

Raymond KAPRAL¹ and Styliani CONSTA²

¹University of Toronto, Department of Chemistry (Canada)

²University of Western Ontario, Department of Chemistry (Canada)

CLASSICAL AND QUANTUM CHEMICAL RATE CONSTANTS FOR REACTIONS IN CONDENSED PHASES

Received 14 June 2002

ABSTRACT: Methods for the computation of rate constants that characterize quantum and classical reactions occurring in the condensed phase are discussed. While expressions for these transport properties are well known, their computation presents challenges for simulation since reactive events often occur rarely, and the long time scales that are typical for reactive processes are not accessible using simple molecular dynamics methods. Furthermore, the reaction coordinate in a condensed phase system may be a complex many-body function of the system's degrees of freedom. The study of chemical rate processes in quantum mechanical systems presents additional challenges. Except for systems with few degrees of freedom, such quantum rate processes cannot be simulated because of the difficulties in solving the time dependent Schrödinger equation for a condensed phase system. For situations where a quantum rate process takes place in an environment that may be treated classically to a good approximation, mixed quantum-classical approaches provide a route to study such systems. Some of the issues that arise in the theoretical description and computer simulation of rare classical and quantum reactive events are discussed in this paper. [*Chem. Educ. Res. Pract. Eur.*, 2002, 3, 253-268]

KEYWORDS: *chemical rate constants; chemical reactions; condensed matter; projection operator methods; quantum rate coefficients; mixed quantum-classical dynamics; computer simulation methods*

1. INTRODUCTION

An important part of chemistry is the study of the transformations of matter through chemical reactions. The mechanisms by which chemical reactions take place and the rates at which they occur are central aspects of the discipline deserving study. Part of the challenge of chemical kinetics is the unraveling of reaction mechanisms. This is a difficult problem since many mechanisms may be consistent with a phenomenological rate law. If the elementary processes that contribute to mechanism are known, the macroscopic rate equations for the elementary steps are usually assumed to be given by the phenomenological equations of mass action kinetics. These equations express the time rate of change of chemical concentrations (chemical rates) in terms of rate constants times products of chemical concentrations. Experimental techniques exist, and are being developed, that are able to probe reaction dynamics at a (sub)microscopic level. Gas phase reactions have been studied at the molecular level using crossed molecular beams for many years (see standard physical chemistry textbooks, for example, Refs. in [1]). However,

the majority of chemical and biochemical reactions take place in the condensed phase or other complex environments. Solution phase reaction mechanisms can be intricate and may depend in an intimate way on the solvent. Femtosecond optical techniques [2] and other spectroscopies and microscopies are being used to study reactions in liquids and on surfaces [3] at the microscopic level. Such techniques are providing a great deal of insight into how reactions take place on microscopic scales and information on how phenomenological macroscopic descriptions may break down. The challenge for theory in this area is to provide a theoretical underpinning for description of chemical reactions in the condensed phase. These theoretical descriptions may then form the basis for the construction of algorithms for the simulation of reactive dynamics and the computation of chemical rate constants.

Probably the most well-known phenomenological theoretical treatments of condensed phase reactions are Smoluchowski's [4] diffusion equation approach for diffusion-limited reactions and Kramers' [5] Fokker-Planck equation treatment of barrier crossing dynamics. [6] Both of these approaches account for solvent effects through friction or diffusion coefficients. Many current approaches adopt a more molecular point of view and attempt to take into account specific details of the static and dynamic effects of the solvent on the reactive event. Usually, such a program must be implemented through the use of molecular dynamics simulation methods since this is the only way one can treat the details of the intermolecular forces giving rise to both the reactive events and solvent effects on the reaction. In most studies of condensed phase systems, model effective potentials are used to describe the interactions among species and a considerable effort has been devoted to their construction. [7] For small systems it is now possible to use quantum density functional methods to compute the interaction potential in the course of a molecular dynamics simulation and thereby obtain a more realistic treatment of the intermolecular interactions. Methods of this type are especially appropriate for situations when chemical bonds are made or broken.

Since reactive events occur on long time scales one cannot simply carry out a molecular dynamics simulation on a reactive system and hope to see a sufficient number of reactive events to be able to compute the reaction rate. For example, a naive method to compute the rate of a chemical reaction is to simply count how many reactants or products are formed in certain time. Consider a reaction $A \rightleftharpoons B$ and suppose one has chosen some microscopic definition for the A and B species. Then one may carry out a molecular dynamics simulation and count the number $n_{A \rightarrow B}$ of reactive events that occur in time t , taking t sufficiently large to observe a large number of chemical transformations. The reaction rate constant is given by

$$k_{A \rightarrow B} = \frac{n_{A \rightarrow B}}{t}. \quad (1)$$

Such an approach is doomed to fail in most cases since reactive events occur on too long a time scale. Consequently, one must first formulate the statistical mechanics of reactive systems and use the resulting expressions to devise effective simulation methods. This is the topic of this article.

In Sec. II, the derivation of an expression for the classical rate constant is sketched. Quantum rate constants are discussed in Sec. III, while mixed quantum-classical dynamics is the topic of Sec. IV. The conclusions of the paper are given in Sec. V. The discussion of this subject involves some mathematical detail and this paper is not meant to provide uninitiated readers with all details. However, it is hoped that this brief sketch will provide readers with some insight into the issues surrounding the theoretical study of condensed phase rate processes and whet their appetites sufficiently to explore the background literature cited in the text.

2. RATE CONSTANTS FOR CLASSICAL SYSTEMS

Microscopic expressions for chemical rate constants in terms of autocorrelation functions were first derived by Yamamoto [8] in 1960 using linear response theory. These expressions have been re-derived in various ways and form the basis for numerical calculations of rate constants for condensed phase systems. [6, 9] A general method for the derivation of rate laws and rate constants can be formulated using projection operator techniques. [10, 11] This method is summarized below.

