AIP | The Journal of Chemical Physics

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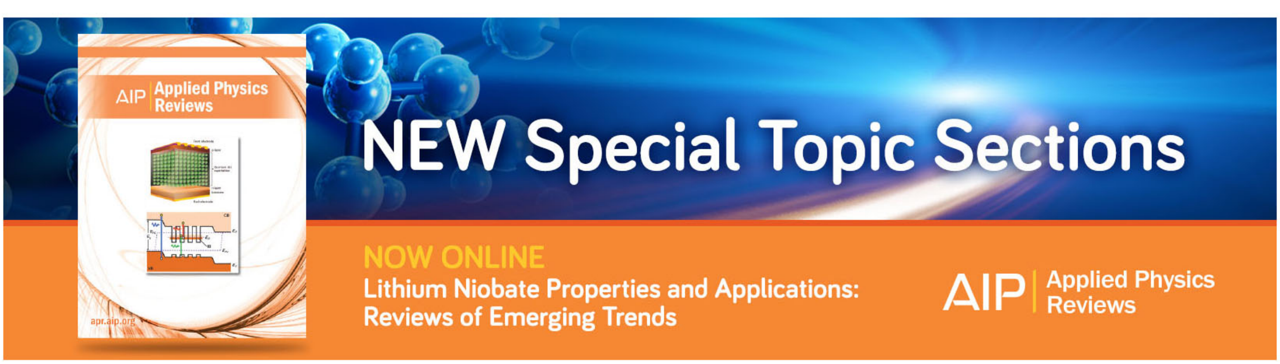
Citation: The Journal of Chemical Physics **145**, 044103 (2016); doi: 10.1063/1.4959124
View online: http://dx.doi.org/10.1063/1.4959124
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/145/4?ver=pdfcov
Published by the AIP Publishing



THE JOURNAL OF CHEMICAL PHYSICS **145**, 044103 (2016)

Asymptotic neutron scattering laws for anomalously diffusing quantum particles

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(Received 10 June 2016; accepted 8 July 2016; published online 25 July 2016)

The paper deals with a model-free approach to the analysis of quasielastic neutron scattering intensities from anomalously diffusing quantum particles. All quantities are inferred from the asymptotic form of their time-dependent mean square displacements which grow $\propto t^{\alpha}$, with $0 \leq \alpha < 2$. Confined diffusion ($\alpha = 0$) is here explicitly included. We discuss in particular the intermediate scattering function for long times and the Fourier spectrum of the velocity autocorrelation function for small frequencies. Quantum effects enter in both cases through the general symmetry properties of quantum time correlation functions. It is shown that the fractional diffusion constant can be expressed by a Green-Kubo type relation involving the real part of the velocity autocorrelation function. The theory is exact in the diffusive regime and at moderate momentum transfers. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4959124]

I. INTRODUCTION

Anomalous diffusion generally refers to the observation that the time-dependent mean square displacement (MSD) of a freely diffusing particle evolves asymptotically as

$$W(t) \overset{t\to\infty}{\sim} 2D_{\alpha}t^{\alpha}, \text{ with } 0 < \alpha < 2. \quad (1)$$

