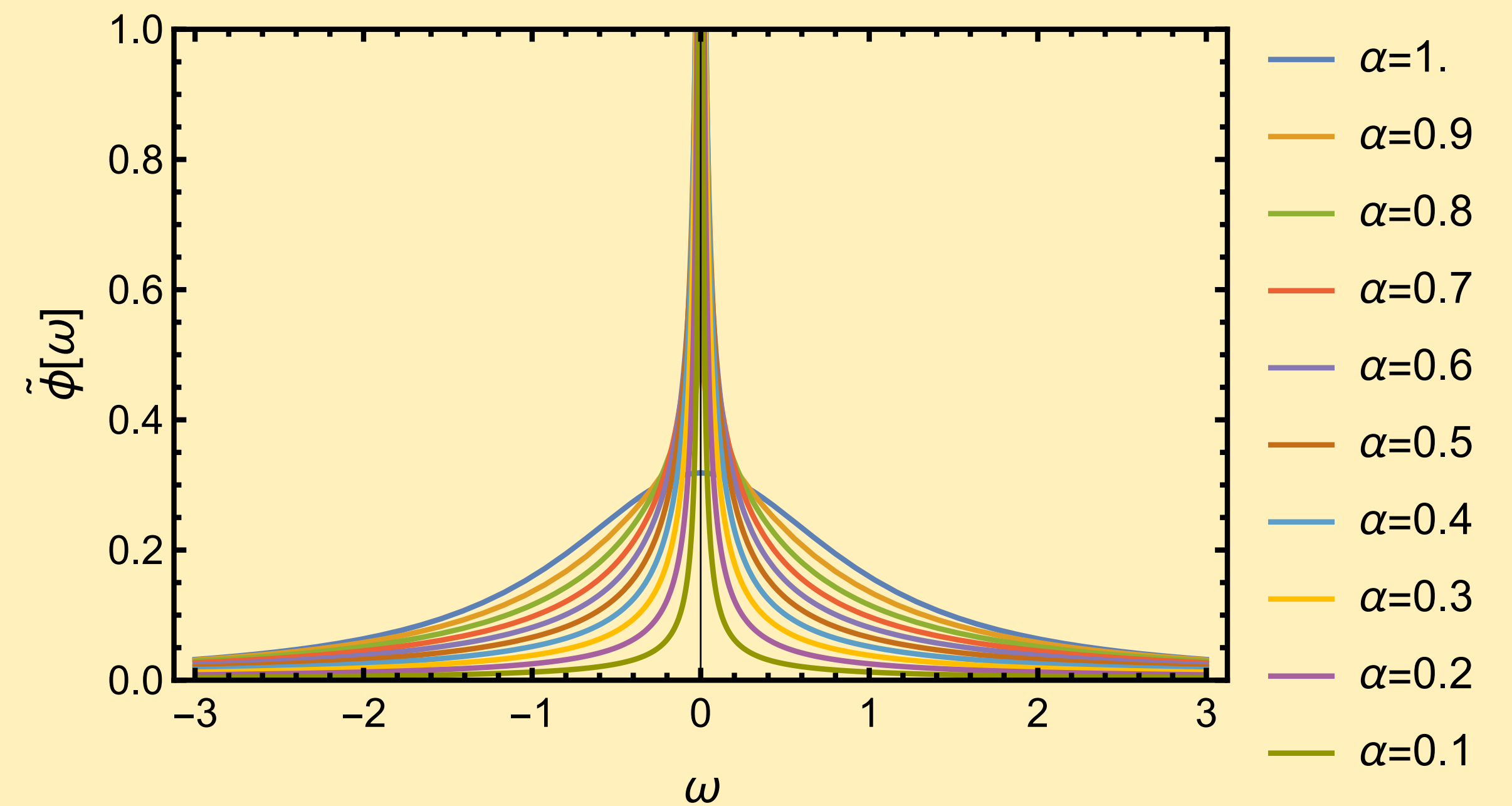
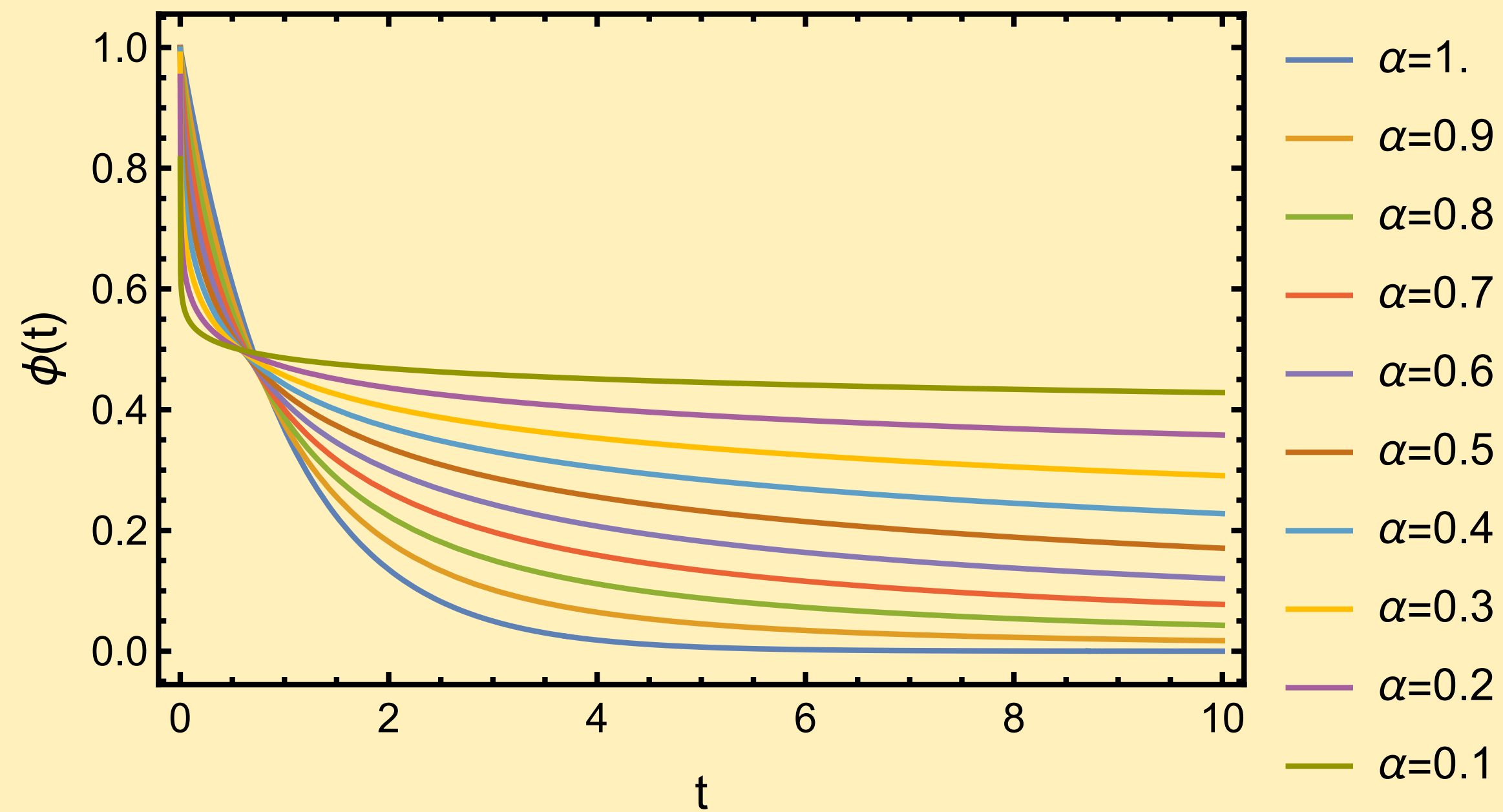
Fractional derivative = memory effects

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

“Stretched” ML function and Fourier spectrum

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

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



Asymptotic Analysis of Quasielastic Neutron Scattering Data from Human Acetylcholinesterase Reveals Subtle Dynamical Changes upon Ligand Binding

M. Saouessi, J. Peters, and G. R. Kneller

J. Chem. Phys., 150(16):161104, avril 2019

$$F(t) = EISF + (1 - EISF)E_{\alpha}\left(-(t/\tau)^{\alpha}\right), \quad \text{fixed } q.$$

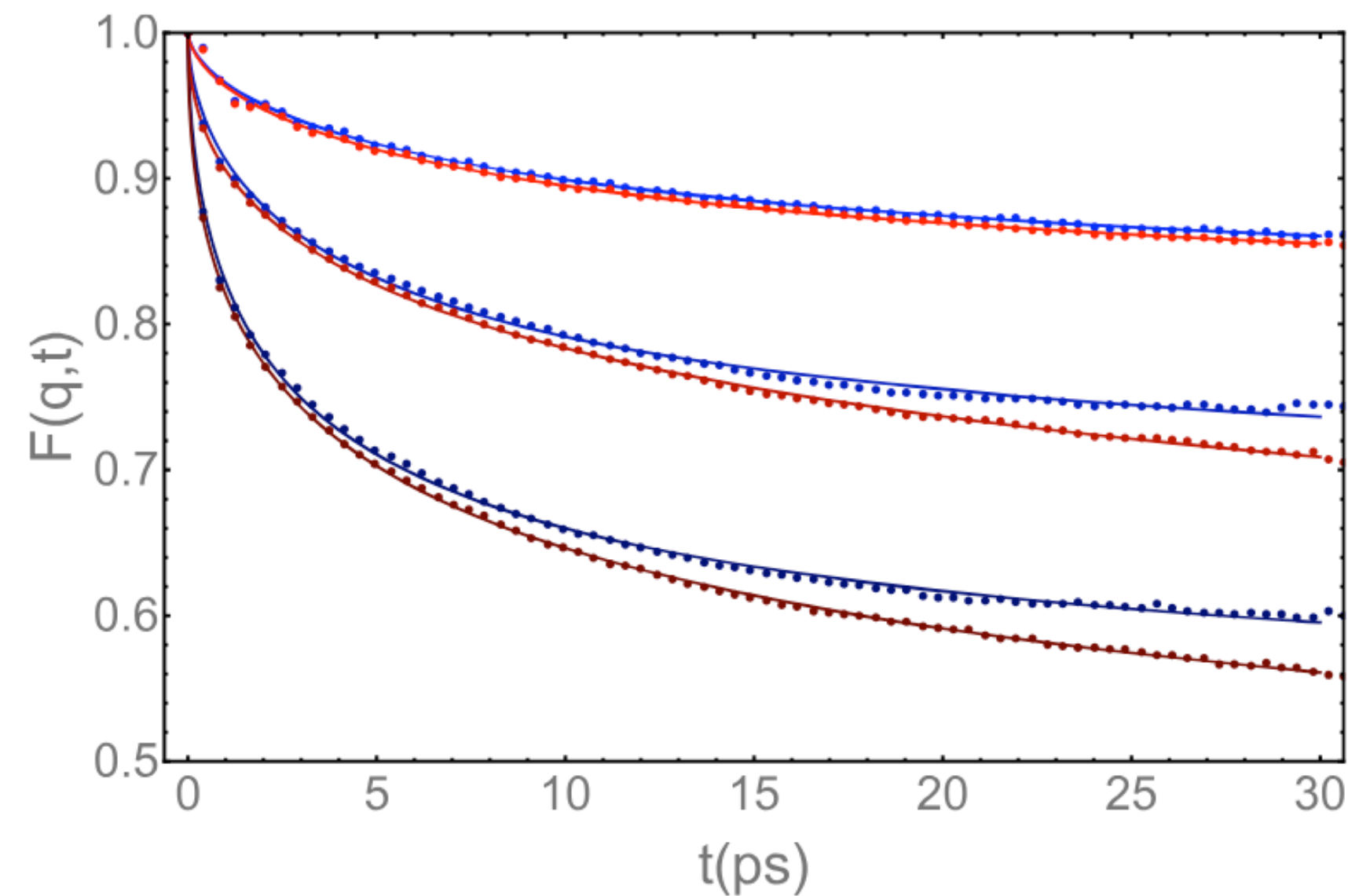
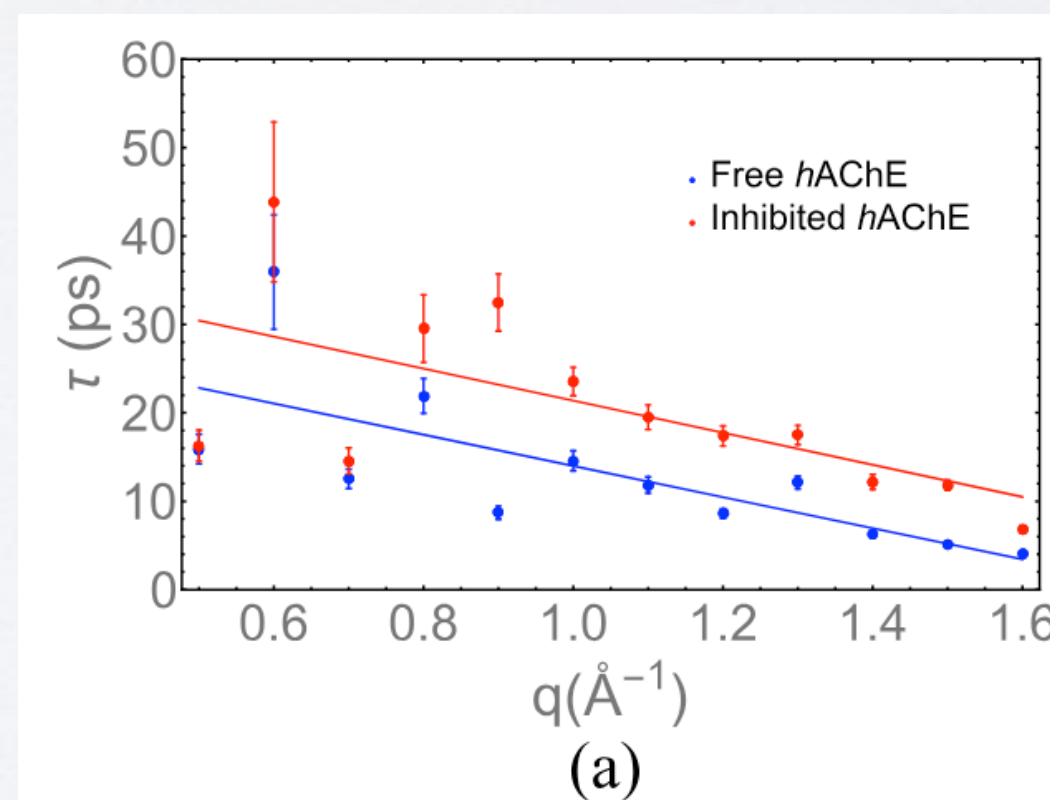
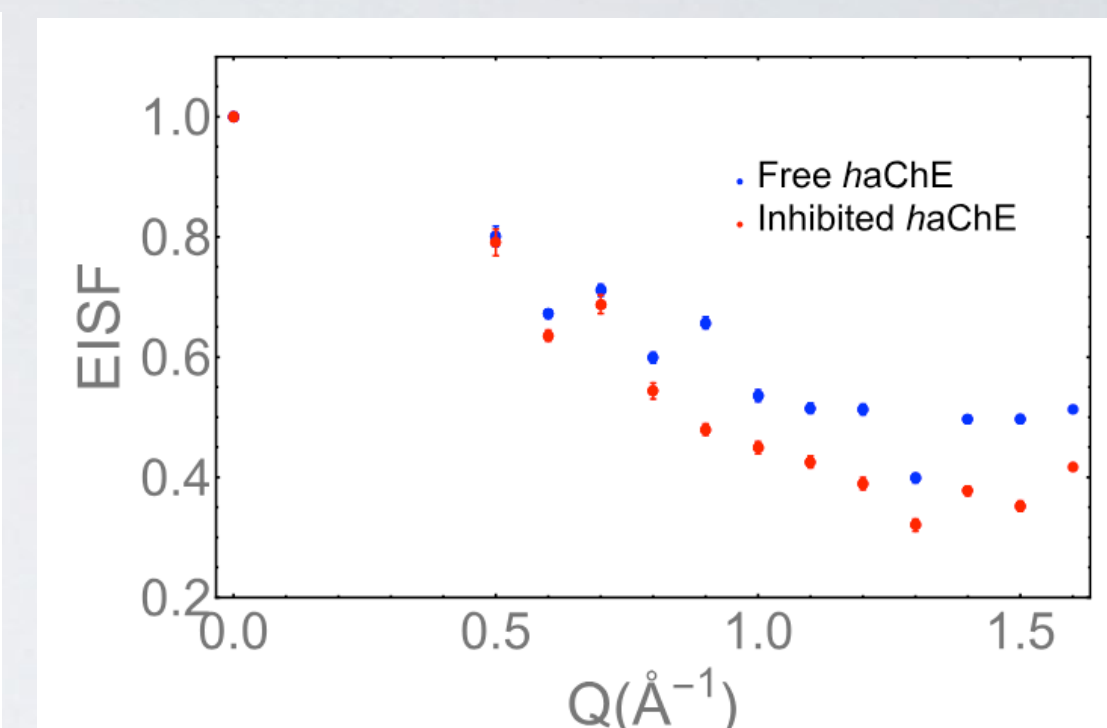
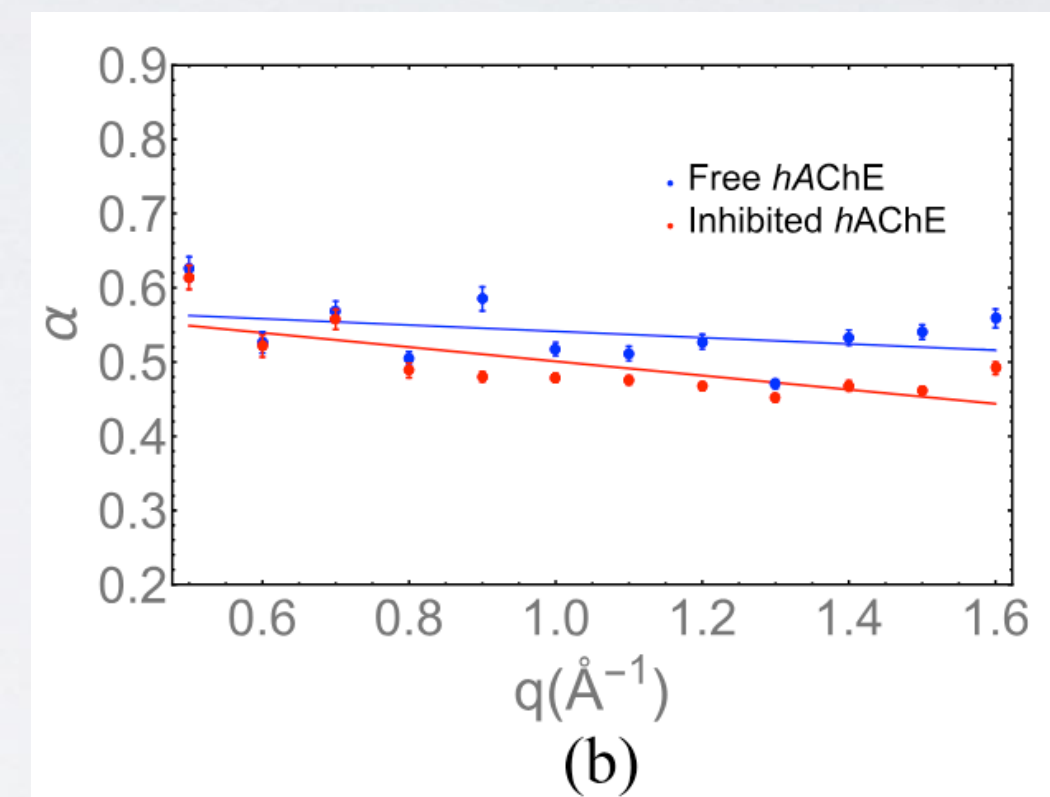
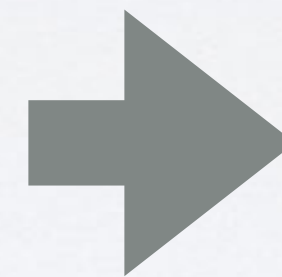


FIG. 1. $F(q, t)$ obtained from the resolution-deconvolved QENS spectra (points) and corresponding model fits (solid lines) for $q = 0.5, 0.9, 1.5 \text{ \AA}^{-1}$ from top to bottom. Blue and red correspond, respectively, to free and HupA-inhibited hAChE



Signature of functional enzyme dynamics in quasielastic neutron scattering spectra: The case of phosphoglycerate kinase

A. N. Hassani, L. Haris, M. Appel, T. Seydel, A. M. Stadler, and G. R. Kneller

The Journal of Chemical Physics, 159(14):141102, 2023

$$F(t) = \underbrace{e^{-Dq^2t}}_{\text{inter-domain}} \times \underbrace{(EISF + (1 - EISF)E_\alpha(-(t/\tau)^\alpha))}_{\text{intra-domain}} \quad (\text{fixed } q)$$

