Using $4R_2/F$ for the span of an F-star we obtain $1/12$ for the ratio of the square of the radius of gyration of an F-star to the square of the spherical span. Thus

$$g_s/g_{sp} = 1 \quad \text{(sea urchin model)} \tag{F4}$$

This result is more simply derived if we orient half of the arms in the $+x$ direction and half in the $-x$ direction. Neither the span nor the radius of gyration is changed by this. Then we see immediately that both the numerator and the denominator of eq F1 are equal to $1/12$.

Both of these cases are subsumed by a generalization to a spherically symmetric distribution function of density given by $\rho(r/R_2)$. We assume that in making an F-star from a 2-star we shrink the distribution function according to

$$\rho(r/R_2) \rightarrow (R_2/R_F)^3 \rho(r/R_F) \tag{F5}$$

The F-star distribution function is shrunk down by a factor R_2/R_F

but at each point the density is increased by a factor $(R_2/R_F)^3$. This ensures that the total number of monomer units is the same in both cases. It is easy to see that if the scaling factors R are proportional to spans that the ratio of eq 25 is then equal to 1.

Let us assume that the center of the star is placed at the origin of a coordinate system and let each arm obey Gaussian statistics. Then the radius of gyration squared of each arm is proportional to the arm length as is the span.

$$g_s/g_{sp} = \frac{S^2(n,F)/R^2(n,F)}{S^2(N/2,2)/R^2(N/2,2)} = \frac{A_n/B_n}{A_{N/2}/B_{N/2}} = 1 \tag{F6}$$

This equation is applicable to the theta region where the arms are invisible to each other.

In the collapse region the sizes are not dependent on F so that the ratio equals 1.

Thus we shall presume that eq 25 is an accurate statement over the whole range of our variables.

Time Correlation Function and Path Integral Analysis of Quantum Rate Constants

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The rate constant for infrequent transitions between stable states in a quantum mechanical system is analyzed. A formulation is provided in which the operation of thermal averaging is separated from the quantum dynamics. The former involves the nonlocal or off-diagonal part of the equilibrium density matrix; the latter, which we call the "z factor", involves the imaginary part of a real time population density matrix. Through analyzing several simple models, the qualitative behavior of the z factor is examined. Approximate theories for the z factor provide a means to estimate quantum rate constants without detailed analysis of the true quantum dynamics. A few such theories are proposed and tested for the Eckart barrier.

I. Introduction

In this paper, we present several results concerning the time correlation function expression for a reaction rate constant.[1] In the particular formulation we describe, the thermal averaging or trace operation is separated from quantum dynamics through the introduction of a quantity we call the "z factor". We describe different dynamical models to illustrate the qualitative behavior of this object, and we show that one can approximate the dynamics and the corresponding z factor to make reasonable estimates of the rate constant. These approximations require equilibrium calculations only, i.e., thermal traces. The qualitative features we illustrate may suggest Monte Carlo sampling procedures by which one might efficiently compute the effects of dynamics on the rate constant. Such procedures would provide a legitimate quantum mechanical analogue of transition-state theory.

In section II, the correlation function expression for the rate constant is analyzed, and an expression involving the z factor is derived and related to earlier work. In section III, the behavior of the z factor is examined for several dynamical models and limits. The rate constant for an Eckart barrier is computed in section IV by using some of the model z factors studied in section III. The paper is concluded in section V with a discussion. The Appendix includes an analysis of multidimensional systems more complex than those described in the main text.

II. Correlation Functions

A. Preliminaries. Consider two stable states, A and B, separated by a barrier located at $q = q^*$ as illustrated in Figure 1.

The variable q is the reaction coordinate. We adopt the convention that state A corresponds to $q < q^*$, and hence the population operator is

$$h_A(q) = 1, \quad q < q^*$$
$$= 0, \quad q > q^* \tag{2.1}$$

Similarly, state B corresponds to $q > q^*$, i.e.,

$$h_B(q) = 1 - h_A(q) \tag{2.2}$$

The equilibrium mole fraction of species A is

$$x_A = \langle h_A \rangle \equiv \text{Tr } h_A e^{-\beta H}/Q \tag{2.3}$$

where H is the Hamiltonian and $Q = \text{Tr } \exp(-\beta H)$.

