Vibrational Relaxation of Diatomic Molecules in Liquids

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Received September 11, 1989 (Revised Manuscript Received February 16, 1990)

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I. Introduction

The problem of vibrational relaxation is of interest for a variety of reasons, most notably because of the importance of energy-transfer processes in chemical reactions. In particular, almost any bond-breaking or bond-forming process requires the transfer of energy either into or out of a molecule's vibrational modes. In liquids, our understanding of this fundamental reaction step is limited by the high density and disordered nature of the medium. For example, the application of isolated binary collision (IBC) models is complicated in liquids by many-body dynamics. Recent interest in theories of vibrational relaxation has been fueled by a variety of new experimental techniques, although the information gained from experiments is still difficult to interpret. One major difficulty in comparing experiments with theories of vibrational relaxation results from a lack of knowledge concerning interaction potentials in solution. For this reason the evaluation of the effectiveness of various theories in treating this problem is based more on a theory's ability to predict trends of density and temperature dependence than on its quantitative agreement with experimentally determined relaxation rates.

There are three regimes of vibrational motion that we will deal with throughout this review, namely, high-frequency, low-frequency, and large-amplitude-motion regimes. The high-frequency regime is strictly quantum mechanical in nature at temperatures most commonly of interest. Isolated binary collision models are effective in treating high-frequency oscillators both because of the possibility of including quantum effects in the coupling and because the assumptions implicit in IBC models are most valid in this limit. The low-frequency regime, not including large-amplitude motion, which will be discussed next, encompasses a much smaller cross section of interesting systems. The low-frequency nature of these systems allows for a classical treatment of the oscillator motion, thus opening up these systems to a variety of classical tools including molecular dynamics and stochastic simulation methods. The questions that remain to be answered in this regime concern the validity of classical approximations to the vibrational motion. The final regime is that of large-amplitude vibrational motions. This regime is extremely important in understanding vibrational energy transfer during chemical reactions, i.e., during bond breaking and bond formation. It is also in some respects the most difficult regime to treat. IBC models break down with large-amplitude vibrational motions, and although the system motions can often be treated classically due to the anharmonicity of the potentials, classical techniques such as stochastic simulation models rely upon assumptions of linear response that become invalid with the large-amplitude motions. Each of these three regimes presents different problems, and each approach to vibrational relaxation has different regions of validity.

This review will cover in detail the period from 1984 to present, for systems of diatomic vibrational population relaxation in simple solvents. Previous work will be referred to often for historical background and theoretical developments. There have been several other review articles published recently,[1] including most recently one by Chesnoy and Gale (1984). Problems of more complicated nature, namely, polyatomic relaxation and the interpretation of experimental results, will not be dealt with exhaustively.

II. Isolated Binary Collision (IBC) Theories

A. General and Early History

It has been 30 years since the isolated binary collision (IBC) theory was proposed to describe vibrational relaxation in liquids.[2,3] Ultrasonic absorption experiments on various liquids were performed, and the results were related to the vibrational relaxation of an oscillator. Experimentally it was found in many cases that the relaxation rate increased linearly with density at low density. As the density increased, however, the rate increased nonlinearly with density. Litovitz believed that the results could be explained by making two assumptions. The first assumption was that the relaxation could be explained by the gas-phase relaxation equation

$$K_{ij} = P_{ij}\nu \qquad (1)$$

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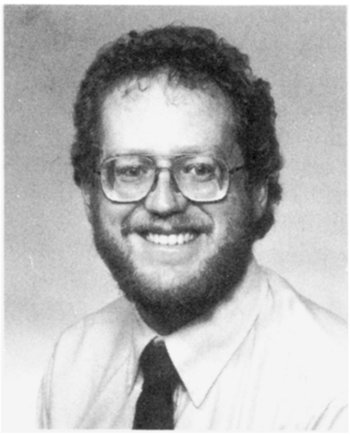
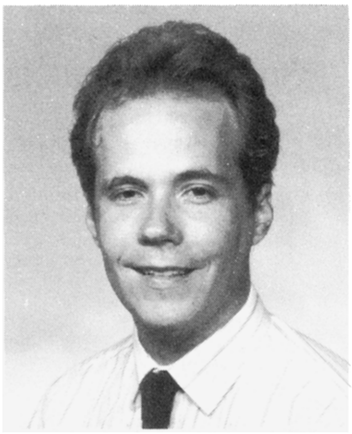
0009-2665/90/0790-0481$09.50/0

