COMMUNICATIONS IN COMPUTATIONAL PHYSICS
Vol. **6**, No. 2, pp. 231-246

Commun. Comput. Phys.
August 2009

Decomposition of Molecular Motions into Translational, Rotational, and Intramolecular Parts by a Projection Operator Technique

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Received 18 June 2008; Accepted (in revised version) 14 August 2008

Communicated by Michel A. Van Hove

Abstract. The motion of the atoms in a molecule may be described as a superposition of translational motion of the molecular center-of-mass, rotational motion about the principal molecular axes, and an intramolecular motion that may be associated with vibrations and librations as well as molecular conformational changes. We have constructed projection operators that use the atomic coordinates and velocities at any two times, $t=0$ and a later time t, to determine the molecular center-of-mass, rotational, and intramolecular motions in a molecular dynamics simulation. This model-independent technique facilitates characterization of the atomic motions within a system of complex molecules and is important for the interpretation of experiments that rely on time correlation functions of atomic and molecular positions and velocities. The application of the projection operator technique is illustrated for the inelastic neutron scattering functions and for the translational and rotational velocity autocorrelation functions.

AMS subject classifications: 81V55

PACS: 34.30.+h, 34.50.Dy, 68.03.Hj, 71.15.Pd

Key words: Molecular dynamics, projection operator, correlation functions, scattering functions, translational motion, rotational motion, intramolecular motion.

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1 Introduction

The dynamics of molecular systems can be probed by different scattering techniques such as inelastic and quasielastic neutron scattering, inelastic helium atom scattering, and infrared and Raman spectroscopy. In each of these cases, the system response can be related

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to a time correlation function of some molecular property, e.g., atom positions, atom velocities, and molecular dipole moments. In particular, the scattered neutron intensity is proportional to the scattering function which is the space- and time-Fourier transform of the dynamical pair distribution function for the atoms in the system. A non-scattering spectroscopic technique like NMR may also be used to probe the dynamics in solids, since the second moment of the NMR absorption spectrum depends on the crystal structure and on any molecular motions that may occur (see, e.g., [1]).

The motion of atoms in a molecule can be a complicated superposition of translational and rotational motions of the whole molecule as well as intramolecular motions. This situation simplifies somewhat in molecular crystals where the translational order and molecular orientations are known. In such cases and at temperatures well below the melting point, a harmonic approximation for the interatomic potential may hold and a normal mode analysis can be applied. For crystalline systems at higher temperatures, a much-used method in the past has been to calculate the scattering functions [2] and/or NMR second moments [1] for simple models of molecular motion, such as uniaxial or spherical rotations or bounded translational motion, and then compare the results with observed spectra to validate them. However, for analyzing complex motions in a given system in any phase and at any temperature, it is desirable to have a general model-independent method that makes no assumptions about the translational ordering and molecular orientations.

In this paper, we describe such a method for analyzing complex molecular motions occurring in a molecular dynamics (MD) simulation. It allows us to project out the center-of-mass motion and rotational motion of the molecule from the atomic positions and velocities at any two times, $t=0$ and a later time t. From the remaining motion, we can determine the intramolecular displacements of the atoms in the specified time interval caused by molecular conformational changes as well as by vibrational and librational excitation. We have applied this technique successfully to our quasielastic neutron scattering studies of intermediate-length alkane molecules adsorbed on solid surfaces [3]-[7]. It has allowed us to determine which type of motion (translational, rotational, or intramolecular) contributes dominantly to the quasielastic spectra. In addition, the velocity and rotational velocity correlation functions have proved useful for characterizing the molecular motions by revealing whether the particular kind of motion is oscillatory, diffusive, or both.

Frequently, the molecular motion of interest can span a broad range of time and length scales. In quasielastic neutron scattering, the instrumental energy resolution and dynamic range determine the slowest and fastest of these motions, respectively, that are accessible experimentally. Thus, being able to analyze MD simulations to determine the time scale of the different types of motion is important in selecting an appropriate instrument. For example, our simulations of adsorbed alkane molecules [3] indicated that intramolecular diffusive motion associated with creation and annihilation of *gauche* defects is rather slow compared to other modes. By using a high-energy-resolution backscattering spectrometer, we were able to find a temperature range where these conformational changes occurred on a nanosecond time scale so that they made the principal contribution to the scattering function within the instrument's dynamic range.

The paper is organized in the following way. In Section 2, we briefly review a few key points about the scattering functions in neutron scattering and describe the construction of projection operators that are used to decompose atomic motions into translational motion of the molecular center-of-mass, rotational motion, and intramolecular atomic displacements. The results are used to determine the signatures of these motions in the inelastic neutron spectra and are illustrated by an example from our simulations of alkane monolayers. In Section 3, we describe the construction of projection operators for the calculation of the center-of-mass and rotational velocity correlation functions, again illustrated by an example from our alkane monolayer simulations.

2 Time correlation functions in neutron scattering

We begin with a brief review of certain aspects of the neutron scattering functions of relevance here [9].

In a neutron scattering experiment, we distinguish between coherent and incoherent scattering. The intensity of the former is proportional to the coherent scattering function $S_{\text{coh}}(\mathbf{q},\omega)$ and that of the latter to the incoherent scattering function $S_{\text{inc}}(\mathbf{q},\omega)$. $\mathbf{q}$ is the wave vector transfer and $\hbar\omega$ the energy transferred by the scattered neutrons. The coherent scattering function represents the collective motions of the atoms in the sample whereas the incoherent scattering function represents single-atom motions. For a fluid and a powder, the orientation of the atom position vectors with respect to the scattering wave vector $\mathbf{q}$ will be random, and the scattered intensity is therefore averaged over all orientations so that the scattering functions will only be a function of the magnitude $|\mathbf{q}|$ of the wave vector transfer. For $\hbar\omega = 0$, the scattering is elastic; and, for $\hbar\omega \to 0$, we describe the scattering as quasielastic and the associated motions as *diffusive*. Examples are translational and rotational diffusive motions.

