Energy Flow during Isomerization Reactions in Liquids

Paul A. Rejto* and David Chandler*

Department of Chemistry, University of California, Berkeley, California 94720

Received: July 15, 1994; In Final Form: September 9, 1994

We introduce a method for trajectory analysis of energy flow during condensed phase chemical dynamics. The method requires specification of a reaction path and consists of monitoring the work done by the reaction path variable on various parts of the system. It is generally applicable to complex systems, is simple to calculate, and provides a consistent method of examining the role of a bath on energy relaxation dynamics. The method is illustrated by studying cyclohexane isomerization in liquid carbon disulfide.

1. Introduction

This paper considers energy flow for a nonlinear dynamical system weakly coupled to a bath. The condition of weak coupling corresponds to the Lindemann—Hinshelwood regime of chemical kinetics. This regime is, of course, pertinent to gas phase chemical dynamics. In recent years, it has been shown that it can be relevant to condensed phase kinetics as well. In particular, the nonstatistical effects of intramolecular dynamics characteristic of this regime reveal themselves in the pressure dependence of measured rate constants.

Quantitative studies of these kinetics require trajectory calculations starting at the transition state. The analysis of these trajectories for polyatomic solutes in a liquid is difficult because the pertinent dimensionality is high. In the strong coupling, or Kramers regime, the analysis is less difficult because trajectories passing over a transition state are so rapidly committed to a stable state that only a small region of configuration space is relevant. Our purpose in this paper is to present a methodology for analyzing pathways in systems with large relevant regions of configuration space.

The method focuses attention on the work done by the reacting species as the reaction coordinate changes. To best illustrate the different types of trajectories that start at the transition state, they are divided into three types. The first are trajectories that obey Wigner’s fundamental hypothesis; namely, they begin at the transition state with their velocity pointing toward either reactant or product and equilibrate without recrossing the transition state as either reactant or product, respectively. Trajectories that recross the transition state are divided into two subtypes: the transient portion of the trajectory between the start and the final recrossing of the transition state as well as the committed portion of the trajectory between the last recrossing of the transition state and the end.

As an illustration, the isomerization of cyclohexane in carbon disulfide is studied. For this system, trajectories of the first and third type transfer energy to the solvent while trajectories of the second type absorb energy from the solvent. We discuss the relative energy transfer from the reaction coordinate to the bath and to the other modes of the cyclohexane molecule and propose a physical model that explains significant qualitative features of the relative energy transfer. A simple collision model rationalizes the density dependence of the energy transfer rate.

2. Work

Consider a Hamiltonian system arbitrarily divided into two parts, solute and bath. For isomerizations in liquids, the solute is defined to be the molecule undergoing isomerization, and the bath is the liquid. Suitable generalizations could be made for processes that are not unimolecular. Suppose that there are \( S \) solute atoms and \( B \) bath atoms, with a total of \( N = S + B \) atoms. In general, the Hamiltonian may then be decomposed as

\[
H = H_s + H_b + \Delta V(q_s^B)
\]  

where

\[
H_s = \sum_{i=1}^{S} \frac{p_i^2}{2m_i} + V_s(q_s)
\]  

and

\[
H_b = \sum_{i=S+1}^{S+B} \frac{p_i^2}{2m_i} + V_b(q_b)
\]

are the separate Hamiltonians of the solute and bath, respectively, and \( \Delta V \) is the coupling between them.

The net work done by the solute on the bath (or, more precisely, the negative work done by the bath on the solute) during a trajectory of time \( t \) is

\[
W(t) = \delta \int_0^t \frac{\partial \Delta V}{\partial q_s} dq_s ds
\]

At equilibrium, it must vanish. Away from equilibrium, however, its behavior is nontrivial. If the solute is hotter than the bath, energy will transfer from the solute to the bath until the temperatures of the two subsystems are equal. In this case, the energy transfer corresponds to the solute doing work on the bath, i.e., \( W(t) > 0 \).

Note the Hamilton’s equations imply that

\[
dW/dt + dH_s/dt = 0
\]

A similar statement connecting \( dW/dt \) with \( dH_b/dt \) does not, however, follow from mechanics alone. Equation 5 is in essence the first law of thermodynamics. From the second law, considering an ensemble where the system is hotter than the bath, heat is transferred from the system to the bath until the total is equilibrated. Such an ensemble is created by placing
the reacting system at its transition state. In that case, when \( \Delta H_s < 0 \), where the first law implies \( W > 0 \), it follows that \( \Delta H_s \) averaged over the nonequilibrium ensemble of trajectories is positive.