The strategy behind this type of calculation relies on the generalization of the classical theory of Brownian motion. [12] If one considers the motion of a Brownian particle with velocity u and mass M in a fluid, according to the phenomenological theory of Brownian motion, the Langevin equation describing its dynamics reads,

$$M \frac{du(t)}{dt} = -\zeta u(t) + f(t), \quad (2)$$

where ζ is the friction coefficient and $f(t)$ is a random force. The random force is taken to be a gaussian random variable with white noise spectrum and is related to the friction constant by the fluctuation-dissipation relation, $\langle f(t)f(t') \rangle = 2k_B T \zeta \delta(t-t')$, where T is the temperature, k_B Boltzmann's constant and $\delta(t)$ is the Dirac delta function. Zwanzig [13] and Mori [14] provided a microscopic derivation of such equations, generalized to any dynamical variable, and relaxed the condition that the random force correlations decay instantaneously as reflected by the δ -function correlations. Such a generalized Langevin equation approach may be used to derive macroscopic rate laws and microscopic expressions for rate constants.

The starting point for such a derivation is the Liouville equation for the evolution of a classical dynamical variable A ,

$$\frac{dA(t)}{dt} = \sum_i \left(\frac{\partial H}{\partial q_i} \frac{\partial A}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial A}{\partial q_i} \right) = \{H, A\} = iLA(t), \quad (3)$$

where the second equality defines the Poisson bracket and the third equality defines the Liouville operator L . Since the Liouville operator does not depend on the time, the solution of this equation is

$$A(t) = e^{iLt} A(0). \quad (4)$$

In applications of the projection operator method, the dynamical variables of the system are separated into two sets: a set of slowly varying variables and a set a rapidly varying variables. A projection operator is constructed that projects the full classical dynamics onto subspace of the slow variables. Let A be the set of slow variables. A projection operator onto A can be constructed in the following way:

$$P = (\cdot, A^*)(A, A^*)^{-1} A, \quad (5)$$

where the notation (\cdot, \cdot) denotes an inner product. The inner product is defined to be an equilibrium average and for any two dynamical variables W and V is given by

$$(W, V^*) = \int W V^* \rho_0 d\Gamma, \quad (6)$$

where ρ_0 is the equilibrium distribution function and $d\Gamma$ is the phase space volume element. When P acts on any dynamical variable, the result is proportional to A : it projects out of the variable the slowly varying component that is parallel to A . The complement of the projection operator P is $Q = 1 - P$ that projects onto the space orthogonal to A .

The generalized Langevin equation is now easily written for the set A of dynamical variables using just two pieces of information. First, since by definition $P + Q = 1$, we may write the Liouville operator as $iL = iPL + iQL \equiv iL_P + iL_Q$. Second, for any operators C and D we have the operator identity,

$$e^{(C+D)t} = \int_0^t d\tau e^{(C+D)\tau} C e^{D(t-\tau)} + e^{Dt}. \quad (7)$$

Then, using these results, we can write

$$\begin{aligned} \frac{dA(t)}{dt} &= e^{iLt} iLA = e^{iLt} iL_P A + e^{iLt} iL_Q A \\ &= e^{iLt} iL_P A + \int_0^t d\tau e^{iL\tau} iL_P e^{iL_Q(t-\tau)} iL_Q A + e^{iL_Q t} iL_Q A, \end{aligned} \quad (8)$$

where we have let $C = iL_P$ and $D = iL_Q$. If we now substitute the definition of the projection operator in eq. (5) we obtain the generalized Langevin equation,

$$\frac{dA(t)}{dt} = i\Omega A(t) - \int_0^t d\tau K(\tau) A(t-\tau) + F(t), \quad (9)$$

where

- $i\Omega = (iLA(0), A^*)(A, A^*)^{-1}$ is termed the frequency matrix;
- $F(t) = e^{iQLt} Q iLA$ is the random force;
- $K(\tau) = -(F(\tau), F^*(0))(A, A^*)^{-1}$ is the memory kernel.

Equation (9) holds for any set of dynamical variables A .

To illustrate the derivation of the macroscopic rate law, consider again the simple situation where two chemical species interconvert,



and recall the phenomenological description of the rate of this reaction. Let the average number of A (B) molecules in the system at time t be $\bar{N}_A(t)$ ($\bar{N}_B(t)$) and their values at chemical equilibrium be \bar{N}_A^{eq} (\bar{N}_B^{eq}). The mass action rate law for this system is

$$\begin{aligned} \frac{d\bar{N}_A(t)}{dt} &= -k_f \bar{N}_A(t) + k_r \bar{N}_B(t), \\ \frac{d\delta\bar{N}_A(t)}{dt} &= -(1 + K_{eq}^{-1}) k_f \delta\bar{N}_A(t). \end{aligned} \quad (11)$$

In the second line of this equation we used the fact that $\delta\bar{N}_B = -\delta\bar{N}_A$ and definition of the equilibrium constant and the detailed balance condition, $K_{eq} = \frac{k_f}{k_r} = \frac{\bar{N}_B^{eq}}{\bar{N}_A^{eq}}$.

To derive this chemical rate law from the microscopic equations of motion, it is only necessary to choose microscopic A variables that correspond to chemical species and substitute these dynamical variables in eq. (9). The choice of microscopic chemical species variables can be a difficult task and some examples will be given below. Suppose we know the microscopic expressions for the dynamical variables N_A (N_B) which correspond to the number of molecules of A (B). These variables depend in general on the positions and momenta of the particles in the system and their average values correspond to the $\bar{N}_A(t)$ ($\bar{N}_B(t)$) that enter the phenomenological rate law. The deviations of these dynamical variables from their average values at equilibrium, \bar{N}_A^{eq} (\bar{N}_B^{eq}), are denoted $\delta N_A = N_A - \bar{N}_A^{\text{eq}}$ ($\delta N_B = N_B - \bar{N}_B^{\text{eq}}$). Substituting δN_A and δN_B for A in eq. (9) we obtain, after some algebra, the generalized Langevin equation for the reactive system,

$$\frac{d\delta N_A(t)}{dt} = -(1 + K_{\text{eq}}^{-1}) \int_0^t d\tau K(\tau) \delta N_A(t - \tau) + F(t), \quad (12)$$

where

$$\bullet K = (F(\tau), (iL\delta N_A)^*)(\delta N_A, \delta N_A^*)^{-1} = (F(\tau), (\delta \dot{N}_A)^*)(\delta N_A, \delta N_A^*)^{-1}.$$

The frequency term in eq. (9) is zero as a result of time reversal symmetry and the random force is given by $F(\tau) = e^{iQL\tau} iL\delta N_A$.