Here D_{α} is the (fractional) diffusion constant and the MSD is defined as an ensemble average, $W(t) = \langle (x(t) - x(0))^2 \rangle$. For simplicity we consider the projection of the motion on an arbitrary direction "x" in space, supposing that the system under consideration is isotropic. The case $\alpha = 1$ corresponds to "normal diffusion," or Brownian motion, and is described by the well-known diffusion models of Einstein, Langevin, and Wiener.[1,2] In the past, various extensions, such as fractional Brownian motion[3] and the Continuous Time Random Walk (CTRW),[4] have been proposed to include also anomalous diffusion.[5–8] The underlying physical assumption in all Brownian dynamics type models is a time scale separation between the "slow" motions of the diffusing particle and the "fast" motions of the molecules in the environment, which are modeled as noise. However, neither the assumption of such a time scale separation nor model assumptions about the dynamics of the diffusing particles are necessary to describe diffusion processes in general and anomalous diffusion in particular. The key elements that characterize the diffusion type for a tagged particle are the asymptotic forms of its velocity autocorrelation function (VACF) and the associated memory kernel. The latter defines the relaxation of the VACF in Zwanzig's (exact) generalized Langevin equation[9–11] and reflects the structural dynamics of the local "cage"[12] in which the particle diffuses. In this model-free description of diffusion processes, one may also consider very light particles, such as hydrogen atoms, where even quantum effects may be important. Experimentally, the diffusion of hydrogen atoms can be ideally studied by quasielastic neutron scattering (QENS), taking advantage of their large scattering cross section for neutrons. The neutron scattering theory developed by Rahman and Sjølander[13] shows that QENS gives access to the MSD of diffusing atoms and molecules if one assumes moderate momentum transfers, such that the neutron intermediate scattering function can be treated in the Gaussian approximation. The overwhelming part of QENS studies has, however, been analyzed in the framework of Van Hove's theory,[14] employing classical diffusion models for the space and time-dependent Van Hove correlation functions.[15] In contrast to Rahman's approach, the assumption of the classical limit is here essential for the physical interpretation of QENS spectra. This implies not only to neglect intrinsic quantum effects of the scattering system but also to disregard the purely kinematic recoil effect, which can be important for scattering atoms with low effective masses.

The aim of this paper is to develop an alternative, model-free route to the interpretation of QENS experiments which is not based on particular models, but uses instead the asymptotic "universal" form of the relevant mean square displacements. The idea is to combine the classical work of Rahman and Sjølander with the asymptotic analysis of anomalous diffusion processes which has been presented more recently in Ref. 9 and which can be straightforwardly extended to include also quantum effects.

A. Mean square displacement

The mean square displacement (MSD) of a quantum particle is defined through a quantum ensemble average, whose explicit form reads

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

Here $\hat{\rho}$ stands for the density operator,

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}, \tag{3}$$

and $\hat{x}(t)$ is the position operator of the tagged particle in the Heisenberg picture,

$$\hat{x}(t) = e^{\frac{it}{\hbar}\hat{H}} \hat{x} e^{-\frac{it}{\hbar}\hat{H}}. \tag{4}$$

As usual, "tr" denotes the trace, $\hat{H}$ is the Hamiltonian of the system, and $\beta = (k_B T)^{-1}$, with k_B and T being, respectively, the Boltzmann constant and the absolute temperature in Kelvins. The density operator $\hat{\rho}$ fulfills the normalization condition $\mathrm{tr}\{\hat{\rho}\} = 1$ and therefore $Z = \mathrm{tr}\{e^{-\beta\hat{H}}\}$. It follows from the hermiticity of $\hat{H}$ and $\hat{x}$ that $W(t) \geq 0$. Writing

$$\hat{x}(t) - \hat{x}(0) = \int_0^t d\tau\, \hat{v}(\tau),$$

where

$$\hat{v}(t) \equiv \frac{d\hat{x}(t)}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{x}(t)]$$

is the velocity (operator) of the diffusing particle, the MSD may be written as a double time integral

$$W(t) = \int_0^t \int_0^t d\tau_2\, d\tau_1\, c_{vv}(\tau_2, \tau_1), \tag{5}$$

where $c_{vv}(\tau_2, \tau_1)$ is the two-point velocity autocorrelation function (VACF),

$$c_{vv}(\tau_2, \tau_1) = \mathrm{tr}\{\hat{\rho}\, \hat{v}(\tau_2)\hat{v}(\tau_1)\}. \tag{6}$$

As in the classical case, the VACF is stationary, i.e., invariant with respect to a common translation of both time arguments. It may thus be parametrized by a single lag time, $\tau \equiv \tau_1 - \tau_2$,

$$c_{vv}(\tau_2, \tau_1) = c_{vv}(0, \tau_1 - \tau_2) \equiv c_{vv}(\tau). \tag{7}$$