Since the hydrogen atom has a very large incoherent scattering length compared to the coherent scattering lengths for both hydrogen and carbon atoms, neutron scattering will be strongly dominated by the incoherent scattering when hydrogen atoms are present as in alkane molecules. That dominance may be suppressed by replacing the hydrogen atoms with deuterium atoms so that the coherent scattering function may be probed.

The scattering function $S_{\text{coh}}(\mathbf{q},\omega)$ is the time-Fourier transform of the intermediate scattering function $F(\mathbf{q},t)$

$$S_{\text{coh}}(\mathbf{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \exp(-i\omega t) F(\mathbf{q},t) \tag{2.1}$$

which is given by the expression

$$F(\mathbf{q},t)=\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}b_ib_j<\exp(i\mathbf{q}\cdot(\mathbf{r}_i(t)-\mathbf{r}_j(0)))>, \tag{2.2}$$

where b_i and b_j are the neutron scattering lengths. This function is readily calculable from a time series of atomic positions $\mathbf{r}_j(t)$ as generated in an MD simulation. The sum extends over all N atoms in the system, and the brackets $<\cdots>$ indicate an ensemble average. The double summation over atoms and the argument of the exponential function show that this function is related to the collective motion of atoms in the sample, since it includes a time correlation between the position coordinates of different atoms.

The incoherent, or *self*-scattering, function is the time-Fourier transform of the intermediate *self*-scattering function $F_s(\mathbf{q},t)$

$$S_{\text{inc}}(\mathbf{q},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\exp(-i\omega t)F_{\text{s}}(\mathbf{q},t) \tag{2.3}$$

which is given by the expression

$$F_s(\mathbf{q},t)=\frac{1}{N}\sum_{j=1}^{N}b_j<\exp(i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0)))>. \tag{2.4}$$

This function is also readily calculable from a time series of atomic positions $\mathbf{r}_j(t)$ as generated in an MD simulation. The single summation over atoms and the argument of the exponential function show that this function is related to single atom motions, since it only includes a time correlation between the position coordinates of the same atom.

For a later discussion, let us rewrite the intermediate self-scattering function in the following way

$$\begin{aligned}&F_s(\mathbf{q},t)=F_s(\mathbf{q},\infty)+F_s'(\mathbf{q},t) \quad \text{with}\\ &F_s'(\mathbf{q},t)\to 0 \quad \text{for} \quad t\to\infty.\end{aligned} \tag{2.5}$$

Then the incoherent scattering function will be

$$S_{\text{inc}}(\mathbf{q},\omega)=2\pi F_s(\mathbf{q},\infty)\delta(\omega)+S_{\text{inc}}'(\mathbf{q},\omega). \tag{2.6}$$

This shows that the incoherent scattering function, and hence the incoherent scattering may consist of two contributions. The first term on the right hand side gives an elastic contribution when $F_s(\mathbf{q},\infty)$ is different from zero. This will be the case when the atoms perform bounded motion about their original positions as in rotational or vibrational motion. When this is not the case, there is no elastic contribution, since $F_s(\mathbf{q},\infty)$ will be zero as in translational diffusive motion. The second term in the expression gives the frequency-dependent part of the scattering function and reflects the type of motion involved.

2.1 Projection operator

Any motion of the atoms in a molecule may be described as a combination of a molecular center-of-mass motion, a molecular rotational motion, and an intramolecular motion [10].

Let $\mathbf{r}_{im}(t)$ be the position vector of atom i with mass m_i in molecule m at time t. Then the center-of-mass position vector of molecule m is given by the expression

$$\mathbf{R}_m(t)=\frac{\sum_{i=1}^{M} m_i \mathbf{r}_{im}(t)}{\sum_{i=1}^{M} m_i}, \tag{2.7}$$

where M is the number of atoms in the molecule. The translational motion of the molecule is determined by following $\mathbf{R}_m(t)$ as function of time t. Now let us introduce the atomic position vectors $\mathbf{s}_{im}(t)$ relative to the center-of-mass position of the molecule by

$$\mathbf{s}_{im}(t)=\mathbf{r}_{im}(t)-\mathbf{R}_m(t). \tag{2.8}$$

The rotational motion of a molecule is described in the following way. At time $t=0$, let the three orthonormal principal axes of inertia be $\mathbf{e}_1(0)$, $\mathbf{e}_2(0)$ and $\mathbf{e}_3(0)$, such that

$$[\mathbf{e}_1(0),\mathbf{e}_2(0),\mathbf{e}_3(0)]=[\mathbf{i},\mathbf{j},\mathbf{k}][E(0)]. \tag{2.9}$$

Here $\mathbf{i},\mathbf{j},\mathbf{k}$ are the basis vectors for the laboratory-fixed Cartesian coordinate system. The elements of the ith column of the (3×3) matrix $E(0)$ are the Cartesian coordinates of the ith principal axis $\mathbf{e}_i(0)$; they are determined by a diagonalization of the inertia tensor $\underline{\underline{\mathbf{I}}}(0)$ for the molecule at time $t=0$ and given by the three orthonormal eigenvectors [10]. Note that $\underline{\underline{\mathbf{I}}}(0)$ may be written in Dyadic notation as

$$\underline{\underline{\mathbf{I}}}(0)=\sum_{i=1}^{M}[m_i(|\mathbf{s}_{im}(0)|^2\underline{\underline{\mathbf{1}}}-\mathbf{s}_{im}(0)\mathbf{s}_{im}(0))]. \tag{2.10}$$

