

# Inelastic neutron scattering from damped collective vibrations of macromolecules

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## Abstract

The present article describes the theory of neutron scattering from harmonically vibrating molecules in the framework of classical Langevin and Smoluchowski dynamics. For both levels of description, the input quantities are a positive definite matrix of force constants and a positive definite friction matrix. Starting from the Fokker–Planck equation of the Ornstein–Uhlenbeck process, the intermediate scattering functions for coherent and incoherent scattering as well as related static correlation functions are derived. It is demonstrated that the Langevin description on a coarse-grained time scale is identical with the Smoluchowski description if friction dominates. Inelastic neutron spectra are discussed in terms of the coherent and incoherent dynamic structure factors and the vibrational density of states. It is shown that incorporating friction on the atomic level is not equivalent to broadening the lines of the corresponding normal mode spectrum. The theory is applicable to low frequency and large amplitude motions of macromolecules as proteins and DNA. Vibrations at higher frequencies can be treated as long as they can be described in the classical approximation. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Inelastic neutron scattering; Langevin modes; Normal modes

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## 1. Introduction

Inelastic and quasielastic scattering of thermal neutrons are well established and powerful techniques to study the dynamics of molecular liquids, solids, and disordered systems on the atomic scale [1,2]. The theoretical foundations of neutron scattering from condensed matter have been developed in the 1950s. In 1954 van Hove published a famous article on the theory of inelastic neutron scattering from a system of interacting particles in which the differential scattering cross-section is expressed in terms of time correlation functions of the particle density [3]. If quantum properties of the scattering system can be neglected, the van Hove correlation functions can be interpreted as time-dependent pair correlation functions and thus have a direct physical meaning. Whereas van Hove aimed at interpreting thermal neutron scattering from essentially classical liquids, Glauber and Zemach developed the theory of neutron vibrational spectroscopy for solids and diluted molecular gases [4,5]. The dynamics of these systems has to be described by

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quantum mechanics, and the van Hove correlation functions have no longer a convenient interpretation. However, in contrast to liquids, vibrating systems are often well described by a harmonic potential energy surface. Therefore, normal mode techniques can be applied to compute the scattering law of solids and vibrating molecules.

In the course of time inelastic neutron scattering has been applied to more and more complex systems, such as polymers [6] and proteins [7,8]. Most proteins fold into very compact and extremely stable structures making them reliable for their various biological tasks. From a biological point of view the large-amplitude modes at low frequencies are the most important ones. Therefore it is not surprising that the harmonic model has been widely used as a first approximation to describe in particular protein dynamics around a stable native structure, although protein dynamics also exhibits diffusive motions [9–11]. The reviews of Smith and Martel [7,8] show applications of the harmonic model to protein dynamics and corresponding neutron scattering experiments. A recent example related to Mössbauer and Raman spectroscopy from myoglobin is presented in Ref. [12]. Formally, the theory of Glauber and Zemach can be applied to molecules of any size, i.e. also to large macromolecules such as proteins composed of several tens or hundreds of amino acids. A straightforward application to bovine pancreatic trypsin inhibitor (BPTI), a small protein consisting of 58 amino acids, can be found in Ref. [13]. In contrast to the energy surface of small molecules, proteins are expected to have a “rugged” energy surface with many minima (“conformational substates”), separated by small barriers [14–16]. The roughness of the energy surface may be characterized by a fractal dimension [17]. It is not obvious that the motion in a local minimum, as it is considered by normal mode analysis, is in some way representative for the delocalized large amplitude modes since the local potential does not necessarily reflect the global features of the energy surface. Nevertheless, it seems reasonable to approximate the latter by a quadratic potential, ensuring that the protein keeps a fixed average structure [16]. The simplest method to take into account the roughness of the effective potential, as well as coupling to the environment, is to introduce friction into the model.

The purpose of this paper is to derive the dynamic structure factor for inelastic neutron scattering from harmonically vibrating molecules in the presence of friction, using the concept of Langevin modes introduced by Lamm and Szabo [18]. Since the important modes at large amplitudes and low frequencies are strongly over-damped, the essential dynamics is described by purely diffusive Brownian dynamics in configuration space, which greatly simplifies the calculations. The corresponding Fokker–Planck equation is then the Smoluchowski equation instead of the Kramers equation, and I call the corresponding modes “Brownian modes”. To study the influence of atomic friction on the dynamic structure factor in a systematic way, an analytical form for the dynamic structure factor and the density of states is derived. The paper is organized as follows: Section 2 contains a brief description of the dynamical model for the scattering system – the Ornstein–Uhlenbeck process, and a compilation of the essential quantities measured in inelastic neutron scattering. In Section 3 the intermediate scattering function is derived for the regimes of Langevin and Smoluchowski dynamics, respectively. The analytical form of the corresponding dynamic structure factors as well as the vibrational density of states are discussed in Section 4, and Section 5 contains the final discussion and the conclusions.

## 2. Theoretical background and definitions

### 2.1. Inelastic neutron scattering

The fundamental quantity measured by inelastic scattering of thermal neutrons is the dynamic structure factor,  $\mathcal{S}(\mathbf{q}, \omega)$ . Its arguments are the momentum and energy transfer in units of  $\hbar$ . The dynamic structure factor can be expressed as the time Fourier transform of the so-called intermediate scattering function,  $\mathcal{F}(\mathbf{q}, t)$ , which describes time correlations between the positions of the atoms in the sample,

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

The intermediate scattering function splits into a coherent and an incoherent part,

$$\overline{\mathcal{F}}(\mathbf{q}, t) = \overline{\mathcal{F}}_{\text{coh}}(\mathbf{q}, t) + \overline{\mathcal{F}}_{\text{inc}}(\mathbf{q}, t), \quad (2)$$

which read explicitly

$$\overline{\mathcal{F}}_{\text{coh}}(\mathbf{q}, t) = \sum_{\alpha, \beta} b_{\alpha, \text{coh}} b_{\beta, \text{coh}} \langle \exp(i\mathbf{q}^T \cdot \mathbf{R}_{\beta}(t)) \exp(-i\mathbf{q}^T \cdot \mathbf{R}_{\alpha}(0)) \rangle, \quad (3)$$

$$\overline{\mathcal{F}}_{\text{inc}}(\mathbf{q}, t) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 \langle \exp(i\mathbf{q}^T \cdot \mathbf{R}_{\alpha}(t)) \exp(-i\mathbf{q}^T \cdot \mathbf{R}_{\alpha}(0)) \rangle. \quad (4)$$

Here and in the following Greek indices label atoms,  $b_{\alpha, \text{coh}}$  is the coherent scattering length of atom  $\alpha$ ,  $b_{\alpha, \text{inc}}$  its incoherent scattering length, and  $\mathbf{R}_{\alpha}(t)$  its position operator in the Heisenberg representation. Values for the scattering lengths can be found in standard books on neutron scattering [1,2]. The brackets in Eqs. (3) and (4) denote quantum statistical averages, and the superscript T of a vector indicates a transposition. It should be noted that  $\overline{\mathcal{F}}_{\text{coh}}(\mathbf{q}, t)$  probes collective motions, whereas  $\overline{\mathcal{F}}_{\text{inc}}(\mathbf{q}, t)$  probes only single-particle motions. The quantum correlation functions can be replaced by their classical counterparts if the scattering system can be described by classical mechanics and if recoil effects can be neglected [19]. The framework of classical mechanics is appropriate for an harmonic system if the spacing of the energy levels is small compared to  $k_{\text{B}}T$ ,

$$\hbar\omega_n \ll k_{\text{B}}T. \quad (5)$$

Here,  $k_{\text{B}}$  denotes the Boltzmann constant and  $T$ , the temperature in Kelvin. Recoil effects depend in general on the mass of the scattering atom and the potential energy function of the system. For harmonically bound scatterers one obtains a global correction factor  $\exp(\hbar\omega/2k_{\text{B}}T)$  for the dynamic structure factor [19]. Therefore the recoil correction can be neglected for harmonic systems if one considers energy transfers of the order of the characteristic frequencies fulfilling (5).

From Eqs. (3) and (4) one obtains two static correlation functions which are frequently considered in neutron scattering experiments: the static structure factor,  $\mathcal{S}(\mathbf{q}) = \overline{\mathcal{F}}_{\text{coh}}(\mathbf{q}, 0)$ , and the elastic incoherent structure factor,  $\text{EISF}(\mathbf{q}) = \lim_{t \rightarrow \infty} \overline{\mathcal{F}}_{\text{inc}}(\mathbf{q}, t)$ . They read explicitly

$$\mathcal{S}(\mathbf{q}) = \sum_{\alpha, \beta} b_{\alpha, \text{coh}} b_{\beta, \text{coh}} \langle \exp(-i\mathbf{q}^T \cdot [\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}]) \rangle, \quad (6)$$

$$\text{EISF}(\mathbf{q}) = \sum_{\alpha} b_{\text{inc}, \alpha}^2 |\langle \exp(-i\mathbf{q}^T \cdot \mathbf{R}_{\alpha}) \rangle|^2. \quad (7)$$

Assuming thermal equilibrium for the scattering system, the time arguments of the positions can be omitted, such that all time correlation functions depend only on time differences. To obtain the expression for the EISF one uses that the positions become decorrelated for  $t \rightarrow \infty$ . The EISF probes the accessible configuration space of the scattering atoms [2]. It vanishes if the atomic motion in the scattering system is unbounded, as in liquids. Writing  $\overline{\mathcal{F}}_{\text{inc}}(\mathbf{q}, t) = \text{EISF}(\mathbf{q}) + \overline{\mathcal{F}}'_{\text{inc}}(\mathbf{q}, t)$ , one finds that

$$\mathcal{S}_{\text{inc}}(\mathbf{q}, \omega) = \text{EISF}(\mathbf{q})\delta(\omega) + \mathcal{S}'_{\text{inc}}(\mathbf{q}, \omega), \quad (8)$$

where  $\delta$  denotes the Dirac distribution. This relation shows that the EISF describes indeed elastic incoherent scattering.  $\mathcal{S}'_{\text{inc}}(\mathbf{q}, \omega)$  contains all the remaining information about inelastic and quasi-elastic processes, describing vibrational and diffusive motion, respectively.

For systems undergoing vibrational dynamics it is convenient to introduce the *dynamic form factors*,  $f_{\alpha\beta}(\mathbf{q}, t)$ , describing correlations between the atomic displacements  $\mathbf{u}_\alpha$  and  $\mathbf{u}_\beta$ . Writing

$$\mathbf{R}_\alpha(t) = \mathbf{R}_\alpha^{\text{eq}} + \mathbf{u}_\alpha(t), \quad (9)$$

where  $\mathbf{R}_\alpha^{\text{eq}}$  is the equilibrium position of atom  $\alpha$ , one defines

$$f_{\alpha\beta}(\mathbf{q}, t) = \langle \exp(-i\mathbf{q}^T \cdot [\mathbf{u}_\alpha(0) - \mathbf{u}_\beta(t)]) \rangle. \quad (10)$$

The intermediate scattering functions are then linear combinations of the  $f_{\alpha\beta}$ ,

$$\mathcal{F}_{\text{coh}}(\mathbf{q}, t) = \sum_{\alpha, \beta} b_{\alpha, \text{coh}} b_{\beta, \text{coh}} \exp(-i\mathbf{q}^T \cdot [\mathbf{R}_\alpha^{\text{eq}} - \mathbf{R}_\beta^{\text{eq}}]) f_{\alpha\beta}(\mathbf{q}, t), \quad (11)$$

$$\mathcal{F}_{\text{inc}}(\mathbf{q}, t) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 f_{\alpha\alpha}(\mathbf{q}, t). \quad (12)$$

According to Eqs. (11) and (12) the static correlation functions  $\mathcal{S}(\mathbf{q}) = \mathcal{F}_{\text{coh}}(\mathbf{q}, 0)$  and EISF( $\mathbf{q}$ ) =  $\lim_{t \rightarrow \infty} \mathcal{F}_{\text{inc}}(\mathbf{q}, t)$  take the form

$$\mathcal{S}(\mathbf{q}) = \sum_{\alpha, \beta} b_{\alpha, \text{coh}} b_{\beta, \text{coh}} \exp(-i\mathbf{q}^T \cdot [\mathbf{R}_\alpha^{\text{eq}} - \mathbf{R}_\beta^{\text{eq}}]) f_{\alpha\beta}(\mathbf{q}, 0), \quad (13)$$

$$\text{EISF}(\mathbf{q}) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 f_{\alpha\alpha}(\mathbf{q}, \infty). \quad (14)$$

Note that  $f_{\alpha\alpha}(\mathbf{q}, 0) = 1$ . The form factors express all static and dynamic correlations relevant to neutron scattering. The case  $f_{\alpha\beta} = 1$  corresponds to a situation where all atomic displacements are frozen. In such a static model the coherent part of  $\mathcal{F}(\mathbf{q}, t)$  describes neutron diffraction from molecules without internal motion and the incoherent part gives simply a constant background.