Using the stationarity of the VACF in expression (5) and performing the variable change $(\tau_1, \tau_2) \to (u, v)$, with $u = \tau_1 - \tau_2$, $v = \tau_2$, it is easy to see that

$$W(t) = \int_0^t du\, (t - u)\{c_{vv}(u) + c_{vv}(-u)\}.$$

In contrast to its classical counterpart, the quantum VACF is not symmetric in time, but fulfills instead the symmetry relation

$$c_{vv}(-t) = c_{vv}^*(t) = c_{vv}(t + i\beta\hbar). \tag{8}$$

The quantum VACF is a complex function whose real and imaginary parts are, respectively, even and odd functions in time,

$$c_{vv}^{(R)}(t) = \frac{1}{2}\big(c(t) + c(-t)\big), \tag{9}$$

$$c_{vv}^{(R)}(t) = \frac{1}{2i}\big(c(t) - c(-t)\big), \tag{10}$$

such that its Fourier transform (see Section II C) is real. With (8) the MSD can be written in two equivalent forms,

$$W(t) = 2\int_0^t du\, (t - u) c_{vv}^{(R)}(u), \tag{11}$$

$$W(t) = \int_0^t du\, (t - u)\{c_{vv}(u) + c_{vv}(u + i\beta\hbar)\}, \tag{12}$$

from which the classical convolution integral[16] is retrieved in the limit $\hbar \to 0$.

B. Kubo relation for D_α

For the following considerations, we will use relation (1) in a slightly generalized form:

$$W(t) \overset{t\to\infty}{\sim} 2L(t) D_\alpha t^\alpha \quad (0 \leq \alpha < 2). \tag{13}$$

The case $\alpha = 0$ is here explicitly included. Formally, $L(t)$ belongs to the class of slowly growing functions,[17] which fulfill $\lim_{t\to\infty} L(\lambda t)/L(t) = 1$ for any $\lambda > 0$. In the following, $L(t)$ is chosen to be a positive function which tends to a plateau value:

$$\lim_{t\to\infty} L(t) = 1. \tag{14}$$

Only its asymptotic form matters and in some cases we simply use $L(t) \equiv 1$. Following the reasoning in Ref. 9, a Green-Kubo type relation for the fractional diffusion coefficient can be derived in exactly the same way as in the classical case. Using Karamata's asymptotic analysis,[17] the asymptotic form (13) of the MSD in the time domain implies that its Laplace transform, $\tilde{W}(s) = \int_0^\infty dt\, \exp(-st) W(t)$ ($\Re(s) > 0$), behaves for small s as

$$\tilde{W}(s) \overset{s\to 0}{\sim} 2L(1/s) D_\alpha \frac{\Gamma(1+\alpha)}{s^{1+\alpha}} \tag{15}$$

and vice versa. $\tilde{W}(s)$ can here be replaced by the Laplace transform of expression (11),

$$\tilde{W}(s) = \frac{2\tilde{c}_{vv}^{(R)}(s)}{s^2}, \tag{16}$$

and with $\lim_{s\to 0} L(1/s) = 1$, one obtains

$$D_\alpha = \lim_{s\to 0} \frac{s^{\alpha-1}}{\Gamma(1+\alpha)} \tilde{c}_{vv}^{(R)}(s).$$

In the time domain this becomes the desired generalized Kubo relation,

$$D_\alpha = \frac{1}{\Gamma(1+\alpha)} \int_0^\infty dt \;\; {}_0\partial_t^{\alpha-1} c_{vv}^{(R)}(t), \tag{17}$$

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

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

C. Asymptotic form of the VACF

The asymptotic form of the VACF must be discussed separately for its real and imaginary parts. Concerning the real part, it follows from (11) that $c_{vv}^{(R)}(t) = W''(t)/2$ and with (13) one obtains

$$c_{vv}^{(R)}(t) \overset{t\to\infty}{\sim} D_\alpha L(t) \alpha(\alpha - 1) t^{\alpha-2}. \tag{19}$$