Charles B. Harris was born in 1940 and received his B.S. at The University of Michigan in 1963. He studied with Prof. F. A. Cotton at M.I.T., where he received his Ph.D. in 1966. From 1966 to 1967 he was an Atomic Energy Commission Fellow, working jointly between Chemistry and Physics at M.I.T. In 1967 he joined the faculty at the University of California at Berkeley. He became an Alfred P. Sloan Fellow in 1970, received the Humbolt Award from the Federal Republic of Germany in 1980–1981, was a Miller Research Professor at the University of California at Berkeley in 1984, and was awarded the Pittsburgh Conference Spectroscopy Award in 1990. His research interests include the study of energy-transfer processes in the condensed phase and on surfaces and studies of the statistical or dynamical basis of chemical reactions in the condensed phase on ultrafast time scales.



David E. Smith received his B.A. in chemistry from Colorado College in 1984 and joined Prof. Charles Harris' research group at the University of California at Berkeley the following fall. His research interests in Prof. Harris' group included both experimental and theoretical studies of simple chemical reactions in liquids. He completed his Ph.D. in the fall of 1989 and is presently pursuing postdoctoral studies with Prof. Tony Haymet at the University of Utah.



Daniel J. Russell received his B.S. in chemistry from the University of Chicago in 1984 and joined Prof. Charles Harris' research group at the University of California at Berkeley. He is currently finishing his thesis, and his research interests in Prof. Harris' group focused on applying simple models of vibrational relaxation in liquids to both experiments and molecular dynamics simulations of vibrational relaxation.

where K_{ij} is the rate of relaxation from vibrational state i to j. P_{ij} is the gas-phase probability of changing from vibrational state i to j given a collision with one molecule averaged over oscillator phase, impact parameter, and a Maxwell–Boltzmann distribution of velocity. ν is the collision frequency. Notice that P_{ij} is only temperature dependent, whereas ν is both density and temperature dependent. The second assumption Litovitz made was that ν is not given by the ideal gas collision rate in the dense phase, but that the volume the molecules take up must be taken into account in calculating the collision rate. An example of one of the collision rate formulas used at the time is

$$\nu \approx V/(\rho^{-1/3} - \sigma) \tag{2}$$

Note that this is the average velocity (V) divided by the mean free path of a molecule in a moving-wall cage.[2] One problem with this formulation is that the mean free path should be proportional to ρ^{-1} as $\rho \rightarrow 0$, but where this transition occurs is not defined.

According to early IBC proponents, one only had to correctly calculate the collision frequency in order to predict the vibrational relaxation. However, there were more assumptions than Litovitz and Madigosky stated in the original papers. Fixman and Zwanzig objected that IBC neglected the constant collective random force on the vibration, the possibility that in the liquid the collisions may not be independent due to a nonrandom phase of the oscillator during collisions, and that collisions may overlap in time.[4,5] Fixman modeled the collective random force due to the solvent as a force with a white noise spectrum. His calculation showed that the white noise random force is very efficient at relaxing the oscillator. However, the white noise random force overestimates the high-frequency random forces in a liquid, as Fixman noted, and the model's criticism of IBC was rebuffed by Herzfeld.[6] Zwanzig approached the problem from a time correlation function perspective where the rate should be proportional to

$$\int \mathrm{d}t \, \exp(i\omega t) \langle F(t) \, F(0) \rangle \tag{3}$$

where ω is the frequency of the oscillator and $F(t)$ is the force on the oscillator at time t. Zwanzig then assumed that the force on the oscillator could be decomposed into isolated events at some time t_k.

$$F(t) = \sum_k f(t - t_k) \tag{4}$$

$$\langle F(t) \, F(t + \tau) \rangle = \sum_{k \neq j} \sum \langle f(t - t_k) \, f(t + \tau - t_j) \rangle + \sum_k \langle f(t - t_k) \, f(t + \tau - t_k) \rangle \tag{5}$$