## 2.2. Macromolecular dynamics as Ornstein–Uhlenbeck process

In the following we will be concerned with the dynamics of macromolecules about their equilibrium structure. The configuration of the molecular system is described by  $N$  atomic positions,  $\mathbf{R}_1, \dots, \mathbf{R}_N$ . In the case of Langevin dynamics (LD) the dynamical variables are the atomic displacements,  $\mathbf{u}_\alpha = \mathbf{R}_\alpha - \mathbf{R}_\alpha^{\text{eq}}$  ( $\alpha = 1, \dots, N$ ), and the corresponding velocities. The regime of Smoluchowski dynamics (SD) applies to strongly over-damped motions on a coarse-grained time scale. It describes motions in configuration space only, i.e. one considers only  $3N$  and not  $6N$  dynamical variables. Throughout this paper mass-weighted coordinates and velocities are used, e.g.

$$\mathbf{R}_\alpha = \sqrt{m_\alpha} \tilde{\mathbf{R}}_\alpha, \quad (15)$$

where  $m_\alpha$  is the mass of atom  $\alpha$ , and the tilde denotes the usual, non-weighted coordinates.

On both the Langevin and the Smoluchowski level of description the time evolution of an harmonic system is described by an Ornstein–Uhlenbeck process which has been extensively discussed in the literature [20–22]. The stochastic differential equation describing the Ornstein–Uhlenbeck process reads for  $n$  variables,  $x_1, \dots, x_n$ ,

$$x_i(t_0 + \Delta t) = x_i(t_0) - A_{ij} x_j(t_0) \Delta t + \xi_i(t_0). \quad (16)$$

The  $\xi_i$  ( $i = 1, \dots, n$ ) are stochastic variables with

$$\langle \xi_i(t) \rangle = 0, \quad (17)$$

$$\langle \xi_i(t) \xi_j(t') \rangle = 2B_{ij} \Delta t \delta(t - t'). \quad (18)$$

The vector  $-A_{ij}x_j$  describes the drift of the system and the  $n^2$  coefficients  $B_{ij}$  define the fluctuations of the dynamical variables. For both LD and SD the first  $3N$  variables are  $x_1 = u_{1,x}, \dots, x_{3N} = u_{N,z}$  and for LD one defines in addition  $x_{3N+1} = \dot{u}_{1,x}, \dots, x_{6N} = \dot{u}_{N,z}$ . The whole set of dynamical variables is denoted by  $x$ . Both  $\mathbf{A} \equiv [A_{ij}]$  and  $\mathbf{B} \equiv [B_{ij}]$  can be expressed in terms of a positive definite friction matrix,  $\gamma$ , and a positive definite matrix of force constants,  $\mathbf{K}$ , with elements

$$K_{ij} = \left. \frac{\partial^2 V}{\partial R_i \partial R_j} \right|_{\mathbf{R}^{\text{eq}}}. \quad (19)$$

Here  $V \equiv V(\mathbf{R})$  denotes the potential function and the index ‘ $\mathbf{R}^{\text{eq}}$ ’ indicates that  $\mathbf{K}$  is to be evaluated at a stable equilibrium position. The vector  $\mathbf{R} = (\mathbf{R}_1^T, \dots, \mathbf{R}_N^T)^T$  comprises all particle positions. Since  $\mathbf{K}$  is supposed to be positive definite the molecules are assumed not to perform global rotations and translations. Such a situation is e.g. encountered in neutron scattering from hydrated protein powders as they are often used to study internal protein dynamics. The relations between the mass-weighted and the standard form of  $\mathbf{K}$  and  $\gamma$  are  $\mathbf{K} = \mathbf{M}^{-1/2} \tilde{\mathbf{K}} \mathbf{M}^{-1/2}$  and  $\gamma = \mathbf{M}^{-1/2} \tilde{\gamma} \mathbf{M}^{-1/2}$ , respectively. The tilde labels again non-weighted quantities.

In the case of LD  $\mathbf{A}$  and  $\mathbf{B}$  are  $6N \times 6N$  matrices with the following block structure:

$$\mathbf{A}_{\text{LD}} = \begin{pmatrix} \mathbf{0} & -\mathbf{1} \\ \mathbf{K} & \gamma \end{pmatrix}, \quad \mathbf{B}_{\text{LD}} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & k_B T \gamma \end{pmatrix}. \quad (20)$$

For SD  $\gamma$  and  $\mathbf{K}$  are given by the  $3N \times 3N$  matrices

$$\mathbf{A}_{\text{SD}} = \gamma^{-1} \cdot \mathbf{K}, \quad \mathbf{B}_{\text{SD}} = k_B T \gamma^{-1}. \quad (21)$$

The Fokker–Planck equation corresponding to Eq. (16) reads

$$\frac{\partial P}{\partial t} = A_{ij} \frac{\partial}{\partial x_i} (x_j P) + B_{ij} \frac{\partial^2 P}{\partial x_i \partial x_j}. \quad (22)$$

Summation over pairwise like indices is implicitly assumed. In Eq. (22)  $P \equiv P(x, t | x', t')$  denotes the conditional probability to find the system in position  $x$  at time  $t$ , given it was in position  $x'$  at time  $t' < t$ . The initial condition reads therefore  $P(x, t' | x', t') = \delta(x - x')$ , with  $\delta(x - x') = \prod_{i=1}^n \delta(x_i - x'_i)$ .

### 2.2.1. The transition probability

The solution of Eq. (22) is known to be a stationary Gaussian with  $P(x, t | x', t') = P(x, t - t' | x', 0)$ . Setting  $t' = 0$ , one has [21]

$$P(x, t | x', 0) = (2\pi)^{-n/2} (\det \boldsymbol{\sigma}(t))^{-1/2} \exp \left( -\frac{1}{2} (x_i - G_{il}(t)x'_l) [\boldsymbol{\sigma}^{-1}(t)]_{ij} (x_j - G_{jm}(t)x'_m) \right), \quad (23)$$

where  $n$  is the number of degrees of freedom ( $n = 3N$  for SD and  $n = 6N$  for LD) and the matrix  $\mathbf{G} = [G_{ij}]$  is defined as

$$\mathbf{G}(t) = \exp(-\mathbf{A}t). \quad (24)$$

The mean positions

$$M_i(t) \equiv \langle x_i(t) \rangle = G_{il}(t)x'_l \quad (25)$$

define the center of the Gaussian for a given initial configuration,  $x'$ , and  $\boldsymbol{\sigma}(t) = [\sigma_{ij}(t)]$  is the corresponding variance,

$$\sigma_{ij}(t) = \langle [x_i(t) - \langle x_i(t) \rangle][x_j(t) - \langle x_j(t) \rangle] \rangle. \quad (26)$$

Note that  $M_i(t)$  and  $\sigma_{ij}(t)$  are averages over  $x$  for a given  $x'$ . The  $\sigma_{ij}$  can be expressed in terms of the propagator  $\mathbf{G}$  and the fluctuation (diffusion) matrix  $\mathbf{B}$  and do not depend on  $x'$ ,

$$\sigma_{ij}(t) = 2 \int_0^t d\tau G_{ik}(\tau) B_{kl} G_{jl}(\tau). \quad (27)$$

The dynamics of  $M_i$  and  $\sigma_{ij}$  is determined by the equations of motion

$$\dot{M}_i = -A_{ij}M_j, \quad (28)$$

$$\dot{\sigma}_{ij} = -A_{ik}\sigma_{kj} - A_{jk}\sigma_{ki} + 2B_{ij}, \quad (29)$$

which are obtained by inserting Eq. (23) as an ansatz into the Fokker–Planck equation (22) [21]. The above differential equations are to be solved with the initial conditions  $M_i(0) = x'_i$  and  $\sigma_{ij}(0) = 0$ . This yields the solutions (25) and (27).

From Eq. (23) the equilibrium distribution  $P_{\text{eq}}(x)$  is found by taking the limit  $t \rightarrow \infty$ ,

$$P_{\text{eq}}(x) = (2\pi)^{-n/2} (\det \boldsymbol{\sigma}(\infty))^{-1/2} \exp \left( -\frac{1}{2} x_i [\boldsymbol{\sigma}^{-1}(\infty)]_{ij} x_j \right). \quad (30)$$

Here one supposes that the real parts of the eigenvalues of  $\mathbf{A}$  are positive. Therefore  $\mathbf{G}(t)$  vanishes in the limit  $t \rightarrow \infty$  and one obtains from Eqs. (25) and (26)

$$\sigma_{ij}(\infty) = \langle x_i x_j \rangle. \quad (31)$$

Using Eq. (29) together with  $\dot{\sigma}_{ij}(\infty) = 0 = -A_{ik}\sigma_{kj}(\infty) - A_{jk}\sigma_{ki}(\infty) + 2B_{ij}$ , one finds that

$$\boldsymbol{\sigma}_{\text{LD}}(\infty) = k_{\text{B}} T \begin{pmatrix} \mathbf{K}^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \quad \boldsymbol{\sigma}_{\text{SD}}(\infty) = k_{\text{B}} T \mathbf{K}^{-1}. \quad (32)$$

Finally, for finite  $t$ ,  $\boldsymbol{\sigma}$  may be written in the useful form

$$\sigma_{ij}(t) = \sigma_{ij}(\infty) - G_{ik}(t) \sigma_{kl}(\infty) G_{jl}(t). \quad (33)$$

### 3. Intermediate scattering function and dynamic form factors

According to Eqs. (11) and (12) the intermediate scattering functions are linear combinations of the dynamic form factors,  $f_{\alpha\beta}$ , which contain the relevant information about the molecular system under consideration. In this section the  $f_{\alpha\beta}$  will be derived for an Ornstein–Uhlenbeck process of the atomic displacements. Their basic form is the same for LD and SD and the transition between the two regimes becomes clear if one uses the spectral representation of the matrices  $\boldsymbol{\sigma}(\infty)$  and  $\mathbf{A}$ , entering the distribution function  $P(x, t|x', t')$ . The resulting spectral representation of the form factors allows also to derive convenient expressions for numerical calculations.

### 3.1. Deriving the $f_{\alpha\beta}$ for an Ornstein–Uhlenbeck process

To obtain the  $f_{\alpha\beta}$  defined in Eq. (10) for the Ornstein–Uhlenbeck process, it is convenient to introduce the vectors  $\mathbf{Q}^{(\alpha)}$  which have the components

$$\mathcal{Q}_i^{(\alpha)} = m_\alpha^{-1/2} \delta_{\{3(\alpha-1)+j,i\}} q_j, \quad i = 1, \dots, 3(6)N, \quad j = 1, 2, 3. \quad (34)$$

They contain the momentum transfer vector,  $\mathbf{q}$ , and are constructed such that  $\mathbf{x}^T \cdot \mathbf{Q}^{(\alpha)} = m_\alpha^{-1/2} \mathbf{u}_\alpha^T \cdot \mathbf{q} = \tilde{\mathbf{u}}_\alpha^T \cdot \mathbf{q}$  is dimensionless, where  $\mathbf{x} = (x_1, \dots, x_n)^T$  and  $m_\alpha$  is the mass of atom  $\alpha$ . Definition (34) says that the length of the  $\mathbf{Q}^{(\alpha)}$  depends on the context and is “automatically” adapted to the size of the vector or the matrix with which it is multiplied. This avoids the introduction of a third  $\mathcal{Q}$ -vector of length  $3N$  to be used in the context of LD where  $\mathcal{Q}_i^{(\alpha)} = 0$  for  $i = 3N + 1, \dots, 6N$ .