We use here that $t^n L^{(n)}(t) \overset{t\to\infty}{\sim} 0$ for slowly growing functions which fulfill in addition $\lim_{t\to\infty} L(t) = 1$. The asymptotic regime can be estimated through $t \gg \tau_v$, where[18]

$$\tau_v = \left(\frac{D_\alpha}{\langle v^2 \rangle}\right)^{\frac{1}{2-\alpha}}. \tag{20}$$

Here $\langle v^2\rangle = k_B T/m$ is the mean square velocity, with m being the mass of the diffusing particle. Relation (20) is an identity for normal diffusion and an exponentially decaying VACF of the form $c_{vv} = \langle v^2\rangle \exp(-t/\tau_v)$. It is important to note that the asymptotic form (19) is only a *necessary* condition for anomalous diffusion with an exponent α. Karamata's theorem[17] can also be used to prove that (19) is in addition sufficient for $1 < \alpha < 2$. The reader is here referred to Ref. 9, where the classical VACF must be replaced by the real part of its quantum version.

The asymptotic form of the imaginary part of the VACF can be deduced from symmetry relations, (8). For this purpose we express the VACF by the contour integral $c_{vv}(t) = \frac{1}{2\pi i}\oint ds\, e^{st}\tilde{c}_{vv}(s)$, which shows that

$$c_{vv}(t + i\beta\hbar) \longleftrightarrow e^{i\beta\hbar s}\tilde{c}_{vv}(s). \tag{21}$$

It follows then from symmetry properties (8) that

$$\tilde{c}_{vv}^{(R)}(s) = \left(\frac{1 + e^{i\beta\hbar s}}{2}\right)\tilde{c}_{vv}(s),$$
$$\tilde{c}_{vv}^{(I)}(s) = \left(\frac{1 - e^{i\beta\hbar s}}{2i}\right)\tilde{c}_{vv}(s),$$

and consequently

$$\tilde{c}_{vv}^{(I)}(s) = -\tan\left(\frac{\beta\hbar s}{2}\right)\tilde{c}_{vv}^{(R)}(s). \tag{22}$$

Defining d/dt as a left derivative,

$$\frac{df(t)}{dt} = \lim_{h\to 0}\frac{f(t) - f(t-h)}{h},$$

one obtains from (22) by inverse Laplace transform

$$c_{vv}^{(I)}(t) = -\tan\left(\frac{\beta\hbar}{2}\frac{d}{dt}\right)c_{vv}^{(R)}(t). \tag{23}$$

Inserting here relation (19) leads to

$$c_{vv}^{(I)}(t) \overset{t\to\infty}{\sim} -\frac{\beta\hbar}{2}L(t)D_\alpha\,\alpha(\alpha-1)(\alpha-2)t^{\alpha-3}, \tag{24}$$

where only the first order correction in $\hbar$ is needed for the asymptotic form. The imaginary part of the VACF decays asymptotically faster than the real part and noting that $0 \le \alpha < 2$, its sign is the same as for the real part.

II. QUASIELASTIC NEUTRON SCATTERING

A. Basic relations

As mentioned in the Introduction, quasielastic neutron scattering is a unique tool for studying diffusive motions on the atomic scale, in particular for hydrogen atoms and hydrogenous systems. The incoherent neutron scattering cross section for hydrogen being largely dominant with respect to the incoherent and coherent scattering cross sections of all other atoms, only the self-scattering from the hydrogen atoms is probed in this case. The differential scattering cross section for the scattering of thermal neutrons is generally written in the form

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k}{k_0}S(\mathbf{q},\omega), \tag{25}$$

where ω and $\mathbf{q}$ are, respectively, the energy and momentum transfer from the neutron to the sample in units of $\hbar$. The information about the scattering system is carried by the dynamic structure factor, $S(\mathbf{q},\omega)$, which is the Fourier transform of a time correlation function involving the positions of the scattering atoms. Concentrating here for simplicity only on the self-scattering from a single "representative" (hydrogen) atom, we have

$$S(\mathbf{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}F(\mathbf{q},t), \tag{26}$$

$$F(\mathbf{q},t) = \left\langle \exp\left(-i\mathbf{q}\cdot\hat{\mathbf{r}}(0)\right)\exp\left(i\mathbf{q}\cdot\hat{\mathbf{r}}(t)\right)\right\rangle. \tag{27}$$

