

MODEL-FREE APPROACH TO QUASIELASTIC NEUTRON SCATTERING FROM ANOMALOUSLY DIFFUSING QUANTUM PARTICLES*

GERALD KNELLER

Centre de Biophysique Moléculaire CNRS
Rue Charles Sadron, 45071 Orléans, France

and

Synchrotron SOLEIL, Saint Aubin — BP 48, 91192 Gif-sur-Yvette, France
and

Université d'Orléans, Avenue du Parc Floral, 45067 Orléans, France

(Received April 27, 2018)

This paper resumes and extends recent work by the author on the dynamics of anomalously diffusing quantum particles that is probed by the quasielastic neutron scattering from complex molecular systems. A model-free description of the observed quasielastic neutron scattering spectra is developed which is valid for moderate momentum transfers.

DOI:10.5506/APhysPolB.49.893

1. Introduction

Anomalous free diffusion is an ubiquitous phenomenon which is characterised by a non-linear growth of the mean-square displacement of the diffusing particles with lag time, $W(t) \equiv \langle (x(t) - x(0))^2 \rangle \sim t^\alpha$, where $0 < \alpha < 2$. The regimes $0 < \alpha < 1$ and $1 < \alpha < 2$ are, respectively, referred to as sub- and superdiffusion, and the case of $\alpha = 1$ corresponds to normal diffusion which is described by the historic models of Fick and Einstein [1, 2]. Although the number of publications concerning anomalous diffusion literally exploded during the last 30 years, the phenomenon has been already observed in 1935 by Freundlich and Krüger, who reported on subdiffusion of quinones in electrolyte solutions [3]. A recent review on anomalous diffusion can be found in Ref. [4].

The models for anomalous diffusion which have been developed so far are essentially concerned with systems whose dynamics can be described by the

* Presented at the XXX Marian Smoluchowski Symposium on Statistical Physics, Kraków, Poland, September 3–8, 2017.

laws of classical physics. The incorporation of quantum effects is an additional challenge from a theoretical point of view and of practical importance for quasielastic neutron scattering (QENS) from complex condensed matter systems. QENS is used to study the diffusive dynamics in these systems on the atomic scale and the accessible time and length scales vary, respectively, from pico- to nanoseconds and from 0.1 to 10 nanometers [5]. In hydrogen-rich samples essentially the self-dynamics of the hydrogen atoms is probed, which exhibits anomalous diffusion and slow multiscale relaxation if complex molecular systems such as proteins and biological membranes are concerned. Since hydrogen atoms have low masses, quantum effects play a potential role and have effectively been observed by elastic incoherent neutron scattering [6]. A theoretical description of QENS from complex molecular systems which addresses both anomalous diffusion and quantum effects is presented in this paper, which is based on recent publications by the author on that subject [7–9].

2. Mean-squared displacement of quantum particles

The fundamental observable in a trajectory-based description of diffusion processes is the mean-squared displacement (MSD) of the diffusing particles

$$W_{\text{cl}}(t) = \langle (x(t) - x(0))^2 \rangle_{\text{cl}} . \quad (1)$$

Here and in the following, we consider the atomic scale and $\langle \dots \rangle_{\text{cl}}$ defines a classical equilibrium ensemble average over the phase-space coordinates of the atoms in the system under consideration. One writes explicitly

$$W_{\text{cl}}(t) = \int d\Gamma \rho(\Gamma) (x(\Gamma, t) - x(\Gamma))^2 , \quad (2)$$

where $\Gamma = (x, p)$ comprises all coordinates x and momenta p of all atoms and