Zwanzig defined the second part of the equation as the binary part of the force on the oscillator. He found that the binary part dominates relaxation when

$$\omega \tau_c \gg 1 \tag{6}$$

where ω is the oscillator frequency and τ_c is the time between events. Herzfeld convinced Zwanzig that this was consistent with IBC if τ_c is the time between effective events.[6] According to Herzfeld, the molecules that were studied were high-frequency oscillators and relaxed very slowly; therefore the time between effective events was very long. Zwanzig agreed that IBC was internally consistent.[7] Several authors have examined interference effects and have come to about the same conclusion.[1b,d,8,9]

B. Statistical Mechanics and IBC

IBC remained stable until 1971, when Davis and Oppenheim used a master equation approach to describe vibrational relaxation in a liquid in the weak-coupling limit.[10,11] Again their theory, as in earlier ones, applies only to high-frequency oscillators. They pointed out that using weak-coupling theories may not be appropriate, because even though relaxation is slow, the forces that cause the relaxation are strong. They derived an equation that was forced into a binary form and found that

$$K_l/K_g = (\rho_l/\rho_g)g_l(R^*)/g_g(R^*) \qquad (7)$$

K_l is the rate for the liquid where the ij subscript has been dropped, K_g is the gas rate, ρ_l is the liquid density, ρ_g is the gas density, $g_l(R^*)$ is the radial distribution function for that liquid density evaluated at some R^*, and $g_g(R^*)$ is the gas radial distribution function evaluated at R^*. R^* is the turning point for the most effective collisions, and it is assumed that this region is small. This is only valid for spherical molecules with small-amplitude vibrations. Equation 7 could have been derived by incorporating into IBC Einwohner and Alders models for collision rates in a liquid.[12] A very intuitive development of this is given by Delalande and Gale.[13] Notice that unlike the earlier equation for the rate by Litovitz, this incorporates the structure of the liquid. At this point experimentalists had started to look at vibrational relaxation with more specific techniques than ultrasound. Unlike the ultrasound studies, the use of lasers allowed experimentalists to study the relaxation of diatomics. The first experiments by Calaway and Ewing of the vibration to translation relaxation of N_2 in liquid N_2 served not only as a simple system to test the above ideas but showed the enormous range over which vibrational relaxation takes place.[14,15] A good review of the above theoretical and experimental techniques is given by Chesnoy and Gale.[1a]

C. Reexamination of Assumptions (Post-1984 Work)

After 1984 IBC was applied to the relaxation of many simple molecules; however, most of the experiments were vibration to vibration relaxation and not as simple to model as vibration to translation relaxation. In many experiments, IBC was used to explain the data and the basic theory was usually not questioned, only the effect of anisotropy, how hard or soft potentials affected the relaxation, how to calculate $g(R^*)$, and what R^* to use.[16-34] One major change was a paper by Chesnoy and Weis[8] studying the density dependence of relaxation times. They performed a molecular dynamics simulation of a Lennard-Jones fluid and calculated two force autocorrelation functions as a function of density

$$F(t) = \langle \sum_b f(r_b(t)) \sum_c f(r_c(0)) \rangle \qquad (8a)$$

$$F_b(t) = \langle \sum_b f(r_b(t))\, f(r_b(0)) \rangle \qquad (8b)$$

where $F(t)$ is the total force autocorrelation, $F_b(t)$ is the binary force autocorrelation, and $f(t)$ is the coupling from the Lennard-Jones liquid to the oscillator at time t. From these correlation functions and the Golden Rule they calculated the relaxation rate

$$1/T_1 \approx \int \mathrm{d}t\ e^{i\omega t}F(t) \qquad (9)$$

Basically the component of the force autocorrelation spectrum at the oscillator frequency determines relaxation. They found that the binary force autocorrelation function frequency spectrum was very similar to the total force autocorrelation function frequency spectrum, all the way to frequencies of $\approx$10 cm^{-1}. This would extend the validity of IBC calculations to near-resonant vibration to vibration relaxation and perhaps to dephasing.[35-37]