In order to obtain the macroscopic chemical rate law from the generalized Langevin equation we must first construct the equation for the average values of the chemical species numbers. In analogy with macroscopic chemical studies, we suppose that an initial non-equilibrium ensemble is constructed where only the chemical concentrations are specified and all other degrees of freedom are assumed to be in equilibrium. The average of the dynamical variable at time t over this ensemble will be denoted by the same symbol as the average concentration in the phenomenological law, $\bar{N}_A(t)$. The average of the random force is zero in this ensemble since it is orthogonal to the chemical species variables. Finally, if one assumes that the memory kernel decays much more rapidly than the species concentrations, an assumption whose validity rests on the fact that species concentrations are the only slow variables in the system, the chemical species number may be removed from under the integral and the integral extended to infinity. The result of these operations is the macroscopic chemical rate law,

$$\frac{d\delta \bar{N}_A(t)}{dt} = -(1 + K_{\text{eq}}^{-1}) \left[\int_0^\infty d\tau K(\tau) \right] \delta \bar{N}_A(t). \quad (13)$$

By comparison with the phenomenological rate law in eq. (11), one obtains the rate constant as the time integral of the random flux autocorrelation function,

$$k_f = \int_0^\infty d\tau K(\tau). \quad (14)$$

The rigorous definition of the rate kernel involves the propagator e^{iQLt} that involves projected dynamics; however, usually one computes unprojected (natural) evolution where the rate kernel is given by the same expression as for projected dynamics, but the propagator e^{iQLt} is replaced by e^{iLt} . We denote the rate kernel using unprojected dynamics by \tilde{K} . Some care must be used in the evaluation of the rate kernel when this approximation is used since the infinite

time integral of $\tilde{K}(\tau)$ is zero. (For a derivation of this result see Ref. [15, 11]). The computation of the rate constant rests on the existence of a plateau value. If the time scale for the decay of the memory kernel is t_{mic} and that of the chemical concentrations is t_{chem} and these two time scales are widely separated, then one can define a time t^* such that $t_{mic} \ll t^* \ll t_{chem}$. In such a circumstance one may approximate the rate coefficient by

$$k_f \approx k_f(t^*) = \int_0^{t^*} d\tau \tilde{K}(\tau) = \int_0^{t^*} d\tau (\delta \dot{N}_A(\tau), (\delta \dot{N}_A)^*)(\delta N_A, \delta N_A^*)^{-1}. \quad (15)$$

In order to illustrate the use of this formula in a simple context suppose a one-dimensional reaction coordinate $\xi(q_1, q_2, \dots)$ is known and can be used to characterize the passage from A to B species. We have noted that this variable may be a complicated function of the positions of the molecules in the system. The dynamical variable corresponding to species A is $N_A(t) = \theta(\xi(t) - \xi^\ddagger)$ so that when $\xi(t) < \xi^\ddagger$ we have species A and species B for $\xi \geq \xi^\ddagger$. Here $\theta(x)$ is the Heaviside function. In this case the time-dependent rate constant (eq. (15) with $t^* \rightarrow t$) takes the form,

$$k_f(t) = \left(\frac{1}{\bar{N}_A^{eq}} + \frac{1}{\bar{N}_B^{eq}} \right) \langle \dot{\xi} \delta(\xi - \xi^\ddagger) \theta(\xi(t) - \xi^\ddagger) \rangle, \quad (16)$$

where we have performed the time integral to obtain this expression.

In computer simulations, the rate constant is usually computed in two steps. First, the $t = 0$ value of the rate constant is calculated in the following way: suppose we consider a time $t = 0 + \epsilon \equiv 0+$ where ϵ is a small positive number. Equation (16) may be written as

$$k_f^{TST} = k_f(0+) = \left(\frac{1}{\bar{N}_A^{eq}} + \frac{1}{\bar{N}_B^{eq}} \right) \langle \dot{\xi} \delta(\xi - \xi^\ddagger) \theta(\dot{\xi}) \rangle, \quad (17)$$

which is just the transition state theory expression, k_f^{TST} , for the rate constant. [9, 16] The full time-dependent rate constant may then be expressed as,

$$k_f(t) = k_f^{TST} \kappa(t), \quad (18)$$

Here $\kappa(t)$ ($0 < \kappa(t) \leq 1$) is the transmission coefficient. The assumptions that underlie the transition state theory (TST) are discussed in standard physical chemistry textbooks [1]. The transition state of the reaction is found by computing the free energy along the reaction coordinate (RC) ξ . From a knowledge of the free energy at the barrier top and the equilibrium statistical averages in eq. (18) one may calculate k_f^{TST} . One of the assumptions of TST is that the trajectories that arrive at the barrier top with velocities directed towards the product state will end in the product state: recrossings of the free energy barrier are neglected. For reactions in the condensed phase this assumption often breaks down and the recrossing corrections may change the value of the TST estimate. If the changes are too large this signals a poor choice of reaction coordinate. Recrossing corrections are taken into account by the transmission coefficient, $\kappa(t)$, which is computed by monitoring $\theta(\xi(t) - \xi^\ddagger)$ for a large number of trajectories that evolve starting from the barrier top. The transmission coefficient will decay with time and if the time scale separation discussed above exists, the rate coefficient can be determined from the plateau value of $\kappa = \kappa(t^*)$ and the value of k_f^{TST} .