$$\rho(\Gamma) = \exp(-\beta H(\Gamma))/Z \quad (3)$$

is the equilibrium distribution function. $H(\Gamma)$ denotes the classical Hamilton function and $Z = \int d\Gamma \exp(-\beta H(\Gamma))$ the classical partition function. As usual $\beta = (k_{\text{B}}T)^{-1}$, where k_{B} and T are, respectively, the Boltzmann constant and the absolute temperature in Kelvins. For simplicity, we consider here one-dimensional motion, where $x(\Gamma)$ is the position of the tagged particle defined by the initial point Γ in phase space, and $x(\Gamma, t)$ is the corresponding position after time t . The latter is obtained by solving the Hamiltonian equations of motion $\dot{x} = \partial H / \partial p$ and $\dot{p} = -\partial H / \partial x$. Formally, one may write $x(\Gamma, t) = \exp(it\mathcal{L})x(\Gamma)$, where $\mathcal{L} = -i\{\partial H / \partial P \times \partial / \partial X - \partial H / \partial X \times \partial / \partial P\}$ is the Liouville operator.

In the quantum regime, we write

$$W(t) = \left\langle (\hat{x}(t) - \hat{x}(0))^2 \right\rangle, \tag{4}$$

where $\hat{x}(t)$ is the Hermitian position operator of the diffusing particle, and $\langle \dots \rangle$ denotes a quantum mechanical ensemble average

$$W(t) = \text{tr} \left\{ \hat{\rho} (\hat{x}(t) - \hat{x}(0))^2 \right\}. \tag{5}$$

Here, $\hat{\rho}$ is the equilibrium density operator

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}, \tag{6}$$

\hat{H} is the Hamiltonian of the system and $Z = \text{tr}\{e^{-\beta \hat{H}}\}$ is the quantum partition function. The symbol “tr” denotes the trace and

$$\hat{x}(t) = e^{\frac{it}{\hbar} \hat{H}} \hat{x} e^{-\frac{it}{\hbar} \hat{H}}. \tag{7}$$

Both the classical and the quantum MSD are intimately related to the velocity autocorrelation function (VACF). Writing $x(t) - x(0) = \int_0^t d\tau v(\tau)$, it follows in the classical case that

$$W_{\text{cl}}(t) = 2 \int_0^t d\tau (t - \tau) c_{vv}^{(\text{cl})}(\tau), \tag{8}$$

where

$$c_{vv}^{(\text{cl})}(t) = \langle v(0)v(t) \rangle_{\text{cl}}. \tag{9}$$

Here, the stationarity of the VACF has been used, *i.e.* $\langle v(t_0)v(t_1) \rangle_{\text{cl}} = \langle v(0)v(t_1 - t_0) \rangle_{\text{cl}}$, which leads also immediately to the symmetry relation

$$c_{vv}^{(\text{cl})}(-t) = c_{vv}^{(\text{cl})}(t). \tag{10}$$

The quantum VACF,

$$c_{vv}(t) = \langle \hat{v}(0)\hat{v}(t) \rangle, \tag{11}$$

is instead a complex function fulfilling the symmetry relations

$$c_{vv}(-t) = c_{vv}^*(t) = c_{vv}(t + i\beta\hbar). \tag{12}$$

We note here arbitrary that quantum time correlation functions $c_{AB}(t)$ verify the symmetry relations $c_{AB}^*(t) = c_{BA}(-t)$ and $c_{AB}(-t) = c_{BA}(t + i\beta\hbar)$. Since the quantum VACF is a complex function and since the MSD must be

real, relation (8) cannot be generalised to the quantum case by exchanging the classical VACF with its quantum counterpart. Using that $\hat{x}(t) - \hat{x}(0) = \int_0^t d\tau \hat{v}(\tau)$, in analogy with the classical case, one obtains here

$$W(t) = 2 \int_0^t d\tau (t - \tau) c_{vv}^{(R)}(\tau), \quad (13)$$

observing that $\hat{v}(0)$ and $\hat{v}(t)$ do not commute. The real VACF in expression (8) is here thus replaced by the real part of its complex quantum counterpart.