We may invert Eq. (2.9) and find

$$[\mathbf{e}_1(0),\mathbf{e}_2(0),\mathbf{e}_3(0)][E(0)]^{-1}=[\mathbf{i},\mathbf{j},\mathbf{k}]. \tag{2.11}$$

At some later time t, the three principal axes of inertia are $\mathbf{e}_1(t)$, $\mathbf{e}_2(t)$ and $\mathbf{e}_3(t)$ as determined by diagonalizing $\underline{\underline{\mathbf{I}}}(t)$; that is,

$$[\mathbf{e}_1(t),\mathbf{e}_2(t),\mathbf{e}_3(t)]=[\mathbf{i},\mathbf{j},\mathbf{k}][E(t)]. \tag{2.12}$$

The relative position vector $\mathbf{s}_{im}(0)$ may be written in terms of Cartesian components arranged in the (3×1) column matrix $[s_{im}(0)]$ as

$$\mathbf{s}_{im}(0)=[\mathbf{i},\mathbf{j},\mathbf{k}][s_{im}(0)] \tag{2.13}$$

and, from Eq. (2.11), in the basis of $\mathbf{e}_1(0),\mathbf{e}_2(0),\mathbf{e}_3(0)$ as

$$\mathbf{s}_{im}(0)=[\mathbf{e}_1(0),\mathbf{e}_2(0),\mathbf{e}_3(0)][E(0)]^{-1}[s_{im}(0)]. \tag{2.14}$$

If the displacement of the *i*th atom in molecule m from time $t=0$ to time t is given by a rigid rotation of the molecule, as defined by the principal axes of inertia at $t=0$ and t, then the relative coordinates of atom i in the $\mathbf{e}_1(t),\mathbf{e}_2(t),\mathbf{e}_3(t)$ coordinate system will be the same as in the $\mathbf{e}_1(0),\mathbf{e}_2(0),\mathbf{e}_3(0)$ coordinate system, that is

$$\begin{aligned}\mathbf{s}^r_{im}(t)&=[\mathbf{e}_1(t),\mathbf{e}_2(t),\mathbf{e}_3(t)][E(0)]^{-1}[s_{im}(0)]\\&=[\mathbf{i},\mathbf{j},\mathbf{k}][E(t)][E(0)]^{-1}[s_{im}(0)]\\&\equiv[\mathbf{i},\mathbf{j},\mathbf{k}]Rot_m(t,0)[s_{im}(0)],\end{aligned}\tag{2.15}$$

where we have used Eq. (2.12). $\mathbf{s}^r_{im}(t)$ is the position vector of atom i in molecule m relative to the center-of-mass position at time t after the molecule has performed a rigid rotation between time $t=0$ and time t.

$Rot_m(t,0)$ is a projection operator given by the (3×3) matrix operator

$$Rot_m(t,0)=[E(t)][E(0)]^{-1}\tag{2.16}$$

and may be used to determine the position vector, relative to the center-of-mass, of atom i in a molecule that performs a rigid rotation, as defined by the rotation of the principal axes of inertia, from time $t=0$ to time t about the center-of-mass of the molecule.

For a rigid molecule, the atomic motion is a superposition of the center-of-mass motion and the rigid rotational motion of the molecule, so starting at time $t=0$, we must have $\mathbf{s}_{im}(t)=\mathbf{s}^r_{im}(t)$ at time t, because the relative atomic position vector at t is only determined by the rotational motion of the molecule in that time interval. This is usually not true for a flexible molecule where there also may be intramolecular atomic displacements, $\mathbf{s}^{int}_{im}(t)$, in that time interval, so we may in general write

$$\mathbf{s}_{im}(t)=\mathbf{s}^r_{im}(t)+\mathbf{s}^{int}_{im}(t),\tag{2.17}$$

which defines the intramolecular atomic displacement vector.

Thus, starting at time $t=0$, we may write the atomic position vectors at any later time t as a sum of the molecular-center-of-mass position vector at time t and the relative position vector $\mathbf{s}_{im}(t)$ [Eq. (2.8)] which again may be written as a sum of the relative position vector associated with a rigid rotation of the molecule from time $t=0$ to time t and an intramolecular atomic displacement vector in that time interval [Eq. (2.17)], that is

$$\mathbf{r}_{im}(t)=\mathbf{R}_m(t)+\mathbf{s}_{im}(t)=\mathbf{R}_m(t)+\mathbf{s}^r_{im}(t)+\mathbf{s}^{int}_{im}(t).\tag{2.18}$$

For $t=0$, we see from Eq. (2.16) that the $Rot_m(0,0)$ matrix is the unit matrix such that $\mathbf{s}^r_{im}(0)=\mathbf{s}_{im}(0)$ according to Eq. (2.15), and we may write Eq. (2.18) as

$$\mathbf{r}_{im}(0)=\mathbf{R}_m(0)+\mathbf{s}_{im}(0)+\mathbf{s}^{int}_{im}(0)=\mathbf{R}_m(0)+\mathbf{s}_{im}(0).\tag{2.19}$$

When we compare this equation with Eq. (2.8) at time $t=0$, we see that $\mathbf{s}^{int}_{im}(0)=0$ to make the two equations identical. That makes sense, since $\mathbf{s}^{int}_{im}(t)$ is an intramolecular displacement vector caused by intramolecular motions from time $t=0$ to time t but at time $t=0$ there has not yet been a displacement of the atoms.