One of the difficulties in the study of the reaction rates is the search for a suitable reaction coordinate. A ‘good’ RC may involve the solvent degrees of freedom in addition to the degrees of freedom of the reacting species. Often it is a challenging problem to find such an RC. Recently, approaches for the computation of the reaction rate without using a reaction coordinate have been explored [17, 18].

2.1 Example: Fragmentation of aqueous droplets containing several sodium ions

An example of a chemical reaction is presented [19] which illustrates the two steps that are used for the computation of the rate constant; i.e., i) the construction of a free energy profile that gives the probability of finding the system with certain values of the reaction coordinate and allows one to compute k_f^{TST} and, ii) the computation of the transmission coefficient.

Consider a small droplet that consists of few hundreds of water molecules and few sodium ions. The droplet fragments because of the repulsive interactions among the sodium ions. For

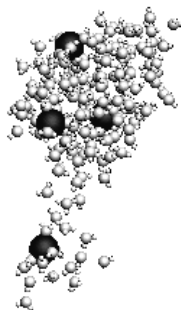


FIGURE 1: *Snapshot of a cluster that consists of 180 water molecules and four Na^+ ions. Large black colored spheres represent Na^+ , small gray spheres, O, and light gray spheres, H. The spheres that represent Na^+ are enhanced to improve visualization.*

certain ratios of number of sodium ions to water molecules the droplet may be stable for several nanoseconds and direct MD simulations indicate that in this case fragmentation is the slowest process in the system. Here a specific cluster size of 180 water molecules and 4 sodium ions is considered. Fragmentation is caused by infrequent shape fluctuations. It is observed that during the fragmentation the shape of the droplet changes dramatically as shown in Fig. 1: an ion protrudes from the droplet while it is still connected by ‘strings’ of water molecules to the remaining part of the droplet. A ‘good’ RC should describe the fluctuations that lead to fragmentation. Since in these fluctuations the entire system participates, a RC is introduced that takes into account the solvent molecules, in addition to the sodium ions. The RC is as follows: a fictitious particle is considered that travels from one sodium ion to another. The particle jumps from molecule i to j with probability P_{ij}

$$P_{ij} = A \exp(-r_{ij}^2/d^2) \quad (19)$$

where A and d are constants determined by few trials in the simulations (typical values used in the simulations are $A = 0.1$ and $d = \sigma$, σ is the diameter of a water molecule). The value of the RC is given by the average first passage time in this fictitious transfer process. When the cluster has a dumbbell shape with ions found in different lobes, many jumps are needed before the fictitious particle finds a path that connects the two ions. In this case the RC has large

value. When the cluster is compact the number of jumps and the value of the RC are smaller. In practice the average number of jumps is found from the transition probability matrix. This reaction coordinate treats all ions equivalently and does not restrict the number of ions that are allowed to leave the cluster. The free energy profile along this RC for a cluster that consists of 180 water molecules and 4 Na^+ is shown in Fig. 2.

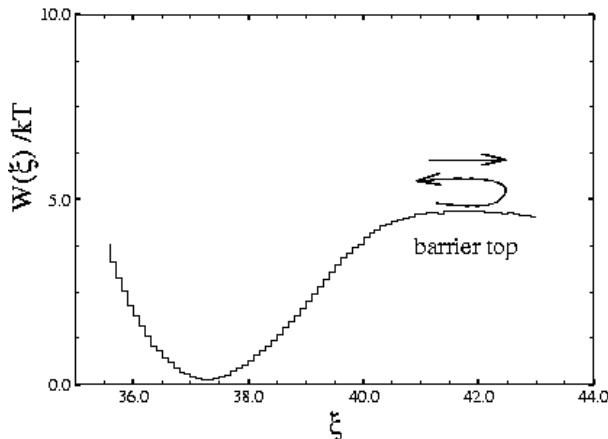


FIGURE 2: Free energy (reversible work) profile (solid line) for a cluster with 180 water molecules that contain 4 Na^+ ions. The staircase form of the curve arises from the histogram method used to determine $P(\xi)$, the probability density to observe a value ξ of the reaction coordinate. The error bar represents $0.2kT$. The arrows at the barrier top are schematic representations of the MD trajectories with velocities towards the products that start at the barrier and may move to the product state or recross and return to the reactants.

Starting from configurations at the free energy barrier top, several thousands of constant energy MD trajectories were evolved for 30 ps. The transmission coefficient shown in Fig. 3 was computed using eq. (18). Figure 3 shows that a plateau is reached after a transient time of 5 ps which is the relaxation time for microscopic molecular motions. The transmission coefficient, $\kappa = 0.05$, is given by the plateau value. The small value of the transmission coefficient indicates that the recrossing corrections are large and consequently corrections to the TST estimate of the rate constant are significant. Analysis of the trajectories may indicate whether the RC describes sufficiently the fluctuations relevant to the reaction.

3. RATE CONSTANTS FOR QUANTUM SYSTEMS

While condensed phase reactions may often be described in terms of classical mechanics, there are many instances where the quantum mechanical character of the system plays an essential role. Examples include ammonia conformational changes that occur as a result of tunneling processes, as well as proton and electron transfer processes. A considerable research effort has been devoted to the study of rate constants in quantum systems (see, for example, Refs. [20]).