Here $\langle\ldots\rangle$ denotes a quantum ensemble average and $\hat{\mathbf{r}}(t)$ is the time-dependent position operator of the scattering atom. The time correlation function $F(\mathbf{q},t)$ is referred to as intermediate scattering function.

For the following considerations we use the cumulant expansion of $F(q,t)$ which has been introduced by Rahman and Sjølander:[13]

$$F(q,t) = \exp\left(i\frac{\hbar q^2 t}{2m}\right)\exp\left(\sum_{n=0}^{\infty}(iq)^n\gamma_n(t)\right). \tag{28}$$

Here $q \equiv q_x$ is the projection of the momentum transfer vector on the direction of motion and the phase factor $\exp\left(i\hbar q^2 t/(2m)\right)$ describes the recoil effect in the collision between the neutron and a scattering atom of mass m. The information about the scattering system is contained in the cumulants $\gamma_n(t)$, which are defined in terms of n-fold integrals over n-point velocity time correlation functions. The first few cumulants read explicitly,

$$\gamma_1(t) = \mu_1(t),$$
$$\gamma_2(t) = \frac{1}{2}\left(2\mu_2(t) - \mu_1(t)^2\right),$$
$$\gamma_3(t) = \frac{1}{3}\left(\mu_1(t)^3 - 3\mu_2(t)\mu_1(t) + 3\mu_3(t)\right),$$
etc.

where the $\mu_n(t)$ are given by

$$\mu_n(t) = \int_0^t\int_0^{t_1}\ldots\int_0^{t_{n-1}} dt_1\ldots dt_n\,\langle\hat{v}(t_1)\ldots\hat{v}(t_n)\rangle. \tag{29}$$

The Gaussian approximation of the intermediate scattering function corresponds to setting $\gamma_{2k}(t) \approx 0$ for $k > 1$, which is justified for moderate momentum transfers. Assuming in addition that the scattering system is isotropic, it follows that all $\mu_n(t)$ with an odd index n vanish, and the Gaussian approximation of the intermediate scattering function becomes

$$F_{\mathrm{GA}}(q,t) \approx \exp\left(i\frac{\hbar q^2 t}{2m}\right)\exp\left(-q^2\mu_2(t)\right). \tag{30}$$

On account of the stationarity of the VACF, the double integral $\mu_2(t)$ can be written in the form of a convolution integral,

$$\mu_2(t) = \int_0^t d\tau_1\,(t-\tau_1)c_{vv}(\tau_1). \tag{31}$$

We note finally that a general relation between the intermediate scattering function and the VACF can be derived from

(28), (30), and (31),

$$c_{vv}(t) = -\lim_{q\to 0}\{q^{-2}\partial_t^2 F(q,t)\}, \tag{32}$$

knowing that $F(q,t) = F_{\mathrm{GA}}(q,t)$ for small q.

B. Asymptotic form of $F(q,t)$

One could be tempted to write $\mu_2(t) = W(t)/2$ in expression (30), but this relation does not hold since $\mu_2(t)$ contains the *full* VACF and not just its real part. A relation between $\mu_2(t)$ and $W(t)$ can though be established by noting that the Laplace transform of $\mu_2(t)$ is given by

$$\tilde{\mu}_2(s) = \frac{\tilde{c}_{vv}(s)}{s^2} = \frac{1}{s^2}\left(1 - i\tan\left(\frac{\beta\hbar s}{2}\right)\right)\tilde{c}_{vv}^{(R)}(s)$$
$$= \left(1 - i\tan\left(\frac{\beta\hbar s}{2}\right)\right)\frac{\tilde{W}(s)}{2}.$$