Previous studies of molecular energy flow have focused on the work done by individual atoms.\(^{11}\) Rather than decompose \( W(t) \) into atomic contributions, we consider the work done by the reaction coordinate \( \theta \) on the bath, defined to be

\[
W_\theta(t) = \int_0^t \frac{\partial V}{\partial \theta} \, ds
\]

The work done by the remaining solute coordinates other than the reaction coordinate is

\[
W_r(t) = W(t) - W_\theta(t)
\]

For conservative Hamiltonians, the equilibrium ensemble averages are

\[
\langle W_\theta(t) \rangle = \langle W_r(t) \rangle = 0
\]

For trajectories started at the transition state, one expects that the work done by the reaction coordinate will be largest at short times because the molecule starts at the transition state with considerable excess potential energy. Furthermore, if coupling to the remaining coordinates is stronger than coupling to the solvent, one expects the energy transfer rate from the remaining coordinates to the solvent to increase as the reaction coordinate transfers energy to them. In the absence of the bath, intramolecular coupling can lead to relaxation. The functions \( W_\theta(t) \) and \( W_r(t) \) provide a measure of the bath's influence on intramolecular relaxation.

### 3. Trajectories

Trajectories that begin at the transition state are the trajectories required to compute the dynamical correction factors.\(^{12-14}\) They are typically divided into two types. Those that begin with an initial velocity pointing toward the reactant or product, and equilibrate as reactant or product, respectively, are called transition state theory trajectories because transition state theory is exact for such trajectories. Those that are not of this type are called non-transition state theory trajectories.

Trajectories that recross the transition state if little or no energy is transferred to the bath are the trajectories that violate the RRKM tenet of statistical behavior.\(^3\) To monitor the work done by the reaction coordinate, in this case, it is convenient to partition trajectories on the details of their short-time equilibration dynamics. In particular, trajectories are divided into three types. Statistical trajectories are those that equilibrate without recrossing the transition state. Trajectories that recross the transition state one or more times are divided into two types. The first type consists of the portion of the trajectory that starts from the transition state and undergoes recrossings until it recrosses the transition state for the final time. We call these transient trajectories. The second type consists of the portion of the trajectory from the time at which the final recrossing of the transition state occurs until the end of the trajectory. We call these committed trajectories. See Figure 1 for an illustration of the partitioning of a recrossing trajectory into transient and committed trajectories.

If little energy relaxation occurs during transient trajectories, then committed and statistical trajectories are expected to be similar since both involve equilibration with no recrossing of the transition state. They need not be identical, however, since the statistical trajectories are equilibrated at the transition state, while the committed trajectories are part of a nonequilibrium swarm of trajectories in the process of equilibrating.

### 4. Cyclohexane in Carbon Disulfide

As noted above, we use the isomerization of cyclohexane in liquid carbon disulfide to illustrate this analysis. The system has been the subject of detailed experimental\(^6\) and theoretical\(^5,15,16\) studies. An intramolecular potential with generalized coordinates for cyclohexane have been developed by Pickett and Strauss.\(^{17}\) Reactive flux correlation functions determined by molecular\(^{13}\) and stochastic dynamics\(^{16}\) are well fit by a strong collision model.\(^{5,16,18}\) This fit suggests that trajectories starting at the transition state move on a surface of roughly constant energy until a strong coupling of short duration time occurs with solvent molecules. During such an event, akin to a collision, the solvent molecule absorbs energy from the reactant and induces the cyclohexane to equilibrate in one of the two stable states. If no "collision" occurs, the trajectory continues to evolve and may recross the transition state. This picture has been supported by a limited analysis of the molecular dynamics simulation results.\(^{15}\) The current work extends that analysis.

The molecular model of cyclohexane used in this study consists of six united carbon atoms for a total of 12 intramolecular degrees of freedom. The bath consists of 250 rigid carbon disulfide molecules. Trajectories start from the transition state of the reaction coordinate, and the energy relaxation is monitored as a function of density to determine the differences between statistical, transient, and committed trajectories. The densities studied are \( \rho = 1.0, 1.3, 1.4 \) and 1.5 g/cm\(^3\). At each density, 1000 trajectories are examined; the same trajectories considered in ref\(^5\). For simulation details, see that paper.