Using definition (34), the form factors can be cast into the same form for both LD and SD,

$$f_{\alpha\beta}(\mathbf{q}, t) = \int \int dx dx' P(x, t; x', t') \exp\left(i\mathcal{Q}_k^{(\beta)} x_k\right) \exp\left(-i\mathcal{Q}_l^{(\alpha)} x'_l\right). \quad (35)$$

$P(x, t; x', t')$  is the *joint two-point probability* describing the stochastic dynamics of the displacements. It is assumed that the time arguments are ordered such that  $t \geq t'$ . Applying Bayes’ rule, the joint probability can be decomposed as  $P(x, t; x', t') = P(x, t|x', t')P(x', t')$ . One assumes now that the scattering system is in equilibrium. Therefore  $P(x', t') = P_{\text{eq}}(x')$ , and  $P(x, t|x', t')$  depends only on time differences,  $P(x, t|x', t') = P(x, t - t'|x', 0)$ . The time origin,  $t'$ , can always be chosen to be zero and needs not be explicitly indicated in expression (35). The integrals in the above expression for  $f_{\alpha\beta}$  can now be rearranged to give

$$f_{\alpha\beta}(\mathbf{q}, t) = \int dx' \exp\left(-i\mathcal{Q}_l^{(\alpha)} x'_l\right) P_{\text{eq}}(x') \int dx \exp\left(i\mathcal{Q}_k^{(\beta)} x_k\right) P(x, t|x', 0).$$

Defining  $\tilde{g}(\mathcal{Q}) = \int dx \exp(-i\mathcal{Q}_l x_l) g(x)$  as the Fourier transform of a function  $g(x)$ , the second integral is recognized to be the Fourier transform of  $P(x, t|x', 0)$  with respect to  $x$ , where  $\mathbf{Q} = -\mathbf{Q}^{(\beta)}$ . Since  $P(x, t|x', 0)$  is a Gaussian, its Fourier transform has again Gaussian shape,

$$\tilde{P}(\mathcal{Q}, t|x', 0) = \exp(-i\mathcal{Q}_k G_{kl}(t)x'_l) \exp\left(-\frac{1}{2}\mathcal{Q}_k \sigma_{kl}(t)\mathcal{Q}_l\right),$$

and one finds the intermediate result

$$f_{\alpha\beta}(\mathbf{q}, t) = \exp\left(-\frac{1}{2}\mathcal{Q}_k^{(\beta)} \sigma_{kl}(t)\mathcal{Q}_l^{(\beta)}\right) \int dx' \exp\left(-i\left[\mathcal{Q}_l^{(\alpha)} - G_{kl}(t)\mathcal{Q}_k^{(\beta)}\right]x'_l\right) P_{\text{eq}}(x').$$

The remaining integral over  $x'$  is the Fourier transform of  $P_{\text{eq}}(x')$  for  $\mathbf{Q} = \mathbf{Q}^{(\alpha)} - \mathbf{G}^T(t) \cdot \mathbf{Q}^{(\beta)}$ . From Eq. (30) one finds

$$\tilde{P}_{\text{eq}}(\mathcal{Q}) = \exp\left(-\frac{1}{2}\mathcal{Q}_k \sigma_{kl}(\infty)\mathcal{Q}_l\right),$$

and  $f_{\alpha\beta}(\mathbf{q}, t)$  takes the form

$$f_{\alpha\beta}(\mathbf{q}, t) = \exp\left(-\frac{1}{2}\mathcal{Q}_k^{(\beta)} \sigma_{kl}(t)\mathcal{Q}_l^{(\beta)}\right) \exp\left(-\frac{1}{2}\left(\mathcal{Q}_k^{(\alpha)} - G_{mk}(t)\mathcal{Q}_m^{(\beta)}\right)\sigma_{kl}(\infty)\left(\mathcal{Q}_l^{(\alpha)} - G_{nl}(t)\mathcal{Q}_n^{(\beta)}\right)\right).$$

A more convenient form is obtained by inserting the decomposition (33) of  $\sigma(t)$  into the above expression. In addition one may use that the correlation functions of the dynamical variables is given by (see Refs. [20,21] and Appendix A)

$$c_{ij}(t) = \langle x_i(t)x_j(0) \rangle = G_{im}(t)\sigma_{mj}(\infty). \quad (36)$$

This allows to cast  $f_{\alpha\beta}(\mathbf{q}, t)$  into the form

$$f_{\alpha\beta}(\mathbf{q}, t) = \exp\left(-\frac{1}{2}\left[\mathcal{Q}_k^{(\alpha)}\sigma_{kl}(\infty)\mathcal{Q}_l^{(\alpha)} + \mathcal{Q}_k^{(\beta)}\sigma_{kl}(\infty)\mathcal{Q}_l^{(\beta)}\right]\right) \exp\left(\mathcal{Q}_k^{(\beta)}c_{kl}(t)\mathcal{Q}_l^{(\alpha)}\right). \quad (37)$$

The diagonal terms,  $f_{\alpha\alpha}$ , take a particularly simple form if they are expressed in terms of the mean-square displacements

$$W_{ij}(t) = \langle [x_i(t) - x_i(0)][x_j(t) - x_j(0)] \rangle = 2\sigma_{ij}(\infty) - c_{ij}(t) - c_{ji}(t). \quad (38)$$

Using Eq. (37) with  $\alpha = \beta$  and the above definition of the coefficients  $W_{ij}(t)$ , one obtains

$$f_{\alpha\alpha}(\mathbf{q}, t) = \exp\left(-\frac{1}{2}\mathcal{Q}_k^{(\alpha)}W_{kl}(t)\mathcal{Q}_l^{(\alpha)}\right). \quad (39)$$

It should be noted that the expressions for the dynamic form factors derived above are valid for positive time arguments. The case of negative time arguments can be handled by using the symmetry relation

$$f_{\alpha\beta}(\mathbf{q}, t) = f_{\beta\alpha}(-\mathbf{q}, -t). \quad (40)$$

This relation is obtained from expression (35), exchanging  $(x, t) \rightarrow (x', t')$ ,  $\alpha \rightarrow \beta$ , and  $\mathbf{q} \rightarrow -\mathbf{q}$ .

Since  $\lim_{t \rightarrow \infty} G_{lm}(t) = \lim_{t \rightarrow \infty} c_{lm}(t) = 0$ , we find from Eq. (37) that each  $f_{\alpha\beta}$  is a product of a time-independent and a time-dependent factor,

$$f_{\alpha\beta}(\mathbf{q}, t) = f_{\alpha\beta}(\mathbf{q}, \infty)f'_{\alpha\beta}(\mathbf{q}, t). \quad (41)$$

Introducing the Debye–Waller factors

$$w_\alpha(\mathbf{q}) = \frac{1}{2}\mathcal{Q}_k^{(\alpha)}\sigma_{kl}(\infty)\mathcal{Q}_l^{(\alpha)}, \quad (42)$$

$f_{\alpha\beta}(\mathbf{q}, \infty)$  may be written in the form

$$f_{\alpha\beta}(\mathbf{q}, \infty) = \exp\left(-[w_\alpha(\mathbf{q}) + w_\beta(\mathbf{q})]\right). \quad (43)$$

The time dependent functions  $f'_{\alpha\beta}(\mathbf{q}, t)$  describe the dynamical correlations,

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp\left(\mathcal{Q}_k^{(\beta)}c_{kl}(t)\mathcal{Q}_l^{(\alpha)}\right). \quad (44)$$

Using that  $G_{ij}(0) = \delta_{ij}$  and therefore  $\lim_{t \rightarrow 0} c_{kl}(t) = \sigma_{kl}(\infty)$ , one finds for  $t = 0$

$$f_{\alpha\beta}(\mathbf{q}, 0) = \exp\left(-\frac{1}{2}\left[\mathcal{Q}_k^{(\alpha)} - \mathcal{Q}_k^{(\beta)}\right]\sigma_{kl}(\infty)\left[\mathcal{Q}_l^{(\alpha)} - \mathcal{Q}_l^{(\beta)}\right]\right). \quad (45)$$

### 3.2. Spectral decomposition of the $f_{\alpha\beta}$

It has been shown above that each dynamic form factor can be written as a product of a static factor  $f_{\alpha\beta}(\mathbf{q}, \infty)$ , involving the matrix  $\sigma(\infty)$ , and a time dependent factor  $f'_{\alpha\beta}(\mathbf{q}, t)$ , involving the correlation matrix  $\mathbf{C}(t)$  of the dynamical variables. The static factors  $f_{\alpha\beta}(\mathbf{q}, \infty)$  are the same for LD and SD. According to Eqs. (42), (43), and (33), they can be expressed in terms of the force constant matrix  $\mathbf{K}$  only. In contrast, the spectral decomposition for the time dependent factors  $f'_{\alpha\beta}(\mathbf{q}, t)$  depends on the dynamical model involved and will be discussed separately.

#### 3.2.1. Static limits $f_{\alpha\beta}(\mathbf{q}, \infty)$ and $f_{\alpha\beta}(\mathbf{q}, 0)$

To compute the static limits of the  $f_{\alpha\beta}$ , the spectral representation of  $k_{\text{B}}T\mathbf{K}^{-1}$  is needed. Since the force constant matrix  $\mathbf{K}$  is by definition positive definite, it can be diagonalized by an orthogonal transformation,

$$\mathbf{K} = \mathbf{D} \cdot \boldsymbol{\Omega}^2 \cdot \mathbf{D}^T, \quad (46)$$



$$\mathbf{\Omega} = \text{diag}(\omega_1, \dots, \omega_{3N}). \quad (47)$$

The columns of  $\mathbf{D} = (\mathbf{d}_1, \dots, \mathbf{d}_{3N})$  are the orthonormal eigenvectors (“normal modes”) of  $\mathbf{K}$ , with  $\mathbf{d}_j^T \cdot \mathbf{d}_k = \delta_{jk}$ , and the  $\omega_j$  ( $\omega_j > 0$ ) are the corresponding “normal frequencies”. Using the normal modes and frequencies one can express any function of the matrix  $\mathbf{K}$  as  $f(\mathbf{K}) = \sum_{j=1}^{3N} f(\omega_j^2) \mathbf{d}_j \cdot \mathbf{d}_j^T$ , in particular

$$\sigma(\infty) = k_B T \sum_{j=1}^{3N} \omega_j^{-2} \mathbf{d}_j \cdot \mathbf{d}_j^T. \quad (48)$$

According to Eqs. (42), (43), and (45), the static limits of the dynamic form factors are then given by

$$f_{\alpha\beta}(\mathbf{q}, \infty) = \exp\left(-\frac{k_B T}{2} \sum_{j=1}^{3N} \omega_j^{-2} \left[ (\mathbf{d}_j^T \cdot \mathbf{Q}^{(\alpha)})^2 + (\mathbf{d}_j^T \cdot \mathbf{Q}^{(\beta)})^2 \right]\right), \quad (49)$$

$$f_{\alpha\beta}(\mathbf{q}, 0) = \exp\left(-\frac{k_B T}{2} \sum_{j=1}^{3N} \omega_j^{-2} \left[ \mathbf{d}_j^T \cdot (\mathbf{Q}^{(\alpha)} - \mathbf{Q}^{(\beta)}) \right]^2\right). \quad (50)$$

### 3.2.2. The $f'_{\alpha\beta}(\mathbf{q}, t)$ for Langevin dynamics

The spectral decomposition of the time-dependent factors  $f'_{\alpha\beta}$  is obtained from expression (44), which reads in matrix form

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp(\mathbf{Q}^{(\beta)T} \cdot \mathbf{C}(t) \cdot \mathbf{Q}^{(\alpha)}). \quad (51)$$

According to relation (36) the correlation matrix of the dynamic variables is given by the product  $\mathbf{C}(t) = \mathbf{G}(t) \cdot \sigma(\infty)$ , where  $\mathbf{G}(t) = \exp(-\mathbf{A}t)$  is the propagator of the mean values of the dynamical variables. In the following it will be assumed that all eigenvalues of  $\mathbf{A}$  are *different*. In this case  $\mathbf{A}$  can be diagonalized [23],

$$\mathbf{A} = \mathbf{U} \cdot \mathbf{\Lambda} \cdot \mathbf{U}^{-1}, \quad (52)$$

$$\mathbf{\Lambda} = \text{diag}(\lambda_1, \dots, \lambda_{6N}). \quad (53)$$

Since  $\mathbf{A}$  is real, all complex eigenvalues must occur in complex conjugate pairs and eigenvectors corresponding to complex conjugate eigenvalues are also complex conjugate. The columns of  $\mathbf{U} = (\mathbf{u}_1, \dots, \mathbf{u}_{6N})$  are the (right) eigenvectors of  $\mathbf{A}$  and the rows of  $\mathbf{U}^{-1}$  are the corresponding left eigenvectors,  $\mathbf{v}_l$  ( $l = 1, \dots, 6N$ ). The right and left eigenvectors form two sets of bi-orthonormal basis vectors of  $\mathcal{R}^{6N}$ ,  $\mathbf{u}_k^T \cdot \mathbf{v}_l = \delta_{kl}$ . Any function of  $\mathbf{A}$  has therefore the spectral representation  $f(\mathbf{A}) = \sum_{k=1}^{6N} f(\lambda_k) \mathbf{u}_k \cdot \mathbf{v}_k^T$ , and one obtains in particular

$$\mathbf{G}(t) = \sum_k \exp(-\lambda_k t) \mathbf{u}_k \cdot \mathbf{v}_k^T. \quad (54)$$