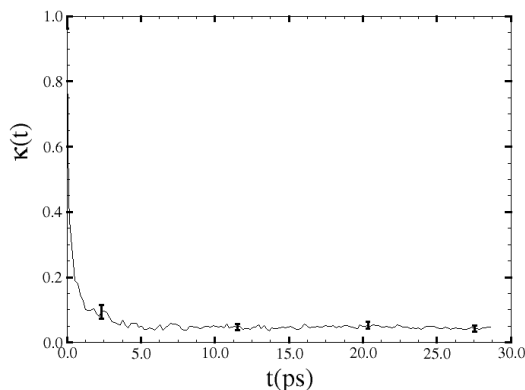


FIGURE 3: *Transmission coefficient $\kappa(t)$ versus time for a cluster of 180 water molecules and four Na^+ ions.*

General expressions for quantum rate constants may be derived using projection operator methods by techniques that parallel those for classical systems. Consequently, here we simply point out some of the differences that arise in quantum mechanics. The dynamical variables corresponding to chemical species are replaced by quantum chemical species operators, \hat{N}_A . We denote an operator by a symbol with a caret. The starting point of the calculation is the quantum mechanical Heisenberg equations of motion for an operator \hat{A} (or the quantum mechanical Liouville equation),

$$\frac{d\hat{A}(t)}{dt} = i\hat{L}\hat{A}(t) = \frac{i}{\hbar}[\hat{H}, \hat{A}], \quad (20)$$

where $\hbar = h/2\pi$ (h is Planck's constant), \hat{H} is the Hamiltonian operator and \hat{L} is the quantum mechanical Liouville operator. One may now carry out calculations like those leading to eq. (15) and the result is [15]:

$$k_f = \frac{1}{i\hbar\beta} \text{Tr}([\delta\hat{N}_A(t^*), \delta\hat{N}_A]\hat{\rho}_{eq})(\delta\hat{N}_A, \delta\hat{N}_A^*)^{-1}. \quad (21)$$

It is necessary to make a few remarks about the nature of the inner product for quantum systems. For classical systems we introduced a nonequilibrium ensemble where only the A dynamical variables deviated from equilibrium. The average of the random force in this ensemble was zero. We want to impose an analogous condition for quantum systems. To this end we suppose that an external force that couples to the \hat{N}_A variable is applied to the system so that the Hamiltonian takes the form, $\hat{\mathcal{H}} = \hat{H} - \hat{N}_A^* \mathcal{F}$. The nonequilibrium canonical distribution for this system is

$$\hat{\rho}_{neq} = \frac{e^{-\beta\hat{\mathcal{H}}}}{\text{Tr}e^{-\beta\hat{\mathcal{H}}}}. \quad (22)$$

If we compute this density to linear order in the external force \mathcal{F} we find,

$$\hat{\rho}_{neq} = \hat{\rho}_{eq} + \int_0^\beta d\lambda e^{-\lambda\hat{H}} \hat{N}_A^* e^{\lambda\hat{H}} \hat{\rho}_{eq}, \quad (23)$$

where

$$\hat{\rho}_{eq} = \frac{e^{-\beta\hat{H}}}{\text{Tr}e^{-\beta\hat{H}}} . \quad (24)$$

If the inner product is defined by

$$(\hat{W}, \hat{V}) = \frac{1}{\beta} \int_0^\beta d\lambda \text{Tr}(\hat{\rho}_{eq} e^{-\lambda\hat{H}} W^* e^{\lambda\hat{H}} \hat{V}) , \quad (25)$$

then the random force will vanish if averaged over this initial nonequilibrium distribution. More extensive discussions of the origin of this Mori inner product may found in Refs. [21] (pp. 28-29 and 100-101) and [15].

4. MIXED QUANTUM-CLASSICAL DYNAMICS

While the quantum expressions for rate constants are the analogs of those for classical systems, it is very difficult to carry out computations using these results except for systems with very few degrees of freedom. Part of the difficulty stems from the fact that it is still practically impossible to compute solutions of the time dependent Schrödinger equation for condensed phase many-body systems. Consequently, many important solution phase reactions where quantum effects play a role cannot be treated in this way. For example, biological systems, where the proton or electron transfer processes that underlie much biological function take place, cannot be treated using full quantum mechanics. As a result of these considerations, one is led to the study of quantum-classical dynamics where certain degrees of freedom (e.g., those for the transferring electron or proton) are treated quantum mechanically but the environment in which these subsystems lie is treated classically. One is now faced with the problem of how to construct a dynamics for quantum-classical systems and formulate the statistical mechanics of these systems.

Starting from the quantum mechanical Liouville equation,

$$\frac{d\hat{\rho}(t)}{dt} = -i\hat{L}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] , \quad (26)$$

the quantum-classical equations of motion may be obtained in the following way. [22, 23] Consider a quantum mechanical system partitioned into two subsystems: the first subsystem contains n particles with masses m and coordinate operators \hat{q} ; the second subsystem comprises N particles with masses M and coordinate operators \hat{Q} . The second subsystem is taken to be an environment or bath with $M \gg m$. The passage to quantum-classical dynamics is made by taking the partial Wigner transform of the quantum Liouville equation. The partial Wigner transformation [24] of the density matrix with respect to the subset of Q coordinates is, [22]

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-3N} \int dz e^{iP \cdot z/\hbar} \langle R - \frac{z}{2} | \hat{\rho} | R + \frac{z}{2} \rangle . \quad (27)$$

In this representation the quantum Liouville equation is,

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} \left((\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W \right) \\ &= -\frac{i}{\hbar} \left(\hat{H}_W e^{\hbar\Lambda/2i} \hat{\rho}_W(t) - \hat{\rho}_W(t) e^{\hbar\Lambda/2i} \hat{H}_W \right) , \end{aligned} \quad (28)$$

where the partially Wigner transformed Hamiltonian is

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R), \quad (29)$$

and \hat{V}_W is the partial Wigner transform of the total potential energy of the system. The operator Λ is the negative of the Poisson bracket operator,

$$\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P. \quad (30)$$

The direction of an arrow indicates the direction in which the operator acts. This transformation has served to replace the coordinate operators of the bath by position and momentum (R, P) variables, the first step towards obtaining a classical description of the bath. Next, we scale distances in terms of the wavelength appropriate for the mass m particles, $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$, where ϵ_0 is a suitable energy unit, scale the momenta of the light and heavy particles by $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$ and $P_M = (M\epsilon_0)^{1/2}$, respectively, and scale time by $t_0 = \hbar/\epsilon_0$. The evolution operator in the quantum Liouville equation may then be expanded in $\mu = (m/M)^{1/2}$ and retaining terms to first order in this quantity we find (in the original unscaled variables), [22]

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} [\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} \left(\left\{ \hat{H}_W, \hat{\rho}_W(t) \right\} - \left\{ \hat{\rho}_W(t), \hat{H}_W \right\} \right) \\ &\equiv -i\hat{\mathcal{L}}\hat{\rho}_W(t). \end{aligned} \quad (31)$$

The last line defines the quantum-classical Liouville operator $\hat{\mathcal{L}}$. The quantum-classical Liouville equation describes the coupled evolution of these two subsystems. As a result of this coupling a purely Newtonian description of the bath dynamics is not possible. Note, however, that if the bath is absent we have the quantum Liouville equation for the quantum subsystem, and, if the quantum subsystem is absent we have the classical Liouville equation for the bath.

