Vibrational relaxation and Bloch–Redfield theory

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Molecular dynamics (MD) simulations are known to be a good calculational tool for many processes in condensed media (both solid and liquid state). This approach allows one to compute such quantities as the density–
density correlation function, dielectric properties of the medium, etc., and to perform calculations in experimentally inaccessible regimes which are often useful tests of simplified theoretical models. But MD simulations, in the usual implementation, are applicable only to processes well described by classical mechanics. Recently there has been renewed interest in processes where quantum-mechanical effects are not negligible. Most of this work has been focused on the charge-transfer problem where one is dealing with many electronic levels, each one consisting of a manifold of vibrational states. A related, but somewhat simpler, problem concerns the manifold of vibrational states for a fixed electronic level. Most studies of electron transfer assume that the vibrational dynamics is classical (see, however, Jean et al. for a treatment using Bloch–Redfield theory which does not make this assumption). Modern spectroscopic techniques are becoming powerful enough to test this assumption and there is current interest in using MD to simulate the cooling of an initially excited molecule.

The early theories of vibrational relaxation of a molecule in solution were mainly applicable to diatomic molecules but did not assume that the oscillator dynamics was classical. Zwanzig used second-order perturbation theory to write down an expression for the decay rate in terms of an (at that time) uncalculable correlation function, assuming that only two states were involved:

\[
\frac{1}{\tau} = \frac{1}{2m\hbar \omega} \int_{-\infty}^{+\infty} ds \ e^{-\iota \omega s} \langle F(s) F(0) \rangle,
\]

where \( m \) is the mass and \( \omega \) is the frequency of the (harmonic) oscillator. Here \( F(t) \) is the force exerted at time \( t \) on the vibrational coordinate by the surroundings, which are assumed to be classical. Similar expressions have been derived for finite temperature by other researchers for quantum baths. MD simulations have also been used to obtain rates for vibrational relaxation but most researchers assumed that the dynamics of the oscillator is classical.

Two important exceptions are the work of Oxtoby et al., who studied dephasing in liquid nitrogen, and of Chesnoy and Weis, where the effect of fluid density on the relaxation and dephasing rates was studied. Both papers present computations of the relevant correlation functions using MD simulations. Whitnell et al. used MD to compute the force autocorrelation function and found that the relaxation rate obtained from MD simulations was well described by the classical analog of Zwanzig’s formula.

Ideally one should perform a purely quantum-mechanical calculation of the complete system. This is, however, prohibitively expensive in CPU time since one has to deal with a few hundred to a few thousand atoms. Thus, it is necessary to make some approximation to reduce the problem to one in which all but a few degrees of freedom (those of the “\( q \) system”) can be described by Newtonian mechanics. For some problems the coupling between the bath and the quantum degrees of freedom is small and one expects that the bath itself is not very much perturbed by the evolution of the \( q \) system. In these cases there exists an approach, developed originally in connection with NMR theory, which is much less CPU intensive. An analysis of NMR relaxation using Bloch–Redfield theory and classical simulations has been reported in the literature. In this approach (Bloch–Redfield theory) one assumes that the state of the bath can be well described at all times by a fixed, thermal equilibrium density matrix, and derives an equation for the “reduced density matrix” of the \( q \) system which involves some correlation functions of operators mixing the \( q \) system and the bath. These correlation functions can then be calculated by MD simulations (assuming the bath to be “classical”) and then used to solve for the evolution of the reduced density matrix. This approach differs from Zwanzig’s in that one deals with the whole vibrational manifold at once instead of just two levels. The advantages of our approach are many: typically one needs to compute a fixed set of correlation functions which are quite independent of the dynamics of the free \( q \) system; once these correlation functions have been computed one can solve for the evolution of the whole reduced density matrix, obtaining not only the evolution of the state populations \( T_1 \), but also the decoherence \( T_2 \) times; the computation of the correlation functions is just an application of the usual MD methods. Bloch–Redfield theory seems promising also in describing time-resolved spectroscopic experiments.
Bloch-Redfield theory\textsuperscript{21,23,24} gives an approximate evolution equation for the density matrix of a system in interaction with a thermal bath. The equation in the interaction representation reads