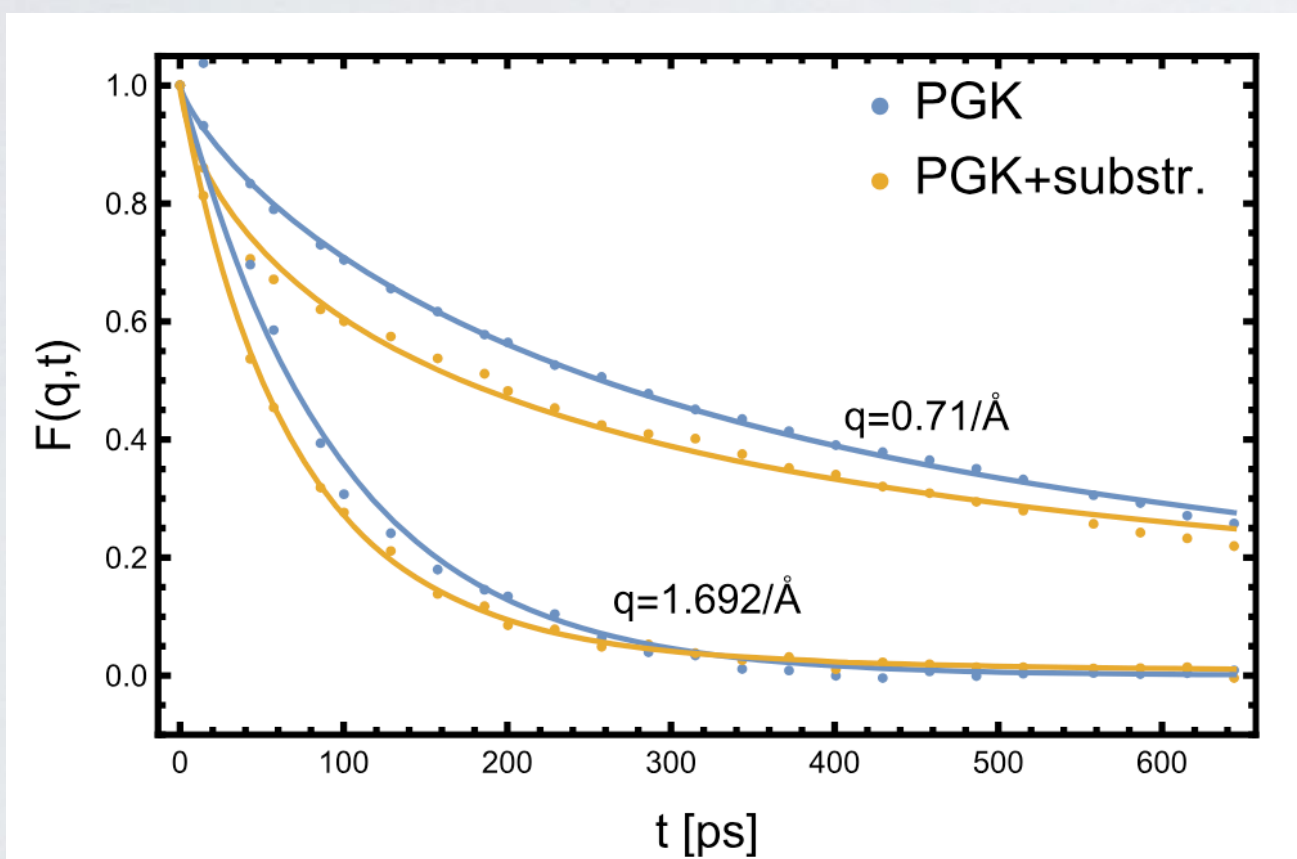
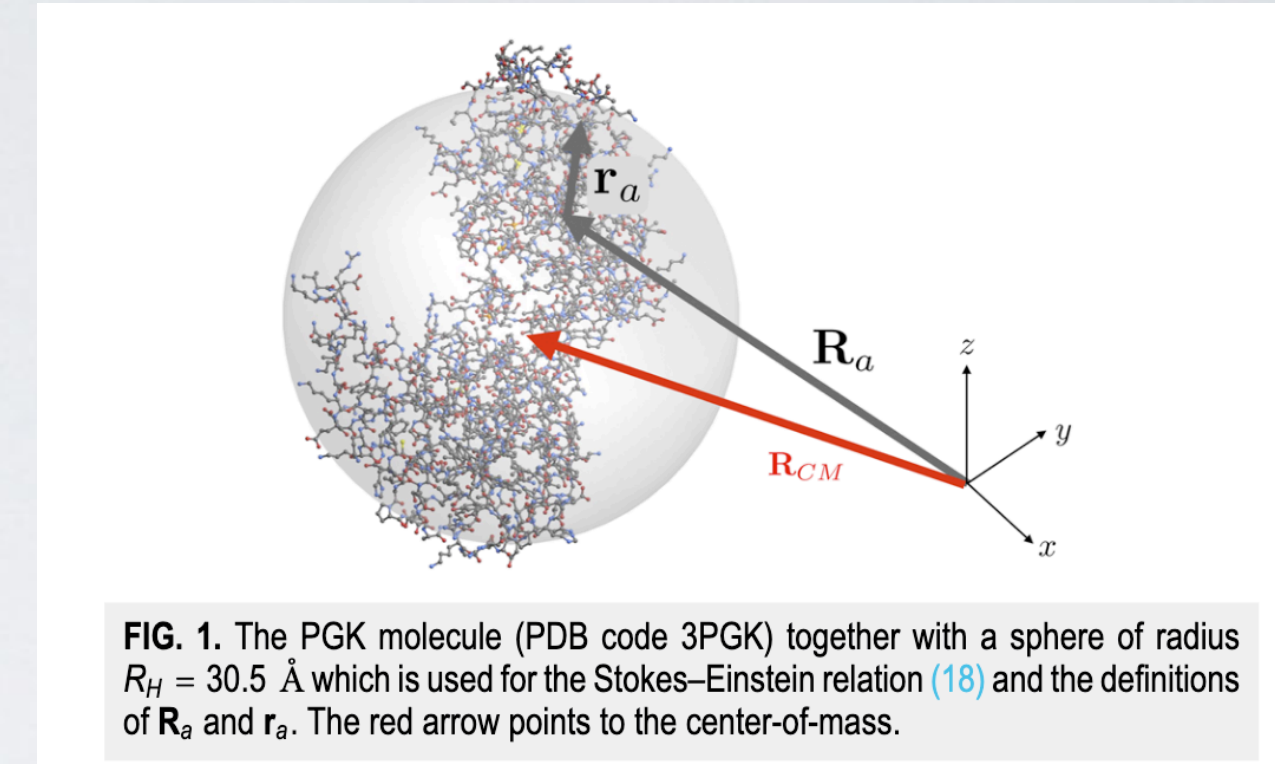
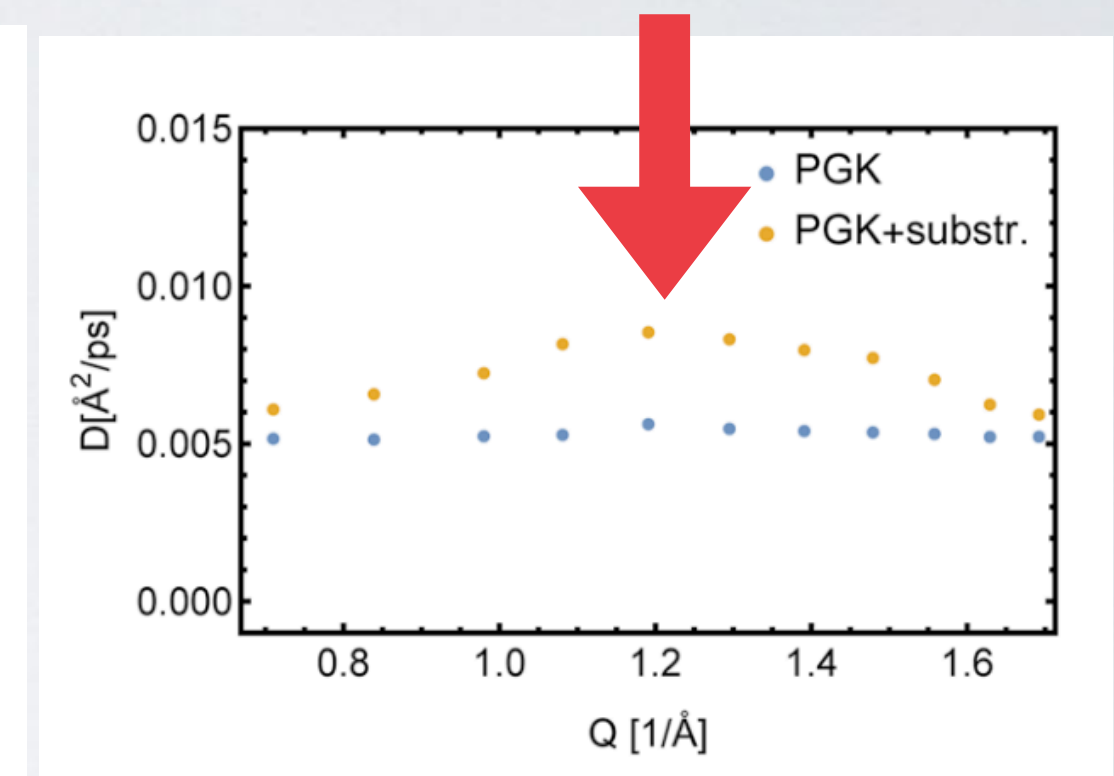
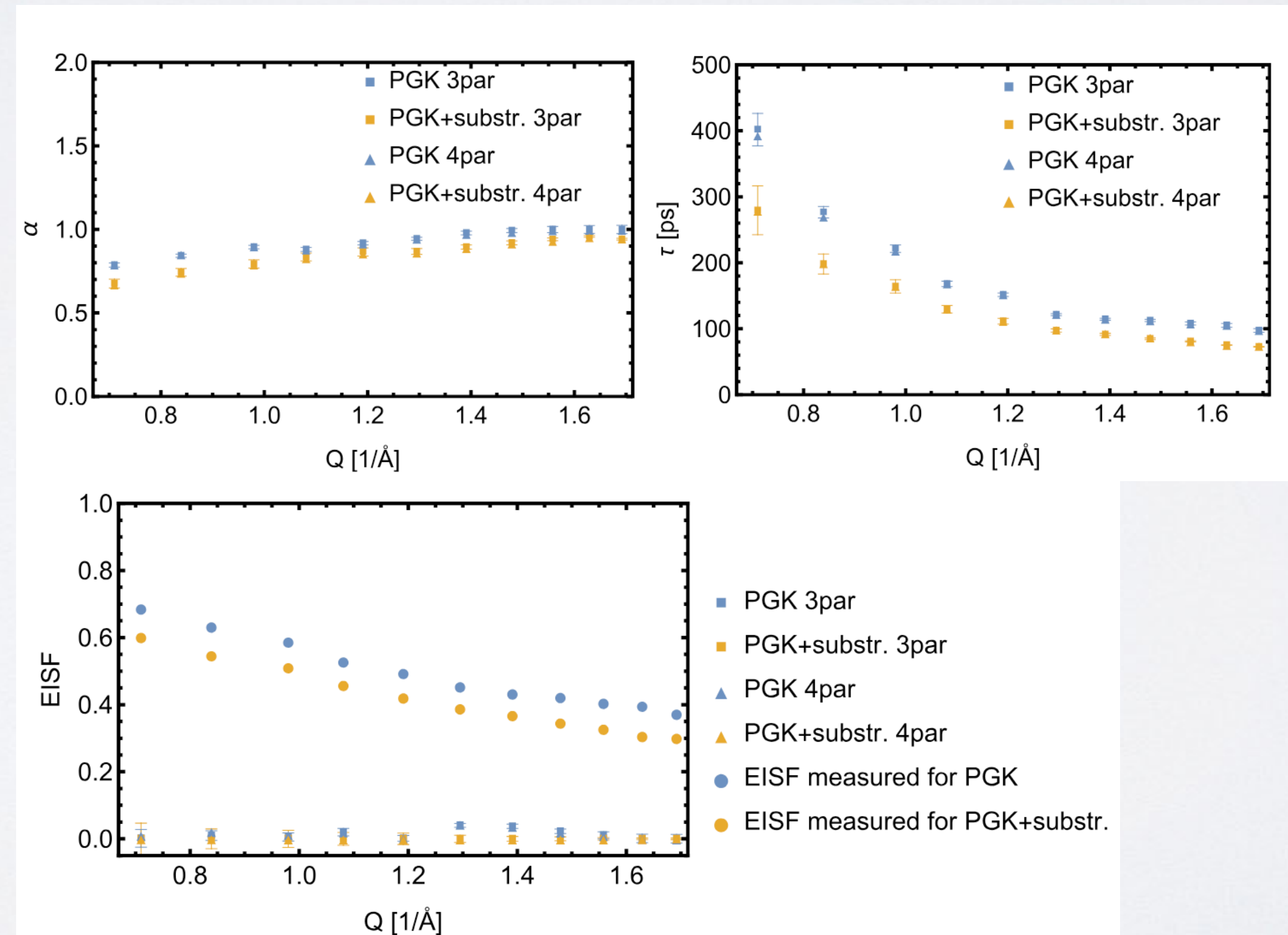
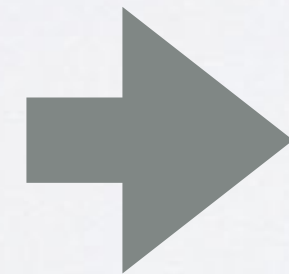


FIG. 3. Resolution-deconvolved $F(q,t)$ of PGK in deuterated solution without and in presence of substrates (blue and yellow dots, respectively) and the corresponding fits (blue and yellow line, respectively).



Relating relaxation rates to the “roughness” of a **classical** energy landscape

The distribution barrier heights corresponds to a distribution of rates for kinetic processes 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**.

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

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

Diffusion in a rough potential

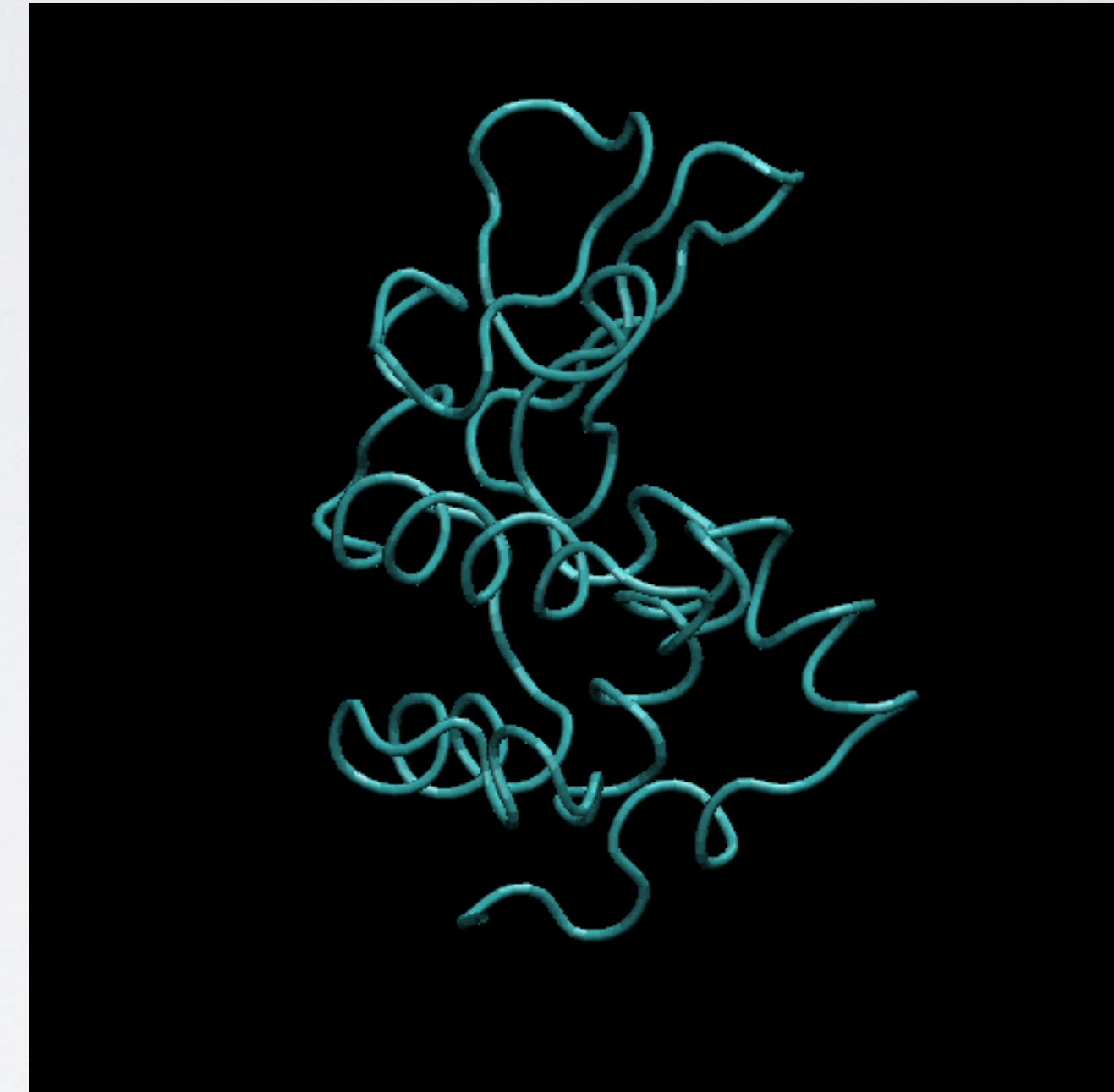
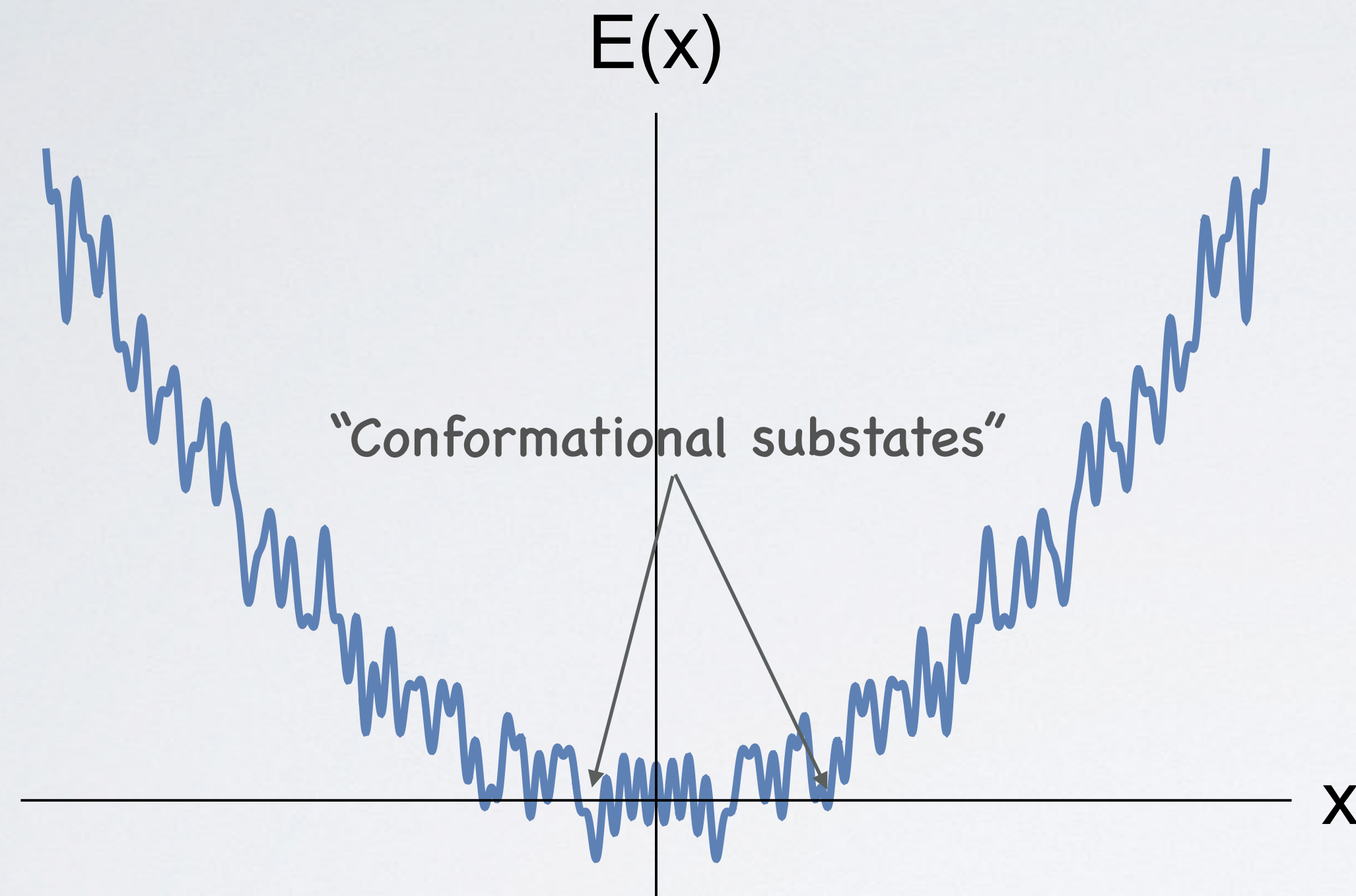
ROBERT ZWANZIG