Figure 2 shows \( W(t) \) at the four densities for the three types of trajectories. At all four densities, the statistical trajectories have positive slope and can be linearly fit, while the transient trajectories exhibit no consistent behavior. For the three lowest densities, the value of \( W(t) \) is consistently negative, while for \( \rho = 1.5 \) g/cm\(^3\), the value is close to zero. For transient trajectories at the lowest densities, the bath does work on the solute despite the fact that there is considerable energy in the solute. In this system, therefore, recrossing coincides with slight energy transfer from the bath to the solute. Committed trajectories are qualitatively and nearly quantitatively similar.
Figure 2. Total work done by the cyclohexane molecule on the bath, $W(t)$, for the statistical, transient, and committed trajectories. (a), (b), (c), and (d) represent solvent densities of 1.0, 1.3, 1.4, and 1.5 g/cm$^3$, respectively. Error bars for statistical trajectories are given at 0.4 and 0.6 ps. Error bars for committed trajectories are given at 0.2 and 0.8 ps. For transient trajectories, error bars are given at 0.1, 0.5, and 0.9 ps. The statistics for transient trajectories are poor at long time because most transient trajectories are of short time duration.

to statistical trajectories. This indicates that no significant relaxation occurs during a transient trajectory: relaxation would cause the committed trajectories to be different from the statistical trajectories.

The relative energy transfer to the bath from the reaction coordinate and the remaining coordinates of the solute is investigated by computing $W_R(t)$ and $W_c(t)$ as a function of density for statistical, transient, and committed trajectories. As with $W(t)$, the statistical trajectories do work on the bath, while for transient trajectories, the bath does work on the reaction coordinate. Again, the statistical and committed trajectories are nearly indistinguishable. Figure 3 shows $W_R(t)$ and $W_c(t)$ for the statistical trajectories as a function of density. The work done by the reaction coordinate is characterized by a sharp positive jump of between 0.5 and 1.0 kcal/mol during the first 0.1 ps, followed by a gradual increase for the remainder of the trajectory. Both the magnitude of the initial jump and the subsequent slope are monotonically increasing functions of density with the exception of the initial jump at $\rho = 1.3$ and 1.4 g/cm$^3$, where the initial jumps are essentially equal. The work done by the remaining coordinates is characterized by a sharp negative jump during the first 0.1 ps, followed again by a gradual increase for the remainder of the trajectory. The magnitude of the jump is between 0.2 and 0.7 kcal/mol and is a monotonically increasing function of density, with the exception of the jumps at $\rho = 1.3$ and 1.4 g/cm$^3$, where the magnitudes of the jumps are essentially equal. The magnitude of the subsequent slope is again a monotonic function of density.

Further, the dominant contribution to the total work done by the solute on the bath in the first picosecond of equilibration is from the reaction coordinate.

5. Discussion

In this final section, we interpret the two most important features of the results we have illustrated in Figure 3. These features are (1) the existence of two time scales for the work curves where large changes in work occur over 0.1 ps followed by slower variations and (2) the initial positive work done by the reaction coordinate on the solvent together with the initial negative work done by the remaining coordinates.

During the first 0.1 ps of a statistical trajectory, the configuration of the cyclohexane changes from one that is at the transition state to one that is either a boat or a chair. The reaction coordinate carves out a new solvation shell for the cyclohexane molecule during this stage of the trajectory. At short time, there is insufficient time for the bath to respond to the motion of the cyclohexane molecule. There is a harmonic restoring force on the reaction coordinate from the bath, and the reaction coordinate does work on the bath. For statistical trajectories, the cyclohexane falls into either the chair or the boat basin and remains there for the duration of the trajectory. After the first 0.1 ps, the reaction coordinate oscillates about either the chair or boat configuration, and the rate of work being done is much slower than during the initial transient period because the solvation shell has already been made. The work increases with
solvent density because the pressure exerted by the solvent on the cyclohexane increases with solvent density, and the magnitude of the harmonic restoring force increases with increasing pressure.

The work done by the cyclohexane molecule on the bath is dominated by the contribution from the reaction coordinate because only this coordinate experiences a harmonic restoring force from the bath. For the other cyclohexane coordinates, there is no harmonic restoring force from the bath because those coordinates are fluctuating and not held fixed at the beginning of the trajectory like the reaction coordinate. During the first 0.1 ps of the trajectory, the force from the bath on the remaining coordinates increases because the reaction coordinate moves them into a region that interacts strongly with the bath. For some of the trajectories, the force from the bath on these coordinates becomes as large or larger than the intramolecular force. When it is larger than the intramolecular force, the remaining coordinates move in the direction of the bath force. In this case, \( f_2 > 0 \), where \( f \) is the force from the bath on these coordinates and \( f_2 \) is the velocity of the other coordinates. For these trajectories, the net work done on the bath is negative. For trajectories that do not have large forces from the bath on the other coordinates, there will be little or no net work done on the bath because \( f \) and \( f_2 \) are essentially uncorrelated. Hence, the total work done by the remaining coordinates on the bath at short time is negative.