Nonequilibrium concentrations ultimately relax in accord with the fluctuation–dissipation theorem

$$\frac{\Delta c_A(t)}{\Delta c_A(0)} \propto \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\tau \, \langle \delta h_A(-i\tau) \, \delta h_A(t) \rangle \tag{2.4}$$

where $\delta h_A(t) = h_A(t) - \langle h_A \rangle$, with the Heisenberg operator

$$h_A(t) = e^{iHt/\hbar} h_A e^{-iHt/\hbar} \tag{2.5}$$

[not to be confused with $h_A(q) = h_A$], and $\Delta c_A(t)$ is the nonequilibrium average of $\delta h_A(t)$. By assuming that the equilibrium concentration in the vicinity of the barrier is negligible (i.e., the

(1) This article is dedicated to Robert Zwanzig who has helped develop the time correlation function formulation of the theory of irreversible processes. Through his writings, the world has learned how to apply this formulation in an amazing variety of useful ways. See, for example, the historically important and pedagogical review: Zwanzig, R. *Annu. Rev. Phys. Chem.* **1965,** *16,* 67.
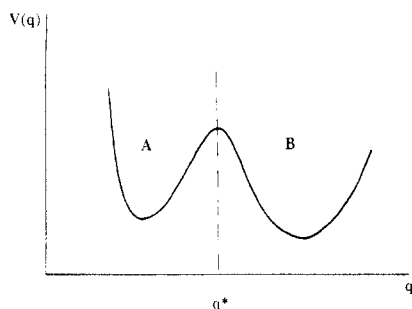
Figure 1. Bistable potential, $V(q)$, with transition surface at $q = q^*$ separating regions of stable states A and B.
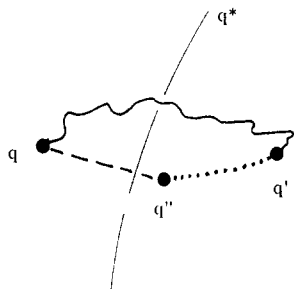

Figure 2. Paths contributing to the rate constant. The solid line depicts the density matrix, $\rho(q,q';\beta)$. The dashed and dotted lines refer to $\langle q|\exp(iH\Delta t/\hbar)|q''\rangle$ and $\langle q''|\exp(-iH\Delta t/\hbar)|q'\rangle$, respectively. The rate constant is obtained from the imaginary part of this diagram after integrating q over all of region A, and sampling q'' and q' over all of region B.

barrier is high), one may show that the proportionality constant for the right-hand side of (2.4) is $(x_A x_B)^{-1} = x_A^{-1}(1 - x_A)^{-1}$.

The negligible concentration of the transition state or barrier region, $q = q^*$, is also associated with the separation of time scales, and this separation of time scales implies the existence of a rate constant.[2] In particular, for a high barrier, there exists a range of plateau times, Δt, which are large compared to transient molecular times, τ_{mol}, yet very small compared to the times between completed reactions. For such times Δt,

$$\frac{\Delta \dot{c}_A(\Delta t)}{\Delta c_A(0)} = -\tau_{rxn}^{-1} = -(k_f + k_b) \qquad (2.6)$$

Therefore, the fluctuation–dissipation theorem along with the detailed balance condition yields

$$k_f = \frac{-1}{\beta \hbar x_A} \int_0^{\beta \hbar} d\tau \, \langle h_A(-i\tau) \, \dot{h}_A(\Delta t)\rangle, \quad \tau_{mol} \ll \Delta t \ll \tau_{rxn} \qquad (2.7)$$

Equation 2.7 is the standard result known since the work of Yamamoto.[3] The curious averaging over imaginary time—the so-called Kubo transform—is often omitted since the complex time correlation function becomes independent of the imaginary time component when $\Delta t \gg \beta \hbar$. We will have more to say about this fact later, but first we will perform the Kubo transform explicitly.

B. Central Result. Due to stationarity,

$$\langle h_A(-i\tau) \, \dot{h}_A(\Delta t)\rangle = -\langle \dot{h}_A(-i\tau) \, h_A(\Delta t)\rangle \qquad (2.8)$$

Therefore, the τ integration in eq 2.5 yields

$$k_f = \frac{1}{x_A}\left\langle \left[\frac{h_A(0) - h_A(-i\beta\hbar)}{i\beta\hbar}\right] h_A(\Delta t)\right\rangle \qquad (2.9)$$

The term in square brackets is like a flux operator. Indeed, for small $\beta\hbar$, the object can be expanded in a Taylor series yielding precisely the flux crossing the surface $q = q^*$. For all values of