University of Maryland, College Park, MD 20742

Proc. Natl. Acad. Sci. USA
Vol. 85, pp. 2029–2030, April 1988
Physics

$$D^* = D \exp[-(\epsilon/k_B T)^2].$$

Energy landscapes – a kinetic picture of protein dynamics and kinetics



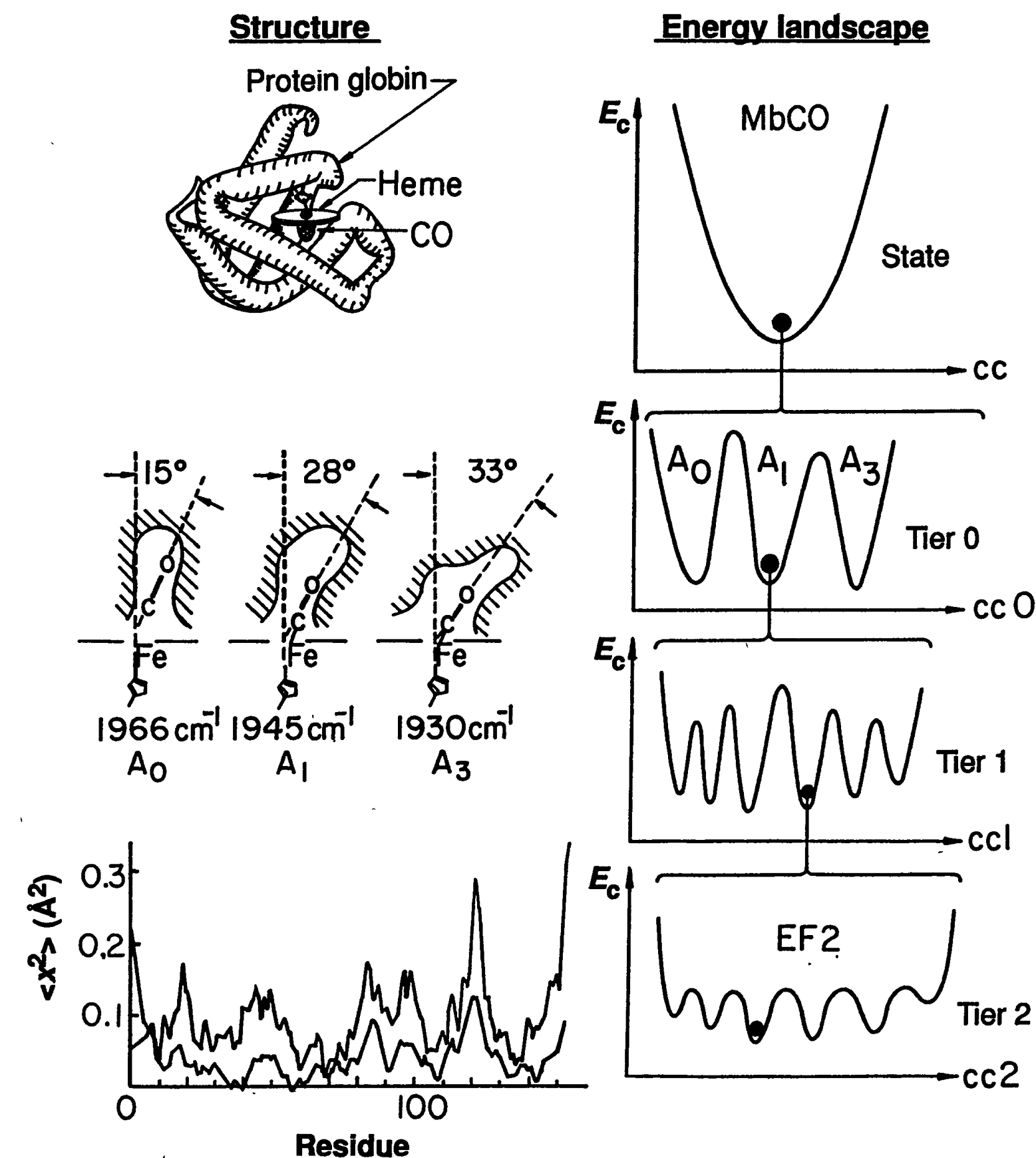
The protein jumps between different minima of the highly multidimensional (free) energy landscape which correspond to similar "conformational substates" (H. Frauenfelder et al, Science 254, 1598 (1991)).

Protein dynamics through jump kinetics

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

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

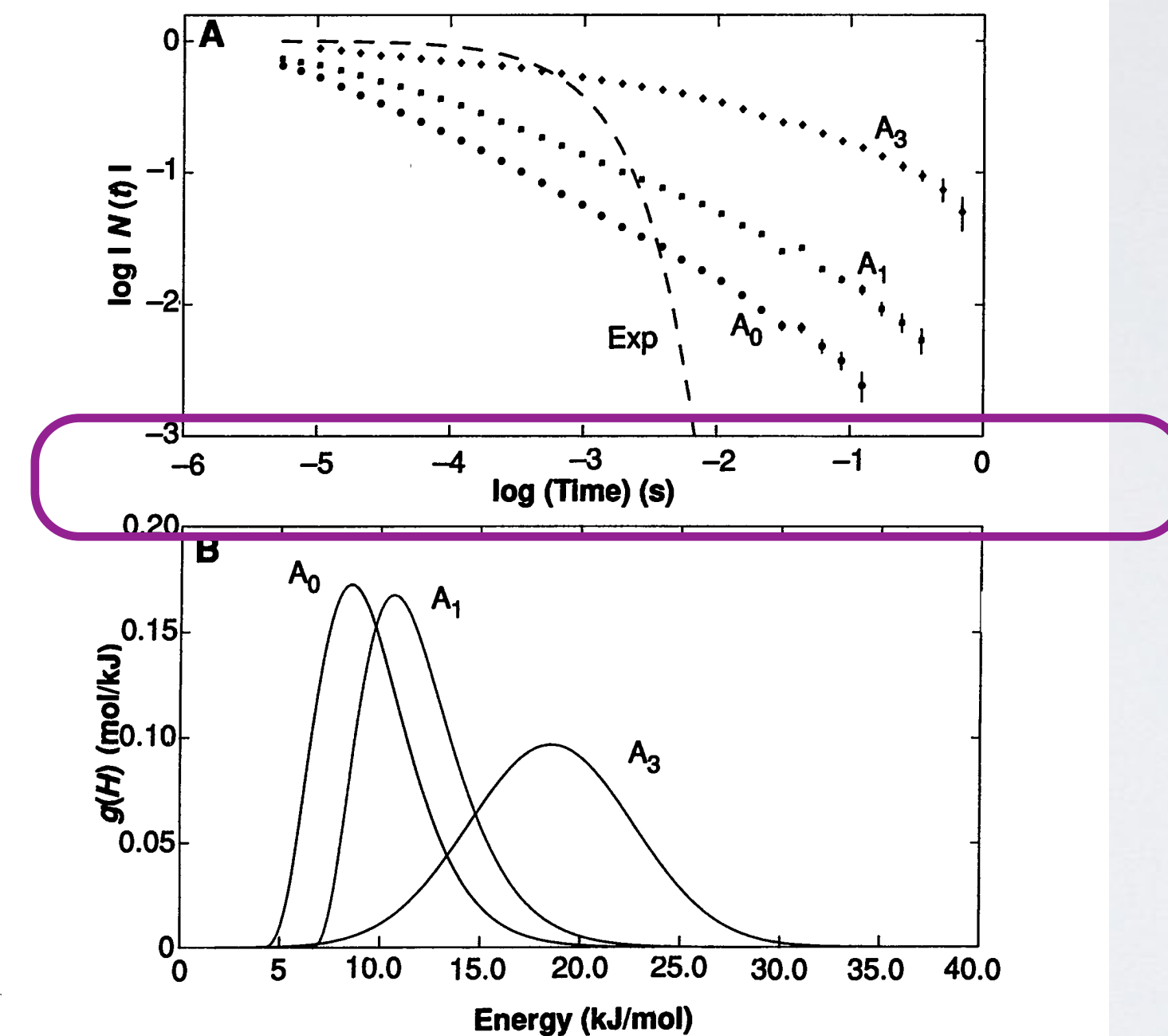
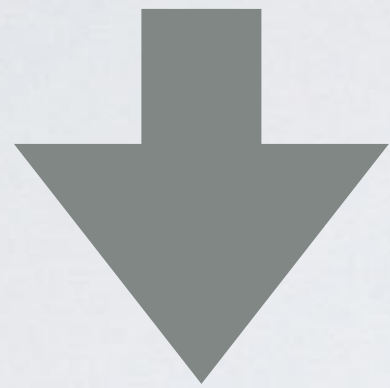


Fig. 2. Rebinding of CO to Mb after photodissociation, measured separately for the substates of tier 0 at pH 5.7. **(A)** $N(t)$ is the fraction of proteins that have not rebound a CO at the time t after photodissociation. All three substates (A₀, A₁, and A₃) rebound nonexponentially in time. **(B)**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

For diffusion in a smooth harmonic potential
(Ornstein-Uhlenbeck process)

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



Diffusion in a rough potential

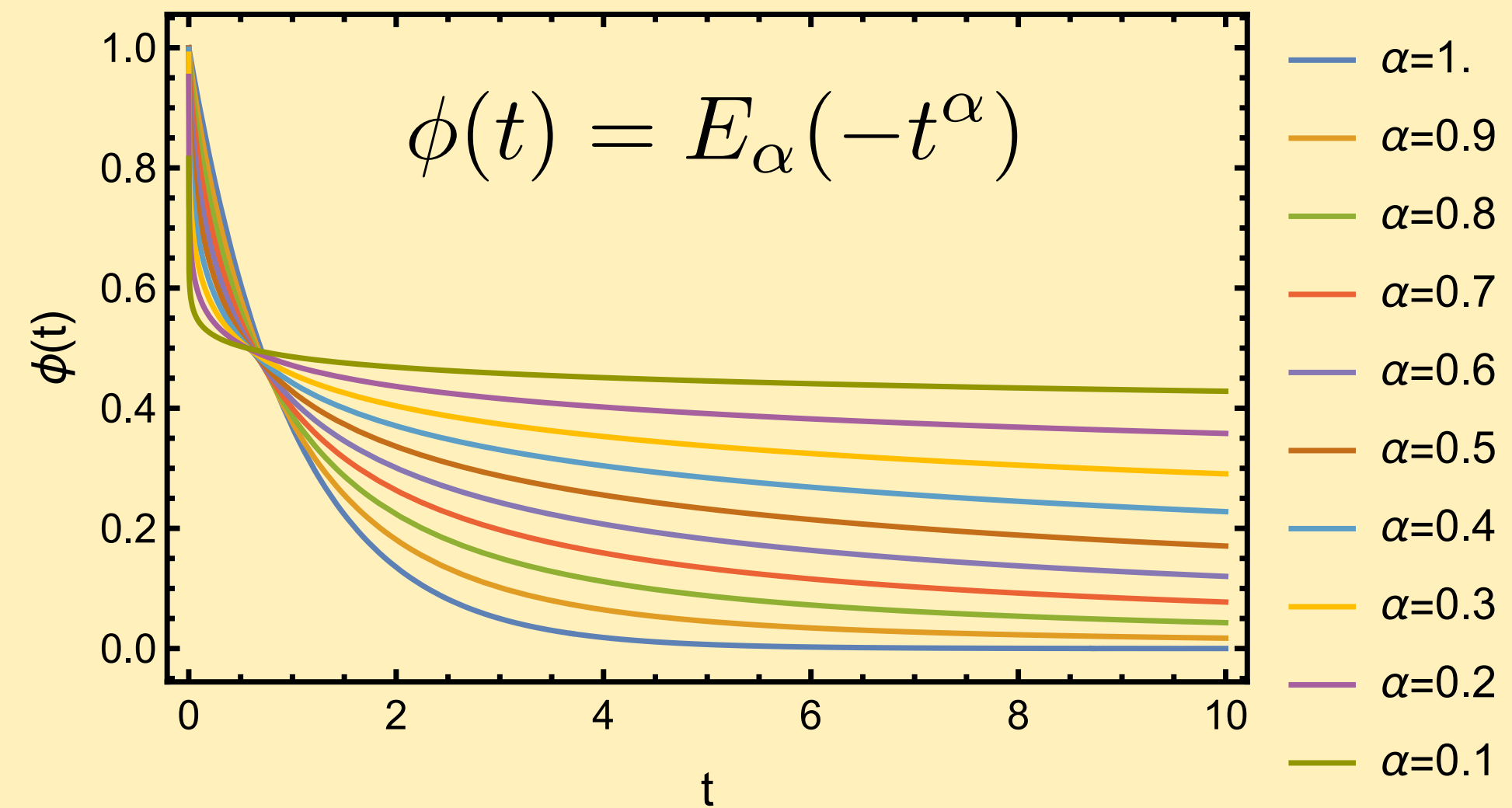
ROBERT ZWANZIG
University of Maryland, College Park, MD 20742

$$D = D_0 e^{-\epsilon^2}$$

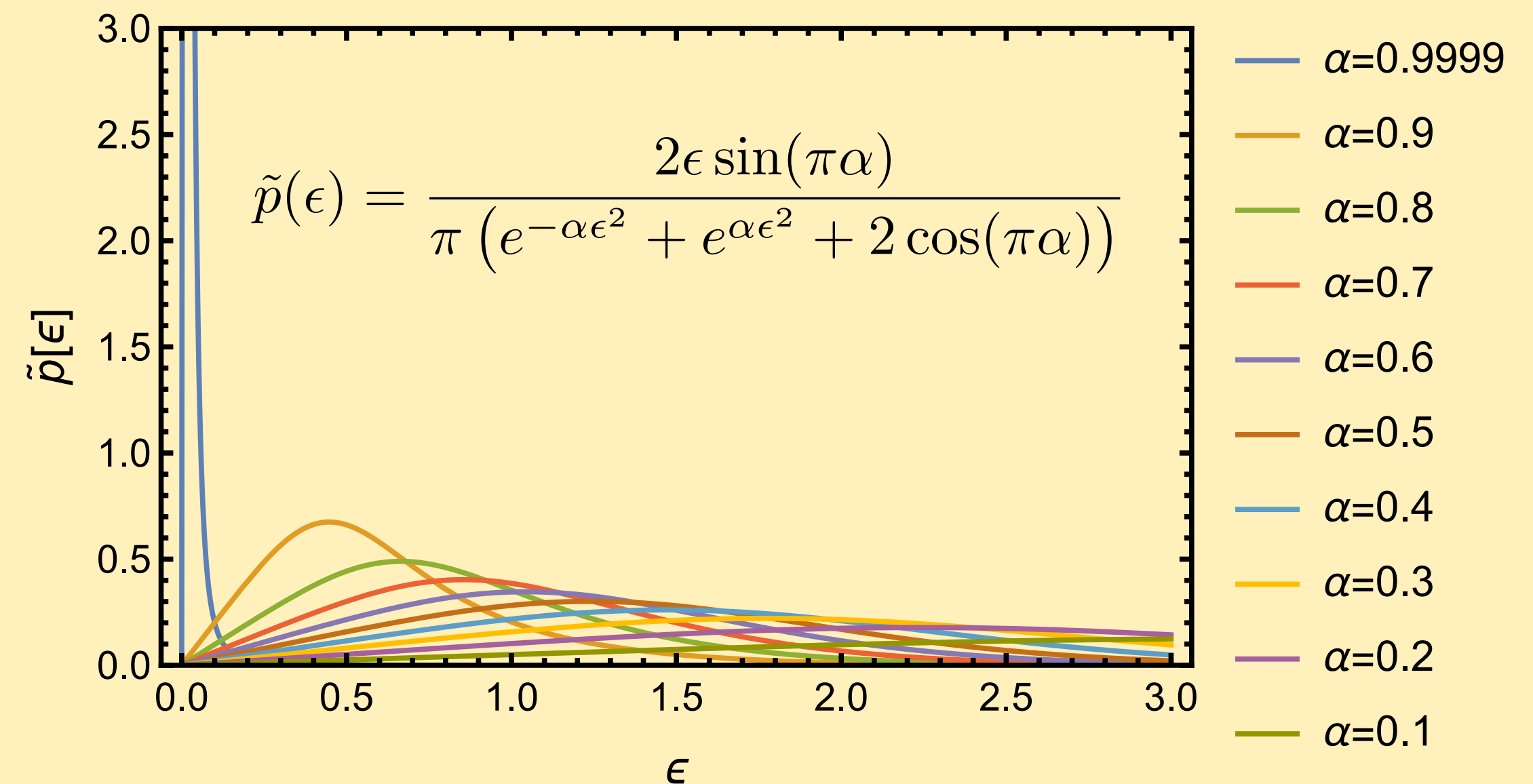
$$\lambda = \lambda_0 e^{-\epsilon^2}$$

Saouessi, Peters &
Kneller, JCP150, 2019.

Relaxation function



Energy barrier distribution

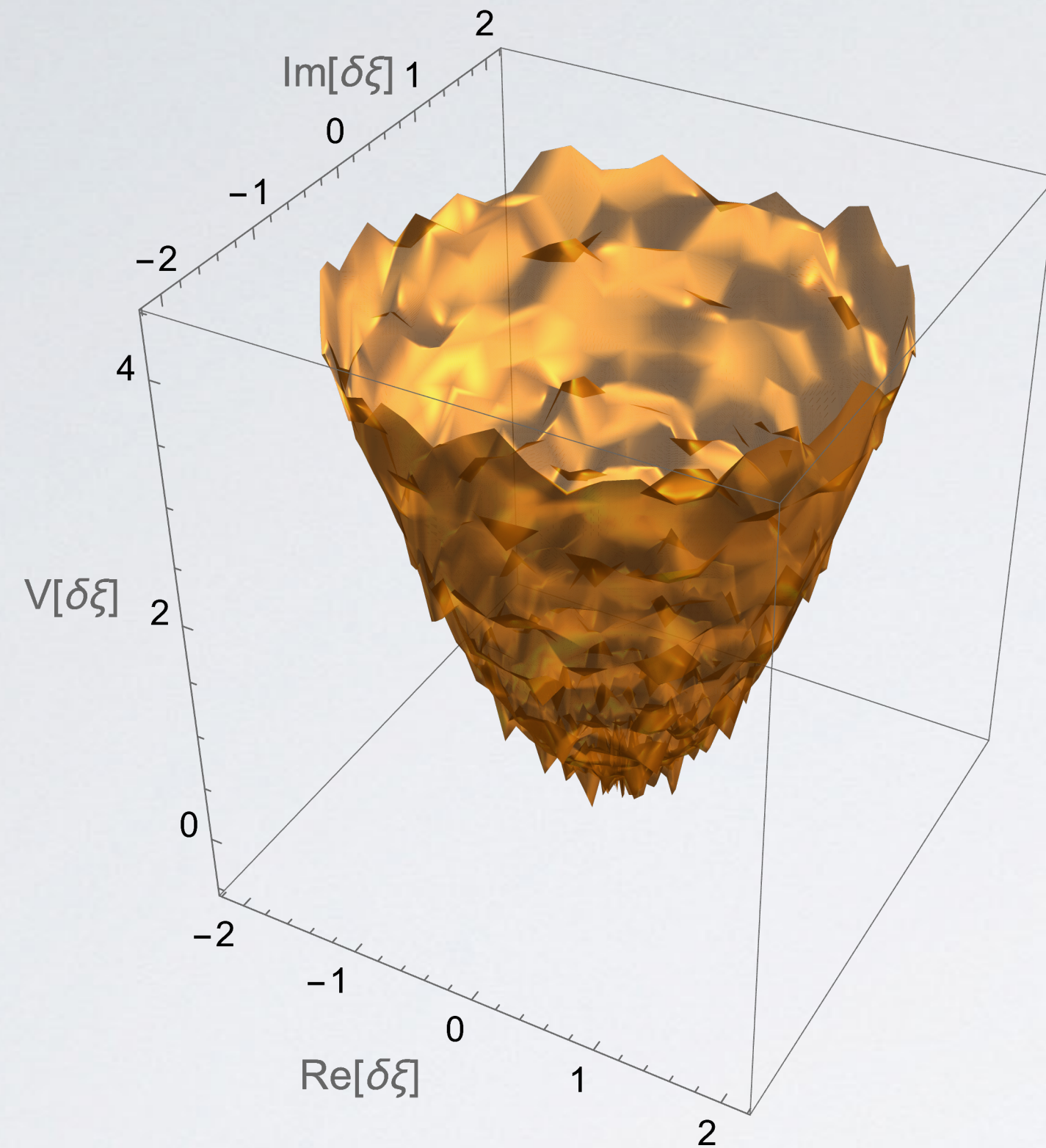


Integrate the momentum transfer q

[1] R. Zwanzig. PNAS USA, 85(7):2029– 2030, Apr. 1988.