In summary, the MD simulation generates the atomic positions at time t starting out with the atomic positions at time $t=0$. From those we may determine the center-of-mass position as function at t using Eq. (2.7), the relative atom position vectors $\mathbf{s}_{im}(t)$ using Eq. (2.8), the relative atom position vectors $\mathbf{s}^r_{im}(t)$ resulting from the rigid rotation of the molecule in the time interval using Eq. (2.15), and the intramolecular displacement $\mathbf{s}^{int}_{im}(t)$ during that time interval using Eq. (2.18). The latter will be zero at any time for rigid molecules.

2.2 Scattering functions

We will in the following use this development to determine the scattering functions for the different kinds of motion.

2.2.1 Overall atomic motion

In a scattering experiment, we monitor the overall atomic motion that is a combination of the center-of-mass, rotational, and intramolecular motions. The intermediate scattering function $F(\mathbf{q},t)$ is defined [Eq. (2.2)] as

$$F(\mathbf{q},t)=\frac{1}{N}<\sum_{i=1}^{N}\sum_{j=1}^{N}b_ib_j\exp[-i\mathbf{q}\cdot(\mathbf{r}_i(t)-\mathbf{r}_j(0))]>, \tag{2.20}$$

where i,j run over all N atoms in the system. For a determination of the contributions to the intermediate scattering function from the center-of-mass, the rotational, and the intramolecular motions, it will be convenient to write the summation differently and explicitly include a summation over molecules n,m, so that we have

$$F(\mathbf{q},t)=\frac{1}{N}<\sum_n\sum_m\sum_i\sum_j b_{im}b_{jn}\exp[-i\mathbf{q}\cdot(\mathbf{r}_{im}(t)-\mathbf{r}_{jn}(0))]>. \tag{2.21}$$

Here the subscript im refers to atom i in molecule m. Index i runs over all atoms in molecule m and j over all atoms in molecule n. Then, using Eqs. (2.18) and (2.19) we may split up the exponential function and write

$$\begin{aligned}F(\mathbf{q},t)=&\frac{1}{N}<\sum_n\sum_m\sum_i\sum_j\{b_{im}b_{jn}\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_n(0))]\\&\times\exp[-i\mathbf{q}\cdot(\mathbf{s}_{im}(t)-\mathbf{s}_{jn}(0))]\}>\\=&\frac{1}{N}<\sum_n\sum_m\sum_i\sum_j\{b_{im}b_{jn}\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_n(0))]\\&\times\exp[-i\mathbf{q}\cdot(\mathbf{s}^r_{im}(t)-\mathbf{s}_{jn}(0))]\times\exp[-i\mathbf{q}\cdot(\mathbf{s}^{int}_{im}(t))]\}>.\end{aligned} \tag{2.22}$$

It is easy to write down similar expressions for the intermediate *self*-scattering function $F_s(\mathbf{q},t)$. We just replace the double summations over molecules and atoms in Eqs. (2.20)-(2.22) with a single summation over molecules and atoms and replace the indices referring to the second summation in the argument of the exponential function with those of the first summation. Thus, the expression that corresponds to Eq. (2.22) for the intermediate *self*-scattering function is

$$\begin{aligned}F_s(\mathbf{q},t)=&\frac{1}{N}<\sum_m\sum_i\{b_{im}b_{im}\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_m(0))]\\&\times\exp[-i\mathbf{q}\cdot(\mathbf{s}_{im}(t)-\mathbf{s}_{im}(0))]\}>\\=&\frac{1}{N}<\sum_m\sum_i\{b_{im}b_{im}\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_m(0))]\\&\times\exp[-i\mathbf{q}\cdot(\mathbf{s}^r_{im}(t)-\mathbf{s}_{im}(0))]\times\exp[-i\mathbf{q}\cdot(\mathbf{s}^{int}_{im}(t))]\}>.\end{aligned}\tag{2.23}$$

If the three contributions to $F(\mathbf{q},t)$ represented by the exponential functions are independent, we may take the ensemble average of each term separately and write the intermediate scattering function as a product of three independent contributions. These contributions correspond to the molecular center-of-mass, rotational, and intramolecular motions including atomic vibrations and librations and molecular conformational changes. Then the total scattering function is a convolution of these three contributions to the intermediate scattering function. However, in most cases, the different types of motion are coupled so that we cannot write $F(\mathbf{q},t)$ as a product of three ensemble averages. Even then, it is still very useful to determine the contributions from the various types of motion to the scattering function, since it is important for interpretation of the observed spectra.

In the following, we will discuss the calculation of the various contributions to the scattering function and have chosen to normalize them all in the same way by introducing the factor $1/N$.