The last major theoretical consideration of IBC was by Dardi and Cukier.[38-40] They calculated the relaxation of a dilute diatomic in a structureless fluid and discuss explicitly all approximations in their calculations and an IBC approach. They examine interference effects as other authors have and assumed again that for high-frequency oscillations this is not a problem. Another assumption is that dynamically correlated collisions are not important. Dynamic correlations are the correlations between successive elastic collisions. The nondynamic effects of correlated elastic collisions should be taken into account by the radical distribution function. No one has examined the effects of dynamic correlations on vibrational relaxation, although by its very definition it should not be important. Also it is not clear that a Maxwell–Boltzmann distribution in velocity exists around the oscillator, although some work indicates this is true as long as the transition probability is small.[41,42] Another assumption implicit in all IBC models is that vibrational relaxation is a Markov process. Finally, they propose that a weak-coupling assumption can be made, unlike Davis and Oppenheim. Gas-phase calculations have shown the weak-coupling approximation to work well, if the elastic cross section is much smaller than the inelastic cross section and the elastic and inelastic potentials are chosen correctly.[43,44] Cukier et al.'s final paper attacks the scaling of vibrational relaxation by the radial distribution function. They calculate the relaxation of an oscillator in a dilute gas using their formalism and show that the result is the standard dilute gas rate constant. They perform the same calculations for a liquid and find that to do the correct averaging the R^* of $g(R^*)$ must be chosen so large that $g(R^*) \approx 1$. They believe that there is no basis for using the ratio of $g_l(R^*)$ to $g_g(R^*)$ to explain the nonlinearity of relaxation vs density. One possible criticism of their calculation is that they must assign a transition probability R as a function of P(momentum) and b(impact parameter), $R(P,b)$. Unfortunately, they approximate $R(P,b)$ as a constant in b up to $b_{\max}$, where it drops to zero. This functional form is highly unlikely for vibrational relaxation, and most previous authors have assumed that

$R(P,b)$ is sharply peaked at $b = 0$. It is generally accepted that hard direct collisions are responsible for the majority of relaxation. As noted earlier to prove or disprove many of these theories a density-dependent study is needed.

The relaxation of I_2 in Xe is a good test case for many reasons. The vibrational frequency is very low (214 cm^{-1} at the bottom of the well) and the solvent is simple to describe. Brown et al. have examined the vibrational relaxation of I_2 after geminate recombination by molecular dynamics.[45,46] A density-dependent study was performed and it was found that the relaxation in four densities was qualitatively the same and could be overlapped by scaling the relaxation in time. This could be explained by IBC if there was a way to quantitatively predict the scaling factors. In order to test the application of IBC to this system, a collinear gas-phase simulation of the relaxation of I_2 by Xe was completed.[46] Quantitatively, the IBC results could not model the relaxation by a physically meaningful collision rate. The collision rate in the liquid could be defined as the flux of Xe atoms through a sphere of reasonable radius centered on each of the I atoms; this was calculated in the molecular dynamics simulation. It was found for a reasonable radius that the collision rate was ≈ 2 ps^{-1}; however, for the IBC calculation to overlap the molecular dynamics results a collision rate of ≈ 4 ps^{-1} was needed. The IBC calculation was a collinear calculation, and therefore a steric factor of 1/3 is usually applied; this would imply that to match the molecular dynamics, a collision factor of 12 ps^{-1} would be needed. The largest problem with this comparison is that the I_2 has a very large amplitude oscillation at the top of the well and IBC theory may not be applicable. The probability of relaxation for the higher vibrational states can with difficulty be found experimentally or predicted; however, if the oscillation of the vibration is very large, as in I_2 at the top of the well, the frequency of collisions and characteristics of the collisions will be determined by the I_2 motion and not the solvent. At the top of the well molecular dynamics shows a definite phase relationship between the I_2 and the solvent. Further studies on the relaxation at the bottom of the well are in progress to see if they can be explained quantitatively by IBC.