[2] M. Saouessi, J. Peters, and G. R. Kneller. J. Chem. Phys. 150(16):161104, 2019.

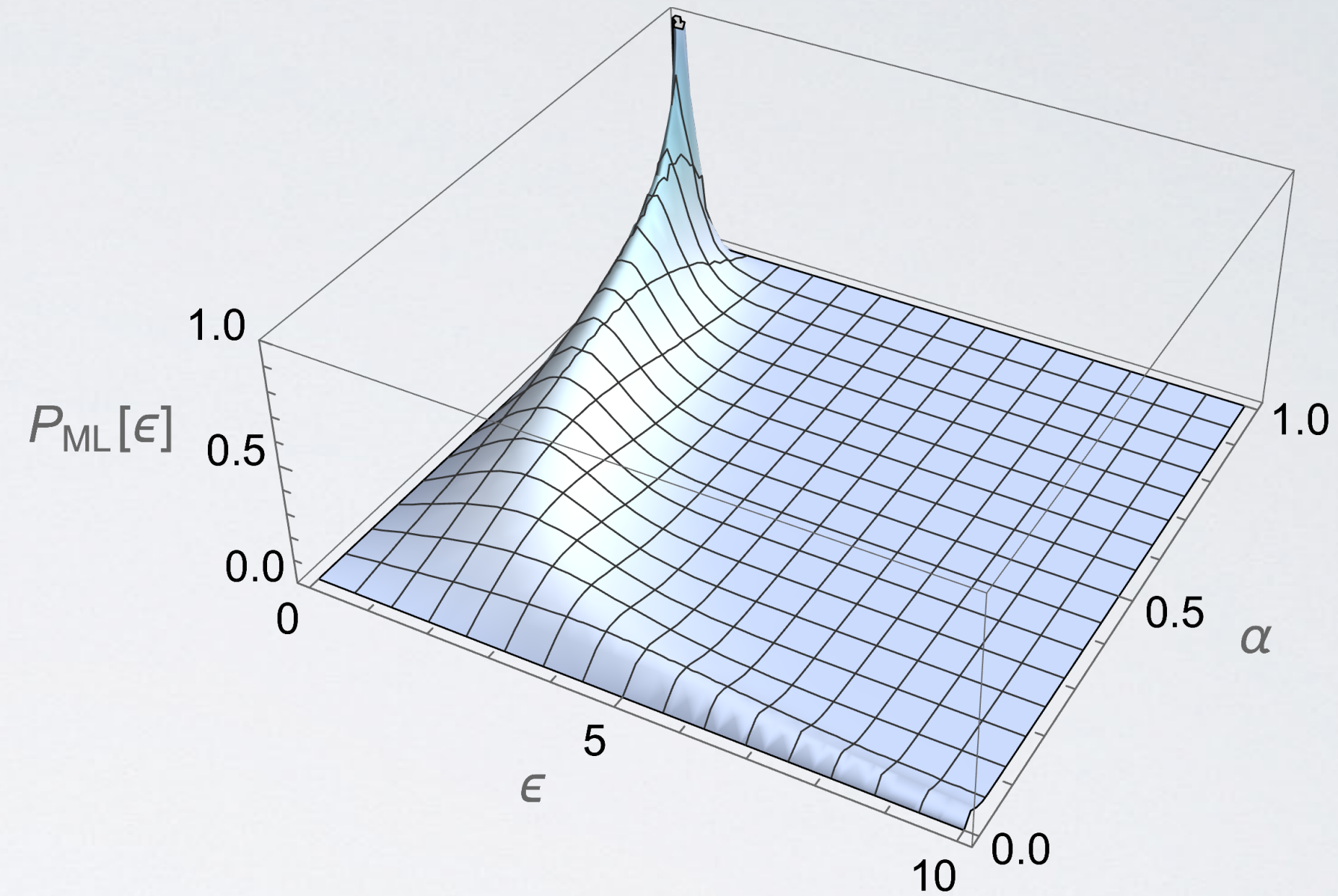
[3] A. N. Hassani, et al. J. Chem Phys., 152(2):025102, 2022.



Dynamical variable:

$$\xi(\mathbf{q}, t) = e^{i\mathbf{q} \cdot \mathbf{R}_j(t)}$$

$$\delta\xi(\mathbf{q}, t) = \xi(\mathbf{q}, t) - \langle \xi(\mathbf{q}, t) \rangle$$



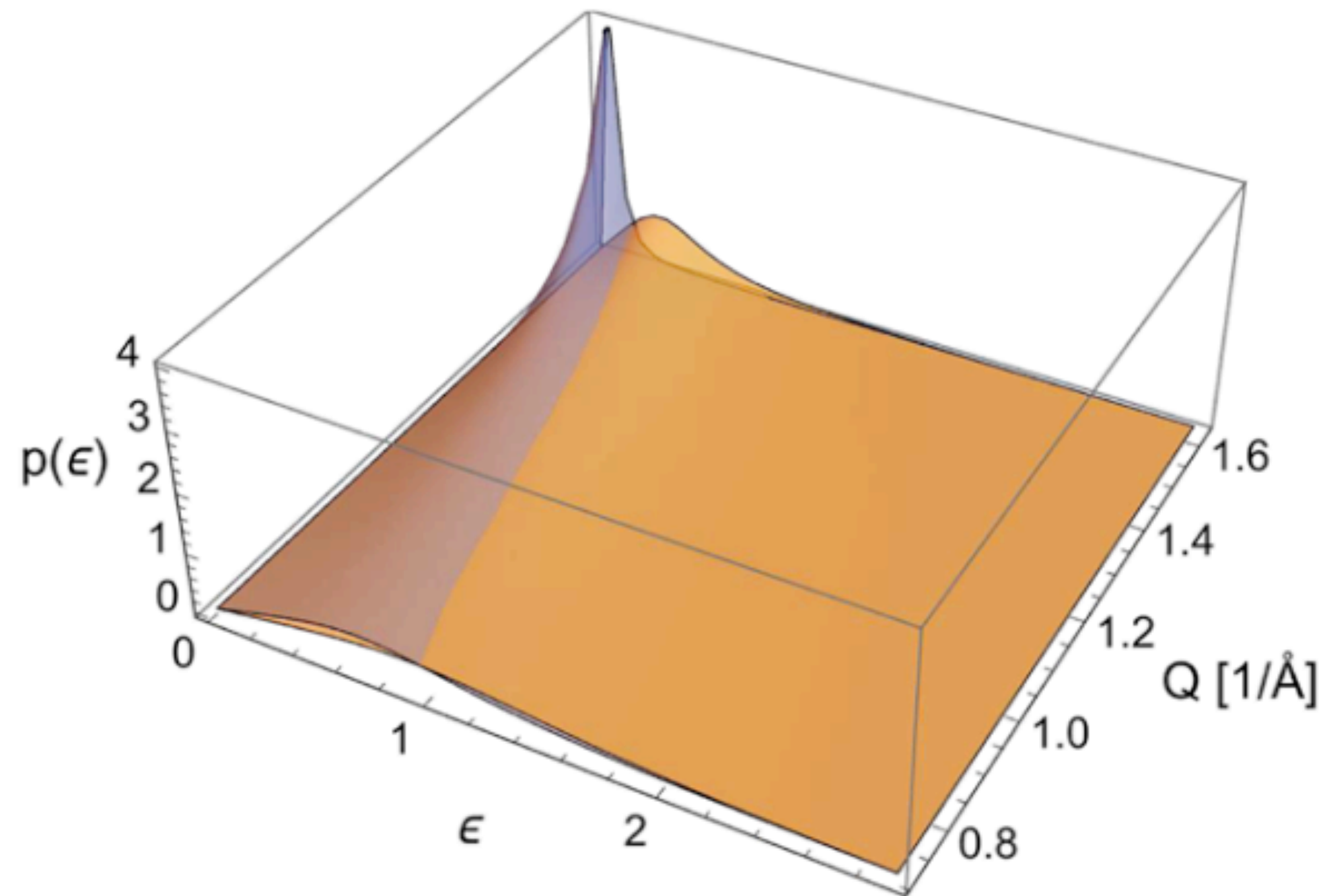
Distribution of barrier heights

$$P_{ML}(\epsilon, \alpha) = \frac{2\epsilon \sin(\pi\alpha)}{\pi (e^{-\alpha\epsilon^2} + e^{\alpha\epsilon^2} + 2 \cos(\pi\alpha))}$$

Signature of functional enzyme dynamics in quasielastic neutron scattering spectra: The case of phosphoglycerate kinase

A. N. Hassani, L. Haris, M. Appel, T. Seydel, A. M. Stadler, and G. R. Kneller

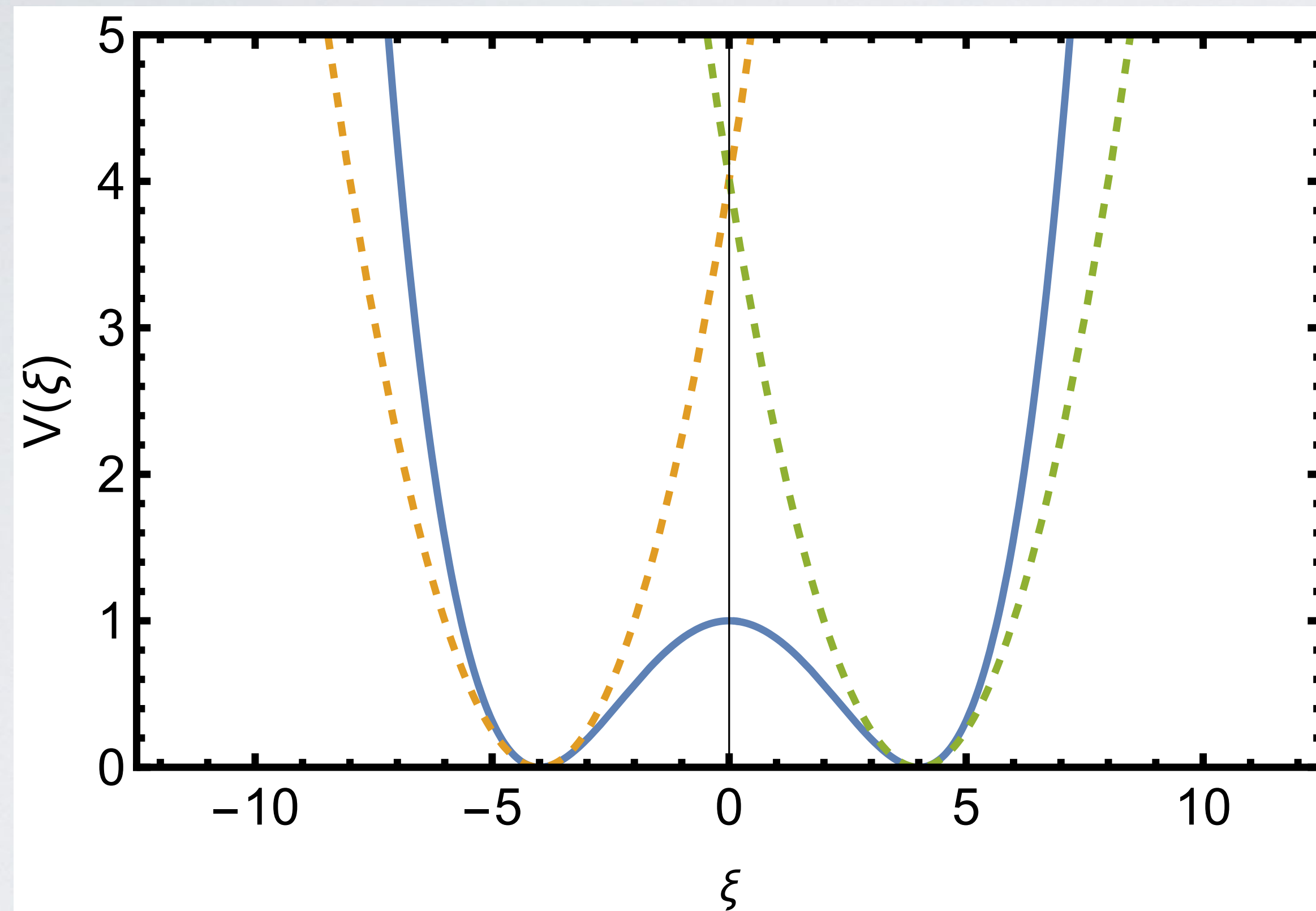
The Journal of Chemical Physics, 159(14):141102, 2023



Barrier distribution for PGK in presence and absence of reactants (orange and blue surfaces)

QENS from a particle in a simplified but true quantum “energy landscape”

Quartic potential



$$U(x) = \frac{1}{8}b(x-a)^2(x+a)^2 = \hbar\omega_0 V(\xi)$$

Dimensionless coordinates

$$V(\xi) = \frac{1}{16\alpha^2}(\xi - \alpha)^2(\xi + \alpha)^2$$

$$\xi \equiv \sqrt{\frac{2m\omega_0}{\hbar}}x \quad \text{and} \quad \alpha \equiv \sqrt{\frac{2m\omega_0}{\hbar}}a$$

$$\omega_0 \equiv \sqrt{\frac{ba^2}{m}}$$

Approximate solution of the Schrödinger equation

$$\Psi(\xi) \approx c_L \Phi_L^{(n)}(\xi) + c_R \Phi_R^{(n)}(\xi)$$

$$\underbrace{\begin{pmatrix} \langle \Phi_L^{(n)} | \hat{H} | \Phi_L^{(n)} \rangle & \langle \Phi_L^{(n)} | \hat{H} | \Phi_R^{(n)} \rangle \\ \langle \Phi_R^{(n)} | \hat{H} | \Phi_L^{(n)} \rangle & \langle \Phi_R^{(n)} | \hat{H} | \Phi_R^{(n)} \rangle \end{pmatrix}}_{\mathbf{H}_n} \cdot \begin{pmatrix} c_L \\ c_R \end{pmatrix} = \epsilon_n \begin{pmatrix} c_L \\ c_R \end{pmatrix}$$

Tunnel splitting

$$\epsilon_n^{(\pm)} = A_n \pm |B_n|$$

$$\begin{pmatrix} c_L \\ c_R \end{pmatrix} = \left\{ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix} \right\}$$

Quantum oscillator solutions for the left and right well:

$$\Phi_L^{(n)}(\xi) \equiv \Phi_n(\xi + \alpha) \quad \text{and} \quad \Phi_R^{(n)}(\xi) \equiv \Phi_n(\xi - \alpha)$$

$$\mathbf{H}_n = \begin{pmatrix} A_n & B_n \\ B_n & A_n \end{pmatrix} \stackrel{\alpha \rightarrow \infty}{=} \begin{pmatrix} n + 1/2 & 0 \\ 0 & n + 1/2 \end{pmatrix}$$

$$\Psi_n^{(\pm)}(\xi) = C_n^{(\pm)} \frac{1}{\sqrt{2}} (\Phi_n(\xi - \alpha) \pm \Phi_n(\xi + \alpha))$$

$$\lim_{\alpha \rightarrow \infty} C_n^{(\pm)} = 1$$

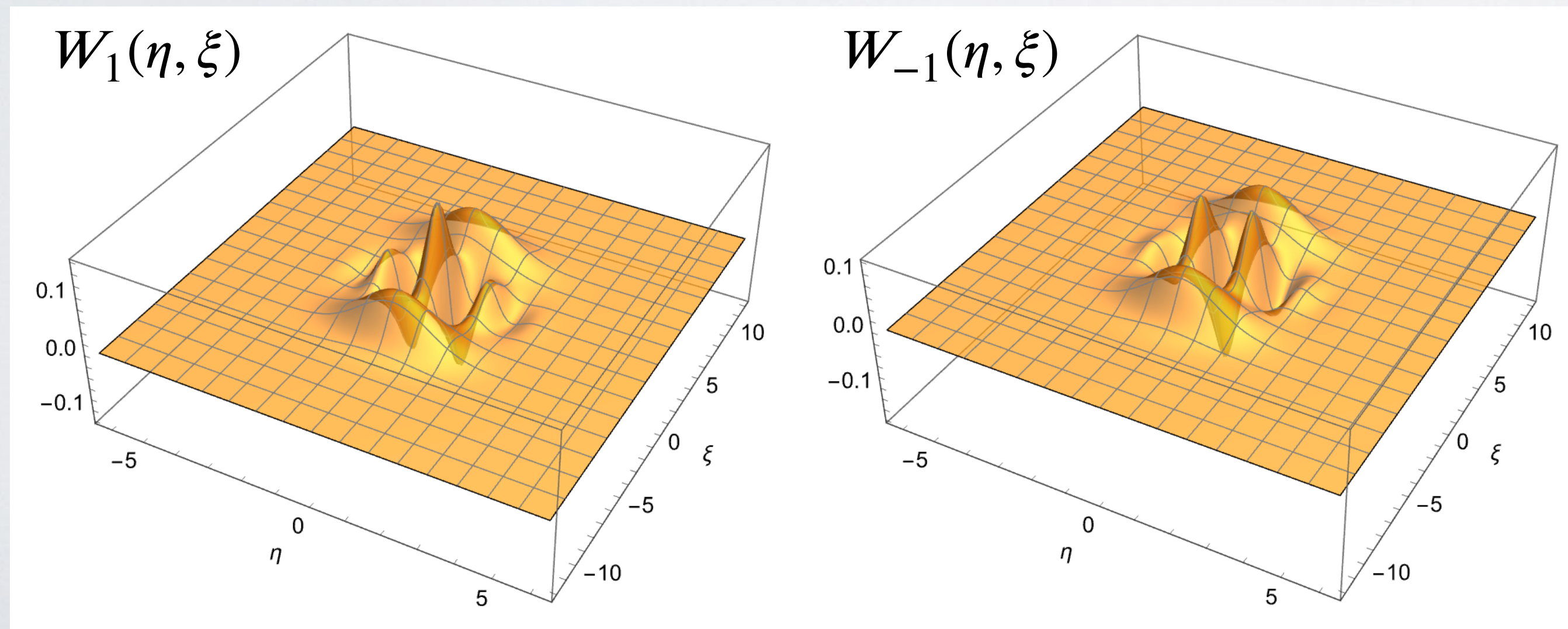
Neutron intermediate scattering function

$$\Psi_{\sigma}(\xi) = \frac{C_{0,\sigma}}{\sqrt{2}} \left(\Phi_0(\xi - \alpha) + \sigma \Phi_0(\xi + \alpha) \right), \quad \sigma \in \{1, -1\}$$

Consider ground state tunnel splitting ($T \rightarrow 0$)

$$F(Q, \tau) = \sum_{\sigma, \sigma'} \frac{e^{-\frac{\epsilon_{\sigma}}{\kappa T}}}{Z} e^{i\Omega_{\sigma'\sigma}\tau} \underbrace{\left\{ 4\pi \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\eta d\xi W_{\sigma'}(\eta + \textcolor{red}{Q}, \xi) W_{\sigma}(\eta, \xi) \right\}}_{|a_{\sigma \rightarrow \sigma'}(Q)|^2}$$

Express transition probabilities through Wigner distributions

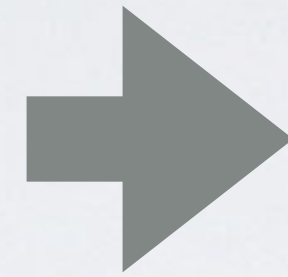


$$\begin{aligned} W_{\sigma}(\eta, \xi) &= \frac{1}{4\pi} \int_{-\infty}^{+\infty} d\xi' e^{\frac{i}{2}\eta\xi'} \Psi_{\sigma}^* \left(\xi + \frac{\xi'}{2} \right) \Psi_{\sigma} \left(\xi - \frac{\xi'}{2} \right) \\ &= \frac{1}{2} \left(W_0(\eta, \xi - \alpha) + W_0(\eta, \xi + \alpha) \right) + \sigma \cos(\eta\alpha) W_0(\eta, \xi) \end{aligned}$$

Background of Wigner distributions

Map wave functions onto “phase space” distributions:

$$\begin{aligned}\psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dp e^{\frac{i}{\hbar}xp} \tilde{\psi}(p) \\ \tilde{\psi}(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx e^{-\frac{i}{\hbar}px} \psi(x)\end{aligned}$$



$$\begin{aligned}W_{\psi}(p, x) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dy e^{\frac{i}{\hbar}py} \psi^* \left(x + \frac{y}{2} \right) \psi \left(x - \frac{y}{2} \right) \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} du e^{-\frac{i}{\hbar}xu} \tilde{\psi}^* \left(p + \frac{u}{2} \right) \tilde{\psi} \left(p - \frac{u}{2} \right)\end{aligned}$$