Relation (22) has here been used to express $\tilde{c}_{vv}(s) = \tilde{c}_{vv}^{(R)}(s) + I\tilde{c}_{vv}^{(I)}(s)$ in terms of $\tilde{c}_{vv}^{(R)}(s)$ only and relation (16) to connect $\tilde{c}_{vv}^{(R)}(s)$ to $\tilde{W}(s)$. In the time domain one obtains thus

$$\mu_2(t) = \frac{1}{2}\left(1 - i\tan\left(\frac{\beta\hbar}{2}\frac{d}{dt}\right)\right)W(t). \tag{33}$$

Interesting for QENS is the behavior of the intermediate scattering function for $t\to\infty$, where the MSD has the form (13). Again only the first order correction with respect to $\hbar$ is needed in (33) to obtain the asymptotic form of $\mu_2(t)$,

$$\mu_2(t) \overset{t\to\infty}{\sim} \left(1 - i\frac{\beta\hbar}{2}\frac{d}{dt}\right)L(t)D_\alpha t^\alpha. \tag{34}$$

In the Gaussian approximation, the asymptotic form of the intermediate scattering function reads thus

$$F_{\mathrm{GA}}(q,t) \overset{t\to\infty}{\sim} \exp\left(i\frac{\hbar q^2}{2m}t\right)\exp\left(-q^2 L(t)D_\alpha t^\alpha\right)$$
$$\times \exp\left(iq^2 L(t)D_\alpha\alpha\frac{\beta\hbar}{2}t^{\alpha-1}\right). \tag{35}$$

Since the recoil factor $\exp(i\hbar q^2 t/2m)$ is only due to the scattering kinematics, true quantum effects are described by the third factor. They may thus be neglected if $\phi(t) \ll 1$, where the time argument is to be replaced by a "collision time." The latter is the flight time of the neutron wave packet through the sample,[19,20] which is determined by the spectral resolution of the monochromator which is used to perform the QENS experiment. Quantum effects can thus be neglected if

$$\phi(t_c) = \alpha D_\alpha q^2\frac{\beta\hbar}{2}t_c^{\alpha-1} \ll 1. \tag{36}$$

Note that $\phi = 0$ if $\alpha = 0$, i.e., for confined diffusion, and that ϕ does not depend on the observation time if $\alpha = 1$, i.e., for normal diffusion.

It is worthwhile noting that expression (35) stays valid in the extreme case where $\alpha = 0$. One considers then spatially confined diffusion where the MSD tends asymptotically to a plateau value. The position $x(t)$ of the diffusing particle may here be referred to a well-defined mean-position and writing $x(t) = u(t) + \langle x\rangle$, the diffusion constant becomes the mean square position fluctuation, $D_0 = \langle u^2\rangle$.[9] Since $\alpha = 0$, the intermediate scattering function has the asymptotic form

$$F_{\mathrm{GA}}(q,t) \overset{t\to\infty}{\sim} \exp\left(i\frac{\hbar q^2 t}{2m}\right)\exp\left(-q^2\langle u^2\rangle L(t)\right). \tag{37}$$

Writing $W(t) = \langle(u(t) - u(0))^2\rangle$, it is easy to see that $L(t)$ describes the relaxation of the real part of the autocorrelation function for the position fluctuations. The MSD can, in fact, be expressed as $W(t) = 2\Re\{c_{uu}(0) - c_{uu}(t)\}$, where $c_{uu}(t) \equiv \langle u(0)u(t)\rangle$. Defining $R(t) = 1 - L(t)$, it follows thus that

$$\Re\{c_{uu}(t)\} \overset{t\to\infty}{\sim} \langle u^2\rangle R(t). \tag{38}$$