III. Computer Simulations

Methods of computer simulation are extremely powerful tools in the study of chemical reactions in solution. This is primarily because of the accessibility of virtually all details of the system motion in such computer experiments. Simulations of vibrational relaxation in liquids have great potential for revealing relevant relaxation mechanisms as well as for giving accurate information on the sensitivity of the relaxation to various system parameters. Thus simulations potentially provide an ideal testing ground for various theoretical models. Yet in practice simulations of vibrational relaxation have proven to be quite difficult to perform for several reasons. First, an accurate treatment of vibrational motion in most systems of interest must be quantum mechanical in nature, and although great progress has been made in recent years in simulating quantum processes, such techniques remain quite computationally burdensome. As a result, most simulations of vibrational relaxation have been restricted to systems for which a classical treatment of vibrational motion is not altogether unreasonable, i.e., to systems with either high temperatures or low vibrational frequencies. Solvents are typically monatomic and therefore also amenable to classical treatments. Second, vibrational relaxation is usually a slow process relative to the vibrational motion and solvent motions, and therefore simulations of relaxation must be performed for long times to give relevant information, making the cost of many such simulations prohibitive. Finally, at least in brute force methods such as molecular dynamics, the system sizes required to give reasonable relaxation results are often quite large even though details of the solvent motion far from the reaction center are seldom of great interest.

A. Molecular Dynamics Simulations

The first molecular dynamics (MD) simulations of vibrational relaxation were reported by Riehl and Diestler in 1976,[47] in which the computational burdens described above were minimized by considering a one-dimensional system of low-frequency (10 cm^{-1}) diatomic oscillators arranged head to tail. The extremely low frequency of the oscillator used in these simulations was necessary to achieve reasonable computational times. Nordholm, Jolly, and Freasier[48] subsequently considered the density dependence of bromine relaxation in argon ranging from gas-phase to moderate liquid-phase densities. The system size was rather small and relaxation was calculated only in the upper portions of the bromine potential where frequencies were fairly low, thus saving computation time and also justifying the classical treatment of the vibration.

More recently, advances in the availability of supercomputers have made possible the first extensive MD simulations of vibrational relaxation in a physically relevant system. Brown, Harris, and Tully[45] have reported a series of simulations of iodine relaxation in liquid xenon out to 500 ps for several densities. The system conditions were chosen to match those in a recent set of experiments by Paige et al.[49,50] The resulting vibrational relaxation curves are quantitatively quite different from experimental observations, being somewhere between a factor of 5 and 10 too fast. The temperature and density dependencies, however, measured as ratios of the relaxation rates, agree quite well with experiments. Quantitative differences can be explained as being due to the extreme sensitivity of simulation results to the potential parameters used and are typically not considered as significant as the ability to reproduce density and temperature trends. An additional source of error in these MD simulations is due to a gradual rise in the temperature of the solvent during each trajectory, a result of the finite system size, with a total temperature rise of about 30 K over the entire relaxation process. This set of simulations provides perhaps the most complete body of information available on the vibrational relaxation of a realistic model system and is proving to be useful in evaluating a variety of theoretical models for vibrational relaxation including IBC[46] and generalized Langevin-based theories.[51,52]

Visscher and Holian[53,54] have performed MD simulations of vibrational energy transfer in high-density, high-temperature systems with the goal of understanding the dynamics of condensed-phase chemical explosions. Their classical treatment is justified by the high system temperatures and pressures. Their work consists first[53] of the evaluation of various thermostating techniques used to accomplish constant-temperature MD simulations, a feature that as seen above would be appealing in a variety of applications. A second set of simulations[54] were performed on a one-dimensional system of diatomic molecules with the purpose of gaining insight into the mechanisms responsible for vibrational to translational energy transfer. The qualitative conclusions they arrive at, that relaxation is most efficient from highly excited molecules due to the anharmonicity of the potentials, is not surprising. The harsh nature of their "explosive" system makes comparison with other systems quite difficult. These same conditions do, however, provide an interesting test of some theories in a regime where they are not expected to hold, i.e., IBC theories at very high densities.