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dp dx W_{\psi}(p, x) = 1, \quad W_{\psi}(p, x) \in \mathbb{R}.$$

Map wave functions onto “phase space” distributions:

$$\langle a \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dp dx W(p, x) a(p, x) \quad \text{if } a(p, x) = f(x) + g(p)$$

Transition probabilities

$$|\langle \phi | \psi \rangle|^2 = 2\pi\hbar \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dp dx W_{\phi}(p, x) W_{\psi}(p, x)$$

On the Quantum Correction For Thermodynamic Equilibrium

By E. WIGNER

Department of Physics, Princeton University

(Received March 14, 1932)

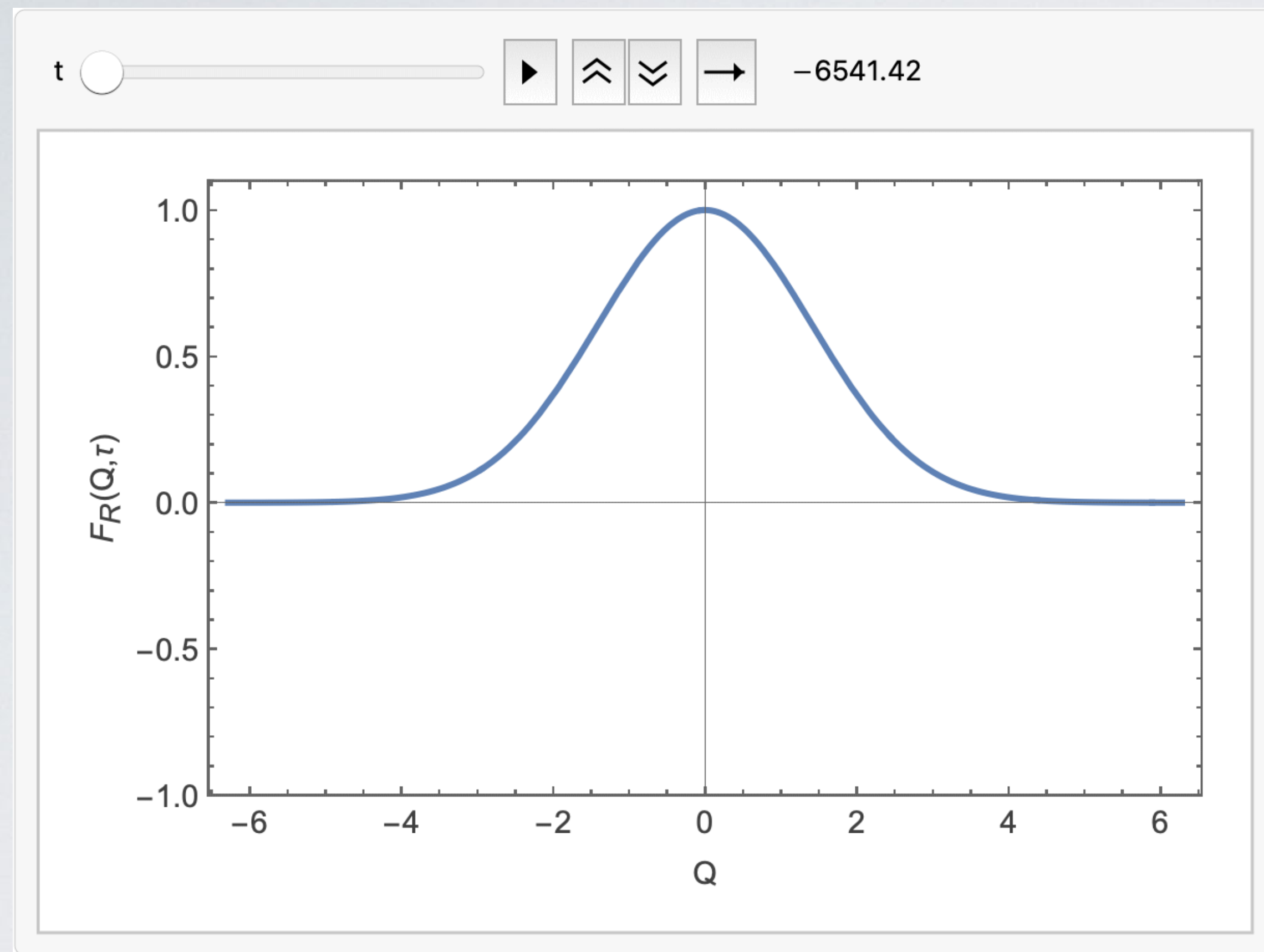
The probability of a configuration is given in classical theory by the Boltzmann formula $\exp [-V/hT]$ where V is the potential energy of this configuration. For high temperatures this of course also holds in quantum theory. For lower temperatures, however, a correction term has to be introduced, which can be developed into a power series of h . The formula is developed for this correction by means of a probability function and the result discussed.

$$\rho(p, x) = \frac{1}{Z} \sum_n e^{-\beta E_n} W_n(p, x)$$

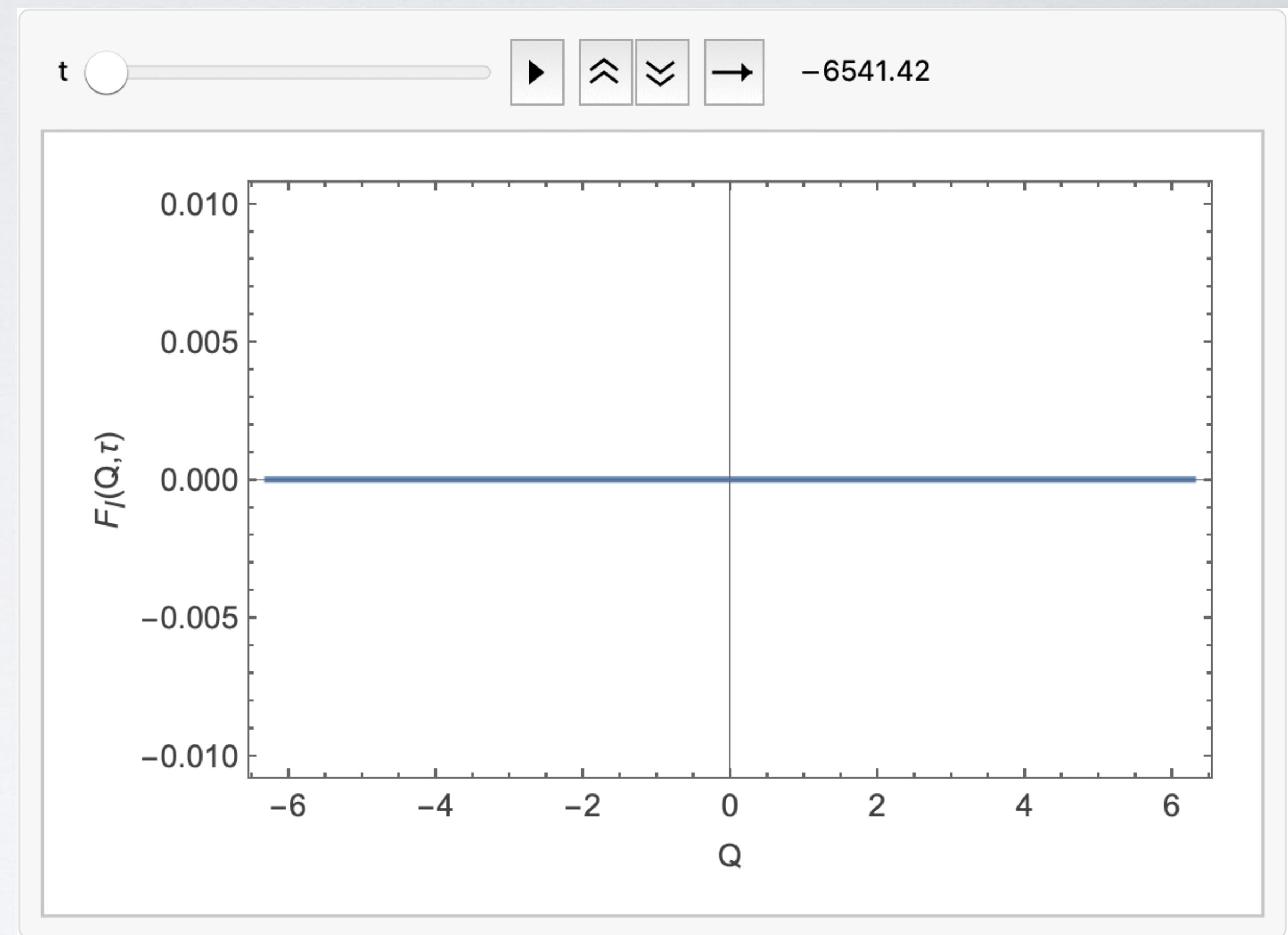
$$W_n(p, x) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dy e^{\frac{i}{\hbar}py} \phi_n^* \left(x + \frac{y}{2} \right) \phi_n \left(x - \frac{y}{2} \right)$$

$$\hat{H}\phi_n(x) = E_n\phi_n(x)$$

$$\text{Re}[F(q, t)]$$



$$\text{Im}[F(q, t)]$$



Van Hove's theory of neutron scattering

PHYSICAL REVIEW

VOLUME 95, NUMBER 1

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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)



A REMARK ON THE TIME-DEPENDENT PAIR DISTRIBUTION

by LÉON VAN HOVE

Instituut voor theoretische fysica der Rijksuniversiteit, Utrecht, Nederland

Physica, vol. 24, no. 1, pp. 404–408, 1958.

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int d^3q e^{-i\mathbf{q}\cdot\mathbf{r}} F(\mathbf{q}, t)$$

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

Only in the classical framework the VH function $G(\mathbf{r}, t)$ has the meaning of a pair distribution in space and time.

- For the tunnelling particle:

$$G(X, \tau) = \sum_{\sigma, \sigma'} \frac{e^{-\frac{\epsilon_{\sigma}}{kT}}}{Z} e^{i\Omega_{\sigma'} \tau} \left\{ 4\pi \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\eta d\xi W_{\sigma'}(\eta, \xi | \mathbf{X}) W_{\sigma}(\eta, \xi) \right\}$$

$$\begin{aligned} W_{\sigma'}(\eta, \xi | X) &= \frac{1}{4\pi} \int_{-\infty}^{+\infty} d\xi' e^{\frac{i}{2}\xi'\eta} \delta(\xi' - \mathbf{X}) \Psi_{\sigma'}^* \left(\xi + \frac{\xi'}{2} \right) \Psi_{\sigma'} \left(\xi - \frac{\xi'}{2} \right) \\ &= \frac{e^{\frac{i}{2}X\eta}}{4\pi} \Psi_{\sigma'}^* \left(\xi + \frac{X}{2} \right) \Psi_{\sigma'} \left(\xi - \frac{X}{2} \right) \end{aligned}$$

- For a classical particle (Hamiltonian mechanics)

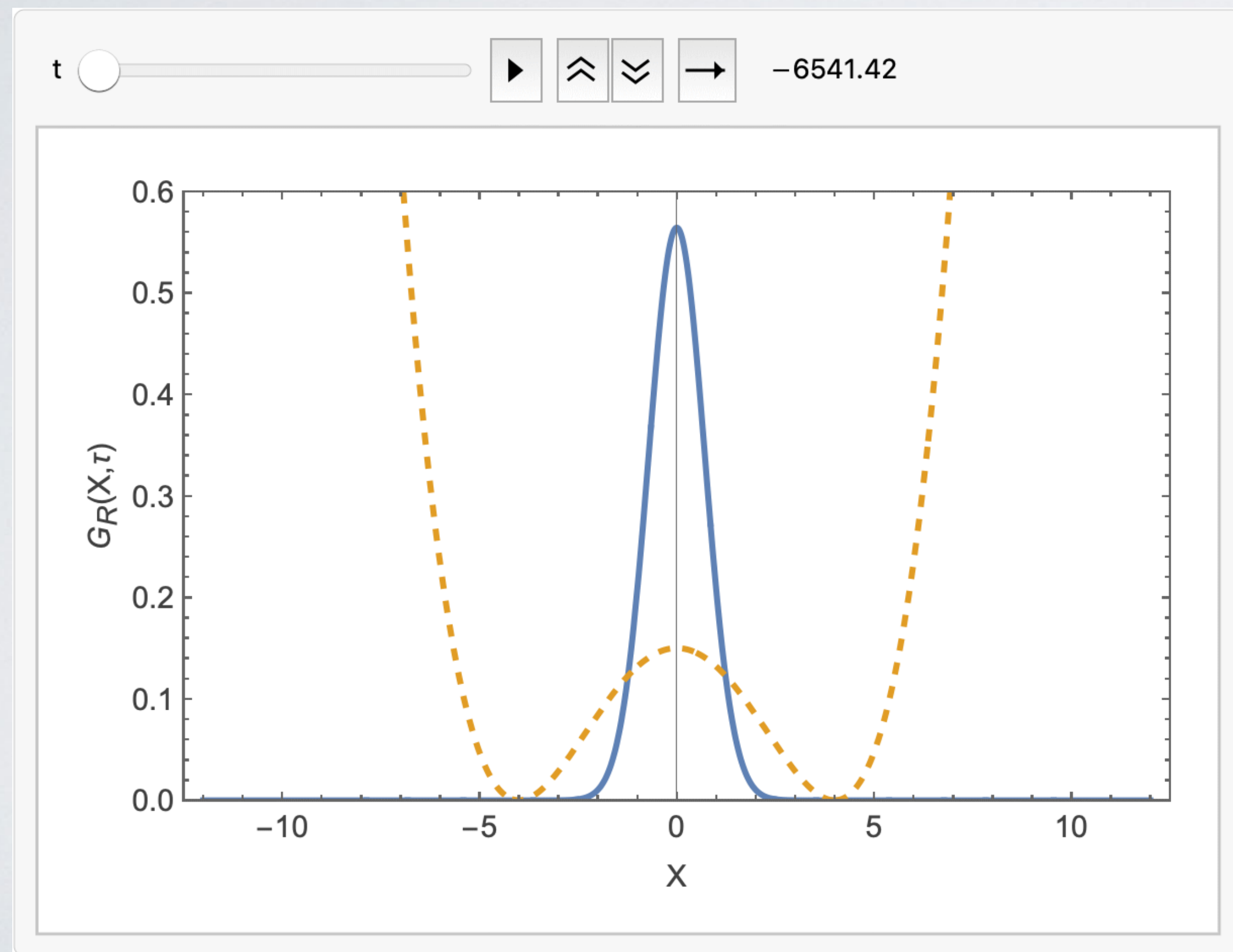
$$G(X, \tau) = \int \int d\eta d\xi \frac{e^{-H(\eta, \xi)}}{Z} \delta(\Xi(\xi, \eta, t) - \mathbf{X}), \quad \Xi(\xi, \eta, 0) = \xi.$$

From Hamiltonian dynamics

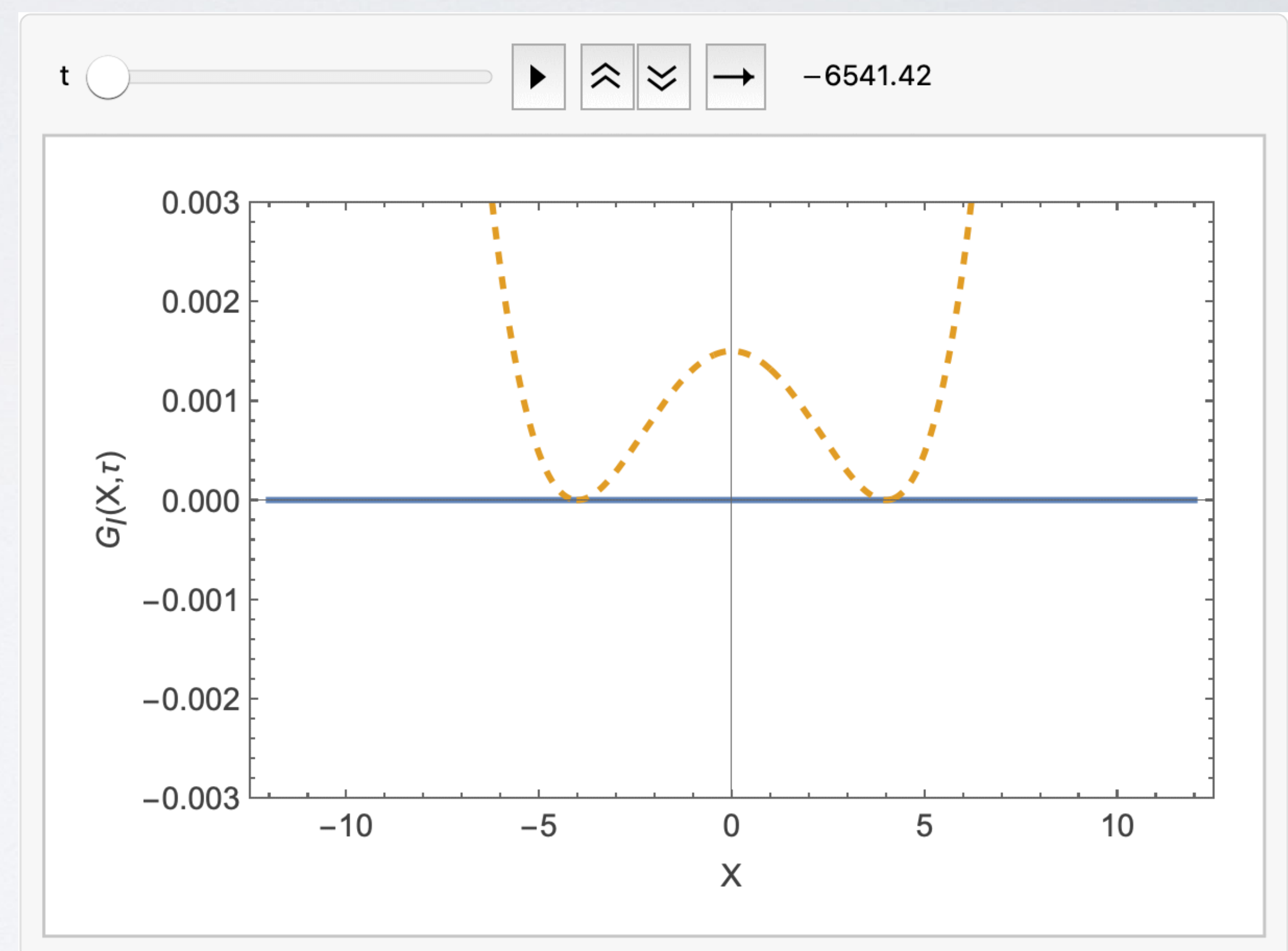
Van Hove function

$$G(X, \tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dq e^{-iQX} F(Q, \tau)$$