3. Asymptotic analysis of anomalous quantum diffusion

3.1. Fractional diffusion constant

It follows from (13) that the MSD of diffusing quantum particles evolves for short times “ballistically”

$$W(t) \stackrel{t \rightarrow 0}{\sim} \langle \hat{v}^2 \rangle t^2, \quad (14)$$

and for long times as $W(t) \sim t^\alpha$. In order to characterise the approach to the asymptotic regime, we write

$$W(t) \stackrel{t \rightarrow \infty}{\sim} 2D_\alpha L(t) t^\alpha, \quad 0 \leq \alpha < 2, \quad (15)$$

where $\lim_{t \rightarrow \infty} L(t) = 1$ and D_α is the fractional diffusion constant with SI units $\text{m}^2/\text{s}^\alpha$. The case of $\alpha = 0$, which corresponds to confined diffusion, is here explicitly included. Formally, $L(t)$ belongs to the class of slowly growing functions, which play an important role in asymptotic analysis [10], and verify the relation $\lim_{t \rightarrow \infty} L(\lambda t)/L(t) = 1$ for any $\lambda > 0$. The standard example is the logarithm, $L(t) = \ln(t)$, but it is obvious that a function which tends asymptotically to a plateau value belongs to the same class of functions. The importance of asymptotic analysis for the theoretical description of diffusion processes relies on the equivalence of (15) with the behaviour of the corresponding Laplace transform for small values of s [7], which is given by

$$\tilde{W}(s) \stackrel{s \rightarrow 0}{\sim} 2L(1/s) D_\alpha \frac{\Gamma(1 + \alpha)}{s^{1+\alpha}}. \quad (16)$$

We recall here that the Laplace transform of a function $f(t)$ is defined through $\tilde{f}(s) = \int_0^\infty dt \exp(-st) f(t)$ ($\Re(s) > 0$). In this context, it is important to note that for arbitrary functions $f(t)$, the behaviour of $\tilde{f}(s)$ for small values of s cannot be obtained from the behaviour of $f(t)$ for long times.

The condition is that the integral $\int_0^t d\tau f(\tau)$ diverges as t goes to infinity. For the MSD, this condition is effectively fulfilled and, therefore, relations (15) and (16) are, indeed, equivalent. This equivalence can be exploited to derive a generalised Kubo formula which holds for anomalously diffusing particles in the quantum case. Starting from (13), one uses that $\tilde{W}(s) = 2\tilde{c}_{vv}^{(R)}(s)/s^2$ or $\tilde{W}(s) = 2\tilde{c}_{vv}^{(R)}(s)/s^2$, and from the combination with the asymptotic expression (16), one finds that $D_\alpha = \lim_{s \rightarrow 0} s^{\alpha-1} \tilde{c}_{vv}^{(R)}(s)/\Gamma(1+\alpha)$. In the time domain, this leads to

$$D_\alpha = \frac{1}{\Gamma(1+\alpha)} \int_0^\infty dt_0 \partial_t^{\alpha-1} c_{vv}^{(R)}(t), \tag{17}$$

where $\partial_t^{\alpha-1}$ denotes here a fractional time derivative of the order of $\alpha - 1$

$$\partial_t^{\alpha-1} c_{vv}^{(R)} = \frac{d}{dt} \int_0^t dt \frac{(t-\tau)^{1-\alpha}}{\Gamma(2-\alpha)} c_{vv}^{(R)}(\tau). \tag{18}$$

Expression (17) is a generalisation of the well-known Green–Kubo relation $D = \int_0^\infty dt c_{vv}(t)$ for the diffusion coefficient of normally diffusing classical particles. For classical dynamical systems, $c_{vv}^{(R)}(t)$ is to be replaced by $c_{vv}^{(cl)}(t)$. The fractional diffusion coefficient defines the time scale for the transition from ballistic to diffusive motion via [7]

$$\tau_v = \left(\frac{D_\alpha}{\langle \hat{v}^2 \rangle} \right)^{\frac{1}{2-\alpha}}. \tag{19}$$