Using formula (32) for  $\sigma(\infty)$  and partitioning the eigenvectors in upper and lower parts,  $\mathbf{u}^T = (\mathbf{u}_a^T, \mathbf{u}_b^T)$  and  $\mathbf{v}^T = (\mathbf{v}_a^T, \mathbf{v}_b^T)$ , yields

$$\mathbf{C}(t) = \begin{pmatrix} \mathbf{C}_{uu}(t) & \mathbf{C}_{uv}(t) \\ \mathbf{C}_{vu}(t) & \mathbf{C}_{vv}(t) \end{pmatrix} = k_B T \sum_{k=1}^{6N} \exp(-\lambda_k t) \begin{pmatrix} \mathbf{u}_{k,a} \cdot \mathbf{v}_{k,a}^T \cdot \mathbf{K}^{-1} & \mathbf{u}_{k,a} \cdot \mathbf{v}_{k,b}^T \\ \mathbf{u}_{k,b} \cdot \mathbf{v}_{k,a}^T \cdot \mathbf{K}^{-1} & \mathbf{u}_{k,b} \cdot \mathbf{v}_{k,b}^T \end{pmatrix}. \quad (55)$$

Since the components  $Q_j^{(\alpha)}$  of  $\mathbf{Q}^{(\alpha)}$  are zero for  $j = 3N + 1, \dots, 6N$ , only the upper left blocks are needed to compute  $f'_{\alpha\beta}(\mathbf{q}, t)$ . To keep a compact form for the expressions to be derived in the following, the quantities:

$$y_{\alpha\beta}^{(k)}(\mathbf{q}) = k_B T \left( \mathbf{v}_{k,a}^T \cdot \mathbf{K}^{-1} \cdot \mathbf{Q}^{(\alpha)} \right) \cdot \left( \mathbf{u}_{k,a}^T \cdot \mathbf{Q}^{(\beta)} \right), \quad k = 1, \dots, 6N, \quad (56)$$

are introduced. It should be noted that here  $\mathbf{Q}^{(\alpha)}$  and  $\mathbf{Q}^{(\beta)}$  have the length  $3N$ . Using this definition,  $f'_{\alpha\beta}$  takes the form

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp \left( \sum_{k=1}^{6N} y_{\alpha\beta}^{(k)}(\mathbf{q}) \exp(-\lambda_k t) \right). \quad (57)$$

Eq. (56) suggests that the left and right eigenvectors of  $\mathbf{A}$  are needed to compute the expressions  $y_{\alpha\beta}^{(k)}(\mathbf{q})$ . By exploiting the block structure of  $\mathbf{A}$  one can derive a more convenient expression, which involves the upper half eigenvectors,  $\mathbf{u}_{k,a}$ , only. Writing  $\mathbf{A} \cdot \mathbf{u}_k = \lambda_k \mathbf{u}_k$  and  $\mathbf{A}^T \cdot \mathbf{v}_k = \lambda_k \mathbf{v}_k$ , with  $\mathbf{A}$  given by definition (20), it follows that (the mode index  $k$  is dropped)

$$\mathbf{u}_b = -\lambda \mathbf{u}_a, \quad (58)$$

$$\mathbf{v}_b = \lambda \mathbf{K}^{-1} \cdot \mathbf{v}_a. \quad (59)$$

These relations allow to derive decoupled equations for each of the upper and lower half eigenvectors:

$$\lambda^2 \mathbf{u}_{a,b} - \lambda \gamma \cdot \mathbf{u}_{a,b} + \mathbf{K} \cdot \mathbf{u}_{a,b} = \mathbf{0}, \quad (60)$$

$$\lambda^2 \mathbf{v}_a - \lambda \mathbf{K} \cdot \gamma \cdot \mathbf{K}^{-1} \cdot \mathbf{v}_a + \mathbf{K} \cdot \mathbf{v}_a = \mathbf{0}, \quad (61)$$

$$\lambda^2 \mathbf{v}_b - \lambda \gamma \cdot \mathbf{v}_b + \mathbf{K} \cdot \mathbf{v}_b = \mathbf{0}. \quad (62)$$

Eq. (59) shows that the vector  $\mathbf{K}^{-1} \cdot \mathbf{v}_a$  appearing in the argument of  $y_{\alpha\beta}^{(k)}(\mathbf{q})$  may be replaced by  $\mathbf{K}^{-1} \cdot \mathbf{v}_a = \lambda^{-1} \mathbf{v}_b$ . Since  $\mathbf{v}_b$  fulfills the same equation as  $\mathbf{u}_a$  – see Eqs. (60) and (62) – the two vectors must be proportional and one can write

$$\mathbf{K}^{-1} \cdot \mathbf{v}_a = \frac{1}{\lambda} \mathbf{v}_b = \frac{c}{\lambda} \mathbf{u}_a, \quad (63)$$

where  $c$  is a constant yet to be determined. This can be achieved by using the normalization conditions  $\mathbf{u}_k^T \cdot \mathbf{v}_l = \delta_{kl}$ . Multiplying the equation for the  $k$ th right eigenvector,  $\mathbf{A} \cdot \mathbf{u}_k = \lambda_k \mathbf{u}_k$ , from the left by the corresponding left eigenvector,  $\mathbf{v}_k$ , and making use of the block structure of  $\mathbf{A}$ , yields (the mode index  $k$  is dropped again)

$$-\mathbf{v}_a^T \cdot \mathbf{u}_b + \mathbf{v}_b^T \cdot \mathbf{K} \cdot \mathbf{u}_a + \mathbf{v}_b^T \cdot \gamma \cdot \mathbf{u}_b = \lambda. \quad (64)$$

With Eqs. (58) and (59) one can derive a normalization condition for any pair  $(\mathbf{u}_{a,b}, \mathbf{v}_{a,b})$ . Using  $\mathbf{v}_b = c \mathbf{u}_a$  with the above normalization condition for  $\mathbf{u}_a$  and  $\mathbf{v}_b$  allows to fix the normalization constant as  $c = 1/(\mathbf{u}_a^T \cdot (\gamma - 2\lambda \mathbf{1}) \cdot \mathbf{u}_a)$ . With Eq. (60) one may also write  $c = \lambda/(\mathbf{u}_a^T \cdot (\mathbf{K} - \lambda^2 \mathbf{1}) \cdot \mathbf{u}_a)$ . From Eqs. (63) and (56) one obtains then two equivalent expressions for  $y_{\alpha\beta}^{(k)}(\mathbf{q})$  in which  $\mathbf{v}_a$  does not appear anymore

$$y_{\alpha\beta}^{(k)}(\mathbf{q}) = k_B T \frac{\left( \mathbf{u}_{k,a}^T \cdot \mathbf{Q}^{(\alpha)} \right) \left( \mathbf{u}_{k,a}^T \cdot \mathbf{Q}^{(\beta)} \right)}{\mathbf{u}_{k,a}^T \cdot (\mathbf{K} - \lambda_k^2 \mathbf{1}) \cdot \mathbf{u}_{k,a}}, \quad (65)$$

$$y_{\alpha\beta}^{(k)}(\mathbf{q}) = k_B T \frac{\left( \mathbf{u}_{k,a}^T \cdot \mathbf{Q}^{(\alpha)} \right) \left( \mathbf{u}_{k,a}^T \cdot \mathbf{Q}^{(\beta)} \right)}{\lambda_k \mathbf{u}_{k,a}^T \cdot (\gamma - 2\lambda_k \mathbf{1}) \cdot \mathbf{u}_{k,a}}. \quad (66)$$

If all modes are under-damped the knowledge of  $3N$  eigenvalues,  $\lambda_j$  ( $j = 1, \dots, 3N$ ), and the corresponding half-eigenvectors,  $\mathbf{u}_{j,a}$ , suffices to compute  $f'_{\alpha\beta}(\mathbf{q}, t)$ . Ordering the eigenvalues of  $\mathbf{A}$  as follows ( $\eta_j \geq 0$ ,  $\Omega_j$  real)

$$\left. \begin{array}{l} \lambda_j = \eta_j + i\Omega_j, \\ \lambda_{3N+j} = \eta_j - i\Omega_j, \end{array} \right\} \quad j = 1, \dots, 3N, \quad (67)$$

we have  $\mathbf{u}_{a,3N+j} = \mathbf{u}_{a,j}^*$ , and therefore

$$y_{\alpha\beta}^{(3N+j)}(\mathbf{q}) = y_{\alpha\beta}^{(j)*}(\mathbf{q}). \quad (68)$$

In case of over-damped modes, where  $\Omega_j$  becomes imaginary, there is no longer a simple relation between  $\mathbf{u}_{a,3N+j}$  and  $\mathbf{u}_{a,j}$  that could be exploited on a purely numerical basis.

The denominators in Eqs. (65) and (66) cannot become zero if all eigenvalues are different, as postulated. To see that one may look at Eqs. (60)–(62) which show that  $\mathbf{u}_{a,b}$ ,  $\mathbf{v}_b$ , and  $\mathbf{K}^{-1}\mathbf{v}_a$  are all solutions of the same eigenvalue problem. Multiplying Eq. (60) for given eigenvalue  $\lambda_j$  from the left by  $\mathbf{u}_{j,a}^H$ , where the superscript H denotes the Hermitian transposed, and setting  $\mathbf{u}_{j,a}^H \cdot \mathbf{u}_{j,a} = 1$  for convenience, yields a quadratic equation for  $\lambda_j$ ,

$$\lambda_j^2 - a_j \lambda_j + b_j = 0. \quad (69)$$

Here  $a_j = \mathbf{u}_{j,a}^H \cdot \boldsymbol{\gamma} \cdot \mathbf{u}_{j,a} = a_{3N+j}$  and  $b_j = \mathbf{u}_{j,a}^H \cdot \mathbf{K} \cdot \mathbf{u}_{j,a} = b_{3N+j}$  are real and positive since  $\mathbf{K}$  and  $\boldsymbol{\gamma}$  are positive definite. Excluding  $\mathbf{u}_a = \mathbf{0}$ , the denominators of the two equivalent expressions (65) and (66) can vanish only if Eq. (69) has a twofold degenerate solution, i.e. in the aperiodic limit where  $a_j^2/4 = b_j$  and  $\lambda_{3N+j} = \lambda_j$ . This situation is, however, excluded since  $\mathbf{A}$  is by definition non-degenerate.

### 3.2.3. The $f'_{\alpha\beta}(\mathbf{q}, t)$ in the low friction limit

In the limit of vanishing friction the classical limit of the intermediate scattering functions derived by Glauber and Zemach for coupled harmonic oscillators must be retrieved. This is indeed the case. One finds from Eq. (60) that

$$\mathbf{K} \cdot \mathbf{u}_a = -\lambda^2 \mathbf{u}_a. \quad (70)$$

If  $\mathbf{u}_a$  is chosen to be a unit vector,  $\mathbf{u}_a^T \cdot \mathbf{u}_a = 1$ , (the norm of  $\mathbf{u}_a$  is arbitrary), one can identify  $\mathbf{u}_{a,j} = \mathbf{d}_j$  and  $\lambda_j = i\omega_j$  for  $j = 1, \dots, 3N$ . Here  $\mathbf{d}_j$  and  $\omega_j$  are the normal modes and frequencies corresponding to the force constant matrix  $\mathbf{K}$ . The remaining  $3N$  eigenvalues and eigenvectors are  $\lambda_{3N+j} = -i\omega_j$  and  $\mathbf{u}_{a,3N+j} = \mathbf{u}_{a,j}$ . The last relation holds since  $\mathbf{u}_{a,j} = \mathbf{d}_j$  are real vectors. It then follows from Eq. (65) that

$$y_{\alpha\beta}^{(j)}(\mathbf{q}) = \frac{k_B T}{2\omega_j^2} (\mathbf{d}_j^T \cdot \mathbf{Q}^{(\alpha)}) (\mathbf{d}_j^T \cdot \mathbf{Q}^{(\beta)}), \quad (71)$$

$$y_{\alpha\beta}^{(3N+j)}(\mathbf{q}) = y_{\alpha\beta}^{(j)}(\mathbf{q}), \quad (72)$$

and the time-dependent parts of the dynamic form factors take the form

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp \left( \sum_{j=1}^{3N} 2y_{\alpha\beta}^{(j)}(\mathbf{q}) \cos \omega_j t \right). \quad (73)$$

Writing  $f_{\alpha\beta}(\mathbf{q}, t) = f_{\alpha\beta}(\mathbf{q}, \infty) f'_{\alpha\beta}(\mathbf{q}, t)$ , the dynamic form factors derived by Glauber and Zemach [5] are retrieved, replacing quantum thermal averages by classical ones. Since here  $\hbar\omega_k \ll k_B T$ , the  $f'_{\alpha\beta}$  are even in time.