The nature of quantum-classical dynamics is clarified if the evolution of the density matrix is expressed in terms of an ensemble of trajectories. Equation (31) is independent of the basis used to represent the quantum subsystem, and any convenient basis may be chosen to study the evolution. We use an adiabatic basis. At each coordinate point R of the classical bath we define the Hamiltonian

$$\hat{h}_W(R) = \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R), \quad (32)$$

whose eigenvalue problem

$$\hat{h}_W(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle, \quad (33)$$

yields the adiabatic states and energies. In this adiabatic basis the density matrix has matrix elements $\rho_W^{\alpha\alpha'}(R, P, t) = \langle \alpha; R | \hat{\rho}_W(R, P, t) | \alpha'; R \rangle$.

Taking matrix elements of Eq. (31) and letting $\rho_W^{\alpha\alpha'}(R, P) = \langle \alpha; R | \hat{\rho}_W(R, P) | \alpha'; R \rangle$, we obtain the adiabatic representation of the equation of motion for the mixed quantum-classical system,

$$\frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} = \sum_{\beta\beta'} -i\mathcal{L}_{\alpha\alpha', \beta\beta'} \rho_W^{\beta\beta'}(R, P, t). \quad (34)$$

The mixed quantum-classical Liouville operator in the adiabatic basis is,

$$-i\mathcal{L}_{\alpha\alpha', \beta\beta'} = (-i\omega_{\alpha\alpha'} - iL_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha', \beta\beta'}. \quad (35)$$

The first term on the r.h.s. is a classical evolution operator containing the mean of the Hellmann-Feynman forces for states α and α' ,

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} \left(F_W^\alpha + F_W^{\alpha'} \right) \cdot \frac{\partial}{\partial P}, \quad (36)$$

where $F_W^\alpha = -\langle \alpha; R | \frac{\partial \hat{V}_W(\hat{q}, R)}{\partial R} | \alpha; R \rangle = -\langle \alpha; R | \frac{\partial \hat{H}_W(R)}{\partial R} | \alpha; R \rangle$ is the Hellmann-Feynman force. If $\alpha = \alpha'$ then

$$iL_{\alpha\alpha} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + F_W^\alpha \cdot \frac{\partial}{\partial P} \equiv iL_\alpha, \quad (37)$$

is the standard classical evolution operator with the Hellmann-Feynman force for state α . The second term on the r.h.s. of Eq. (35) contributes only if $\alpha \neq \beta$ or $\alpha' \neq \beta'$ and is defined by

$$J_{\alpha\alpha', \beta\beta'} = -\frac{P}{M} \cdot d_{\alpha\beta} \left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} - \frac{P}{M} \cdot d_{\alpha'\beta'}^* \left(1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta}, \quad (38)$$

and the quantity $S_{\alpha\beta}$ is defined as

$$S_{\alpha\beta} = (F_W^{\alpha\beta} - F_W^\alpha \delta_{\alpha\beta}) \left(\frac{P}{M} \cdot d_{\alpha\beta} \right)^{-1} = (E_\alpha - E_\beta) d_{\alpha\beta} \left(\frac{P}{M} \cdot d_{\alpha\beta} \right)^{-1}. \quad (39)$$

Here $\omega_{\alpha\alpha'}(R) = (E_\alpha(R) - E_{\alpha'}(R))/\hbar$ and the non-adiabatic coupling matrix element given by

$$d_{\alpha\alpha'} = \langle \alpha; R | \frac{\partial}{\partial R} | \alpha'; R \rangle. \quad (40)$$

This term is responsible for the momentum transfer to and from the bath that accompanies quantum transitions. The quantity $S_{\alpha\beta}$ has appeared in Tully's theory[25, 26] of non-adiabatic surface hopping dynamics as the momentum jump that the bath particles experience when a quantum transition occurs.

Approximate surface-hopping methods have been developed for studying non-adiabatic dynamics. [27, 25, 26, 28, 29, 30] The quantum-classical Liouville equation can be solved by iteration in a power series in J in order to obtain an exact solution for the density matrix in terms of surface hopping trajectories. [22, 31, 33, 32] The first terms of this series are,

$$\rho_W^{\alpha\alpha'}(R, P, t) = e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})t} \rho_0^{\alpha\alpha'}(R, P) + \sum_{\beta\beta'} \int_0^t dt' e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t')} J_{\alpha\alpha', \beta\beta'} e^{-(i\omega_{\beta\beta'} + iL_{\beta\beta'})t'} \rho_0^{\beta\beta'}(R, P) + \dots \quad (41)$$

It is easy to give a physical interpretation of the terms in this solution. Figure 4 shows one of the trajectory segments contributing to the second order term in the series solution for density matrix. We wish to compute the value of the $(\alpha\alpha)$ component of the density matrix at phase point (R, P) at time t . The phase point (R, P) is evolved backward in time on the E_α potential energy surface until time t'' where a quantum transition to adiabatic state β occurs. At this time the operator $J_{\alpha\alpha, \beta\beta}$ acts, for example, to change the state of the second index of the density matrix, $(\alpha\alpha) \rightarrow (\alpha\beta)$; a corresponding continuous change occurs in the bath momentum determined by the momentum derivative in the J operator. States α and β are now coherently coupled. The phase point evolves backward in time on the mean of the E_α and E_β potential energy surfaces between time t'' where the quantum transition occurred and time t' where another quantum transition takes place. During this time interval a phase factor arising from the $i\omega_{\alpha\beta}$ factor accumulates its value and reflects the coherent evolution of