2.2.2 Center-of-mass motion

This contribution may be written

$$\begin{aligned}F_{CM}(\mathbf{q},t)&=\frac{1}{N}<\sum_n\sum_m\sum_i\sum_j b_{im}b_{jn}\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_n(0))]>\\&=\frac{1}{N}<\sum_n\sum_m B_nB_m\exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_n(0))]>,\end{aligned}\tag{2.24}$$

where we have defined the molecular scattering lengths as

$$B_n=\sum_j b_{jn};\quad B_m=\sum_j b_{jm}.\tag{2.25}$$

For the intermediate *self*-scattering function, we have

$$\begin{aligned} F_{s,CM}(\mathbf{q},t) &= \frac{1}{N} < \sum_m \sum_i b_{im} b_{im} \exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_m(0))] > \\ &= \frac{1}{N} < \sum_m B_m^2 \exp[-i\mathbf{q}\cdot(\mathbf{R}_m(t)-\mathbf{R}_m(0))] > . \end{aligned} \tag{2.26}$$

2.2.3 Rotational and intramolecular motion

According to Eq. (2.22), this contribution may be written as

$$F_{roint}(\mathbf{q},t) = \frac{1}{N} < \sum_n \sum_m \sum_i \sum_j b_{im} b_{jn} \exp[-i\mathbf{q}\cdot(\mathbf{s}_{im}(t)-\mathbf{s}_{jn}(0))] >; \tag{2.27}$$

and for the intermediate *self*-scattering function we have [Eq. (2.23)]

$$F_{s,roint}(\mathbf{q},t) = \frac{1}{N} < \sum_m \sum_i b_{im} b_{im} \exp[-i\mathbf{q}\cdot(\mathbf{s}_{im}(t)-\mathbf{s}_{im}(0))] > . \tag{2.28}$$

2.2.4 Rotational motion

This contribution is given by [Eq. (2.22)]

$$F_{rot}(\mathbf{q},t) = \frac{1}{N} < \sum_n \sum_m \sum_i \sum_j b_{im} b_{jn} \exp[-i\mathbf{q}\cdot(\mathbf{s}^r_{im}(t)-\mathbf{s}_{jn}(0))] >; \tag{2.29}$$

and the intermediate *self*-scattering function is given by Eq. (2.23)

$$F_{s,rot}(\mathbf{q},t) = \frac{1}{N} < \sum_m \sum_i b_{im} b_{im} \exp[-i\mathbf{q}\cdot(\mathbf{s}^r_{im}(t)-\mathbf{s}_{im}(0))] > . \tag{2.30}$$

2.2.5 Intramolecular motion

This contribution is given by Eq. (2.22)

$$F_{int}(\mathbf{q},t) = \frac{1}{N} < \sum_n \sum_m \sum_i \sum_j b_{im} b_{jn} \exp[-i\mathbf{q}\cdot(\mathbf{s}^{int}_{im}(t))] > . \tag{2.31}$$

The intermediate *self*-scattering function is given by

$$F_{s,int}(\mathbf{q},t) = \frac{1}{N} < \sum_m \sum_i b_{im} b_{im} \exp[-i\mathbf{q}\cdot(\mathbf{s}^{int}_{im}(t))] > . \tag{2.32}$$

We note that the result only depends on im and that we do not need to sum over jn. This may seem surprising but is a consequence of $\mathbf{s}^{int}_{im}(t)$ not being a position vector, like the other vectors, but a displacement vector determined relative to a given time origin $t=0$.

2.2.6 Example

As an example of the rotational and intramolecular scattering function, let us consider our simulations of the squalane monolayer [6,7,11]. Squalane [$C_{30}H_{62}$ or (2,6,10,15,19,23-hexamethyltetracosane] is a branched alkane with twenty-four carbon atoms in its backbone and six methyl side groups located symmetrically along its length. When bound to a solid surface by van der Waals forces at low temperature, it forms a crystalline structure with a two-molecule rectangular-centered unit cell [6]. At 225 K, the monolayer undergoes a transition from a crystalline phase to a smectic phase, where the molecules are arranged in lamellae with some translational disorder within the lamellae in the direction parallel to the long axis of the molecule. A top-down snapshot of the simulation cell containing the squalane molecules is shown in Fig. 1 at a temperature of 300 K [6]. The molecules are depicted by the bonds between carbon atoms, and we see how the molecules are arranged in lamellae.

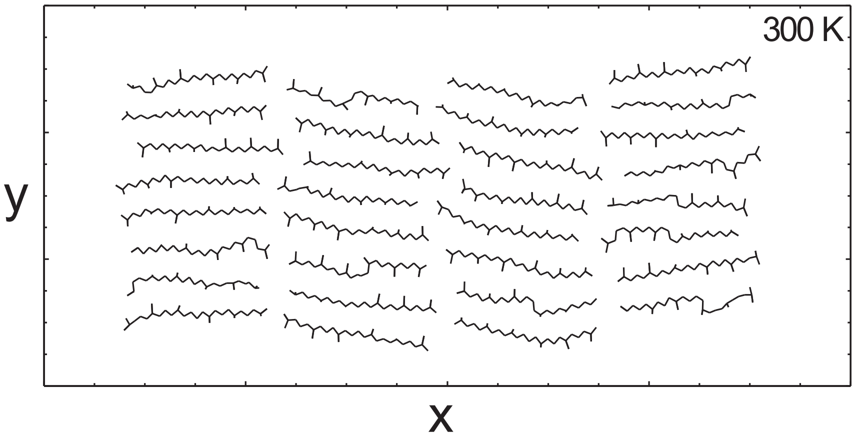

Figure 1: A top-down view of the simulation cell with squalane molecules at 300 K [11].

In Fig. 2, we show the intermediate *self*-scattering functions for the rotational motion of the molecules, the intramolecular motions, and the combined rotational and intramolecular (internal) motions. All correlation functions are seen to be unity at $t=0$ consistent with the normalization factor that we introduced for each of the correlation functions. After an initial decrease with time, each of the correlation functions levels out at some non-zero value. These are examples of $F_s(|\mathbf{q}|,\infty)$ in Eq. (2.5) being different from zero, since, in rotational and intramolecular motions, the atomic motions are bounded about their original positions. Therefore, we have an elastic, in addition to the quasielastic, contribution to the scattered intensity. We also note that the product of the rotational and intramolecular scattering functions are not quite equal to the internal contribution, indicating that there is a slight coupling between the two kinds of motions as discussed in relation to Eq. (2.23).