$\text{Re}[G(X, \tau)]$



$\text{Im}[G(X, \tau)]$



A REMARK ON THE TIME-DEPENDENT PAIR DISTRIBUTION

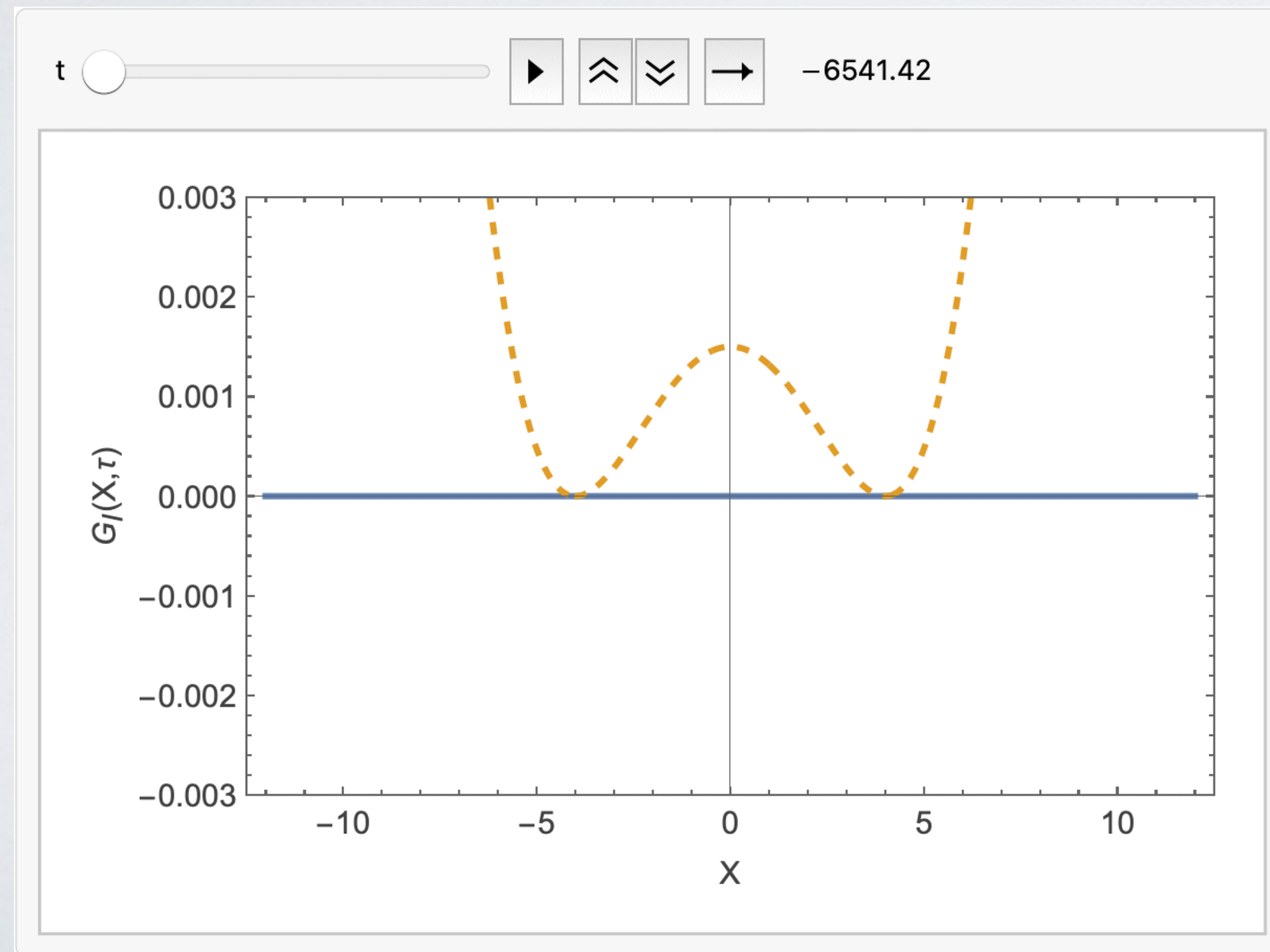
by LÉON VAN HOVE

Instituut voor theoretische fysica der Rijksuniversiteit, Utrecht, Nederland

Physica, 24(1):404–408, 1958

$$n(\mathbf{r}, t) = \rho_0 - (2\pi a \hbar^2 / m) \rho_0 \int_{-\infty}^t dt' G_1(\mathbf{r} - \mathbf{r}_{t'}, t - t'). \quad (13)$$

$$G_1(x, t) \equiv \text{Im}[G(x, t)]$$



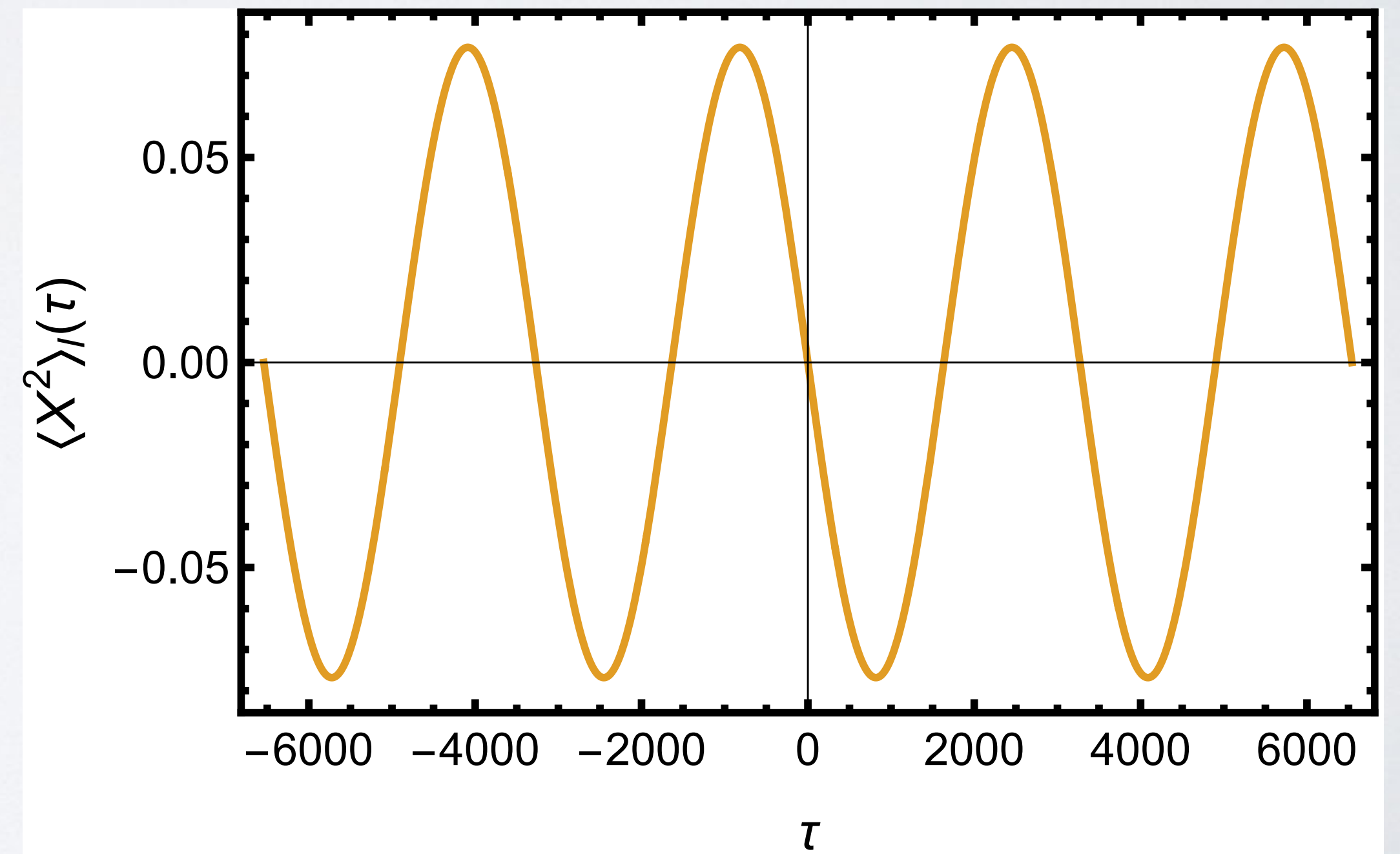
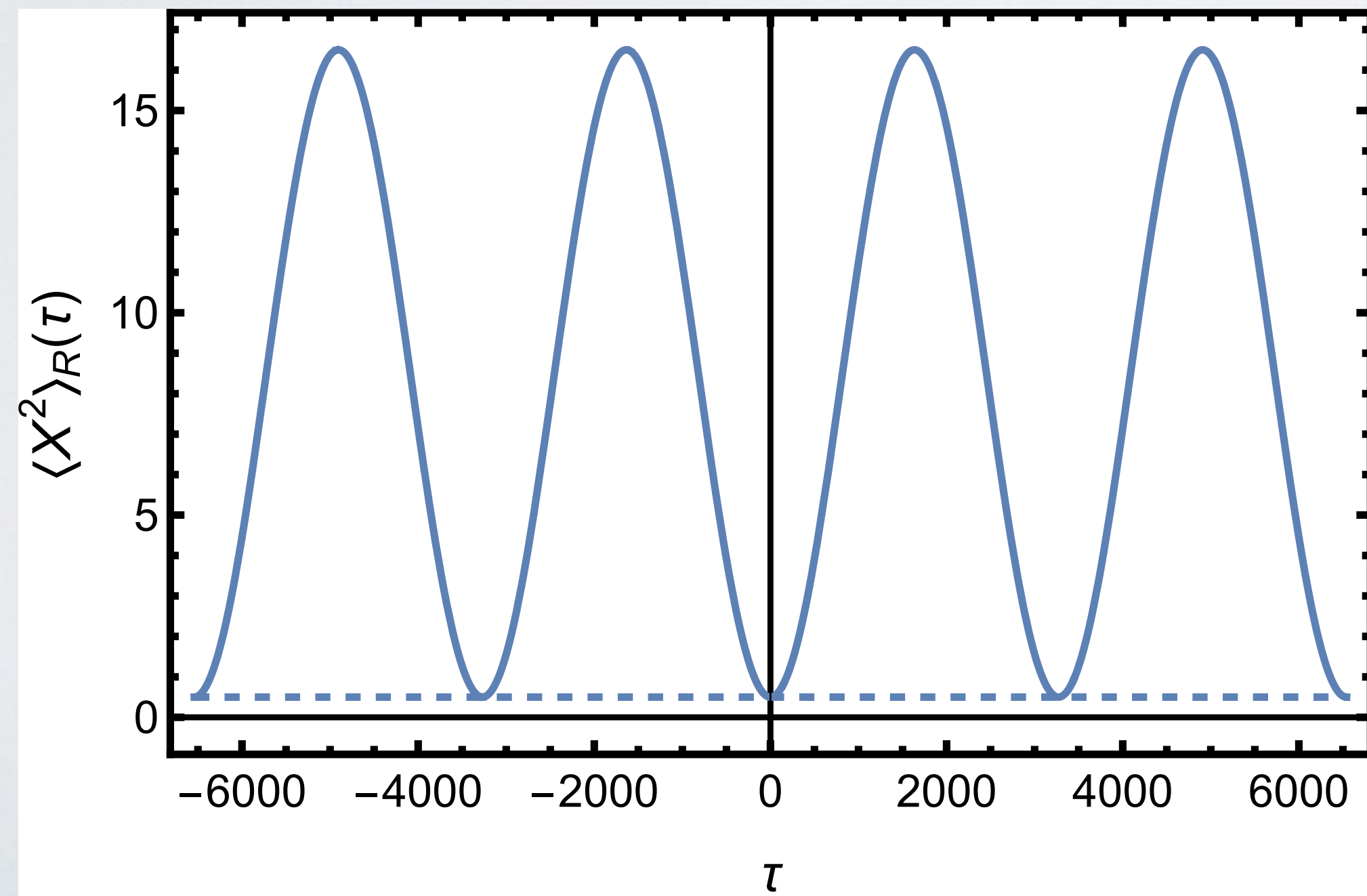
The imaginary part of the VH function determines the density perturbation induced by the neutron kick.

Mean squared displacement

$$\langle X^2(\tau) \rangle = \int_{-\infty}^{+\infty} dX X^2 G(X, \tau)$$

$$G(X, \tau) = G_R(X, \tau) + iG_I(X, \tau)$$

$$\langle X^2(\tau) \rangle_{R/I} = \int_{-\infty}^{+\infty} dX X^2 G_{R/I}(X, \tau) = -\frac{\partial^2}{\partial Q^2} F_{R/I}(Q, \tau) \Big|_{Q=0}$$



Details for the real part¹

$$\langle X^2(\tau) \rangle_R = \langle X^2 \rangle_{\text{zpf}} + A_R \sin\left(\frac{\Omega \tau}{2}\right)^2$$

$$\lim_{\alpha \rightarrow \infty} \Omega = 0 \quad \text{and} \quad \lim_{\alpha \rightarrow 0} \Omega = \infty$$

$$A_R \stackrel{\alpha \rightarrow \infty}{\sim} \alpha^2 \quad \text{and} \quad A_R \stackrel{\alpha \rightarrow 0}{\sim} 1$$

$$\langle X^2 \rangle_{\text{zpf}} \rightarrow \begin{cases} 1 & \text{for } \alpha \rightarrow 0 \\ 1/2 & \text{for } \alpha \rightarrow \infty \end{cases}$$

In physical units:

$$\langle x^2 \rangle_{\text{zpf}} \rightarrow \begin{cases} \frac{\hbar}{2m\omega_0} & \text{for } a \rightarrow 0 \\ \frac{\hbar}{4m\omega_0} & \text{for } a \rightarrow \infty \end{cases}$$

Zero-point fluctuation of
the quantum oscillator

$$\Omega = \epsilon_+ - \epsilon_- = \frac{e^{-\frac{\alpha^2}{2}} \left| -3\alpha^4 + 2\alpha^2 + 3 \right|}{8\alpha^2}$$

$$A_R = \left(\frac{1}{e^{\alpha^2} - 1} + 1 \right) \alpha^2$$

$$\langle X^2 \rangle_{\text{zpf}} = \frac{1}{4} \left(\alpha^2 \operatorname{csch}\left(\frac{\alpha^2}{2}\right) \tanh\left(\frac{\Omega}{2\alpha^2 kT}\right) + 2 \right)$$

¹All calculations have been performed with Wolfram Mathematica.

Details for the imaginary part¹

$$\langle X^2(\tau) \rangle_I = A_I \sin(\Omega \tau)$$

$$\lim_{\alpha \rightarrow \infty} \Omega = 0 \quad \text{and} \quad \lim_{\alpha \rightarrow 0} \Omega = \infty$$

$$A_I \stackrel{\alpha \rightarrow \infty}{\sim} 0 \quad \text{and} \quad A_I \stackrel{\alpha \rightarrow 0}{\sim} -1/2$$

$$\Omega = \epsilon_+ - \epsilon_- = \frac{e^{-\frac{\alpha^2}{2}} \left| -3\alpha^4 + 2\alpha^2 + 3 \right|}{8\alpha^2}$$

$$A_I = -\frac{1}{4}\alpha^2 \left(\coth\left(\frac{\alpha^2}{2}\right) + 1 \right) \operatorname{sgn}(\Omega) \tanh\left(\frac{\Omega}{2\alpha^2 \kappa T}\right)$$

¹All calculations have been performed with Wolfram Mathematica.

The impact of damping/dissipation....

$$\langle X^2(\tau) \rangle_{R/I} = 2 \int_0^t dt' (t - t') c_{vv}^{(R)}(t')$$

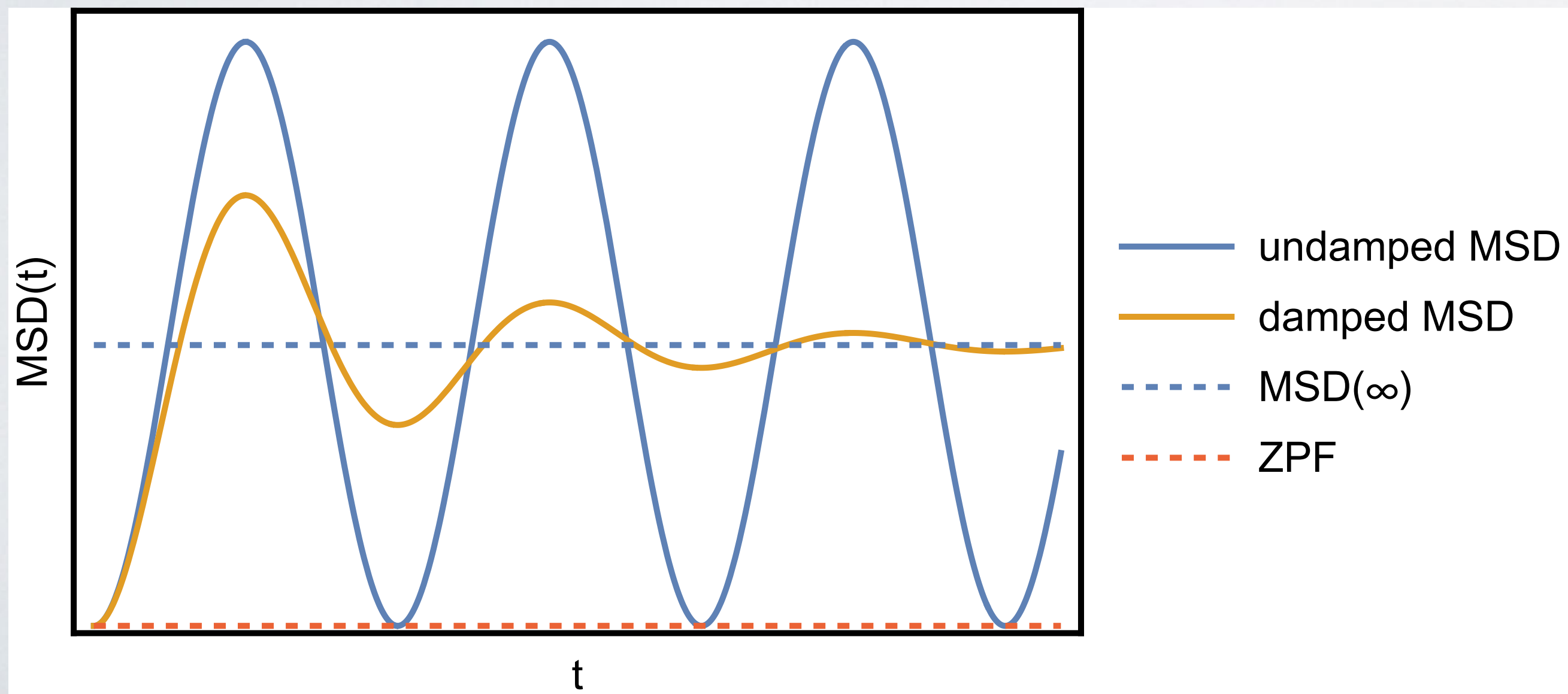
$$c_{vv}^{(R)}(t) = \text{Re}[\langle \hat{v}(0) \hat{v}(t) \rangle], \quad \hat{v}(t) = \frac{i}{\hbar} [\hat{H}, \hat{x}(t)]$$

$$c_{vv}^{(R)}(t) = \frac{1}{2} \epsilon \delta'(t) + \cos(\Omega t)$$

Undamped

$$c_{vv}^{(R)}(t) = \frac{1}{2} \epsilon \delta'(t) + \frac{e^{-\eta t} (\Omega \cos(t\Omega) - \eta \sin(\Omega t))}{\Omega}$$

Damped



Undamped:

$$\langle X^2(t) \rangle_R = \epsilon + \frac{2}{\Omega^2} (1 - \cos(\Omega t))$$

Damped:

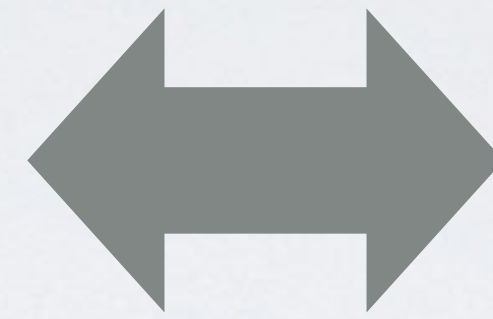
$$\langle X^2(t) \rangle_R = \epsilon + \frac{2}{\eta^2 + \Omega^2} \left(1 - e^{-\eta t} \left(\frac{\eta \sin(t\Omega)}{\Omega} + \cos(\Omega t) \right) \right)$$