### 3.2.4. The $f'_{\alpha\beta}(\mathbf{q}, t)$ for Smoluchowski dynamics

In the Smoluchowski description the  $f'_{\alpha\beta}$  are calculated through

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp(\mathbf{Q}^{(\beta)\text{T}} \cdot \mathbf{C}_{\text{SD}}(t) \cdot \mathbf{Q}^{(\alpha)}), \quad (74)$$

where  $\mathbf{C}_{\text{SD}}(t)$  is given by (see Eqs. (36), (32), (24), and (21))

$$\mathbf{C}_{\text{SD}}(t) = k_{\text{B}}T \sum_{j=1}^{3N} \exp(-\lambda_j t) (\mathbf{u}_j \cdot \mathbf{v}_j^{\text{T}}) \mathbf{K}^{-1}. \quad (75)$$

Here the spectral decomposition

$$\mathbf{A}_{\text{SD}} = \sum_{j=1}^{3N} \lambda_j \mathbf{u}_j \cdot \mathbf{v}_j^{\text{T}} \quad (76)$$

is used, where  $\mathbf{A} = \boldsymbol{\gamma}^{-1} \cdot \mathbf{K}$  and  $\mathbf{u}_j$  and  $\mathbf{v}_j$  are the right and left eigenvectors of  $\mathbf{A}$ , respectively,

$$\mathbf{A}_{\text{SD}} \cdot \mathbf{u}_j = \lambda_j \mathbf{u}_j, \quad (77)$$

$$\mathbf{A}_{\text{SD}}^{\text{T}} \cdot \mathbf{v}_j = \lambda_j \mathbf{v}_j. \quad (78)$$

As for LD, the right and left eigenvectors are bi-orthonormal, i.e.  $\mathbf{u}_j^{\text{T}} \cdot \mathbf{v}_k = \delta_{jk}$ . The matrix  $\mathbf{A}_{\text{SD}}$  can always be diagonalized since it is the product of two positive definite matrices [23]. The functions  $f'_{\alpha\beta}(\mathbf{q}, t)$  take the same form as for LD, except that only one branch of real positive eigenvalues exists,

$$f'_{\alpha\beta}(\mathbf{q}, t) = \exp\left(\sum_{j=1}^{3N} y_{\alpha\beta}^{(j)}(\mathbf{q}) \exp(-\lambda_j t)\right). \quad (79)$$

To derive expressions for the  $y_{\alpha\beta}^{(j)}(\mathbf{q})$  one starts from the definition  $y_{\alpha\beta}^{(j)}(\mathbf{q}) = k_{\text{B}}T (\mathbf{v}_j^{\text{T}} \cdot \mathbf{K}^{-1} \cdot \mathbf{Q}^{(\alpha)}) \cdot (\mathbf{u}_j^{\text{T}} \cdot \mathbf{Q}^{(\beta)})$ , which is the analogue of definition (56). Here  $\mathbf{K}^{-1} \cdot \mathbf{v}_j$  can be expressed by a vector which is proportional to the corresponding right eigenvector  $\mathbf{u}_j$ . One can easily verify that  $\mathbf{K}^{-1} \cdot \mathbf{v}_j$  fulfills Eq. (77), and therefore  $\mathbf{K}^{-1} \cdot \mathbf{v}_j = c \mathbf{u}_j$ . The constant  $c$  is determined from the normalization condition  $\mathbf{u}_j^{\text{T}} \cdot \mathbf{v}_j = 1$ . One obtains  $c = (\mathbf{u}_j^{\text{T}} \cdot \mathbf{K} \cdot \mathbf{u}_j)^{-1}$ , and the functions  $y_{\alpha\beta}^{(j)}(\mathbf{q})$  take the equivalent forms

$$y_{\alpha\beta}^{(j)}(\mathbf{q}) = k_{\text{B}}T \frac{(\mathbf{u}_j^{\text{T}} \cdot \mathbf{Q}^{(\alpha)}) (\mathbf{u}_j^{\text{T}} \cdot \mathbf{Q}^{(\beta)})}{\mathbf{u}_j^{\text{T}} \cdot \mathbf{K} \cdot \mathbf{u}_j}, \quad (80)$$

$$y_{\alpha\beta}^{(j)}(\mathbf{q}) = k_{\text{B}}T \frac{(\mathbf{u}_j^{\text{T}} \cdot \mathbf{Q}^{(\alpha)}) (\mathbf{u}_j^{\text{T}} \cdot \mathbf{Q}^{(\beta)})}{\lambda_j \mathbf{u}_j^{\text{T}} \cdot \boldsymbol{\gamma} \cdot \mathbf{u}_j}. \quad (81)$$

In the last equation it was used that  $\mathbf{K} \cdot \mathbf{u}_j = \boldsymbol{\gamma} \cdot \mathbf{A}_{\text{SD}} \cdot \mathbf{u}_j = \lambda_j \boldsymbol{\gamma} \cdot \mathbf{u}_j$ .

### 3.2.5. Transition from Langevin to Smoluchowski dynamics

The dynamic form factors for SD can also be obtained within the Langevin description, considering a situation where friction is dominating. All vibrational modes are then strongly over-damped and both roots of Eq. (69) are real. Using the ordering scheme (67) one has  $\lambda_j = \eta_j - \tilde{\Omega}_j$  and  $\lambda_{3N+j} = \eta_j + \tilde{\Omega}_j$  ( $j = 1, \dots, 3N$ ), where  $\eta_j = a_j/2$  and  $\tilde{\Omega}_j = (a_j^2/4 - b_j)^{1/2}$ . Here is again  $a_j = \mathbf{u}_{j,a}^{\text{H}} \cdot \boldsymbol{\gamma} \cdot \mathbf{u}_{j,a} = a_{3N+j}$  and  $b_j = \mathbf{u}_{j,a}^{\text{H}} \cdot \mathbf{K} \cdot \mathbf{u}_{j,a} = b_{3N+j}$ . For  $\|\boldsymbol{\gamma}\| \gg \|\mathbf{K}\|$  ( $\|\dots\|$  denotes a suitable matrix norm)  $b_j$  is much smaller than  $a_j$

and  $\lambda_j$  is close to zero, whereas  $\lambda_{3N+j}$  is close to  $2\eta_j$ . On a coarse-grained time scale with observation intervals  $\Delta t \gg 1/\eta_j$  ( $j = 1, \dots, 3N$ ) the correlation matrix defined in Eq. (55) can be approximated by

$$\mathbf{C}(t) \approx k_B T \sum_{j=1}^{3N} \exp(-\lambda_j t) \begin{pmatrix} (\mathbf{u}_{j,a} \cdot \mathbf{v}_{j,a}^T) \cdot \mathbf{K}^{-1} & (\mathbf{u}_{j,a} \cdot \mathbf{v}_{j,b}^T) \\ (\mathbf{u}_{j,b} \cdot \mathbf{v}_{j,a}^T) \cdot \mathbf{K}^{-1} & (\mathbf{v}_{j,b} \cdot \mathbf{v}_{j,b}^T) \end{pmatrix}. \quad (82)$$

Only the upper left block of  $\mathbf{C}(t)$  is needed to compute  $f'_{\alpha\beta}$ , and one gets

$$f'_{\alpha\beta}(\mathbf{q}, t) \approx \exp \left( \sum_{j=1}^{3N} y_{\alpha\beta}^{(j)}(\mathbf{q}) \exp(-\lambda_j t) \right). \quad (83)$$

Since  $\lambda_j$  is small for  $j = 1, \dots, 3N$ , the quadratic term in the denominators of expressions (65) and (66) may be neglected, i.e.

$$y_{\alpha\beta}^{(j)}(\mathbf{q}) \approx k_B T \frac{(\mathbf{u}_{j,a}^T \cdot \mathbf{Q}^{(\alpha)}) (\mathbf{u}_{j,a}^T \cdot \mathbf{Q}^{(\beta)})}{\mathbf{u}_{j,a}^T \cdot \mathbf{K} \cdot \mathbf{u}_{j,a}}, \quad (84)$$

$$y_{\alpha\beta}^{(j)}(\mathbf{q}) \approx k_B T \frac{(\mathbf{u}_{j,a}^T \cdot \mathbf{Q}^{(\alpha)}) (\mathbf{u}_{j,a}^T \cdot \mathbf{Q}^{(\beta)})}{\lambda_j \mathbf{u}_{j,a}^T \cdot \boldsymbol{\gamma} \cdot \mathbf{u}_{j,a}}, \quad (85)$$

where  $j = 1, \dots, 3N$ . It is easy to see that for high friction the  $\mathbf{u}_{j,a}$  tend to the right eigenvectors of  $\mathbf{A}_{SD}$  and the  $\mathbf{v}_{j,a}$  to the corresponding left eigenvectors. Setting  $\lambda^2 = 0$  in Eq. (60) and multiplying with  $\boldsymbol{\gamma}^{-1}$  from the left yields (the mode indices are dropped)

$$\underbrace{\boldsymbol{\gamma}^{-1} \cdot \mathbf{K}}_{\mathbf{A}_{SD}} \cdot \mathbf{u}_a \approx \lambda \mathbf{u}_a. \quad (86)$$

Similarly one finds from Eq. (61) by multiplication with  $\mathbf{K} \cdot \boldsymbol{\gamma}^{-1} \cdot \mathbf{K}^{-1}$  that

$$\underbrace{\mathbf{K} \cdot \boldsymbol{\gamma}^{-1}}_{\mathbf{A}_{SD}^T} \cdot \mathbf{v}_a \approx \lambda \mathbf{v}_a. \quad (87)$$

Comparing now expressions (80) and (81) for the  $y$ -functions of SD with Eqs. (84) and (85), respectively, shows that SD and strongly over-damped LD on a coarse-grained time scale yield the same dynamic form factors.

#### 4. Dynamic structure factor

According to Eq. (1) the dynamic structure factor,  $\mathcal{S}(\mathbf{q}, \omega)$ , is obtained from the intermediate scattering function by a Fourier transform in time. The straightforward approach is to perform the Fourier transform numerically, e.g. by using the fast Fourier transform technique [24]. From a practical point of view this is, indeed, the best way [25]. The analytical approach is, however, important to discuss theoretical aspects of Langevin and Brownian modes, as compared to conventional normal mode analysis.

#### 4.1. Partial dynamic structure factors

As the intermediate scattering function splits into a coherent and an incoherent part,  $\mathcal{S}_{\text{coh}}(\mathbf{q}, \omega)$  and  $\mathcal{S}_{\text{inc}}(\mathbf{q}, \omega)$  are defined as the corresponding Fourier transforms. With Eqs. (11) and (12) one obtains

$$\mathcal{S}_{\text{coh}}(\mathbf{q}, \omega) = \sum_{\alpha, \beta} b_{\alpha, \text{coh}} b_{\beta, \text{coh}} \exp\left(-i\mathbf{q}^T \cdot [\mathbf{R}_{\alpha}^{\text{eq}} - \mathbf{R}_{\beta}^{\text{eq}}]\right) s_{\alpha\beta}(\mathbf{q}, \omega), \quad (88)$$

$$\mathcal{S}_{\text{inc}}(\mathbf{q}, t) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 s_{\alpha\alpha}(\mathbf{q}, t), \quad (89)$$

where the functions  $s_{\alpha\beta}(\mathbf{q}, \omega)$  are the Fourier cosine transforms of the dynamic form factors,  $f_{\alpha\beta}(\mathbf{q}, \omega)$ ,

$$s_{\alpha\beta}(\mathbf{q}, \omega) = f_{\alpha\beta}(\mathbf{q}, \infty) s'_{\alpha\beta}(\mathbf{q}, \omega), \quad (90)$$

$$s'_{\alpha\beta}(\mathbf{q}, \omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \int_0^{\infty} dt \exp(-\epsilon t) \cos \omega t f'_{\alpha\beta}(\mathbf{q}, t). \quad (91)$$

Here it was used that the dynamic form factors are even functions in time. This follows from the symmetry relation (40) and from the additional symmetries  $f_{\alpha\beta}(-\mathbf{q}, t) = f_{\alpha\beta}(\mathbf{q}, t)$  and  $f_{\beta\alpha}(\mathbf{q}, t) = f_{\alpha\beta}(\mathbf{q}, t)$ . The factor  $\exp(-\epsilon t)$  ( $\epsilon \rightarrow 0+$ ) ensures the existence of the cosine transforms in case of vanishing friction.