B. Stochastic Simulations

An interesting alternative to MD simulations is provided by stochastic simulation techniques, in which the solvent dynamics are modeled by some sort of stochastic equations of motion while the solute motion is treated explicitly as in MD. The most common approaches to stochastic modeling of the solvent begin with the generalized Langevin equation (GLE), as first developed by Mori, Kubo, and Zwanzig.[55-57] The GLE can be written in scalar form for a single particle of mass m as

$$m\dot{v}(t) = -\int_{t_0}^{t} \mathrm{d}t'\, m\gamma(t')\, v(t-t') + R(t) \qquad (10)$$

where $R(t)$ is the "random" force and the convolution integral is the dissipative force. It can be further shown that $R(t)$ and the memory function $\gamma(t)$ are related by the second fluctuation dissipation theorem[57]

$$\langle R(t')\, R(t'+t)\rangle = k_{\mathrm{B}}Tm\gamma(t) \qquad (11)$$

where the brackets indicate an ensemble average, k_{B} is Boltzmann's constant, and T is the temperature. The GLE is particularly useful in that it easily lends itself to approximation. $R(t)$ can be represented as a Gaussian random force, and the memory function $\gamma(t)$, which in essence contains all relevant information about the full many-body dynamics of the solvent, can be approximated by a variety of simple functional forms, thus making evaluation of the GLE a relatively simple task. Stochastic simulations have both advantages and disadvantages when compared with MD. The most obvious advantage is in their potential computational efficiency. The stochastic model for the solvent can be developed to arbitrary accuracy providing a balance between adequate solvent modeling and computational complexity. Information about relevant solute–solvent interactions can also be readily obtained through evaluation of the effectiveness of various solvent models in the stochastic simulations. The primary disadvantage of stochastic models is that potentially useful information about the solvent dynamics is lost when the solvent is not treated explicitly. There is also some uncertainty in stochastic simulation results associated both with the assumption of solvent linear response, implicit in the GLE, and with the approximations in the solvent model. Thus the two techniques seem to be complementary in nature rather than competitors.

The most thoroughly developed stochastic simulation technique is the MTGLE work of Adelman and coworkers.[58-60] Their approach consists of reformulating the generalized Langevin equation into an equivalent set of linear coupled equations that govern the motion of an infinite chain of harmonically bound "atoms". The individual chain atoms are related intuitively to successive solvation shells in the liquid. The computational efficiency of the technique is derived from the ability to truncate the harmonic chain after a very few atoms. Parameters for the harmonic chain are determined from equilibrium pair distribution functions for the system of interest. The pair distribution functions can in turn either be calculated explicitly from a molecular dynamics simulation or approximated analytically, the latter being much more efficient. The MTGLE technique has been applied to the vibrational relaxation of iodine in a variety of Lennard-Jones solvents by Brooks, Balk, and Adelman.[59,60] Results are qualitatively quite reasonable though only calculated for relaxation in the upper portions of the well. There were no reported studies of density or temperature dependence.

More recent work by Adelman and Balk[61-63] has been directed toward extending the MTGLE approach to include molecular solvents. Such an extension is not at all trivial because of the need to realistically include vibrational structure in the solvent. Even ignoring the difficulties inherent in treating these modes classically, the high-frequency nature of the vibrations is not amenable to MTGLE techniques as originally formulated. The work of Adelman and Balk accomplishes the necessary modifications, yet implementation of their model requires in addition a knowledge of the random force autocorrelation function of the molecule, which is, at present, unavailable. Thus this promising extension of a computationally efficient algorithm to simulations of vibrational relaxation in molecular solvents remains essentially untested.

Smith and Harris[51,52] have recently applied a stochastic simulation technique of similar spirit to the problem of iodine vibrational relaxation. Input into these simulations comes directly from a MD simulation of single iodine atom dissolved in Lennard-Jones xenon at equilibrium. These simulations contain the same potential parameters as the full-scale MD simulations of Brown et al.[45] and no other adjustable parameters. This close connection allows for both a direct and a meaningful comparison of the stochastic and MD simulation results, providing for an interesting evaluation of stochastic methods in general. Results are shown in Figure 1 in comparison with MD simulation results of Brown et al. As can be clearly seen, the stochastic simulation results are in very good agreement with MD, lending credibility to this and related techniques that rely upon an assumption of solvent linear response. As it is developed to this point, this technique requires explicit calculation of atomic force autocorrelation functions, albeit for single atoms at equilibrium, and thus the computational burdens are not completely negligible. (The computational requirements are still