Here, $\langle \hat{v}^2 \rangle = k_B T/m$ is the mean-squared velocity, where m is the mass of the diffusing particle, and expression (19) is motivated by the exponentially decaying VACF of a Brownian particle, where $c_{vv}(t) = \langle v^2 \rangle \exp(-\gamma t)$ and $\tau_v = \gamma^{-1}$. Using the characteristic time τ_v , we can more precisely define that $t \xrightarrow{\sim} \infty$ and $s \xrightarrow{\sim} 0$ mean, respectively, $t \gg t_v$ and $|s| \ll 1/t_v$.

The generalised Kubo formula (17) for the fractional diffusion constant holds also in the case of $\alpha = 0$, which corresponds to confined diffusion. Here, the mean position of a diffusing particle is well-defined and the dynamics of the diffusing quantum particle may be described by the operator $\hat{u}(t) = \hat{x}(t) - \langle \hat{x} \rangle$, noting that $W(t) = \langle (\hat{u}(t) - \hat{u}(0))^2 \rangle$. The diffusion constant for confined diffusion can be derived from expression (17) by following the argumentation in Ref. [7], with the classical VACF being replaced by the real part of its quantum counterpart. The result is

$$D_0 = \langle \hat{u}^2 \rangle, \tag{20}$$

and the characteristic time scale of the VACF is here given by

$$\tau_v = \sqrt{\frac{\langle \hat{u}^2 \rangle}{\langle \hat{v}^2 \rangle}}. \quad (21)$$

The simple example of a harmonic quantum oscillator of mass m and (angular) frequency Ω in thermal equilibrium shows that (21) is meaningful. Here, we have $\langle \hat{v}^2 \rangle = k_B T/m$ and $\langle \hat{u}^2 \rangle = k_B T/(m\Omega^2)$, such that $\tau_v = 1/\Omega$.

3.2. Long-time tails of the VACF

The asymptotic form (15) of the MSD entails particular forms for the long-time tails of the real and imaginary part of the VACF, respectively. It follows from (13) that $c_{vv}^{(R)}(t) = W''(t)/2$ and with (15), one finds, therefore, that the real part of the VACF decays for long times as

$$c_{vv}^{(R)}(t) \stackrel{t \rightarrow \infty}{\sim} D_\alpha L(t) \alpha(\alpha - 1) t^{\alpha-2}. \quad (22)$$

The function $L(t)$ can be here treated like a constant since $t^n L^{(n)}(t) \stackrel{t \rightarrow \infty}{\sim} 0$ for slowly growing functions which fulfil in addition $\lim_{t \rightarrow \infty} L(t) = 1$. This is seen as follows: It follows from $\lim_{t \rightarrow \infty} L(\lambda t)/L(t) = 1$ that $\lim_{t \rightarrow \infty} d^n/d\lambda^n \{L(\lambda t)/L(t)\} = \lim_{t \rightarrow \infty} t^n L^{(n)}(\lambda t)/L(t) = 0$. Since this relation is true for any $\lambda > 0$ and since $\lim_{t \rightarrow \infty} L(t) = 1$, we can write $\lim_{t \rightarrow \infty} t^n L^{(n)}(\lambda t) = 0$. Setting now in particular $\lambda = 1$ closes the proof.

The asymptotic form of the imaginary part of the VACF can be derived from (22) and the symmetry relation (12). As outlined in [9], it follows from (12) that the Laplace transforms of the imaginary and real part are related through

$$\tilde{c}_{vv}^{(I)}(s) = -\tan\left(\frac{\beta \hbar s}{2}\right) \tilde{c}_{vv}^{(R)}(s), \quad (23)$$

such that

$$c_{vv}^{(I)}(t) = -\tan\left(\frac{\beta \hbar}{2} \frac{d}{dt}\right) c_{vv}^{(R)}(t) \quad (24)$$

with d/dt being a left derivative. Inserting here expression (22) shows that

$$c_{vv}^{(I)}(t) \stackrel{t \rightarrow \infty}{\sim} -\frac{\beta \hbar}{2} L(t) D_\alpha \alpha(\alpha - 1)(\alpha - 2) t^{\alpha-3}. \quad (25)$$