According to Eqs. (57) and (79), the functions  $f'_{\alpha\beta}(\mathbf{q}, t)$  can be written as a product over contributions from single modes. As it will be shown in Section 4.2.1, it is useful to treat under-damped Langevin modes in terms of complex conjugate pairs. In this case one writes

$$f'_{\alpha\beta}(\mathbf{q}, t) = \prod_{j=1}^{N_{\text{cc}}} f_{\alpha\beta}^{(j, \text{cc})}(\mathbf{q}, t) \prod_{k=1}^{N_{\text{s}}} f_{\alpha\beta}^{(k)}(\mathbf{q}, t). \quad (92)$$

Here  $N_{\text{cc}}$  is the number of conjugate complex pairs and  $N_{\text{s}}$  the number of single modes, with  $2N_{\text{cc}} + N_{\text{s}} = 6N$ . For over-damped Brownian dynamics one has

$$f'_{\alpha\beta}(\mathbf{q}, t) = \prod_{k=1}^{3N} f_{\alpha\beta}^{(k)}(\mathbf{q}, t). \quad (93)$$

It follows from Eq. (92) that the partial dynamic structure factors for LD are convolution products of the form

$$s'_{\alpha\beta}(\mathbf{q}, \omega) \propto s_{\alpha\beta}^{(1, \text{cc})}(\mathbf{q}, \omega) \times \cdots \times s_{\alpha\beta}^{(N_{\text{cc}}, \text{cc})}(\mathbf{q}, \omega) \times s_{\alpha\beta}^{(1)}(\mathbf{q}, \omega) \times \cdots \times s_{\alpha\beta}^{(N_{\text{s}})}(\mathbf{q}, \omega), \quad (94)$$

and for SD one has with Eq. (93)

$$s'_{\alpha\beta}(\mathbf{q}, \omega) \propto s_{\alpha\beta}^{(1)}(\mathbf{q}, \omega) \times \cdots \times s_{\alpha\beta}^{(3N)}(\mathbf{q}, \omega). \quad (95)$$

The functions  $s_{\alpha\beta}^{(j, \text{cc})}(\mathbf{q}, \omega)$  and  $s_{\alpha\beta}^{(k)}(\mathbf{q}, \omega)$  are defined through

$$s_{\alpha\beta}^{(K)}(\mathbf{q}, \omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \int_0^{\infty} dt \exp(-\epsilon t) \cos \omega t f_{\alpha\beta}^{(K)}(\mathbf{q}, t), \quad (96)$$

where  $K$  stands either for a pair of complex conjugate modes or for a single mode.

## 4.2. Partial dynamic structure factors for single modes

### 4.2.1. Under-damped Langevin modes

Here it is convenient to consider a pair of complex conjugate modes, and one defines

$$f_{\alpha\beta}^{(j,\text{cc})}(\mathbf{q}, t) = \exp\left(y_{\alpha\beta}^{(j)}(\mathbf{q}) \exp(-\lambda_j t) + y_{\alpha\beta}^{(j)*}(\mathbf{q}) \exp(-\lambda_j^* t)\right). \quad (97)$$

To obtain a tractable expression for  $f_{\alpha\beta}^{(j,\text{cc})}(\mathbf{q}, t)$  one can use that [26]

$$\exp(z \cos \theta) = I_0(z) + 2 \sum_{n=1}^{\infty} I_n(z) \cos(n\theta), \quad (98)$$

where  $z$  is complex. The functions  $I_n(z)$  are the modified Bessel functions of the first kind. For integer  $n$ ,  $I_n(z) = I_{-n}(z)$ . If we set  $z = 2|y| \exp(-\eta t)$  and  $\theta = \Omega t - \phi$  (indices are dropped), where  $y = |y| \exp(i\phi)$  and  $\lambda = \eta + i\Omega$ , expression (97) can be cast into the form

$$f_{\alpha\beta}^{(j,\text{cc})}(\mathbf{q}, t) = I_0\left(2|y_{\alpha\beta}^{(j)}(\mathbf{q})| \exp(-\eta_j t)\right) = 2 \sum_{n=1}^{\infty} I_n\left(2|y_{\alpha\beta}^{(j)}(\mathbf{q})| \exp(-\eta_j t)\right) \cos\left(n[\Omega_j t - \phi_{\alpha\beta}^{(j)}(\mathbf{q})]\right). \quad (99)$$

According to Eqs. (96) and (99),  $s^{(j,\text{cc})}(\mathbf{q}, \omega)$  can be interpreted as the Laplace transform  $h(t) \rightarrow H(\epsilon)$  of a function  $h(t) = I_n(2y \exp(-\eta t))$  (dropping indices), multiplied by a product of cosine functions. The Laplace variable,  $\epsilon$ , is passed to 0 after the transformation. As described in Appendix B, the Laplace transform of  $I_n(2y \exp(-\eta t))$  can be cast into the form

$$\Psi_n(s; y, \eta) = \int_0^{\infty} dt \exp(-st) I_n(2y \exp(-\eta t)), \quad (100)$$

$$\Psi_n(s; y, \eta) = \sum_{k=0}^{\infty} \frac{(-2\eta)^k I_{n+k}(2y) y^k}{(s + \eta n)(s + [n + 2]\eta) \cdots (s + [n + 2k]\eta)}. \quad (101)$$

Here  $\Re[s] > 0$  and  $n \geq 0$ . Since  $I_n(z) = I_{-n}(z)$ , it follows that

$$\Psi_n(s; y, \eta) = \Psi_{-n}(s; y, \eta), \quad n < 0. \quad (102)$$

Writing the cosines appearing in the Fourier–Laplace transform of  $f_{\alpha\beta}^{(j,\text{cc})}(\mathbf{q}, t)$  in exponential form one finds that

$$s_{\alpha\beta}^{(j,\text{cc})}(\mathbf{q}, \omega) = \sum_{n=-\infty}^{+\infty} \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \exp\left(i n \phi_{\alpha\beta}^{(j)}(\mathbf{q})\right) \Psi_n(\epsilon - i[\omega - n\Omega_j]; |y_{\alpha\beta}^{(j)}(\mathbf{q})|, \eta_j) \right]. \quad (103)$$

For vanishing friction, i.e. for classical normal modes where  $\Omega_j = \omega_j$ , it follows that:

$$\Psi_n(s; y, \eta = 0) = \frac{I_n(2y)}{s}, \quad (104)$$

and  $y > 0$ . Inserting the above expression for  $\Psi(s; y, \eta)$  into Eq. (103) and using the identity

$$\delta(\omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + \omega^2},$$

we retrieve the expressions

$$s_{\alpha\beta}^{(j,cc)}(\mathbf{q}, \omega) = \sum_{n=-\infty}^{+\infty} I_n \left( 2y_{\alpha\beta}^{(j)}(\mathbf{q}) \right) \delta(\omega - n\omega_j) \quad (105)$$

for harmonically vibrating molecules in the classical limit [5].

In the case of very small but non-vanishing friction one needs still only the  $k = 0$  term in series (101), keeping, however,  $\eta$  finite. This yields

$$\Psi_n(s; y, \eta \rightarrow 0) \approx \frac{I_n(2y)}{s + |n|\eta}. \quad (106)$$

Approximating  $\Im[y] \approx 0$ , one obtains

$$s_{\alpha\beta}^{(j,cc)}(\mathbf{q}, \omega) \approx I_0 \left( 2y_{\alpha\beta}^{(j)}(\mathbf{q}) \right) \delta(\omega) + \sum_{n=-\infty}^{+\infty} I_n \left( 2y_{\alpha\beta}^{(j)}(\mathbf{q}) \right) \frac{1}{\pi} \frac{|n|\eta_j}{n^2\eta_j^2 + (\omega - n\omega_j)^2}. \quad (107)$$

The prime indicates that the term  $n = 0$  is to be excluded. Comparison with expression (105) shows that each peak for each normal frequency  $\omega_j$  is broadened with a width (HWHM) of  $|n|\eta_j$ . It should be noted that Eq. (107) is only valid in the low-friction limit.

#### 4.2.2. Over-damped Langevin modes and Brownian modes

It follows from Eq. (67) that for over-damped modes the eigenvalues have the form  $\lambda_j = \eta_j - \tilde{\Omega}_j$  and  $\lambda_{3N+j} = \eta_j + \tilde{\Omega}_j$  where  $j = 1, \dots, 3N$  and  $\tilde{\Omega}_j \equiv |\Omega_j|$ . In contrast to under-damped modes, there is not a simple relation that would allow to obtain the eigenvectors corresponding to  $\lambda_{3N+j}$  from those corresponding to  $\lambda_j$ . In this case one considers a *single* mode,  $k$ , and  $f_{\alpha\beta}^{(k)}$  has the form

$$f_{\alpha\beta}^{(k)}(\mathbf{q}, t) = \lim_{\omega_\epsilon \rightarrow 0} \left\{ \exp \left( y_{\alpha\beta}^{(k)}(\mathbf{q}) \exp(-\lambda_k t) \cos(\omega_\epsilon t) \right) \right\}. \quad (108)$$

To use relation (98), one sets (dropping indices)  $z = y \exp(-\lambda t)$ ,  $\theta = \omega_\epsilon t$ , where  $\omega_\epsilon$  is passed to 0 after application of theorem (98). This yields

$$f_{\alpha\beta}^{(k)}(\mathbf{q}, t) = I_0 \left( y_{\alpha\beta}^{(k)}(\mathbf{q}) \exp(-\lambda_k t) \right) + 2 \sum_{n=1}^{\infty} I_n \left( y_{\alpha\beta}^{(k)}(\mathbf{q}) \exp(-\lambda_k t) \right). \quad (109)$$

For over-damped modes the  $y$ -functions are always real and moreover positive. This follows from Eqs. (65) and (66) for *real* vectors  $\mathbf{u}_{a,k}$ . One obtains from Eq. (103) for purely real eigenvalues,  $\lambda_k$ ,

$$s_{\alpha\beta}^{(k)}(\mathbf{q}, \omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \Psi_0 \left( \epsilon - i\omega; \frac{y_{\alpha\beta}^{(k)}(\mathbf{q})}{2}, \lambda_k \right) + 2 \sum_{n=1}^{\infty} \Psi_n \left( \epsilon - i\omega; \frac{y_{\alpha\beta}^{(k)}(\mathbf{q})}{2}, \lambda_k \right) \right]. \quad (110)$$

Note that the  $y$ -function in the argument of  $\Psi_n$  is divided by two.

All results in this paragraph can be used to treat Brownian modes, the only difference being that there are only  $3N$  Brownian modes which correspond to the first  $3N$  over-damped Langevin modes in case of strongly over-damped motion. The corresponding  $y$ -functions are given by Eq. (80) or Eq. (81).