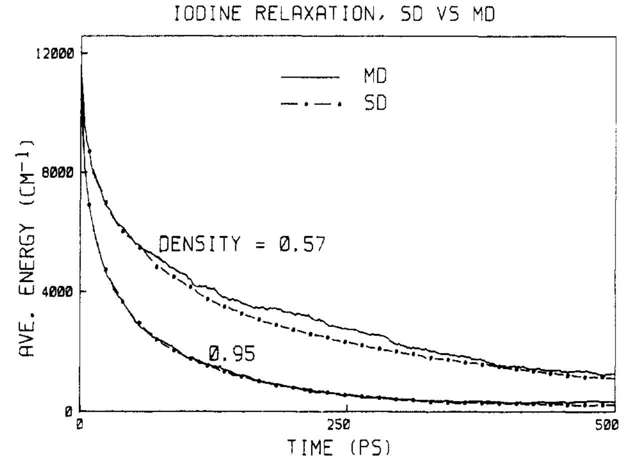


Figure 1. Comparison of stochastic simulation (SD) and molecular dynamics (MD) results for vibrational relaxation of iodine in liquid xenon. Solvent densities simulated correspond to Lennard-Jones reduced densities of $\rho^* = 0.57$ and $\rho^* = 0.95$.

considerably less than in full-scale MD simulations of vibrational relaxation.)

C. Semiclassical Simulations

Herman[64-66] has developed a semiclassical approach to simulating vibrational relaxation of diatomics based on a semiclassical theory of nonadiabatic processes. In this model, time scale arguments are used to separate the "fast" vibrational motion from the slower translational and rotational motions of the solute and solvent. The vibrational motion is treated quantum mechanically using perturbation theory to calculate adiabatic vibrational energies and wave functions. Vibrational relaxation is treated semiclassically through calculation of nonadiabatic couplings which are dependent on slow variable dynamics. Translational and rotational motions in the system are treated classically. This model is applied to the system of bromine in liquid argon with Monte Carlo simulations of the solvent motions being used to calculate the 1 → 0 vibrational transition rate. Results are quantitatively reasonable, although only calculated for a single density and temperature. Further applications of this technique, including temperature and density dependencies, are required for a more effective evaluation of its usefulness. The quantum mechanical treatment of the vibrational motion sets it apart significantly from the other simulation methods discussed in this section.

IV. Continuum Theories

Several theories of vibrational relaxation have been presented that treat the solvent as a viscoelastic continuum.[67-69] An early hydrodynamic model by Metiu, Oxtoby, and Freed[69] related vibrational relaxation times of a harmonic oscillator to the solvent's frequency-dependent shear and bulk viscosities with slip-boundary conditions. The resulting expression for the relaxation rate is

$$\frac{1}{T_1} = \frac{\mathrm{Re}\,[\zeta(\omega_\nu)]}{m} \tag{12}$$

where ω_ν is the harmonic oscillator frequency, m is the atomic mass, and $\zeta(\omega)$ is a function of the shear and bulk viscosities.

TABLE I. Comparison of the Density Dependence of Relaxation Times for Iodine in Lennard-Jones Xenon As Calculated from Molecular Dynamics and the Analytical Method Described by Stote and Adelman[a]

	relax time, ns	
packing fraction	Stote and Adelman	molecular dynamics
0.50	0.647	0.25
0.40	2.04	
0.30	5.23	1.0

[a] Molecular dynamics relaxation times are estimates of the total time required for relaxation from vibrational energies near dissociation to equilibrium, while the results from Stote and Adelman are T_1 times for I_2 at its equilibrium frequency. MD temperature ranges from ~290 K near the top of the I_2 potential well to ~310 K at equilibrium. Stote and Adelman temperature is 298 K. All other system parameters are nearly identical.

A recently developed model by Stote and Adelman[70-72] includes a formula for T_1 that is analogous to eq 12