All faster decaying contributions $\propto t^{\alpha-n}$, with $n = 4, 5, \dots$, can be neglected. Since $0 \leq \alpha < 2$, the signs for the long-time tails of $c_{vv}^{(R)}(t)$ and $c_{vv}^{(I)}(t)$ are

the same and they vanish for $\alpha = 0$ and $\alpha = 1$, *i.e.* for confined and for normal diffusion. Note that

$$\lim_{\hbar \rightarrow 0} c_{vv}^{(1)}(t) = 0, \tag{26}$$

which is consistent with the fact the classical VACF is real, and the corresponding symmetry relation (10) is retrieved from (12).

4. Quasielastic neutron scattering

4.1. Differential cross section and scattering functions

The basic quantity which is observed with QENS experiments and thermal neutron scattering experiments, in general, is the differential scattering cross section

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k}{k_0} S(\mathbf{q}, \omega). \tag{27}$$

The symbols ω and \mathbf{q} denote, respectively, the energy and momentum transfer from the neutron to the sample in units of \hbar . Multiplied by the flux of incoming atoms, the differential scattering cross section defines the number of neutrons which is scattered per second, per solid angle interval $d\Omega$, and per energy transfer interval $d\omega$. The dynamic structure factor, $S(\mathbf{q}, \omega)$, is here the quantity of interest. It carries information about the atomic dynamics in the system of interest in space and time. In the following, we will consider an isotropic scattering system such that the momentum transfer can be chosen to point in the “ x -direction”, $\mathbf{q} = q \mathbf{e}_x$. We assume, in addition, that the scattering results predominantly from hydrogen atoms and, for simplicity, that all hydrogen atoms can be represented by one single atom. The position of the scattering atom along the x -axis is represented by the position operator $\hat{x}(t)$. With these prerequisites, the dynamic structure factor per atom has the form of

$$S(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} F(q, t), \tag{28}$$

where

$$F(q, t) = \langle \exp(-iq\hat{x}(0)) \exp(iq\hat{x}(t)) \rangle \tag{29}$$

is the (incoherent) intermediate scattering function. The latter fulfils the symmetry relation

$$F(q, t) = F(-q, -t + i\beta\hbar), \tag{30}$$

which follows from the symmetry relation $C_{AB}(t) = C_{BA}(-t + i\beta\hbar)$ of quantum time correlation functions and which translates into the detailed balance relation

$$S(q, \omega) = \exp(\beta\hbar\omega)S(-q, -\omega) \quad (31)$$

for the dynamic structure factor. The detailed balance relation expresses that energy gain ($\omega > 0$) of the sample is more likely than energy loss.

An important issue in this context is that the interpretation of QENS experiments usually relies on the replacement of $F(q, t)$ by its classical counterpart

$$F_{\text{cl}}(q, t) = \langle \exp(-iq[x(t) - x(0)]) \rangle_{\text{cl}}. \quad (32)$$

This implies not only neglecting quantum effects in the sample, but also to recoil effects resulting from the momentum transfer from the neutron to the sample. In particular, for hydrogen atoms, this assumption is not necessarily justified. Concerning the sample dynamics, quantum effects play an important role at least at lower temperatures [6]. Low effective masses of hydrogen atoms lead also to recoil effects, which are not true quantum effects, but are accounted for in a quantum description of the neutron scattering intensities [11]. The classical intermediate scattering function and the corresponding dynamic structure factor fulfil the symmetry relations