Confined anomalous diffusion/relaxation corresponds to a slow power law decay of $R(t)$,

$$R(t) \overset{t\to\infty}{\sim} t^{-\beta} \quad (0 < \beta < 1), \tag{39}$$

such that the mean relaxation time, which is defined by the integral $\int_0^\infty dt\, t\, c_{uu}(t)/c_{uu}(0)$, diverges. In this case $R(t)$ is described by a broad spectrum of relaxation rates,

$$R(t) = \int_0^\infty d\lambda\, p(\lambda)\exp(-\lambda t), \tag{40}$$

where the relaxation rate spectrum, $p(\lambda)$, diverges at $\lambda = 0$.[9,21] An example is the position fluctuation autocorrelation function of a particle which diffuses in a harmonic potential and whose dynamics is described by a fractional Ornstein Uhlenbeck process. This is a simple model for the confined multiscale dynamics of atoms in proteins, which is probed by QENS experiments.[22,23]

C. Density of states (DOS)

1. Definition and existence

The density of states (DOS) is essentially the Fourier spectrum of the VACF and it is here defined as

$$g(\omega) = g^{(R)}(\omega) + g^{(I)}(\omega), \tag{41}$$

where

$$g^{(R)}(\omega) = \int_0^\infty dt\ \cos\omega t\, c_{vv}^{(R)}(t), \tag{42}$$
$$g^{(I)}(\omega) = \int_0^\infty dt\ \sin\omega t\, c_{vv}^{(I)}(t). \tag{43}$$

The DOS has a direct relation to the dynamic structure factor,

$$g(\omega) = \frac{1}{2}\lim_{q\to 0}\frac{\omega^2}{q^2}S(q,\omega), \tag{44}$$

which follows from relation (32) and the Fourier integral (26) defining the dynamic structure factor.

To show that $g^{(R)}(\omega)$ and $g^{(I)}(\omega)$ exist for all cases of anomalous diffusion, we introduce a time $\tau > 0$ which is defined as the point on the time axis from which on the asymptotic regimes (19) and (24) are valid for all practical purposes. Since we are only interested in the existence of

$g^{(R/I)}(\omega)$ we may here set $L(t) \equiv 1$, such that

$$g^{(R)}(\omega) = \int_0^\tau dt\, \cos\omega t\, c_{vv}^{(R)}(t) + D_\alpha \alpha(\alpha-1) \int_\tau^\infty dt\, t^{\alpha-2} \cos\omega t, \quad (45)$$

$$g^{(I)}(\omega) = \int_0^\tau dt\, \sin\omega t\, c_{vv}^{(I)}(t) - \frac{\beta\hbar}{2} D_\alpha \alpha(\alpha-1)(\alpha-2) \times \int_\tau^\infty dt\, t^{\alpha-3} \sin\omega t. \quad (46)$$

The integrals $\int_\tau^\infty dt \ldots$ involving the long-time tails of both the real and the imaginary parts of the VACF are determined through the identities

$$\int_\tau^\infty dt\, t^{\alpha-2} \cos\omega t = \frac{\tau^{\alpha-1}}{2} (E_{2-\alpha}(-i\tau\omega) + E_{2-\alpha}(i\tau\omega)),$$
$$\int_\tau^\infty dt\, t^{\alpha-3} \sin\omega t = \frac{\tau^{\alpha-2}}{2i} (E_{3-\alpha}(-i\tau\omega) - E_{3-\alpha}(i\tau\omega)),$$

where $E_\beta(z) = \int_1^\infty dt\, \exp(-zt)/t^\beta$ is the generalized exponential integral.[24,25] For $\alpha < 2$ both above integrals tend to zero as τ tends to infinity and since one can assume that the definite integrals $\int_0^\tau dt\, \cos\omega t\, c_{vv}^{(R)}(t)$ and $\int_0^\tau dt\, \sin\omega t\, c_{vv}^{(I)}(t)$ exist for any reasonable VACF, the existence of both $g^{(R)}(\omega)$ and $g^{(I)}(\omega)$ is ensured.