$$\langle X^2(\infty) \rangle_R = \epsilon + \frac{2}{\eta^2 + \Omega^2}$$

Recoil in QENS

Symmetry relations

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



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

Recoil moment

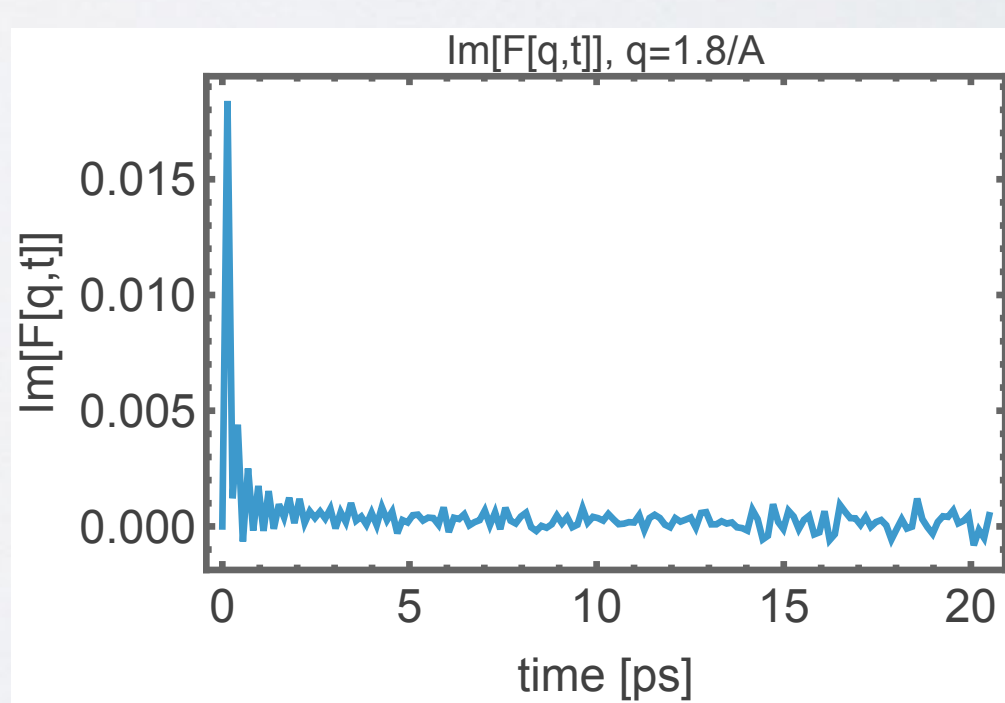
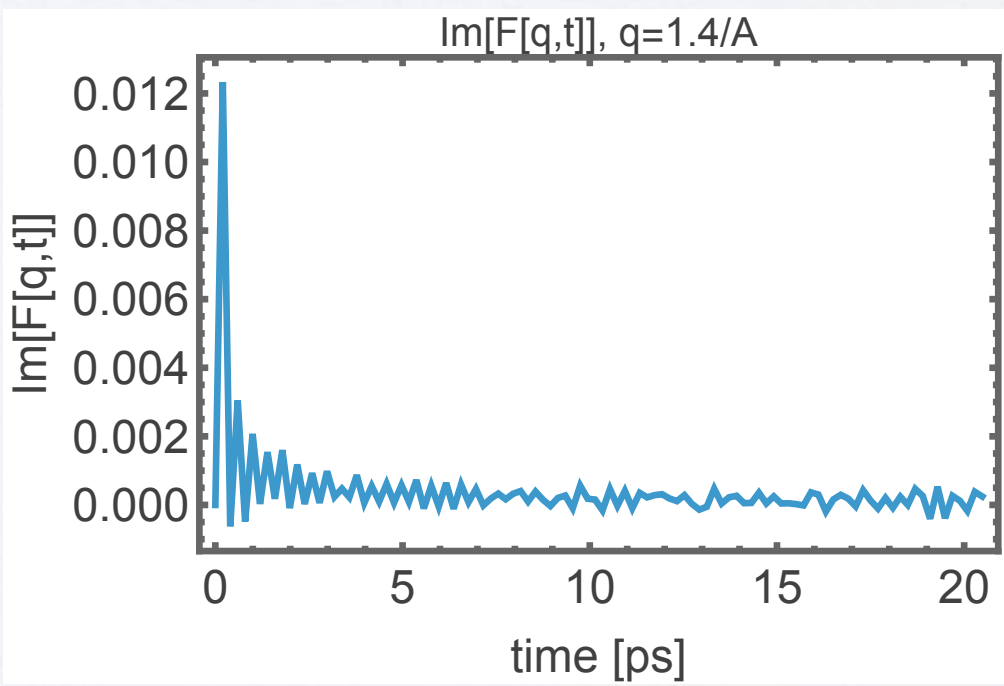
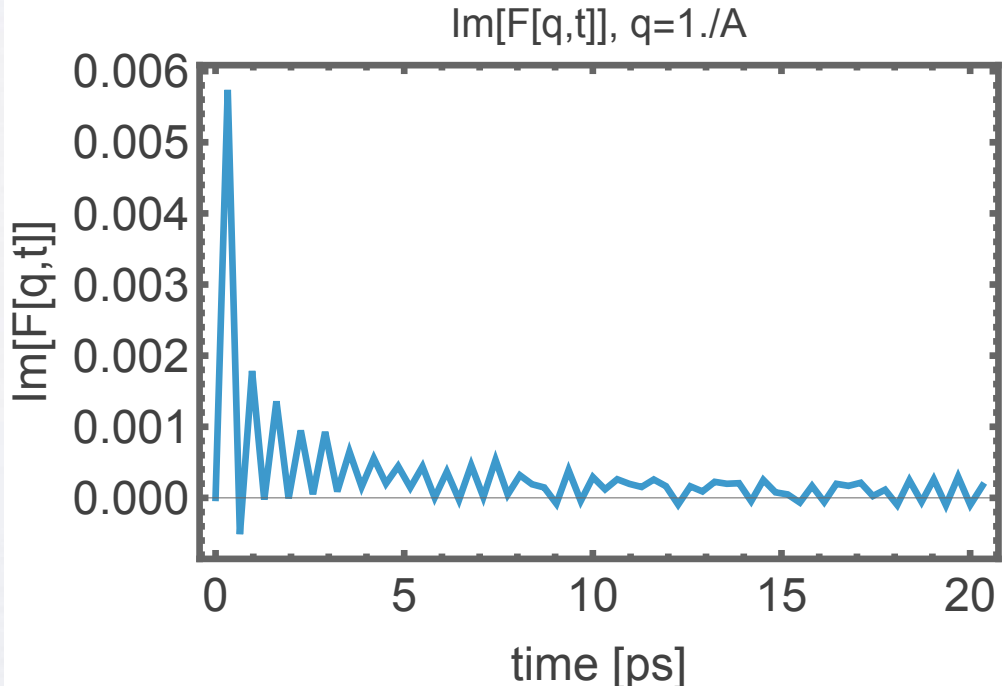
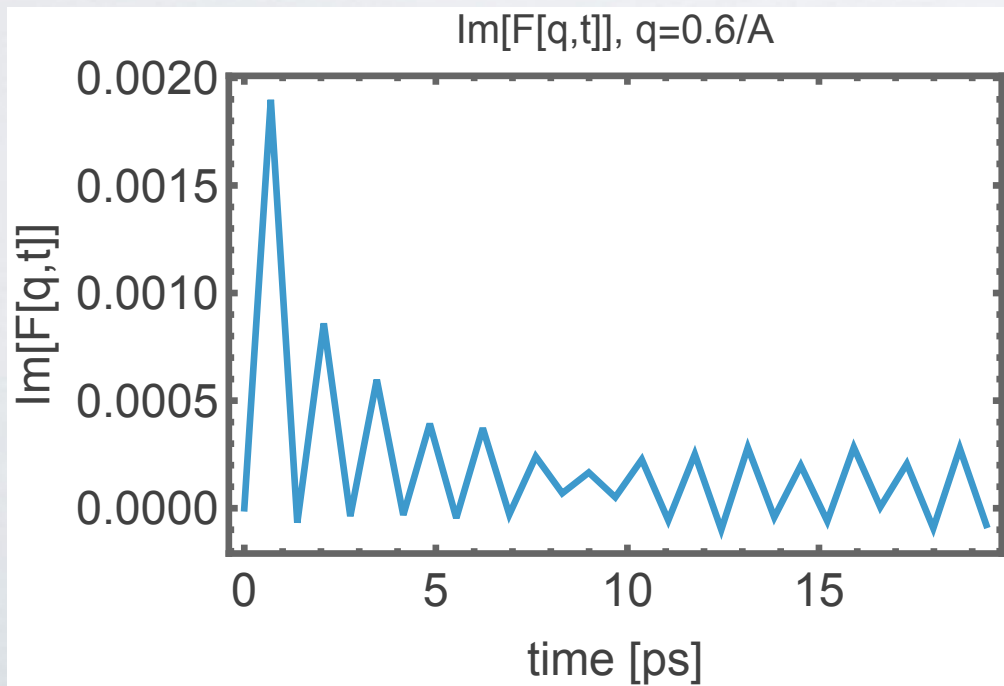
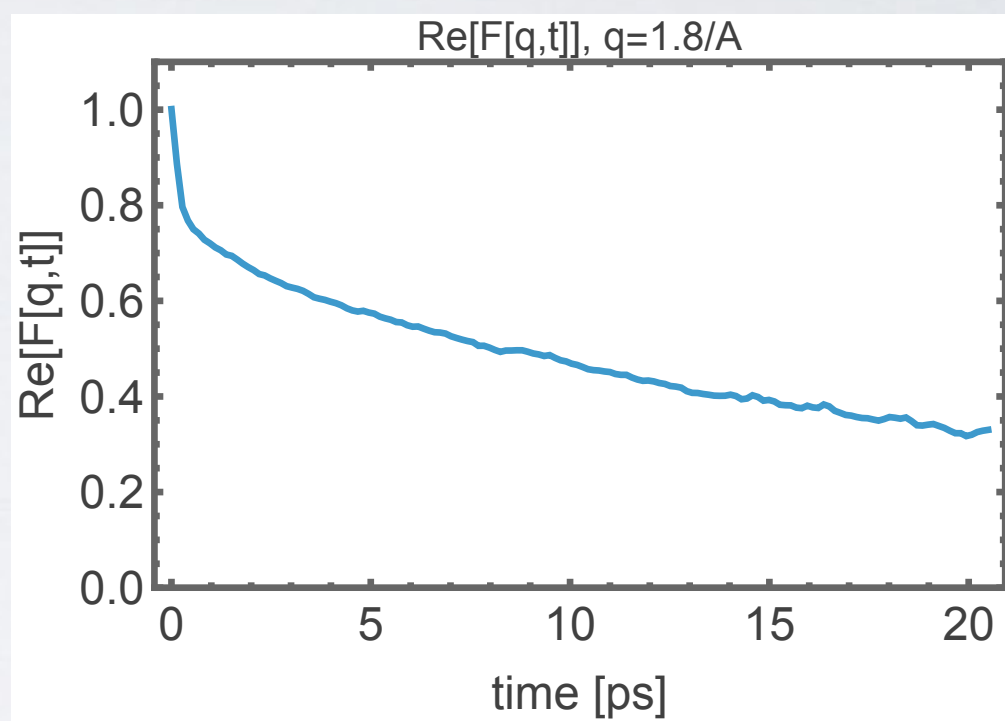
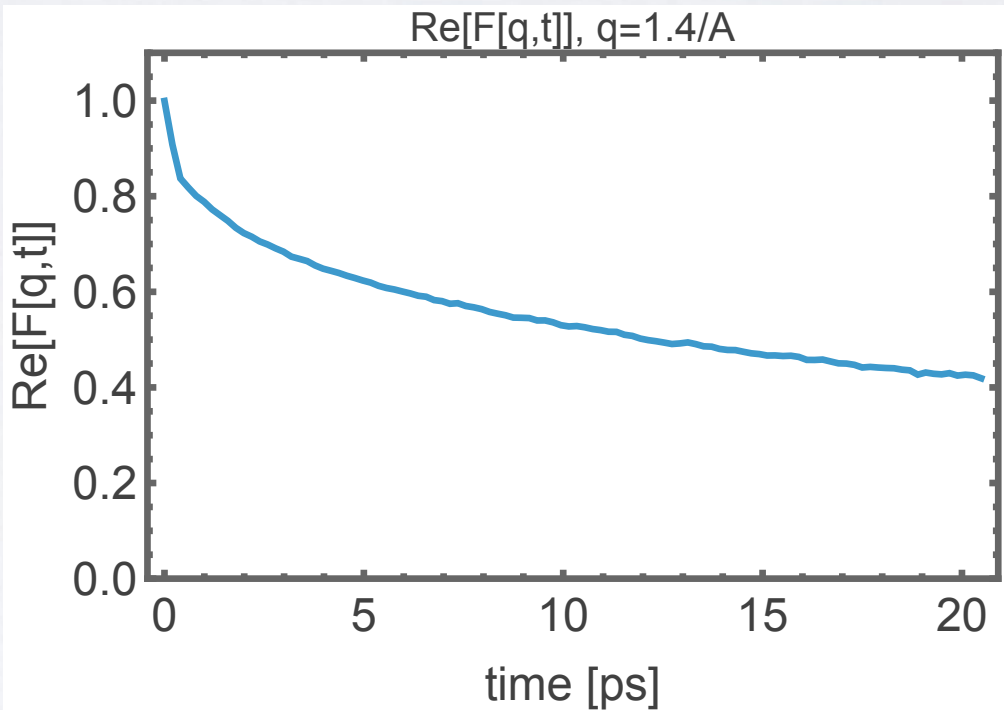
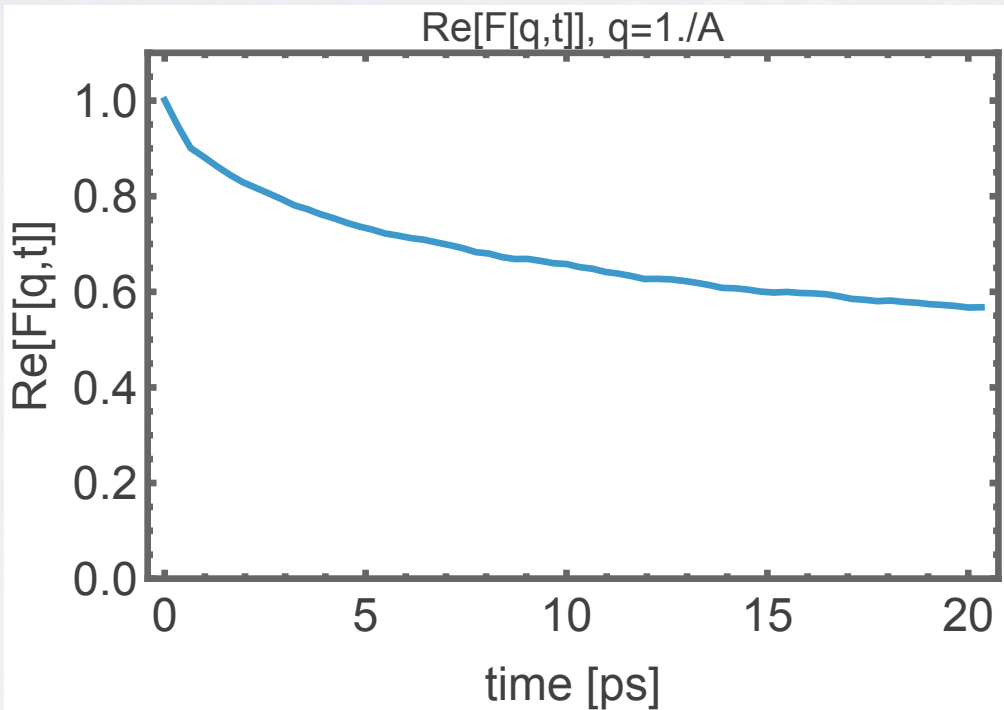
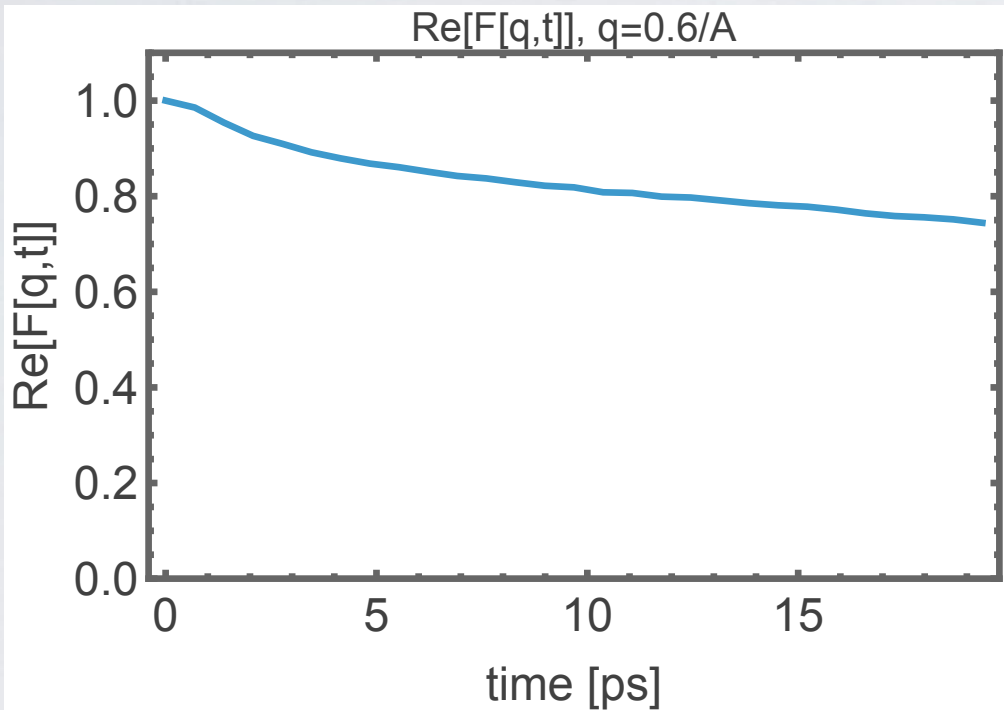
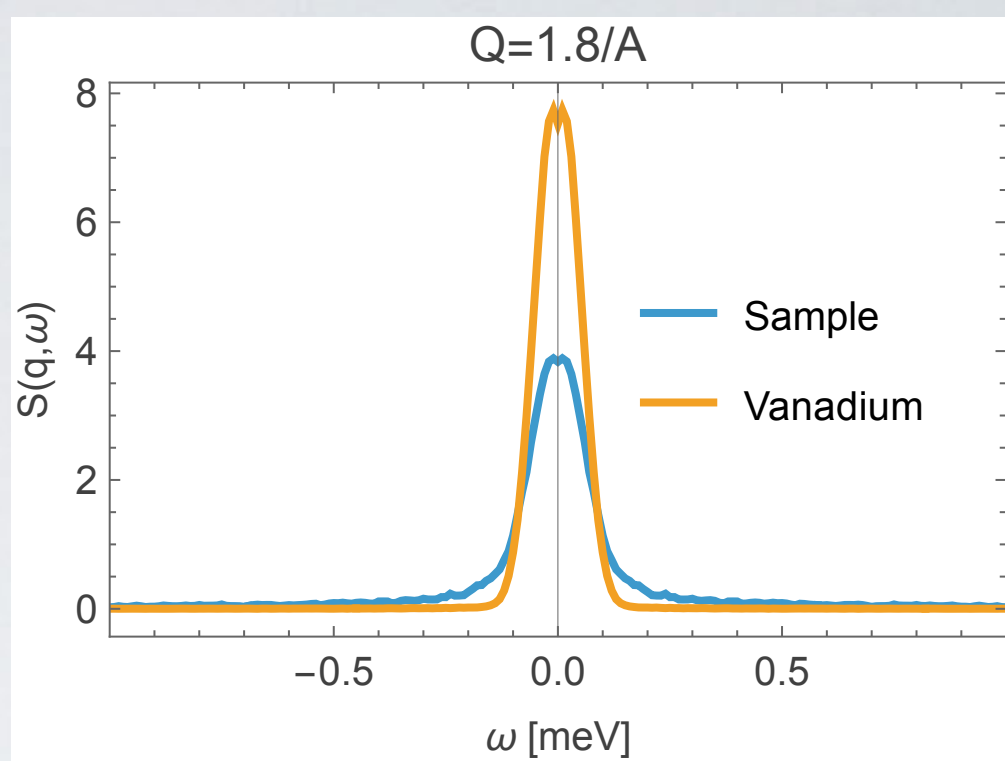
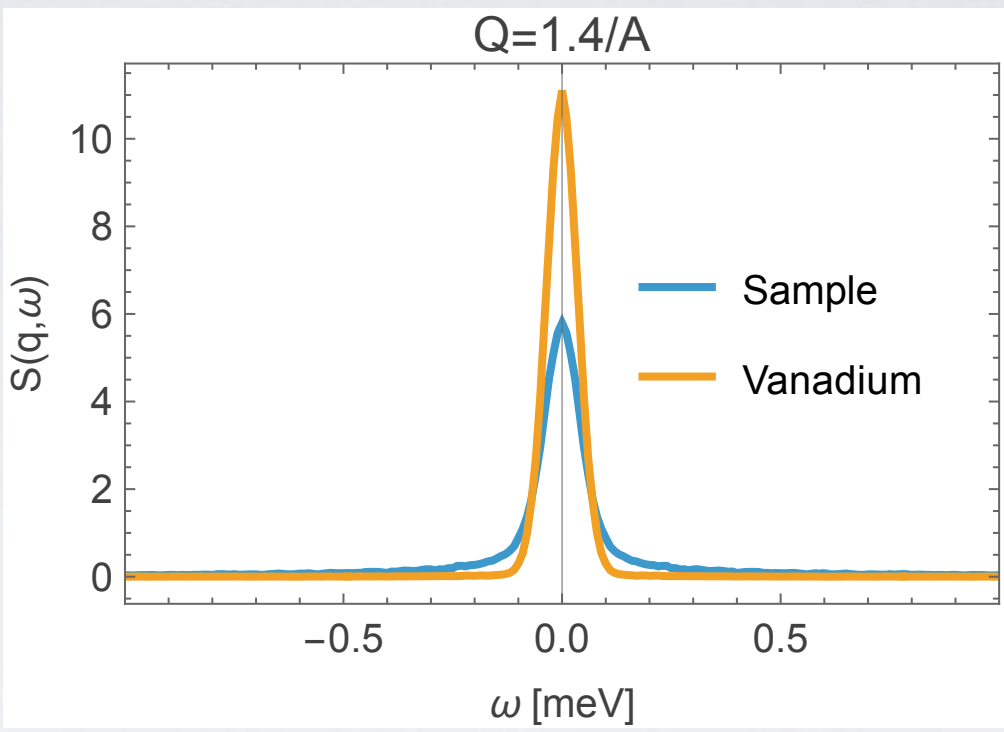
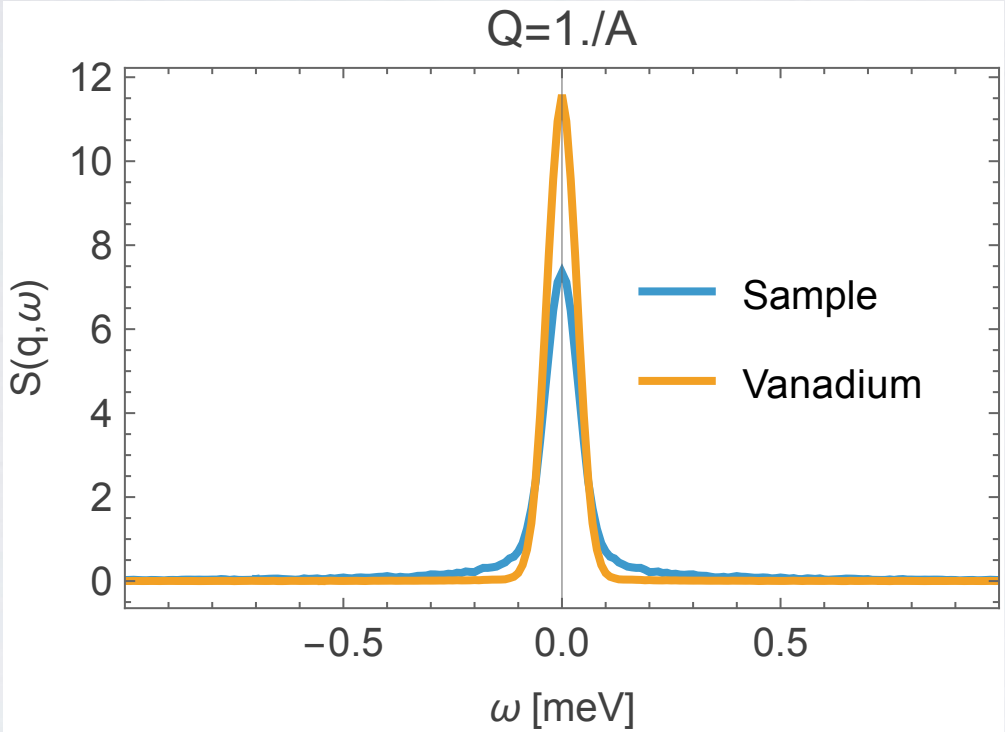
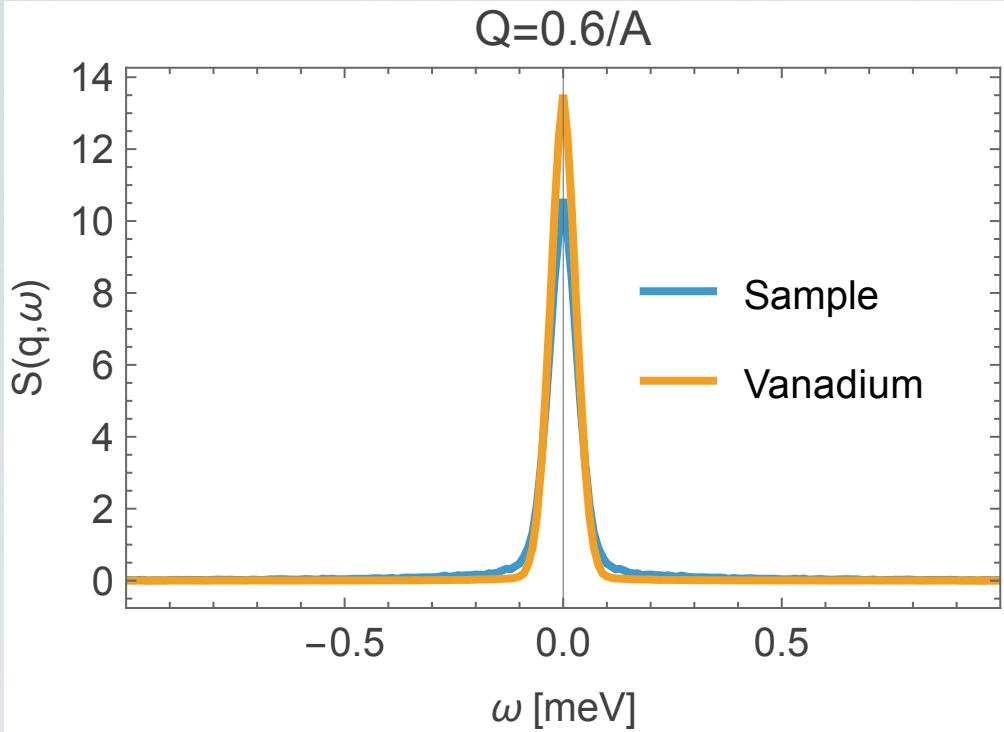
$$\int_{-\infty}^{+\infty} d\omega \, \omega S(\mathbf{q}, \omega) = -i \left. \frac{\partial F(\mathbf{q}, t)}{\partial t} \right|_{t=0} = \sum_j \Gamma_{jj} \frac{\hbar |\mathbf{q}|^2}{2m_j}$$