$$F_{\text{cl}}(q, t) = F_{\text{cl}}(-q, -t), \quad (33)$$

$$S_{\text{cl}}(q, \omega) = S_{\text{cl}}(-q, -\omega). \quad (34)$$

4.2. Asymptotic Gaussian approximation of $F(q, t)$

For moderate momentum transfers, the intermediate scattering function can be approximated by the Gaussian form

$$F_{\text{G}}(q, t) \approx \exp\left(i\frac{\hbar q^2 t}{2m}\right) \exp(-q^2 \mu_2(t)), \quad (35)$$

where $\mu_2(t)$ is given by the convolution integral [12]

$$\mu_2(t) = \int_0^t d\tau_1 (t - \tau_1) c_{vv}(\tau_1). \quad (36)$$

Compared to the quantum MSD given in (13), here the *full* VACF appears and not just its real part. The relation $\mu_2(t) = W(t)/2$ holds thus only in the classical case, where the VACF is real. A general relation between $\mu_2(t)$ and $W(t)$ can be derived by transforming expression (36) into the Laplace domain, $\tilde{\mu}_2(s) = \tilde{c}_{vv}(s)/s^2$. Writing now $\tilde{c}_{vv}(s) = \tilde{c}_{vv}^{(\text{R})}(s) + i\tilde{c}_{vv}^{(\text{I})}(s)$

and using (23), it follows that $\tilde{\mu}_2(s) = (1 - i \tan(\beta\hbar s/2)) \tilde{c}_{vv}^{(R)}(s)/s^2$. On the other hand, we know from (13) that $\tilde{W}(s) = 2\tilde{c}_{vv}^{(R)}(s)/s^2$, such that $\tilde{\mu}_2(s) = \frac{1}{2} (1 - i \tan(\beta\hbar s/2)) \tilde{W}(s)$. In the time domain, we thus obtain

$$\mu_2(t) = \frac{1}{2} \left(1 - i \tan \left(\frac{\beta\hbar}{2} \frac{d}{dt} \right) \right) W(t), \tag{37}$$

noting again that d/dt is a left derivative.

The first factor appearing in (41) is due to the recoil of the scattering atom. Defining

$$s_G(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \exp(-q^2 \mu_2(t)), \tag{38}$$

it follows that the dynamic structure factor takes the form of

$$S_G(q, \omega) = s_G(q, \omega - \omega_r), \tag{39}$$

where

$$\omega_r = \frac{\hbar q^2}{2m} \tag{40}$$

is the average recoil energy of the scattering atom in units of \hbar . The mass m is here an *effective* mass, which is usually larger than the “bare” atomic mass and depends on the motions of the scattering atom which can be excited by the incoming neutrons. In QENS experiments, this energy does not suffice to excite internal vibrations of (sub)molecules, which thus appear as rigid to the incoming neutrons. In this case, m is the Sachs–Teller mass of the scattering atom [13, 14]. Since recoil is a purely kinematic effect, the recoil factor survives in a carefully taken physical classical limit, where the momentum transfer $\Delta p = \hbar q$ is kept *finite*, and the limit $\hbar \rightarrow 0$ concerns only the physical properties of the scattering system [11].

The asymptotic form of $F_G(q, t)$ is derived from (35) by inserting expression (37) for $\mu_2(t)$, with $W(t)$ replaced with expression (15). The resulting asymptotic form of $\mu_2(t)$ is obtained by using only the first term in the Taylor series of the tangent function in (37), which leads to

$$F_G(q, t) \stackrel{t \rightarrow \infty}{\sim} \exp\left(i \frac{\hbar q^2}{2m} t\right) \exp\left(-q^2 \left(1 - i \frac{\beta\hbar}{2} \frac{d}{dt}\right) D_\alpha L(t) t^\alpha\right). \tag{41}$$

Since $F_G(q, t)$ is an even function in q , it follows that

$$F_G(q, -t) = F_G(q, t + i\beta\hbar) \tag{42}$$

on account of the general symmetry relation (30).