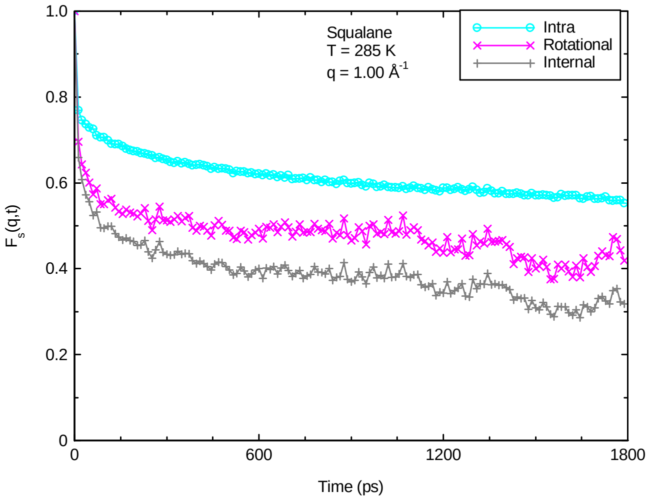

Figure 2: The powder-averaged intermediate *self*-scattering function $F_s(q,t)$ for the squalane molecules in a monolayer film at 280 K in the smectic phase for the rotational, intramolecular and combined rotational and intramolecular (labeled internal in the figure) motion (from [11]). No quantitative uncertainty analysis was performed, but the calculated data points are based on MD simulation results with a standard deviation of the total energy on the 1% level.

3 Velocity correlation functions

The velocity correlation functions are very useful for the characterization of the molecular motions and their time-Fourier transform gives the power spectrum of the motions that may be related to inelastic helium atom scattering spectra. In addition, a determination of the velocity correlation function for the center-of-mass and rotational motions is essential for identifying the types of motions in a system. For example, in systems of the strongly anisotropic alkane molecules, we have found [6, 11] that motions parallel to the long axis of the molecules differ qualitatively from those perpendicular to it (see Fig. 1), the parallel motions being more diffusive in character whereas the perpendicular motions are bounded and oscillatory.

The normalized center-of-mass velocity auto correlation function is given by the expression

$$\mathrm{Cvel}_\alpha(t) = \frac{< V_\alpha(t) V_\alpha(0) >}{< V_\alpha(0) V_\alpha(0) >}, \tag{3.1}$$

where $\alpha = x,y,z$ are the Cartesian components of the center-of-mass velocity of the molecules and the bracket $< \cdots >$ indicates an ensemble average. Instead of determining the velocity correlation function for motions in the three Cartesian directions, we may also determine the correlation function of the total center-of-mass velocity given by

$$\mathrm{Cvel}(t) = \frac{< \mathbf{V}(t) \cdot \mathbf{V}(0) >}{< \mathbf{V}(0) \cdot \mathbf{V}(0) >}. \tag{3.2}$$

For molecular rotational motion, we define the rotational velocity correlation function as

$$\mathrm{Crot}_i(t) = \frac{<\Omega_i(t)\Omega_i(0)>}{<\Omega_i(0)\Omega_i(0)>}, \tag{3.3}$$

where Ω_i is the angular velocity vector for a rigid rotation about an axis defined by the angular velocity vector. Usually, we choose the three principal axis of inertia for rotational motion of the molecule, so Ω_i is the rotational velocity for rotation about the ith principal axis of inertia. We may also determine the overall rotational velocity correlation function as

$$\mathrm{Crot}(t) = \frac{<\mathbf{\Omega}(t)\cdot\mathbf{\Omega}(0)>}{<\mathbf{\Omega}(0)\cdot\mathbf{\Omega}(0)>}. \tag{3.4}$$

The center-of-mass velocity correlation functions may readily be calculated from the center-of-mass velocity for molecule m that may be found directly from Eq. (2.7) by differentiation with respect to time. We have

$$\mathbf{V}_m(t) = \frac{\sum_{i=1}^{M} m_i \mathbf{v}_{im}(t)}{\sum_{i=1}^{M} m_i}, \tag{3.5}$$

where $\mathbf{v}_{im}(t)$ is the velocity of atom i in molecule m at time t. These velocities can be determined in an MD simulation and used in a calculation of the velocity correlation functions given by Eqs. (3.1) or (3.2).

3.1 Projection operator

It is straightforward to determine the rotational velocities about the three principal axes of inertia. First, we determine the center-of-mass coordinates for the molecule at time t using Eq. (2.7); then the atomic position vectors $\mathbf{s}_{im}(t)$ relative to the center-of-mass position are determined from Eq. (2.8). These are used to construct a projection operator that when applied to the atomic velocities will project out the angular velocities for rotation of the molecule about the three principal axes of inertia which are the eigenvectors of the inertia tensor in Eq. (2.10). The relative atom position vectors $\mathbf{s}_{im}(t)$ are then represented in the coordinate system spanned by the principal axes of inertia.