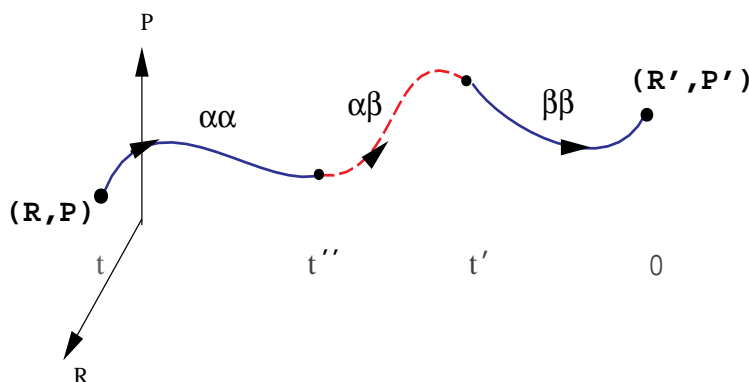


FIGURE 4: Schematic representation of a trajectory that enters into the computation of the density matrix.

the off-diagonal element of the density matrix. At time t' a second quantum transition, e.g., $(\alpha\beta) \rightarrow (\beta\beta)$, occurs. As before the operator $J_{\alpha\beta,\beta\beta}$ determines the nature of this transition and specifies the momentum change in the bath. Due to this second quantum transition the system is once again in a diagonal state $(\beta\beta)$. As a result of this transition back to the diagonal state, no phase factor enters the evolution to time zero on the single adiabatic surface E_β to yield the phase point (R', P') .

The density matrix element at time t can be constructed from an ensemble of such “surface-hopping” trajectories where all possible numbers of quantum transitions to all possible intermediate quantum states at all possible intermediate times are considered. This ensemble of trajectories provides an exact solution of the density matrix in the quantum-classical limit. Surface-hopping methods extend treatments based on simple adiabatic dynamics. In adiabatic dynamics the dynamics takes place on a single potential energy surface and the classical dynamics is Newtonian. The rate constant can be computed using the techniques discussed in Sec. II. Often a classical reaction coordinate may be used; for example, the solvent polarization reaction coordinate [34] has been used to study proton transfer [35] in liquid clusters.

Once the dynamics is known there still remains the problem of the computation of the rate constant. Consequently, in addition to quantum-classical dynamics described above, one must formulate the statistical mechanics of quantum-classical systems to obtain correlation function expressions for the rate constant. The statistical mechanics of quantum-classical systems has been formulated. [33, 23] The use of these quantum-classical correlation function expressions for the computation of condensed phase rate processes is a topic of current research.

5. CONCLUSIONS

The theoretical and computational studies of condensed phase chemical reaction rates address one of the most important aspects of chemistry and chemical physics. Although there has been considerable progress in the field, fundamental problems remain to be resolved. For systems which can be described by classical mechanics, the dynamical description is, in principle,

straightforward since a variety of techniques exist for simulating the classical equations of motion. However, since rate processes are often activated, the choice of a reaction coordinate in a condensed phase system is not always evident. The energy landscape of a many-body system may be complex with many metastable minima. The selection of a (possibly multidimensional) reaction coordinate may be difficult in such cases and the free energy along this multi-dimensional coordinate can exhibit complicated structure. Consequently, challenges for simulation and theory remain.

Mixed quantum-classical dynamics provides a route to simulate quantum rate processes without having to carry out quantum mechanical dynamical simulations on the entire many-body system. The challenges in this area center around the construction of efficient simulation methods for the quantum-classical equations of motion and the computation of transport properties, like the rate constant, for such systems. The quantum-classical equations of motions have properties which differ from both classical mechanics and full quantum mechanics. Further theoretical developments in this field offer many prospects for future research.

We have seen that the theoretical formulation of chemical reaction rates uses concepts from statistical mechanics, quantum mechanics and classical mechanics. The projection methods needed to derive rate constant expressions, while not usually taught in chemistry graduate courses, do not require advanced knowledge and may be introduced easily as part of a physical chemistry course. Using such a formalism one may understand how the phenomenological macroscopic laws of chemical kinetics are obtained from the microscopic equations of motion, either classical or quantum. Furthermore, general microscopic expressions for rate constants are obtained that can be used for either gas phase or condensed phase systems. In suitable limits one can find well known approximate rate constant expressions, such as transition state theory or Kramers' theory expressions. More importantly, the autocorrelation expressions provide the basis for algorithms that can be used in computer simulations of the rate constant. The extensions to quantum processes and, in particular, the introduction of quantum-classical surface-hopping methods will allow one to appreciate the breakdown of adiabatic dynamics and its effect on the reaction rate. As the field matures, it is likely that students will have access to codes that will allow them simulate the effects of non-adiabatic in a classroom setting.

ACKNOWLEDGMENT This research was supported in part by grants from the Natural Sciences and Engineering Research Council of Canada to SC and RK.

CORRESPONDENCE: Raymond KAPRAL, Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada; E-mail: rkapral@gatto.chem.utoronto.ca; Fax number: (416)-978-5325

Raymond KAPRAL is Professor at the Department of Chemistry of the University of Toronto, Canada. He did his Ph.D. at Princeton University and he was Research Associate at Massachusetts Institute of Technology. In 1969 he joined the faculty of the Department of Chemistry of the University of Toronto. Prof. Kapral's research interests are in the area of non-linear dynamics, study of solvent effects in reactions in condensed phase, methods of molecular dynamics for sampling rare events, mesoscopic modeling of condensed phases, development of methods of mixed quantum-classical dynamics. Professor Kapral has received many distinctions and awards: Fellow of the Royal Society of Canada (1996), Fellow of the American Physical Society (1994), of the Chemical Institute of Canada (1996), John C. Polanyi Award (Chemical Society for Chemistry, 1996), Martin Gutzwiller Fellowship of the Max Planck Institute of the

Physics of Complex Systems, Dresden, Germany (2002). Currently, he is in the editorial board of Physical Review E, Theoretical Chemistry Accounts, ChemPhysChem, International Journal of Bifurcation and Chaos.