4.3. Confined diffusion and elastic scattering

For confined diffusion ($\alpha = 0$), the asymptotic form of $F_G(q, t)$ takes the form of

$$F_G(q, t) \stackrel{t \rightarrow \infty}{\sim} \exp\left(i \frac{\hbar q^2}{2m} t\right) \exp(-q^2 L(t) \langle \hat{u}^2 \rangle), \quad (43)$$

where it has been used that $D_0 = \langle \hat{u}^2 \rangle$ and that $L'(t) \stackrel{t \rightarrow \infty}{\sim} 0$. For $t \rightarrow \infty$, the factor $\exp(-q^2 L(t) \langle \hat{u}^2 \rangle)$ tends to the plateau value

$$\text{EISF}(q) = \exp(-q^2 \langle \hat{u}^2 \rangle), \quad (44)$$

which is referred to as elastic incoherent structure factor (EISF) and which gives information about the motional amplitude of the scattering atom. Defining

$$\Delta s_G(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) (\exp(-q^2 \mu_2(t)) - \text{EISF}(q)), \quad (45)$$

the dynamic-structure factor takes the form of

$$S_G(q, \omega) = \text{EISF}(q) \delta(\omega - \omega_r) + \Delta s_G(q, \omega - \omega_r) \quad (46)$$

which shows that the EISF is amplitude of the spectrum of the elastic line shifted by the recoil frequency ω_r . The term *elastic* incoherent structure factor is thus only justified if $\omega_r \approx 0$. The Gaussian form (44) has been abundantly used in the study of biological samples, noting that within a harmonic model the mean position fluctuation $\langle \hat{u}^2 \rangle = k_B T / K$ gives access to the force constant K defining the ‘‘softness’’ of a protein [15].

Noting that $W(t) = \langle (\hat{x}(t) - \hat{x}(0))^2 \rangle = \langle (\hat{u}(t) - \hat{u}(0))^2 \rangle$ and that $\hat{u}(t)$ and $\hat{u}(0)$ do not commute, one finds that the MSD can be here expressed as

$$W(t) = 2 (\langle \hat{u}^2 \rangle - \Re\{c_{uu}(t)\}), \quad (47)$$

where

$$c_{uu}(t) \equiv \langle \hat{u}(0) \hat{u}(t) \rangle \quad (48)$$

is the autocorrelation function of the position fluctuation. Since $\langle \hat{u}^2 \rangle = c_{uu}(0)$, the MSD thus describes the relaxation of $c_{uu}(t)$. Writing

$$\Re\{c_{uu}(t)\} \stackrel{t \rightarrow \infty}{\sim} \langle \hat{u}^2 \rangle R(t), \quad (49)$$

it follows that the function $L(t)$ describing the approach of the MSD to its asymptotic limiting form is given by

$$L(t) = 1 - R(t). \quad (50)$$

4.4. Semiclassical approximation

Taking the classical limit “ $\hbar \rightarrow 0$ ”, it follows from (41) that

$$F_g^{(\text{cl})}(q, t) \stackrel{t \rightarrow \infty}{\sim} \exp(-q^2 D_\alpha L(t) t^\alpha) \quad (51)$$

is the classical intermediate scattering function in the Gaussian approximation. In the spacial case of confined diffusion, one has, in particular, $D_0 = \langle u^2 \rangle_{\text{cl}}$, such that

$$F_g^{(\text{cl})}(q, t) \stackrel{t \rightarrow \infty}{\sim} \exp(-q^2 L(t) \langle u^2 \rangle_{\text{cl}}). \quad (52)$$