Let us first focus on one of the atoms in the molecule. Suppose that the molecule performs a rigid rotation as given by the vector $\mathbf{\Omega}$, then the velocity of the atom is given by

$$\begin{aligned}\mathbf{v}_{im} &= \mathbf{\Omega}\times\mathbf{s}_{im}\\ &= \mathbf{e}_1[\Omega_2 s_{im,3} - \Omega_3 s_{im,2}] + \mathbf{e}_2[\Omega_3 s_{im,1} - \Omega_1 s_{im,3}] + \mathbf{e}_3[\Omega_1 s_{im,2} - \Omega_2 s_{im,1}].\end{aligned} \tag{3.6}$$

The eigenvectors $\mathbf{e}_i$ are functions of time as indicated in Eq. (2.15), but for simplicity of notation this is not shown explicitly here. $s_{im,l}$ is the component of the position vector relative to the center-of-mass along principal axis of inertia $\mathbf{e}_l$. In matrix form, we have

$$\mathbf{v}_{im}=[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]\begin{bmatrix} v_{im,1} \\ v_{im,2} \\ v_{im,3} \end{bmatrix}=[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]\begin{bmatrix} 0 & s_{im,3} & -s_{im,2} \\ -s_{im,3} & 0 & s_{im,1} \\ s_{im,2} & -s_{im,1} & 0 \end{bmatrix}\begin{bmatrix} \Omega_1 \\ \Omega_2 \\ \Omega_3 \end{bmatrix}. \tag{3.7}$$

Thus the relation between the components of the atomic velocity and the rotational velocity in the basis of the principal axes of inertia is given by

$$\begin{bmatrix} v_{im,1} \\ v_{im,2} \\ v_{im,3} \end{bmatrix}=\begin{bmatrix} 0 & s_{im,3} & -s_{im,2} \\ -s_{im,3} & 0 & s_{im,1} \\ s_{im,2} & -s_{im,1} & 0 \end{bmatrix}\begin{bmatrix} \Omega_1 \\ \Omega_2 \\ \Omega_3 \end{bmatrix}. \tag{3.8}$$

A (3×3) matrix, as in Eq. (3.7), is generated for each atom in the molecule and they are put together to form a $(3M\times 3)$ matrix $[rotvel]$ where the first (3×3) block is for atom 1, the next (3×3) block for atom 2, etc. In the same way, we form a $(3M\times 1)$ column matrix $[vel]$ of the components of the atomic velocities, the first (3×1) block is for atom 1, the next (3×1) block for atom 2, etc. Likewise, the (3×1) matrix with the three components of the rotational velocity is written like $[\Omega]$. Then we have

$$[vel]=[rotvel][\Omega]. \tag{3.9}$$

In order to solve this equation, we first need to generate a square matrix in front of the (3×1) Ω column matrix, so we can take the inverse. This is done by multiplication from the left by the transpose of the $(3M\times 3)$ $[rotvel]$ matrix. We find

$$[rotvel]^{\mathrm{T}}[vel]=[rotvel]^{\mathrm{T}}[rotvel][\Omega]. \tag{3.10}$$

The $[rotvel]^T[rotvel]$ matrix is a quadratic (3×3) matrix that may be inverted; and, by multiplying from the left by the inverse of that quadratic matrix, we solve the equation for Ω. We get

$$[\Omega]=[[rotvel]^{\mathrm{T}}[rotvel]]^{-1}[rotvel]^{\mathrm{T}}[vel]. \tag{3.11}$$

This shows that, by applying the matrix operator $[[rotvel]^{\mathrm{T}}[rotvel]]^{-1}[rotvel]^{\mathrm{T}}$ to the atomic velocities, we may project out the rotational velocity of the molecule at a given time for rotation about any of the three principal axes of inertia.

3.2 Example

Let us use the center-of-mass and rotational velocity correlation functions for the squalane molecules in Fig. 1 as an example [6, 11]. In Fig. 3, we show the Cartesian components V_x, V_y, V_z of the center-of-mass velocity correlation function. We note that the correlation functions are very different for the three Cartesian directions. The motion in the z-direction, perpendicular to the surface, clearly has the character of an oscillatory bouncing mode as expected. The motion in the y-direction, perpendicular to the long axis

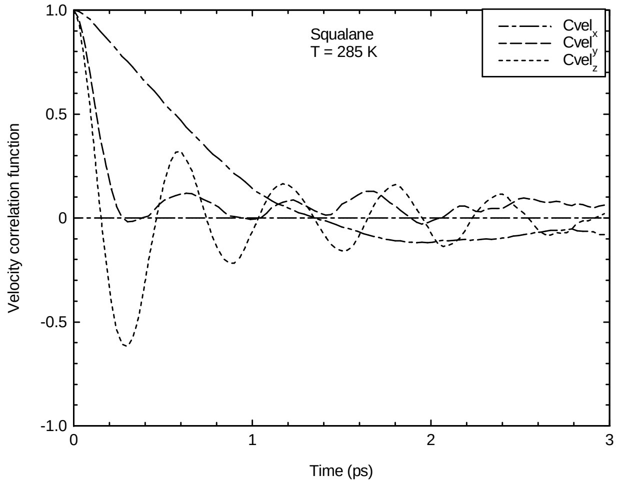

Figure 3: The Cartesian components, V_x, V_y and V_z of the center-of-mass velocity correlation functions of the squalane molecules in Fig. 1 (from [11]). No quantitative uncertainty analysis was performed, but the calculations are based on MD simulation results with a standard deviation of the total energy on the 1% level.