$$T_1 = \frac{2k_BT}{\pi\rho_F(\omega_1)} \tag{13}$$

where k_B is Boltzmann's constant, T is the temperature, and $\rho(\omega)$ is the frequency spectrum of the fluctuating force exerted by the solvent on the vibrational mode. ω_1 is the gas-phase frequency of the oscillator corrected for the centripetal force and interactions with the local solvent environment. In their model, the force autocorrelation function is approximated as a Gaussian and determined from pair potentials and pair correlation functions of the system. The pair correlation functions are in turn determined numerically as solutions of the Percus–Yevick integral equation. Results are given for iodine in several Lennard-Jones (L-J) liquids and bromine in L-J argon. One result for iodine in L-J xenon is compared with the experimental measurement of Paige et al.[49,50] and found to be in reasonable agreement, although it should be noted that the experiments were performed at 280 K and not 306 K as they quote. Comparison with the MD simulations of Brown, Harris, and Tully[45] (BHT) is perhaps more meaningful as both sets of results contain an evaluation of density and temperature dependence of the relaxation rate. The Lennard-Jones parameters in each case are identical except for the L-J ϵ's for the Xe–Xe interaction, which differs slightly (229 K for Stote and Adelman (SA) and 222 K for Brown and co-workers). Relaxation results for the two systems are summarized in Table I. Note that the results for T_1 of the SA analysis are significantly longer than the BHT values, differing by over a factor of 2 at a packing fraction of 0.5 and by a factor of ~5 at a packing fraction of 0.3. SA results are given as the T_1 value for iodine at vibrational frequencies corresponding to relaxation near the bottom of the well, while BHT results are given as the time for the entire relaxation process to occur. Extraction of T_1 values at particular frequencies from the BHT results is not accomplished trivially given the noise in the simulations, but note that the resulting T_1 values would be less than the relaxation times quoted. Therefore the discrepancies between the SA and BHT results are actually greater than seen in Table I. The SA analysis of the density dependence of iodine relaxation was performed at 298 K, compared with 280 K in the MD simulations. This discrepancy is actually lessened by the temperature rise during the MD trajectories discussed above, with the average temperature of the system being $\sim$300 K during the relaxation and reaching a final value of $\sim$310 K. Analysis of temperature dependencies in both systems suggests that temperature differences on the order of 10 K could not account for the observed differences in relaxation results. The SA and BHT results disagree not only in absolute magnitudes but also in their density dependence. The BHT results show an increase in the relaxation rate by a factor of 4 from a packing fraction of 0.3–0.5, while the SA analysis predicts instead an increase by a factor of 8. In summary, the procedure of Stote and Adelman, while giving qualitatively reasonable results, does not give complete agreement with MD simulation results of nearly identical systems. This discrepancy could be due to a variety of approximations in their model, including the calculation of the force autocorrelation functions from the Percus–Yevick equation or the subsequent approximation of that FAF by a Gaussian function. Finally, they claim to have developed a technique that decomposes the relaxation time into components that are due to direct (solute vibrational mode → solvent modes) and indirect (solute vibrational mode → solute translation and rotational modes → solvent modes) coupling mechanisms. This decomposition is misleading, as it does *not* lead to an expression for the total relaxation rate which is the sum of their "direct" and "indirect" relaxation rates, as is only reasonable.

V. Conclusions

The state of the theory of vibrational relaxation at this point must be driven by experiments. Due to the observation that relaxation is very sensitive to the potentials, all the theories examined in this paper are useful only in predicting the density and temperature dependence of relaxation. Unfortunately, there have been very few experiments that provide this information in a system that can be easily modeled. In the classical regime I_2 in liquid Xe has been studied extensively in theory and experiment. This system has been modeled by most of the theories examined in this paper. The most successful model of the relaxation was based on the generalized Langevin equation. This model has reproduced the density trends seen in experiments and has quantitatively reproduced a molecular dynamics simulation of the relaxation of I_2 in Xe. IBC theory, the most prevalent model, failed to model the relaxation, due to the large-amplitude motion of I_2 near dissociation.

IBC theories have been somewhat successful in modeling quantum systems. The ease in applying IBC has made it most prevalent; however, it has been applied in detail differently in many experiments. This difference in application from experiment to experiment is partially due to the lack of a firm theoretical foundation for IBC. This weakness causes the theory to still be attacked theoretically. Other theories to model quantum systems have been confined to semiclassical calculations; however, few of these calculations have been made because of their relative difficulty. Until the relaxation of simple oscillators in simple solvents is understood, it seems that relaxation mechanisms and dynamics of chemical relaxation in larger molecules in molecular solvents will still be a major challenge to experimentalist and theorist alike.

VI. Acknowledgments

This work was supported in part by the Office of Naval Research. We also acknowledge U.S. Army Research Office support under Contract No. DAAL03-86-K-0172.

VII. References

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