Since $F_g^{(\text{cl})}(q, t)$ is a classical time correlation function, it fulfils the symmetry relation

$$F_g^{(\text{cl})}(q, -t) = F_g^{(\text{cl})}(q, t). \quad (53)$$

A semiclassical approximation [17] fulfilling strictly the symmetry relation (42) can be defined by identifying the real and time-symmetric function

$$F_g^{(+)}(q, t) = F_g(q, t + i\beta\hbar/2), \quad (54)$$

with the classical intermediate scattering function

$$F_g^{(+)}(q, t) \approx F_g^{(\text{cl})}(q, t). \quad (55)$$

In the frequency domain, relation (54) corresponds to

$$S_g(q, \omega) \approx \exp(\beta\hbar\omega/2) S_g^{(\text{cl})}(q, \omega) \quad (56)$$

and the semiclassical approximation implies, in particular, that the average recoil energy is not bigger than the thermal energy fluctuations of the scattering atom,

$$\frac{\hbar^2 q^2}{2m} \lesssim k_B T. \quad (57)$$

5. Discussion and conclusion

In this paper, a model-free form of the quantum intermediate scattering function for incoherent neutron scattering has been derived, which is valid for moderate momentum transfers and for time scales beyond the diffusion time scale τ_v which defines the transition from the ballistic to the diffusive regime. Such a description is useful for practical applications if the energy resolution of the spectrometer is much smaller than the energy transfer corresponding to τ_v , since, in this case, the quasielastic line is entirely described by the asymptotic form of the intermediate scattering function. To discuss

this point, we consider two instruments at the Institut Laue–Langevin, which are frequently used for QENS studies on liquids and soft matter systems. The first one is the IN6 spectrometer, which is a time-of-flight instrument, and the second one is the high-resolution backscattering spectrometer IN16 at the same institution. These instruments have energy resolutions of, respectively, $\Delta E = 50 \mu\text{eV}$ and $\Delta E = 0.75 \mu\text{eV}$, which corresponds to time scales of $\tau_T \approx 83 \text{ ps}$ and $\tau_T \approx 55 \text{ ns}$. Even if we consider slow diffusion processes, such as the lateral center-of-mass diffusion of lipid molecules in lipid bilayers, τ_v is of the order of picoseconds [16] and thus much smaller than τ_T . This shows that QENS spectra at moderate momentum transfers, where the Gaussian approximation of the intermediate scattering function is valid, can be conveniently described by the model-free approach presented in this paper.

REFERENCES

- [1] A. Fick, *Ann. Phys.* **170**, 59 (1855).
- [2] A. Einstein, *Ann. Phys.* **322**, 549 (1905).
- [3] H. Freundlich, D. Krüger, *Trans. Faraday Soc.* **31**, 906 (1935).
- [4] R. Metzler, J.H. Jeon, A.G. Cherstvy, *Phys. Chem. Chem. Phys.* **16**, 24128 (2014).
- [5] M. Bée, *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science*, Adam Hilger, Bristol 1988.
- [6] F. Natali *et al.*, *Physica B* **301**, 145 (2001).
- [7] G.R. Kneller, *J. Chem. Phys.* **134**, 224106 (2011).
- [8] G.R. Kneller, *Acta Phys. Pol. B* **46**, 1167 (2015).
- [9] G.R. Kneller, *J. Chem. Phys.* **145**, 044103 (2016).
- [10] J. Karamata, *J. Reine Angew. Math.* **164**, 27 (1931).
- [11] G.R. Kneller, *Mol. Phys.* **83**, 63 (1994).
- [12] A. Rahman, K.S. Singwi, A. Sjölander, *Phys. Rev.* **126**, 986 (1962).
- [13] R.G. Sachs, E. Teller, *Phys. Rev.* **60**, 18 (1941).
- [14] G.R. Kneller, *J. Chem. Phys.* **125**, 114107 (2006).
- [15] G. Zaccai, *Science* **288**, 1604 (2000).
- [16] G.R. Kneller, K. Baczynski, M. Pasenkiewicz-Gierula, *J. Chem. Phys.* **135**, 141105 (2011).
- [17] P. Schofield, *Phys. Rev. Lett.* **4**, 239 (1960).