2. *Detailed balance and small frequencies*

Knowing that both $g^{(R)}(\omega)$ and $g^{(I)}(\omega)$ exist, they can be expressed by the Laplace transformed real (symmetric) and imaginary (antisymmetric) parts of the VACF, respectively,

$$g^{(R)}(\omega) = \Re\{\tilde{c}_{vv}^{(R)}(i|\omega|)\}, \quad (47)$$
$$g^{(I)}(\omega) = -\Im\{\tilde{c}_{vv}^{(I)}(i\omega)\}. \quad (48)$$

Since $\tilde{c}_{vv}^{(I)}(s)$ can be expressed by $\tilde{c}_{vv}^{(R)}(s)$ by means of relation (22), this leads to

$$g^{(I)}(\omega) = \tanh\left(\frac{\beta\hbar\omega}{2}\right) g^{(R)}(\omega), \quad (49)$$

such that the full DOS is given by

$$g(\omega) = \left(1 + \tanh\left(\frac{\beta\hbar\omega}{2}\right)\right) g^{(R)}(\omega). \quad (50)$$

Since $g^{(R)}(\omega)$ is symmetric in ω it follows from the above identity that

$$g(\omega) = e^{\beta\hbar\omega} g(-\omega), \quad (51)$$

which is referred to as a *detailed balance relation*. Quantum effects can thus be neglected if

$$\beta\hbar|\omega| \ll 1. \quad (52)$$

An explicit form for $g(\omega)$ at small ω is easily obtained from the Laplace transformed VACF as small s. Combining relations (15) and (16) and using that $\lim_{s\to0} L(1/s) = 1$, one obtains for the Laplace transform of the real part

$$\tilde{c}_{vv}^{(R)}(s) \overset{s\to0}{\sim} D_\alpha \Gamma(1+\alpha) s^{1-\alpha}. \quad (53)$$

It follows then from (47) that

$$g^{(R)}(\omega) \overset{\omega\to0}{\sim} D_\alpha |\omega|^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) \Gamma(\alpha+1). \quad (54)$$

With definition (20) of the time scale τ_v, the meaning of $\overset{\omega\to0}{\sim}$ is to be understood as

$$|\omega| \ll \frac{1}{\tau_v}. \quad (55)$$

The full asymptotic DOS is finally obtained from (50),

$$g(\omega) \overset{\omega\to0}{\sim} \left(1 + \frac{\beta\hbar\omega}{2}\right) D_\alpha |\omega|^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) \Gamma(\alpha+1), \quad (56)$$

assuming that $\beta\hbar|\omega| \ll 1$. This condition can be translated into $|\omega| \ll 0.13\ \mathrm{THz} \times T[\mathrm{K}]$ or, for the energy transfer, into $|\Delta E| \ll 0.086\ \mathrm{meV} \times T[\mathrm{K}]$.

III. RÉSUMÉ

In this paper exact expressions have been derived for two quantities which are related to quasielastic neutron scattering from anomalously diffusing quantum particles. The first one is the intermediate scattering function at moderate momentum transfers for long times, i.e., in the diffusive regime, and the second one is the Fourier spectrum of the velocity autocorrelation function at small frequencies. Both expressions have been inferred from the asymptotic form of the particle's mean square displacement and they are thus essentially described by two parameters — the fractional diffusion constant, D_α, and the anomaly exponent, α. The asymptotic regimes can be defined through a well-defined characteristic time scale, $\tau_v = \left(D_\alpha/\langle v^2\rangle\right)^{1/(2-\alpha)}$. Except for $\alpha = 1$, the quantum correction of the intermediate scattering function depends on the collision time of the neutron with the sample and the quantum correction of the density of states simply reflects the detailed balance relation. As in the classical case, D_α can be expressed through a generalized Kubo relation. The general form of the QENS intensities can also be used to analyze confined diffusion processes, which correspond to $\alpha = 0$. Here a generic "slowly growing function" describes the asymptotic relaxation of the real part of the autocorrelation function for the position fluctuations and there is no asymptotic quantum correction. The theory thus allows for a "model-free" interpretation of QENS experiments, including anomalous diffusion, confined diffusion, and quantum effects.

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