**Scattering
kinematics**

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

Dynamic structure factors and resolution-corrected intermediate scattering functions for myoglobin in solution

Data from A. M. Stadler, M. M. Koza, and J. Fitter, *J. Phys. Chem.*, 119(1):72-82, 2015

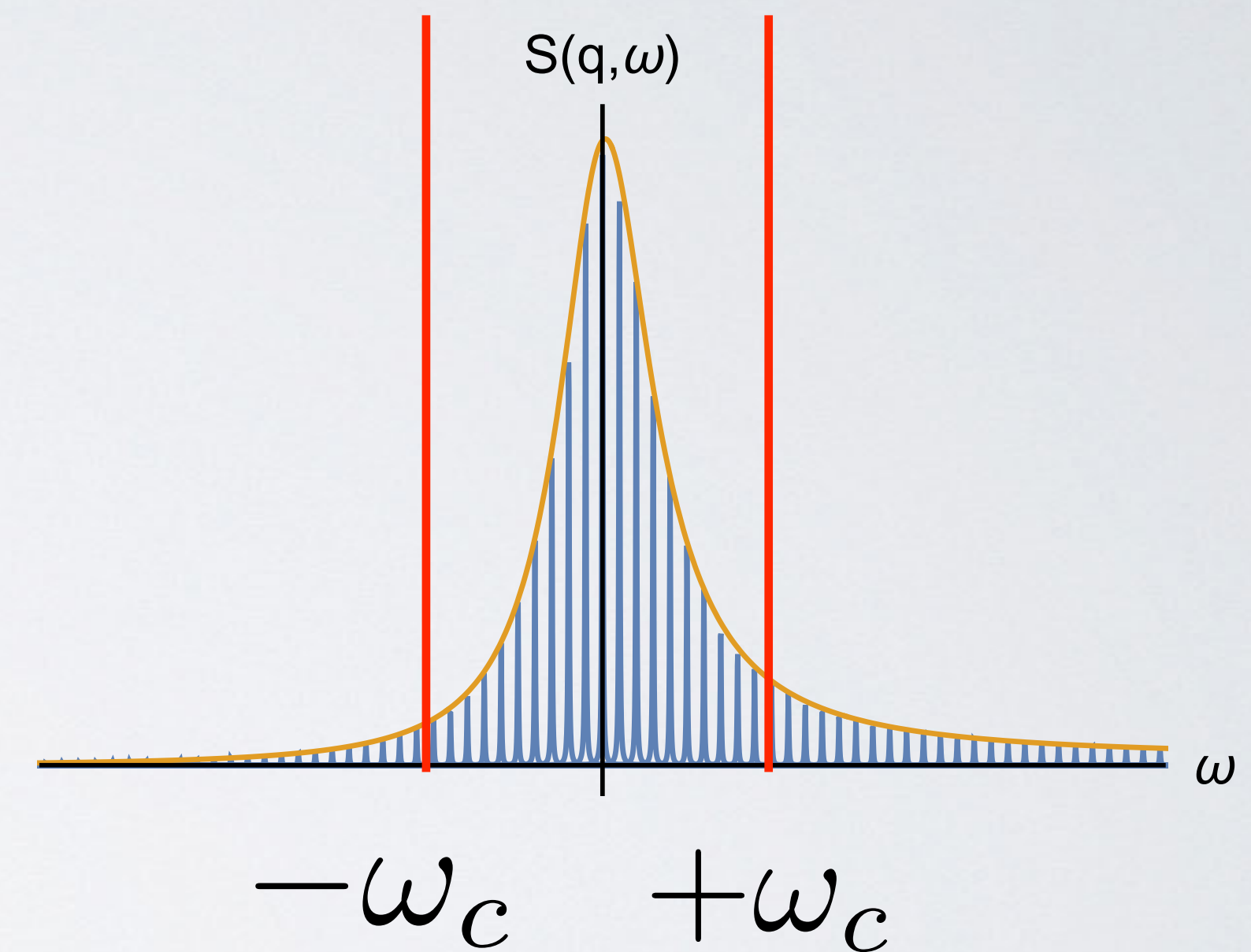


Not accessible to classical simulations: The effective mass

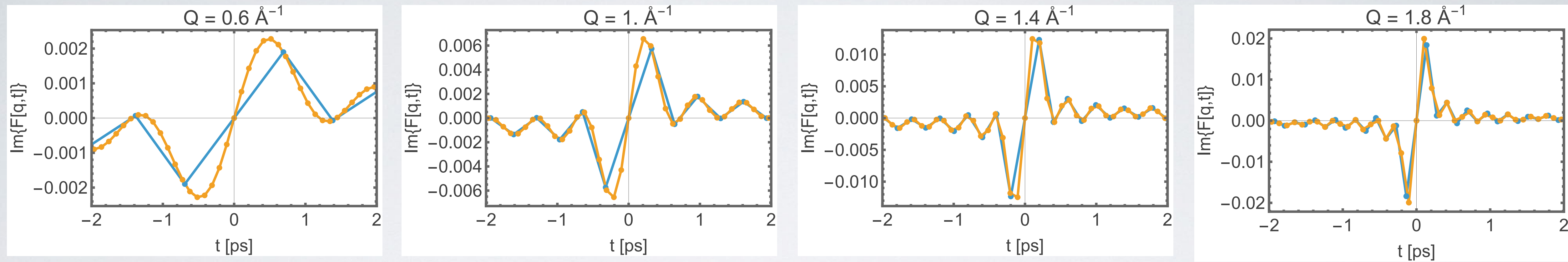
$$\overline{S}(q, \omega) \equiv \frac{1}{4\pi} \int d\Omega_q S(q\mathbf{n}_q, \omega) \quad \text{Angular average}$$

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

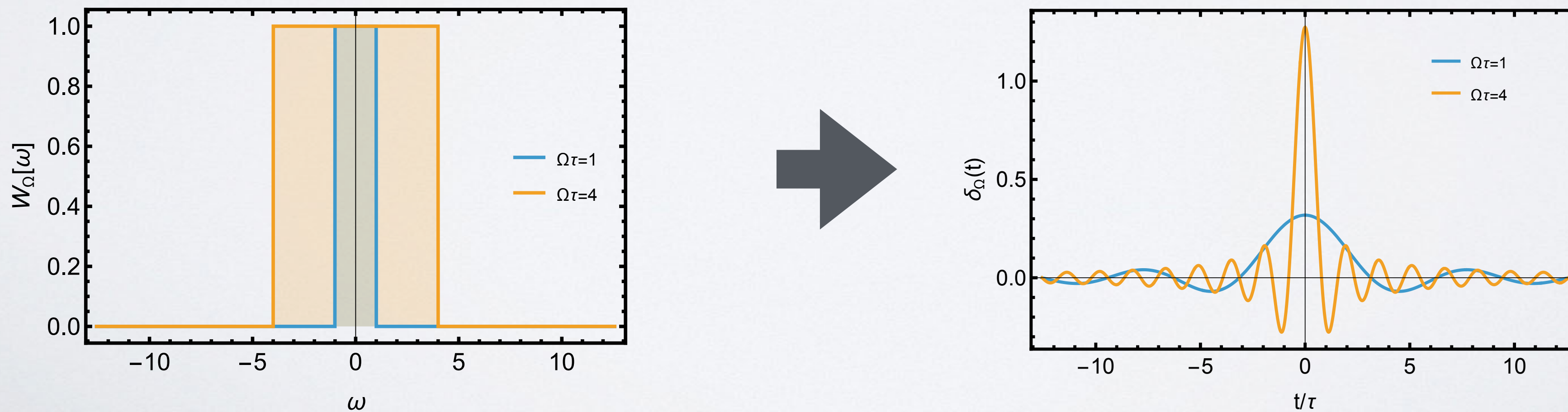
$$M \leq M_{\text{eff}}(q, \omega_c) < \infty$$



$\text{Im}[F(q,t)]$ with and without **zero-padding** of the experimental input spectra (orange & blue lines, respectively):

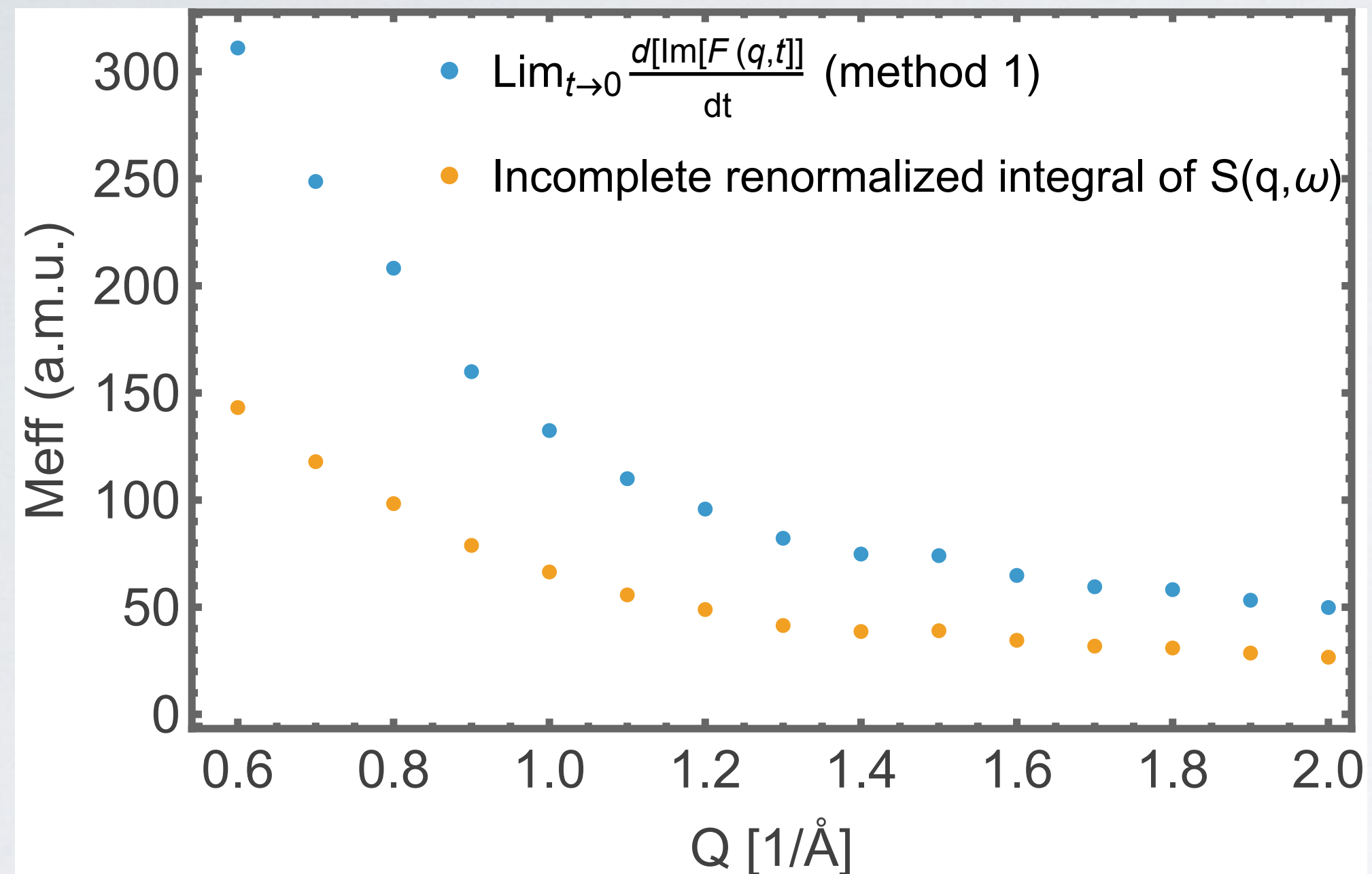


The oscillations are due to the frequency cutoff window of the instrument



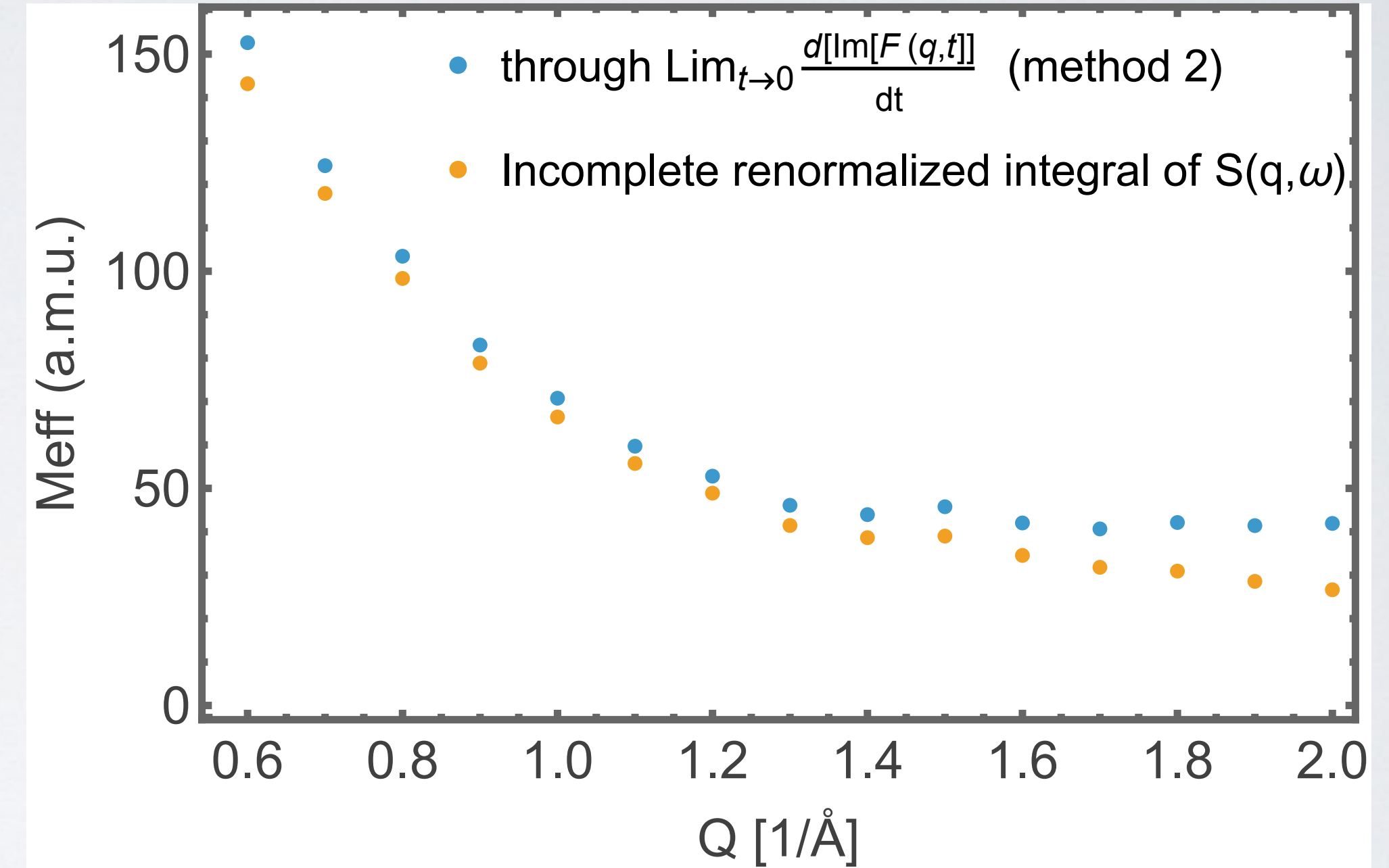
Effective atomic recoil masses for myoglobin in solution

Without zero-padding of the spectra



$$m_{\text{eff}} = 118.849 \text{ u}$$

With zero-padding of the spectra



$$m_{\text{eff}} = 58.7297 \text{ u}$$

Average side-chain mass in proteins: 54-55 u.

Conclusions

- Neutrons “see” quantum states and not trajectories.
- Neutrons are wave packets and probe small systems ($<10^8$ atoms) which are thermostatted by the environment ($\rightarrow$ open systems, relaxation).
- The quantum mechanical and classical interpretation of (quasi-)elastic scattering from proteins lead *a priori* to different functional dependencies on temperature.
- Tunnelling in “rugged” quantum energy landscapes should be considered as a fundamental process in protein dynamics and folding.
- Recoil in QENS is a very small but exploitable effect.

The universe can only be understood after learning the language and becoming familiar with the characters in which it is written. It is written in mathematical language, and the letters are triangles, circles, and other geometric figures, without which it is humanly impossible to understand a single word.

Galileo Gallilei, 1623 treatise *Il Saggiatore* (The Assayer)