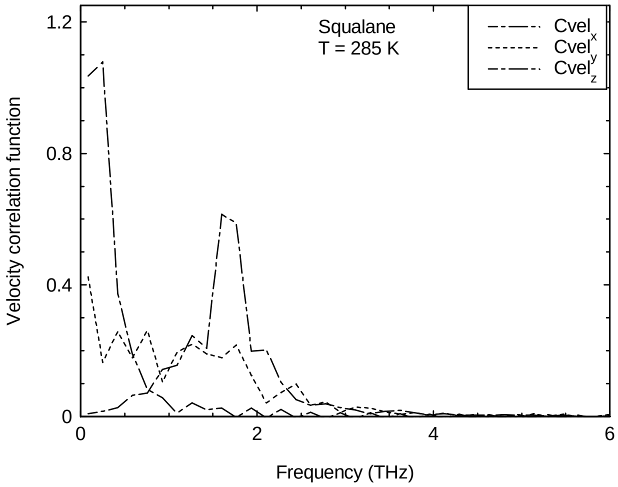

Figure 4: The power spectrum of the velocity correlation functions in Fig. 3 (from [11]). No quantitative uncertainty analysis was performed, but the calculations are based on MD simulation results with a standard deviation of the total energy on the 1% level.

of the molecules, is different and has both an oscillatory and diffusive character. The motion in the x-direction, parallel to the long axis of the molecules, is very different from the other directions in that the motion appears to be mostly diffusive. These features were used to conclude that the molecules form a smectic phase rather than a crystalline phase, since oscillatory behavior would have dominated in a crystalline phase. The power spectrum of the velocity correlation functions in Fig. 4 supports this picture. It will have a non-zero value at zero frequency for a diffusive mode while it will be zero for an oscilla-

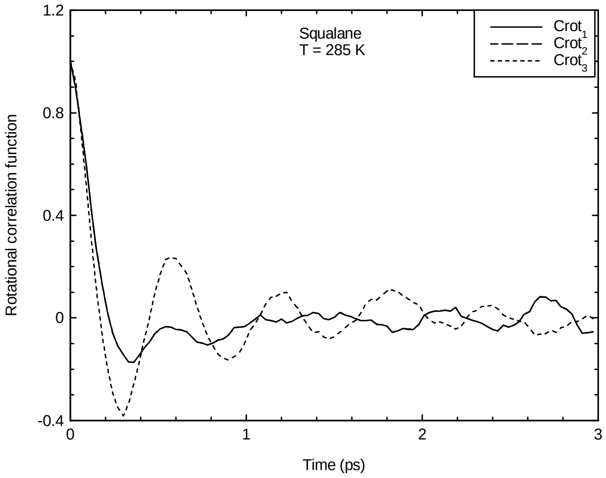

Figure 5: The rotational velocity correlation functions, Rot1, Rot2 and Rot3, for rotations about the principal axes of inertia with descending moments of inertia (from [11]). Note that the Rot1 and Rot2 correlation functions are degenerate and can therefore not be distinguished in the plot. No quantitative uncertainty analysis was performed, but the calculations are based on MD simulation results with a standard deviation of the total energy on the 1% level.

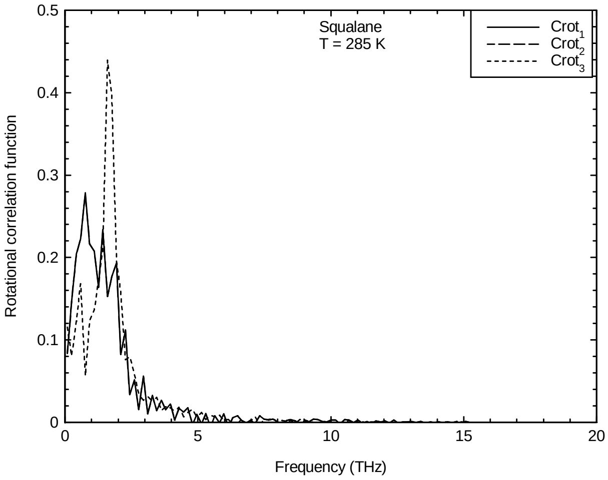

Figure 6: The power spectrum of the rotational velocity correlation functions in Fig. 4 (from [11]). No quantitative uncertainty analysis was performed, but the calculations are based on MD simulation results with a standard deviation of the total energy on the 1% level.

tory mode. In fact, we see a zero value at the origin for the z-motion but not for the x- and y-motions. The peaks in the power spectra for the y- and z-motions give the average oscillatory frequency, and there does not appear to be a peak for motion in the x-direction. However, since it is a smectic phase rather than a fluid, there should also be a peak in the power spectrum for the x-motion. We expect it to be at a very low frequency and below the energy resolution in the simulations.

In Fig. 5, we show the three rotational velocity correlation functions, Crot1, Crot2, Crot3 (Rot1, Rot2, Rot3 respectively in the figure), for rotation about the three principal axes of rotation corresponding to descending moments of inertia. That is, Rot1 and Rot2 correspond to rotations about the two principal axes of inertia that are perpendicular to the long axis of the molecule, while Rot3 corresponds to rotation about the long axis. The results for Rot1 and Rot2 cannot be distinguished. This is because the two moments of inertia are, on the average, the same so that the two motions will be degenerate. The rolling motion about the long axis, Rot3, is clearly distinct from the other rotational motions. It has an oscillatory character as well as a diffusive character like Rot2 and Rot 3. The latter may be seen more easily from the power spectrum of the rotational velocity correlation functions in Fig. 6, where each has a non-zero value at zero frequency. Again, the oscillatory character of the rolling motion about the long axis of the molecule is also clear from the distinct peak in the power spectrum. That character is much less pronounced for the rotational motions about the other axes.

Acknowledgments

This work was supported by the U.S. National Science Foundation under Grants DMR-0411748 and DMR-0705974 and by the U.S. Department of Energy through grant No. DE-FG02-01ER45912.

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