Styliani CONSTA is Assistant Professor at the Department of Chemistry of the University of Western Ontario (UWO), London, Ontario, Canada. She received her Ph.D. at the University of Toronto and did her postdoctoral studies at AMOLF, The Netherlands. In 1999 she joined the faculty of the Department of Chemistry at UWO. Her research interests are : microscopic modeling of chemical reactions in solution; dynamics of phase transitions; development and applications of efficient Monte Carlo schemes for polymer systems. She has been awarded a Marie Curie Fellowship for postdoctoral studies (Europe, 1997) and Premier's Research Excellence Award (Canada, 2002).

REFERENCES

- [1] R. S. Berry, S. A. Rice, J. Ross, 'Physical Chemistry', 2nd ed. Oxford University Press, 2000; R. J. Silbey and R. .A. Alberty, 'Physical Chemistry', 3rd ed. J. Wiley, 2000; L. M. Raff, 'Principles of Physical Chemistry', 1st ed. Prentice-Hall, 2001;
- [2] A. H. Zewail, 'Femtochemistry : ultrafast dynamics of the chemical bond', World Scientific, New Jersey, Singapore, 1994.
- [3] Bonn, M., S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf and G. Ertl, Science **285**, 1042 (1999).
- [4] Smoluchowski, M. V., Ann. Phys. **48**, 1103 (1915).
- [5] H. A. Kramers, Physica **7**, 284 (1940).
- [6] P. Hanggi, P. Talkner, and M. Borkovec, Reviews of Modern Physics **62**, 251 (1990); R. Kapral, Advances in Chemical Physics, **48**, 71 (1981); J. T. Hynes, in The Theory of Chemical Reaction Dynamics, Vo. IV, edited by M. Baer, p. 171, CRC, Boca Raton, FL, (1985); J. T. Hynes, Journal of Statistical Physics **42**, 149 (1986);
- [7] D. Frenkel and B. Smit, 'Understanding Molecular Simulation', Academic Press, 1996.
- [8] T. Yamamoto, Journal of Chemical Physics **33**, 281 (1960).
- [9] D. Chandler, Journal of Chemical Physics **68**, 2959 (1978).
- [10] R. Kapral, Journal of Chemical Physics **56**, 1842 (1972).
- [11] R. Kapral, S. Consta and L. McWhirter, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, Eds. B. J. Berne, G. Ciccotti, D. .F. Coker, pp. 587-616 (1998).
- [12] S. Chandrasekhar, Reviews of Modern Physics **15**, 1 (1943).
- [13] R. Zwanzig, in Boulder Lectures in Theoretical Physics, Vol. III, p. 106, Wiley-Interscience, New York (1961); R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965); R. Zwanzig, Physical Review **124**, 983 (1961).
- [14] H. Mori, Progress of Theoretical Physics (Kyoto) **33**, 423 (1965); **34**, 399 (1965).

- [15] G. Ciccotti, M. Ferrario, D. Laria and R. Kapral in ‘Progress in Computational Physics of Matter: Methods, Software and Applications’ eds. F. Manghi and L. Reatto (1995).
- [16] D. Chandler, ‘Introduction to Modern Statistical Mechanics’, Oxford University Press (1987);
- [17] L. R. Pratt, Journal of Chemical Physics **85**, 5045 (1986).
- [18] C. Dellago, P. G. Bolhuis, D. Chandler, Journal of Chemical Physics **110**, 6617 (1999).
- [19] S. Consta, to appear in THEOCHEM (2002).
- [20] W. H. Miller, S. D. Schwartz, J. W. Tromp, Journal of Chemical Physics **70**, 4889 (1983); P. Pechukas, ‘Dynamics of Molecular Collisions’ Part B, edited by W. H. Miller (Plenum, New York), p. 269 (1976).
- [21] E. Fick and G. Sauermann, ‘The Quantum Statistics of Dynamic Processes’, Springer-Verlag, 1990.
- [22] R. Kapral and G. Ciccotti, Journal of Chemical Physics **110**, 8919 (1999).
- [23] R. Kapral and G. Ciccotti, *A Statistical Mechanical Theory of Quantum Dynamics in Classical Environments*, in eds. M. Mareschal and P. Nielaba, (Springer, Berlin, 2002).
- [24] E. Wigner: Physical Review **40**, 749 (1932).
- [25] J. C. Tully, Journal of Chemical Physics **93**, 1061 (1990).
- [26] J. C. Tully, Faraday Discussions **110**, 407-419 (1998).
- [27] D. S. Sholl and J. C. Tully, Journal of Chemical Physics **109**, 7702 (1998).
- [28] L. Xiao, D. F. Coker, Journal of Chemical Physics **199**, 8646 (1994).
- [29] D. F. Coker, L. Xiao, Journal of Chemical Physics **102**, 496 (1995).
- [30] E. R. Bittner and P. J. Rossky, Journal of Chemical Physics **103**, 8130 (1995); O. V. Prezhdo and P. J. Rossky, Physical Review Letters **81**, 5294 (1998).
- [31] S. Nielsen, R. Kapral and G. Ciccotti, Journal of Chemical Physics **112**, 6543 (2000).
- [32] D. Mac Kernan, G. Ciccotti and R. Kapral: Journal of Chemical Physics. **106**, (2002).
- [33] S. Nielsen, R. Kapral and G. Ciccotti, Journal of Chemical Physics **115**, 5805 (2001).
- [34] R. A. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1963); R. A. Marcus, Journal of Chemical Physics **43**, 2658 (1965).
- [35] S. Consta and R. Kapral, Journal of Chemical Physics **104**, 4581 (1996); *ibid.* **101** 10908 (1994).