After the transient period, the reaction coordinate no longer moves the remaining coordinates into a region that interacts strongly with the bath. Meanwhile, energy is transferred from the reaction coordinate to these coordinates; they become hot relative to the bath and subsequently transfer energy to the bath. The short-time equilibration dynamics of this system should be a generic feature of complex systems relaxing from a high-energy transition state in a dense fluid.

Figure 3. (a) Work done by the reaction coordinate on the bath, \( W_d(t) \). (b) Work done by coordinates other than the reaction coordinate on the bath, \( W_d(t) \). Both (a) and (b) show statistical trajectories at solvent densities of 1.0, 1.3, 1.4, and 1.5 g/cm\(^3\). Error bars are shown at 0.2, 0.4, 0.6, and 0.8 ps, respectively.

A linear fit to the statistical trajectories determines a rate, \( \gamma \), at which the cyclohexane molecule does work on the bath. In view of the separation of time scales, one may assume that this work is performed during distinct strong encounters between the cyclohexane molecule with solvent molecules. The average energy transferred to the bath per strong event (i.e., per collision), \( \alpha \), and the frequency of these events, \( f \), determine \( \gamma \).

\[
\gamma = \alpha f
\]  

An estimate for \( f \) is the Enskog collision frequency for a hard-sphere mixture. Given a sphere of diameter \( \sigma_a \) at infinite dilution in a solvent of spheres of diameter \( \sigma_c \),

\[
f \approx \frac{1}{\sigma_c} \approx \frac{\rho \sigma^2}{g(\sigma)}
\]

where \( \sigma = (\sigma_a + \sigma_c)/2 \). The Mansoori–Carnahan–Starling formula\(^{20} \) for a hard-sphere mixture yields the contact radial distribution function, \( g(\sigma) \). The hard-sphere diameters are determined by requiring that the isothermal compressibility at room temperature for the neat liquids be given by the Carnahan–Starling expression. The relatively small density dependence of the effective hard-sphere diameters\(^{21} \) is neglected. Available data for density and isothermal compressibility\(^{22,23} \) give \( \sigma_a = 5.41 \) Å and \( \sigma_c = 4.31 \) Å. The best fit in eq 9 is achieved with \( \alpha = 0.075 \) kcal/mol per collision. Figure 4 shows the linear fit to the statistical trajectories from simulation and the \( \gamma \) obtained from the simple theory.

The value of \( \alpha \) indicates that about 10 strong or rare events (so-called "collisions") are required to remove \( k_\beta T \) of energy from the reaction coordinate. The time scale for transferring energy from the reaction coordinate to the bath is therefore roughly 10 times longer than that to randomize the center-of-mass momentum of the molecule. It is in this sense that for this system the coupling between the bath and the reaction coordinate is weak. We have adopted a "collision" model to describe the effects of this weak coupling because of the ease with which density variation can be estimated. In principle, a Langevin model might be equally satisfactory.

While the density dependence of the energy transfer rate for this system is a monotonic function of density, other systems may exhibit more complex behavior. For example, competition between long- and short-range forces can in some systems produce relaxation rates that are nonmonotonic functions of pressure.\(^{24} \) The collision model can be generalized to account for this competition.\(^{25} \) For some systems, there will be more than one reaction coordinate, and it will be useful to examine the work functions for each separately. Irrespective of the
particular interpretation that may be needed to understand the relaxation dynamics of other systems, the general method of analysis adopted in this paper should be applicable provided the topography of the potential energy surface is understood well enough that meaningful reaction coordinates can be identified.

Acknowledgment. This research has been supported by NSF. We have benefitted from discussion with Eckart Bindewald.

References and Notes
(7) Kramers, H. A. Physica 1940, 7, 284.
(20) The contact value of the pair distribution function is given by
\[ g(0) = \eta/(1 - \eta)^{-1}(1 - \eta)((\alpha/\eta)(1 + 2\eta) + (\alpha/\eta)(1 - \eta)) + \eta^2(\alpha/\eta)^2), \]
where \( \eta \) is the packing fraction of the liquid. G. A.; Mansoori, N. F.; Camahan, K. E.; Starling, K. E.; Leland, T. W. J. Chem. Phys. 1971, 54, 1523.