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

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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.

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