\[
\rho_{jk}(t) = \sum_{l,k} R_{iljk} e^{(\omega_{jk} + i\omega_{il})t} \rho_{jk}(t),
\]

where the "relation matrix" \(R_{iljk}\) is given by

\[
R_{iljk} = \delta_{ik} \sum_{r} \Gamma_{irr}^{\pm} \delta_{ij} \sum_{r} \Gamma_{krr}^{\pm} + \Gamma_{klj}^{\pm},
\]

\[
\Gamma_{klj}^{\pm} = \frac{1}{\hbar} \langle k | q | l \rangle \langle i | q | j \rangle \int_{0}^{\infty} ds e^{-i\omega_{klj}(F(s)F(0))},
\]

\[
\Gamma_{klj}^{\pm} = \frac{1}{\hbar} \langle k | q | l \rangle \langle i | q | j \rangle \int_{0}^{\infty} ds e^{-i\omega_{klj}(F(0)F(s))}.
\]

In the derivation of this equation many assumptions have been made:\textsuperscript{23,24} (1) The interaction Hamiltonian can be written as \(H_{\text{int}} = q F(t)\) with \(F(t)\) a time-dependent force, which is to be computed with the oscillator frozen at its equilibrium position. (2) The thermal bath remains in thermal equilibrium. (3) The relaxation times of the system under study are much longer than the autocorrelation time of the force. The first assumption, also made by Zwanzig and Whitnell \textit{et al.}, is mostly of a technical nature and presents no problem if the coupling is small. The second assumption, that the thermal bath remains in thermodynamic equilibrium, is expected to be valid if the coupling is small. The third assumption can be checked self-consistently by performing the MD simulations.

The correlation functions appearing in the expressions for \(\Gamma^{\pm}\) are quantum mechanical. Replacing them by their na"ive classical limit violates detailed balance and does not lead to thermodynamic equilibrium.\textsuperscript{16} To go smoothly to the classical limit one rewrites them in terms of the symmetrized correlation function, which is then replaced by the classical autocorrelation function, which can be computed by means of MD.\textsuperscript{16}

If one assumes that the off-diagonal elements of \(\rho\) are negligible compared to the diagonal ones one obtains for the thermodynamic average of the energy \(E = \text{Tr}(\rho H)\) of an harmonic oscillator the following equation

\[
\frac{dE}{dt} = -\gamma \left( E - \frac{\hbar \omega}{e^{\hbar \omega} - 1} \right),
\]

where the decay constant \(\gamma\) is given by

\[
\gamma = \frac{1}{m \hbar \omega} \frac{e^{\hbar \omega} - 1}{e^{\hbar \omega} + 1} \int_{-\infty}^{+\infty} ds e^{-\omega s}(F(s)F(0))_{\text{cl}}.
\]

In the limit \(\hbar \to 0\) one obtains (apart from a factor of 1/2) the same formula as Whitnell \textit{et al.},\textsuperscript{17} whereas in the limit \(\beta \to \infty\) (low temperature) one recovers Zwanzig’s formula.\textsuperscript{13}

We chose as a system a methylchloride molecule immersed in water.\textsuperscript{17} In contrast to Whitnell \textit{et al.},\textsuperscript{17} we took into account the hydrogens explicitly, but considered harmonic bonds. We performed two sets of calculations, both with the "normal" charges of Whitnell \textit{et al.}\textsuperscript{17} one, herc

called the "hf" case, with the oscillator frequency dictated by the normal parameters \((\omega_i = 673 \text{ cm}^{-1})\); and one, herc,
on the "lf" case, with the oscillator force constant reduced by a factor of 10 \((\omega_i = 213 \text{ cm}^{-1})\). The lf simulation serves as a check that at low frequency the classical predictions of Bloch–Redfield theory agree with the results of explicit simulations of the relaxation of energy deposited in the vibrational mode.\textsuperscript{17} Each calculation consisted of two parts; a MD simulation of the vibrational relaxation, and the solution of Redfield’s equations with the appropriate parameters. Note that the correlation function entering the expressions for the relaxation matrix is independent of the vibrational dynamics. The MD simulations were carried out with the program IMPACT developed at Rutgers.\textsuperscript{25}