#### 4.2.3. Small momentum transfers

Consider now the case in which the  $y$ -functions tend to zero. Since  $y \propto q^2$  and  $y \propto k_B T$ , the above mathematical assumption corresponds to the experimental situations of small momentum transfers and/or low temperatures. In general the temperature is not a parameter that can be varied arbitrarily and therefore the small argument approximation will be referred to as an approximation for small momentum transfers (small  $q$  approximation). Using that for  $n \geq 0$  and  $|z| \ll 1$  [26]



$$I_n(z) \approx \frac{(z/2)^n}{n!}, \quad (111)$$

and  $I_n(z) = I_{-n}(z)$  for  $n < 0$ , one can approximate  $I_n(2y) \approx 0$  if  $|n| > 1$ . Therefore

$$\Psi_n(s; y, \eta) \approx \left\{ \begin{array}{ll} \frac{y^{|n|}}{s+|n|\eta}, & |n| = 0, 1 \\ 0, & |n| > 1 \end{array} \right\}, \quad (112)$$

and one obtains

$$s_{\alpha\beta}^{(j,cc)}(\mathbf{q}, \omega) \approx \delta(\omega) + \Re \left[ y_{\alpha\beta}^{(j)}(\mathbf{q}) \right] \frac{1}{\pi} \left\{ \frac{\eta_j}{\eta_j^2 + (\omega - \Omega_j)^2} + \frac{\eta_j}{\eta_j^2 + (\omega + \Omega_j)^2} \right\} \\ + \Im \left[ y_{\alpha\beta}^{(j)}(\mathbf{q}) \right] \frac{1}{\pi} \left\{ \frac{\Omega_j - \omega}{\eta_j^2 + (\omega - \Omega_j)^2} + \frac{\Omega_j + \omega}{\eta_j^2 + (\omega + \Omega_j)^2} \right\} \quad (113)$$

for a pair of under-damped Langevin modes and

$$s_{\alpha\beta}^{(k)}(\mathbf{q}, \omega) \approx \delta(\omega) + y_{\alpha\beta}^{(k)}(\mathbf{q}) \frac{1}{\pi} \frac{\lambda_k}{\lambda_k^2 + \omega^2} \quad (114)$$

for a single over-damped Langevin or Brownian mode. The corresponding approximations for the dynamic form factors follow from Eqs. (99) and (109) or from developing Eqs. (97) and (108) up to linear terms in  $y$

$$f_{\alpha\beta}^{(j,cc)}(\mathbf{q}, t) \approx 1 + 2 \left| y_{\alpha\beta}^{(j)}(\mathbf{q}) \right| \exp(-\eta_j t) \cos \left( \Omega_j t - \phi_{\alpha\beta}^{(j)}(\mathbf{q}) \right), \quad (115)$$

$$f_{\alpha\beta}^{(k)}(\mathbf{q}, t) \approx 1 + y_{\alpha\beta}^{(k)}(\mathbf{q}) \exp(-\lambda_k t). \quad (116)$$

#### 4.3. Density of states

The density of vibrational states (DOS) for an harmonically vibrating system is defined as

$$g(\omega) = \frac{1}{3N} \sum_{j=1}^{3N} \delta(\omega - \omega_j). \quad (117)$$

By construction, the DOS is normalized to one and integration over a finite frequency interval gives the fraction of normal frequencies (vibrational states) contained in that interval. To generalize the DOS to a system with complex eigenfrequencies we define

$$g(\omega) = \frac{1}{n} \text{Tr} \{ \mathbf{g}(\omega) \}, \quad (118)$$

where  $\text{Tr}$  denotes the trace,  $n = 6N$  (LD) or  $n = 3N$  (SD), and  $\mathbf{g}(\omega)$  is the Fourier cosine transform of  $\mathbf{G}(t) = \exp(-\mathbf{A}t)$ ,

$$\mathbf{g}(\omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \int_0^{\infty} dt \exp(-\epsilon t) \cos \omega t \mathbf{G}(t) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \hat{\mathbf{G}}(\epsilon - i\omega) \right]. \quad (119)$$

$\hat{\mathbf{G}}(s)$  is the Laplace transform of  $\mathbf{G}(t)$  and the factor  $\exp(-\epsilon t)$  ensures again the existence of the Fourier cosine transform in case of vanishing friction.  $\hat{\mathbf{G}}(s)$  has a particularly simple form since all eigenvalues of  $\mathbf{A}$  are different,

$$\hat{\mathbf{G}}(s) = \sum_k \frac{\mathbf{u}_k \cdot \mathbf{v}_k^T}{s + \lambda_k}. \quad (120)$$

Each eigenmode gives a simple pole in the  $s$ -plane. To obtain the DOS we insert Eq. (120) into Eq. (119) and take the trace of the resulting expression. Observing that  $\text{Tr}\{\mathbf{u}_k \cdot \mathbf{v}_k^T\} = \mathbf{v}_k^T \cdot \mathbf{u}_k = 1$ , yields

$$g(\omega) = \frac{1}{n} \sum_k \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \frac{1}{\epsilon - i\omega + \lambda_k} \right]. \quad (121)$$

In the limit of LD without friction, where  $\lambda_j = i\omega_j$  for  $j = 1, \dots, 3N$ , and  $\lambda_{3N+j} = -i\omega_j$ , one obtains

$$g(\omega) = \frac{1}{6N} \sum_{j=1}^{3N} \{\delta(\omega - \omega_j) + \delta(\omega + \omega_j)\}. \quad (122)$$

This is exactly Eq. (117), except that here two branches of complex conjugate eigenvalues are considered. Assuming  $N_{cc}$  complex conjugate under-damped Langevin modes with  $\lambda_j = \eta_j + i\Omega_j$  and  $\lambda_{N_{cc}+j} = \eta_j - i\Omega_j$  ( $j = 1, \dots, N_{cc}$ ), and  $N_s$  over-damped modes with eigenvalues  $\lambda_k$ , one finds that

$$g(\omega) = \frac{1}{6N} \left\{ \sum_{j=1}^{N_{cc}} \left( \frac{1}{\pi} \frac{\eta_j}{(\omega - \Omega_j)^2 + \eta_j^2} + \frac{1}{\pi} \frac{\eta_j}{(\omega + \Omega_j)^2 + \eta_j^2} \right) + \sum_{k=1}^{N_s} \frac{1}{\pi} \frac{\lambda_k}{\omega^2 + \lambda_k^2} \right\}. \quad (123)$$

In case of Brownian dynamics all modes are over-damped and therefore

$$g(\omega) = \frac{1}{3N} \sum_{k=1}^{3N} \frac{1}{\pi} \frac{\lambda_k}{\omega^2 + \lambda_k^2}. \quad (124)$$

It is easy to see that  $g(\omega)$  given by either Eq. (123) or Eq. (124) is normalized,

$$\int_{-\infty}^{+\infty} d\omega g(\omega) = 1, \quad (125)$$

since each eigenvalue in the spectrum of  $\mathbf{A}$  yields a normalized Lorentzian. In contrast to the dynamic structure factor, the DOS for a damped harmonic system is obtained by mode-wise broadening of the normal mode spectrum.

#### 4.4. Neutron-weighted density of states for Langevin dynamics

In neutron scattering experiments one often considers the quantity [2]

$$g_n(\omega) = \lim_{q \rightarrow 0} \frac{\omega^2}{q^2} \mathcal{S}_{\text{inc}}(\mathbf{q}, \omega), \quad (126)$$

which is called the neutron-weighted density of states. Since the dynamic structure factor is the Fourier cosine transformed intermediate scattering function, it follows that

$$g_n(\omega) = -\frac{1}{\pi} \lim_{q \rightarrow 0} \frac{1}{q^2} \frac{\partial}{\partial t} \mathcal{F}_{\text{inc}}(\mathbf{q}, t) \Big|_{t=0+} - \frac{1}{\pi} \lim_{q \rightarrow 0} \frac{1}{q^2} \lim_{\epsilon \rightarrow 0} \int_0^{\infty} dt \exp(-\epsilon t) \cos \omega t \left( \frac{\partial^2}{\partial t^2} \mathcal{F}_{\text{inc}}(\mathbf{q}, t) \right). \quad (127)$$

The first term is zero if the intermediate scattering function is even in time and differentiable at  $t = 0$ . This is true if the underlying dynamical model for  $\mathcal{F}(\mathbf{q}, t)$  is based on classical Hamiltonian dynamics. For models with friction, where the equations of motion are not time reversible, the intermediate scattering function is of the form  $\exp(-|t|)$  and hence not differentiable at  $t = 0$ . In this case the time derivative is to be

understood as the right-hand derivative and the first term in Eq. (127) must be kept. Since the limit  $q \rightarrow 0$  is considered, it follows from Eq. (39) that the form factors  $f_{zx}$  can be approximated as

$$f_{zx}(\mathbf{q}, t) \approx 1 - \frac{1}{2} Q_k^{(x)} W_{kl}(t) Q_l^{(x)}.$$

According to Eq. (38) the mean-square displacements are related to the correlation functions through  $W_{ij}(t) = 2\sigma_{ij}(\infty) - c_{ij}(t) - c_{ji}(t)$ . Taking the  $Q$ -vectors as vectors of length  $3N$ , i.e. omitting the zero components for  $j > 3N$ , the correlation matrix can be replaced by the  $3N \times 3N$  correlation matrix of the positions. Therefore one can write ( $k > 0$ )

$$\lim_{q \rightarrow 0} \frac{1}{q^2} \frac{\partial^k}{\partial t^k} \mathcal{F}_{\text{inc}}(\mathbf{q}, t) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 \mathbf{n}_Q^{(\alpha)\text{T}} \cdot \frac{\partial^k}{\partial t^k} \mathbf{C}_{uu}(t) \cdot \mathbf{n}_Q^{(\alpha)},$$

where  $\mathbf{n}_Q^{(\alpha)}$  is the unit vector along  $\mathbf{Q}^{(\alpha)}$  and  $\mathbf{C}_{uu}(t)$  reads according to Eq. (55)

$$\mathbf{C}_{uu}(t) = k_{\text{B}} T \sum_{k=1}^{6N} \exp(-\lambda_k t) \mathbf{u}_{k,a} \cdot \mathbf{v}_{k,a}^{\text{T}} \cdot \mathbf{K}^{-1}.$$

Using that the upper and lower components of the eigenvectors of  $\mathbf{A}$  are related by  $\mathbf{u}_b = -\lambda \mathbf{u}_a$  and  $\mathbf{v}_b = \lambda \mathbf{K}^{-1} \cdot \mathbf{v}_a$ , one finds that

$$\frac{\partial}{\partial t} \mathbf{C}_{uu}(t) = k_{\text{B}} T \sum_{k=1}^{6N} \exp(-\lambda_k t) \mathbf{u}_{k,b} \cdot \mathbf{v}_{k,a}^{\text{T}} \cdot \mathbf{K}^{-1} = \mathbf{C}_{vu}(t), \quad (128)$$

$$\frac{\partial^2}{\partial t^2} \mathbf{C}_{uu}(t) = -k_{\text{B}} T \sum_{k=1}^{6N} \exp(-\lambda_k t) \mathbf{u}_{k,b} \cdot \mathbf{v}_{k,b}^{\text{T}} = -\mathbf{C}_{vv}(t). \quad (129)$$

With Eq. (128) one obtains

$$\lim_{q \rightarrow 0} \frac{1}{q^2} \frac{\partial}{\partial t} \mathcal{F}_{\text{inc}}(\mathbf{q}, t) \Big|_{t=0+} = \sum_{\alpha} b_{\alpha, \text{inc}}^2 \mathbf{n}_Q^{(\alpha)\text{T}} \cdot \mathbf{C}_{vu}(0) \cdot \mathbf{n}_Q^{(\alpha)} = 0,$$

since the cross-correlation matrix  $\mathbf{C}_{vu}(t)$  vanishes for  $t = 0$ . To see this, write  $\mathbf{C}(0) = \mathbf{G}(0) \cdot \boldsymbol{\sigma}(\infty) = \boldsymbol{\sigma}(\infty)$ . The matrix  $\mathbf{C}_{vu}(0)$  is given by the lower left block matrix of  $\boldsymbol{\sigma}(\infty)$  which is zero according to Eq. (32). The neutron-weighted DOS takes thus the form

$$g_n(\omega) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \int_0^{\infty} dt \exp(-\epsilon t) \cos \omega t \left\{ \mathbf{n}_Q^{(\alpha)\text{T}} \cdot \mathbf{C}_{vv}(t) \cdot \mathbf{n}_Q^{(\alpha)} \right\}, \quad (130)$$

$$g_n(\omega) = \sum_{\alpha} b_{\alpha, \text{inc}}^2 \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \mathbf{n}_Q^{(\alpha)\text{T}} \cdot \hat{\mathbf{C}}_{vv}(\epsilon - i\omega) \cdot \mathbf{n}_Q^{(\alpha)} \right]. \quad (131)$$

According to Eq. (130)  $g_n(\omega)$  is the Fourier transform of the averaged velocity autocorrelation function. The average is taken over all atoms, each atom contributing with a weight of  $b_{\alpha, \text{inc}}^2$ . If one assumes that there is only one type of atoms,  $g_n(\omega)$  is simply proportional to the Fourier transform of the velocity autocorrelation function of the atoms. This is a well-known result for liquids and solids, assuming a classical or a quantum mechanical model without friction for the scattering system [27].