All the calculations were performed at a constant temperature \(T = 298 \text{ K}\). The simulations included 203 SPC water molecules with periodic boundary conditions in a box of 18.6206 Å on each side.

To simulate via MD the vibrational relaxation we prepared ten configurations with an energy of about 70 kcal/mol in the vibrational coordinate. Each configuration was used as initial conditions for an MD simulation from which the vibrational energy as a function of time was extracted (see Figs. 2 and 3).

Using the values of the Fourier transform of the force autocorrelation function \((\zeta)\) obtained above we solved Redfield’s equations in each one of the two cases. To do that we had to truncate the infinite dimensional vibrational Hilbert space to a manageable size taking care that no relevant states were left out. For the hf case the initially excited state corresponded to ten quanta and we truncated the Hilbert space to a 15-dimensional space. For the lf case the 34th state was initially occupied and we considered the first 45 states as relevant, in which case we had to solve a system of 2025 coupled differential equations. Since we solved the (truncated) system of Redfield’s equations explicitly we obtained much more information than the energy relaxation. As an illustration we present in Fig. 1 the time evolution of the relevant diagonal elements (population numbers) of \(\rho\) in the hf case. One can also obtain information about dephasing as well as population relaxation by studying the evolution of the off-diagonal elements of \(\rho\). In our case they are initially zero and remain much smaller than the diagonal ones, so that Eq. (3) is applicable. Indeed, it agrees very well with the behavior of the
average energy calculated from the solution of the full system of Redfield’s equations, which is superimposed in Figs. 2 and 3 (the smooth line) with the energy as computed from the classical MD simulations. Note that the smooth line is not the solution of Eq. (3) but is obtained by taking the (weighted) trace of the solution of the full equations (2). We find for the hf case $\tau \sim 10$ ps from Bloch–Redfield theory and $\sim 4$ ps from the MD simulation. For the If case $\tau \sim 1$ ps from both Bloch–Redfield and the MD simulations.

It is clear that for the If case the agreement between the MD simulation and the solution of Redfield’s equations is much better than for the hf case. As discussed before, this is to be expected on general grounds, since the lower the frequency, the more states enter the description and the better a classical description should be. It should be noted that the $\hbar \to 0$ limit of $\gamma$ agrees very well with all the MD simulations. Thus, we conclude that the disagreement, in the high-frequency case, between the classical MD results and the results obtained via Redfield’s equations reflects the importance of quantum effects. The magnitude of these effects (which is, of course, temperature dependent) can be estimated easily from the formula for $\gamma$. (Similar results have been reported for impurities in a lattice by Nitzan et al. 27)

The framework presented in this letter lends itself to the study of other aspects of the vibrational relaxation phenomena. Since the correlation functions entering Eq. (2) are independent of the intramolecular dynamics they need to be computed only once. The only change one has to make is in the matrix elements and the energy spectrum of the oscillator. Thus, this method is particularly well suited to the study of the effects of anharmonicities in the intramolecular potential. Also, given that one obtains the full density matrix as solution to (2) one can obtain information about the coherence time(s), state-to-state dynamics, and the approach to equilibrium. We intend to address these questions in the future.

It is worth mentioning that the assumption that the solute-bath interaction takes the form $qF(t)$ can be relaxed without changing the essential details (although the calculations become much more CPU expensive). One can also extend the method beyond second-order perturbation theory.28 The price one has to pay is the calculation of further correlation functions.
A more detailed presentation of these results will be given elsewhere.

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