We consider now the relation between  $g_n(\omega)$  and  $g(\omega)$ . It follows from Eq. (129) that  $g_n(\omega)$  can be cast into the form of a weighted average over contributions from each mode

$$g_n(\omega) = \sum_{k=1}^{6N} \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \left[ \frac{w_k}{\epsilon - i\omega + \lambda_k} \right]. \quad (132)$$

The weights  $w_k$  have the form

$$w_k = k_B T \sum_{\alpha} b_{\alpha, \text{inc}}^2 \left( \mathbf{u}_{k,b}^{\text{T}} \cdot \mathbf{n}_Q^{(\alpha)} \right) \left( \mathbf{v}_{k,b}^{\text{T}} \cdot \mathbf{n}_Q^{(\alpha)} \right) = -\lambda_k^2 \sum_{\alpha} b_{\alpha, \text{inc}}^2 y_{\alpha\alpha}^{(k)}(\mathbf{n}_q), \quad (133)$$

where  $y_{\alpha\alpha}^{(k)}(\mathbf{q})$  is defined by Eq. (65) or Eq. (66), and  $\mathbf{n}_q$  is the unit vector along  $\mathbf{q}$ . It should be noted that the  $w_k$  are in general complex, i.e. no positive weights in a classical sense. For an isotropic scattering system, e.g. proteins in hydrated powders or a polymer melt, the scattering law will not depend on the direction of  $\mathbf{q}$ , and  $w_k$  can be replaced by its spherical average. With expression (65) for the  $y$ -functions one finds that

$$w_k = \lambda_k^2 \sum_{\alpha} b_{\alpha, \text{inc}}^2 \frac{k_B T}{3} \frac{\text{Tr} \{ (\mathbf{u}_{k,a} \cdot \mathbf{u}_{k,a}^{\text{T}}) \cdot \mathbf{P}^{(\alpha)} \}}{\mathbf{u}_{k,a}^{\text{T}} \cdot (\lambda_k^2 \mathbf{1} - \mathbf{K}) \cdot \mathbf{u}_{k,a}}, \quad (134)$$

where  $\mathbf{P}^{(\alpha)}$  is the projector on the configurational subspace of atom  $\alpha$ . It has the obvious properties

$$\mathbf{P}^{(\alpha)} \cdot \mathbf{Q}^{(\alpha)} = \mathbf{Q}^{(\alpha)}, \quad (135)$$

$$\sum_{\alpha} \mathbf{P}^{(\alpha)} = \mathbf{1}. \quad (136)$$

We now make the assumption that all atoms are of the same type, i.e.  $b_{\alpha, \text{inc}} = b_{\text{inc}}$ . A more realistic situation is that one sort of atoms scatters predominantly and scattering from all other atoms can be neglected. This is the case for systems containing a large amount of hydrogen atoms, such as proteins and DNA molecules. Incoherent scattering from hydrogen dominates by far all other scattering processes. Using Eq. (136) and normalizing  $\mathbf{u}_{k,a}$  to 1, Eq. (134) simplifies to

$$w_k = \frac{k_B T}{3} \frac{b_{\text{inc}}^2 \lambda_k^2}{\mathbf{u}_{k,a}^{\text{T}} \cdot (\lambda_k^2 \mathbf{1} - \mathbf{K}) \cdot \mathbf{u}_{k,a}}. \quad (137)$$

In the limit of vanishing friction one obtains with Eq. (70)

$$w_k = b_{\text{inc}}^2 \frac{k_B T}{6}. \quad (138)$$

Since the weights do not depend on the modes the neutron-weighted DOS is directly proportional to  $g(\omega)$

$$\lim_{\gamma \rightarrow 0} g_n(\omega) = b_{\text{inc}}^2 N k_B T g(\omega). \quad (139)$$

In case of non-vanishing friction  $g_n(\omega)$  is, however, *not* proportional to  $g(\omega)$  since the weights  $w_k$  are mode-dependent.

A final remark concerns the regime of SD. In contrast to LD, the first term in Eq. (127) here does *not* vanish and  $g_n(\omega)$  cannot be proportional to  $g(\omega)$ , even if all weights  $w_k$  were mode-independent. (Using definition (133) with the  $y$ -functions for SD shows that the  $w_k$  are, in fact, always mode-dependent.) In the regime of SD the neutron-weighted DOS is therefore only a formally defined quantity.

## 5. Conclusions

Using the Ornstein–Uhlenbeck process in phase or configuration space as a dynamical model for macromolecular dynamics around a stable equilibrium structure, the intermediate scattering function, the dynamic structure factor, and the vibrational density of states for inelastic neutron scattering have been derived for the regimes of LD and SD. The input parameters are the force constant matrix,  $\mathbf{K}$ , and the drift matrix,  $\mathbf{A}$ , determining the equilibrium properties and the dynamics, respectively. The latter is constructed from  $\mathbf{K}$  and a positive definite friction matrix,  $\gamma$ . Using the spectral decomposition of  $\mathbf{K}$  and  $\mathbf{A}$ , one can derive expressions for the intermediate scattering functions which are suitable for numerical calculations. In the case of LD, it is sufficient to know the eigenvalues of  $\mathbf{A}$  and the upper halves of its right eigenvectors,  $\mathbf{u}_k$ . Considering strongly over-damped LD on a coarse-grained time scale, one retrieves formally the intermediate scattering function of SD. As for normal modes analysis, the intermediate scattering function contains contributions from each pair of atoms (coherent scattering) and from each single atom (incoherent scattering), which are in turn products of contributions for each Langevin or Brownian mode. The dynamic structure factor can be obtained by applying essentially the same “Bessel function trick” known from normal mode calculations. The contributions for the individual modes are, however, no longer delta functions, but series of rational functions in the frequency (energy transfer) in which each term is proportional to a power of the effective friction constant of the mode. Only in the low-friction limit higher powers of these effective friction constants can be neglected, and the contribution from each mode appears to be a broadened normal mode line. In principle, the dynamic structure factor can then be obtained by broadening the normal mode contributions a posteriori. This method is only useful in the low- $q$  limit and has been used to compute inelastic neutron spectra for a small protein (BPTI) [25]. It is, however, inappropriate to describe the effect of larger atomic friction, or even over-damped motions, for larger  $q$ -values. More precisely, the  $\gamma$ -functions should not exceed a value of about 0.5.

Although the model of Langevin and Brownian modes appears to be closer to physical reality than the model of broadened normal modes, the question is still open if the Ornstein–Uhlenbeck has some practical relevance for protein dynamics and how one can obtain useful parameters for the model, especially for the friction matrix. This question will be addressed in a subsequent paper [28]. In this context it is worthwhile mentioning that an “atom” in the dynamical models used in this article might also be a group of physical atoms. In this way a coarse-grained description of a macromolecule can be obtained in time *and* space.

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## Appendix A. Moments of the transition probability

There is a close relation between the moments of the stochastic process described by  $P(x, t; x', 0)$  and the functions  $f_{x\beta}(\mathbf{q}, t)$  since the latter have essentially the form of moment generating functions. Consider first the correlation functions of the positions in phase space,

$$c_{ij}(t) = \langle x_i(t)x_j(0) \rangle.$$

The corresponding generating function, the distribution function  $P(x, t; x', 0)$ , and the correlation functions  $c_{ij}(t)$  are related by

$$M^{(c)}(Q, Q', t) = \int \int dx dx' P(x, t; x', 0) \exp(-i(Q_k x_k + Q'_l x'_l)),$$

$$c_{ij}(t) = -\frac{\partial^2}{\partial Q_i \partial Q'_j} M^{(c)}(Q, Q', t) \Big|_{Q=Q'=0}.$$

Comparing the definition of  $M^{(c)}(Q, Q', t)$  with the one of  $f_{\alpha\beta}(\mathbf{q}, t)$  – see Eq. (35) – shows that the moment generating function have exactly the same form, setting here  $\mathbf{Q}' = \mathbf{Q}^{(\alpha)}$  and  $\mathbf{Q} = -\mathbf{Q}^{(\beta)}$ . Observing that  $\sigma_{kl}(\infty) = \sigma_{lk}(\infty)$  it follows that

$$M^{(c)}(Q, Q', t) = \exp\left(-\frac{1}{2}[Q'_k \sigma_{kl}(\infty) Q'_l + Q_k \sigma_{kl}(\infty) Q_l]\right) \exp(-Q_k G_{km}(t) \sigma_{ml}(\infty) Q'_l),$$

and we obtain the relation

$$c_{ij}(t) = G_{im}(t) \sigma_{mj}(\infty)$$

for the correlation functions [21]. The initial values are  $c_{ij}(0) = \langle x_i x_j \rangle = \sigma_{ij}(\infty)$ , since  $G_{im}(0) = \delta_{im}$  (compare Eq. (31)).

Similarly to  $M^{(c)}(Q, Q', t)$ , one can introduce the generating function for the mean-square displacements

$$W_{ij}(t) = \langle [x_i(t) - x_i(0)][x_j(t) - x_j(0)] \rangle.$$

The generating function is here

$$M^{(d)}(Q, t) = \int \int dx dx' P(x, t; x', 0) \exp(i(Q_k [x_k - x'_k])),$$

and the components of the mean-square displacement tensor are obtained from the relation

$$W_{ij}(t) = -\frac{\partial^2}{\partial Q_i \partial Q_j} M^{(d)}(Q, t) \Big|_{Q=0}.$$

The generating function  $M^{(d)}(Q, t)$  has the same form as the self-terms  $f_{\alpha\alpha}(\mathbf{q}, t)$ , replacing  $\mathbf{Q}^{(\alpha)}$  by  $\mathbf{Q}$ , and one obtains

$$M^{(d)}(Q, t) = \exp\left(-\frac{1}{2} Q_k W_{kl}(t) Q_l\right),$$

$$W_{ij}(t) = 2\sigma_{ij}(\infty) - G_{im}(t) \sigma_{mj}(\infty) - G_{jm}(t) \sigma_{im}(\infty).$$

With  $G_{im}(t) \sigma_{mj}(\infty) = c_{ij}(t)$ , it follows that:

$$W_{ij} = 2\sigma_{ij}(\infty) - c_{ij}(t) - c_{ji}(t),$$

which is an immediate consequence of the definition of the mean-squared displacements.

## Appendix B. Laplace transform of the Bessel functions

To obtain an expression for the Laplace transform

$$\Psi_n(s; y, \eta) = \int_0^\infty dt \exp(-st) I_n(2y \exp(-\eta t)) \quad (\text{B.1})$$

we use the scaling property of the Bessel functions [26],

$$I_n(\lambda z) = \lambda^n \sum_{k=0}^{\infty} \frac{(\lambda^2 - 1)^k (z/2)^k}{k!} I_{n+k}(z). \quad (\text{B.2})$$

Setting  $z = 2y$  and  $\lambda = \exp(-\eta t)$  yields

$$I_n(2y \exp(-\eta t)) = \exp(-n\eta t) \sum_{k=0}^{\infty} \frac{y^k}{k!} I_{n+k}(2y) (\exp(-2\eta t) - 1)^k. \quad (\text{B.3})$$

To perform the Laplace transform of the above function with respect to time one could expand each of the terms  $(\exp(-2\eta t) - 1)^k$  into a sum of powers of  $\exp(-2\eta t)$ , using the binomial formula. The resulting expression does, however, not reflect the fact that Eq. (B.2) is effectively a series which converges rapidly for small  $\eta$  and is thus convenient to discuss the low friction limit. Therefore the closed form of  $g(s)$  is considered in the following:

$$g(s) = \int_0^{\infty} dt \exp(-[s + n\eta]t) (\exp(-2\eta t) - 1)^k. \quad (\text{B.4})$$

Performing the substitution  $u = \exp(-2\eta t)$  yields

$$g(s) = \frac{(-1)^k}{2\eta} \int_0^1 du u^{(s+n\eta)/(2\eta)-1} (1-u)^k. \quad (\text{B.5})$$

Apart from the prefactors, the above integral has the form of the defining equation for the Beta functions [26]

$$B(z, w) = \int_0^1 dt t^{z-1} (1-t)^{w-1} = \frac{\Gamma(z)\Gamma(w)}{\Gamma(z+w)} = B(w, z), \quad (\text{B.6})$$

where  $\Gamma(z)$  is the generalized factorial

$$\Gamma(z) = \int_0^{\infty} dt t^{z-1} \exp(-t). \quad (\text{B.7})$$

Using the above definitions the function  $g(s)$  may be expressed as

$$g(s) = \frac{(-1)^k}{2\eta} B\left(\frac{s+n\eta}{2\eta}, k+1\right). \quad (\text{B.8})$$

Using the properties

$$\Gamma(m+1) = m!, \quad (\text{B.9})$$

$$\Gamma(z+m) = (m-1+z)(m-2+z)\cdots(1+z)\Gamma(1+z), \quad (\text{B.10})$$

of the Gamma function, one can simplify

$$B(z, k+1) = \frac{k!}{(k+z)(k-1+z)\cdots(1+z)z} \quad (\text{B.11})$$

to obtain

$$g(s) = \frac{k!(-2\eta)^k}{(s+n\eta)(s+[n+2]\eta)\cdots(s+[n+2k]\eta)}. \quad (\text{B.12})$$

The Laplace transform of expression (142) yields thus

$$\Psi_n(s; y, \eta) = \sum_{k=0}^{\infty} \frac{(-2\eta)^k I_{n+k}(2y) y^k}{(s + m\eta)(s + [n + 2]\eta) \cdots (s + [n + 2k]\eta)}. \quad (\text{B.13})$$

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