$\beta\hbar$, in general, the term in square brackets has the quality of an odd vector quantity, and it constrains quantum paths to pass through the transition surface. This perspective is made explicit by expressing eq 2.9 in terms of matrix elements. The result is

$$k_f = \frac{1}{Q_A}\int dq \int dq' \left[\frac{h_A(q) - h_A(q')}{i\beta\hbar}\right] \langle q'|e^{-\beta H}|q\rangle \langle q|h_A(\Delta t)|q'\rangle \qquad (2.10)$$

where

$$Q_A = \text{Tr } h_A e^{-\beta H} = \int dq \, h_A(q)\langle q|e^{-\beta H}|q\rangle \qquad (2.11)$$

Finally, since the thermal density matrix, $\rho(q,q';\beta) = \langle q|\exp(-\beta H)|q'\rangle$, is real and even on interchange of q and q', and since $\langle q|h_A(\Delta t)|q'\rangle$ is hermitian, we arrive at

$$k_f = \left(\frac{k_B T}{h}\right)\frac{4\pi}{Q_A}\int dq \int dq' \, h_A(q) \, h_B(q') \, \rho(q',q;\beta) \, z(q,q';\Delta t) \qquad (2.12)$$

where

$$z(q,q';\Delta t) = \text{Im } \langle q|h_A(\Delta t)|q'\rangle$$
$$= -\text{Im } \langle q|h_B(\Delta t)|q'\rangle \qquad (2.13)$$

A diagrammatic representation for the integral in eq 2.12 is illustrated in Figure 2.

Equation 2.12 is a central result of this paper. Notice that the z factor involves the *imaginary part* of an off-diagonal population matrix. Imaginary components are associated with currents. Equally pertinent is that imaginary components are associated with commutators. Indeed, since

$$\langle h_A(-i\beta\hbar) \, h_A(t)\rangle = \langle h_A(t) \, h_A(0)\rangle \qquad (2.14)$$

Equation 2.9 also yields

$$k_f = \frac{1}{\beta x_A}\left(\frac{i}{\hbar}\right)\langle [h_A(\Delta t), h_A(0)]\rangle \qquad (2.15)$$

Alternatively, one may start from eq 2.10 and work backwards by integrating over q and q'. This gives

$$Q_A k_f = \text{Tr } e^{-\beta H}[h_B h_B(\Delta t) - h_B(\Delta t)h_B]/i\beta\hbar \qquad (2.16)$$

from which eq 2.15 also follows immediately.

Classical transition-state theory can be viewed as the short-time approximation to the correlation function expression for k_f.[4] We see, however, from eq 2.15, the well-known fact[5] that the $\Delta t \to 0$ limit does not provide an estimate of the quantum mechanical rate.

C. Other Formulas. In the calculation prescribed by eq 2.12, the z factor is purely dynamical and independent of temperature and all the temperature or thermodynamic state dependence is contained in $\rho(q',q;\beta)$. This factorization, however, is not unique. For example, there is another formula that also employs the z factor to compute k_f. This alternative formula follows from eq 2.5 written as

$$k_f = \frac{1}{\beta\hbar x_A}\int_0^{\beta\hbar} dt \, \langle \dot{h}_B h_B(\Delta t + i\tau)\rangle \qquad (2.17)$$

Note that

$$h_B(\Delta t + i\tau) = e^{-\tau H/\hbar}h_B(\Delta t)e^{\tau H/\hbar}$$
$$= h_B(\Delta t) + \dots \qquad (2.18)$$

where the omitted terms involve the commutator of $h_B(\Delta t)$ with the hamiltonian, H. Since transitions between stable states are infrequent, h_B is very nearly conserved, and the omitted com-

(2) Kapral, R.; Hudson, S.; Ross, J. *J. Chem. Phys.* **1970**, *53*, 4387. Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford University Press: New York, 1987; Section 8.3.

(3) Yamamoto, T. *J. Chem. Phys.* **1960**, *33*, 281.

(4) Chandler, D. *J. Chem. Phys.* **1978**, *68*, 2959. See also; Chandler, D. Reference 2.

(5) Costley, J.; Pechukas, P. *Chem. Phys. Lett.* **1981**, *83*, 139.

mutators in (2.18) make negligible contributions to k_f. That is, their relative contributions are of the order of τ_{mol}/τ_{rxn}. Thus, due to the separation of time scales that secures the very existence of k_f, the correlation function in eq 2.17 is independent of τ. As a result,

$$k_f = \frac{1}{x_A}\langle Fh_B(\Delta t)\rangle = \frac{1}{Q_A} \text{Tr } e^{-\beta H}Fh_B(\Delta t) \qquad (2.19)$$

where

$$F = (i/\hbar)[H,h_B] \qquad (2.20)$$

is the flux operator. The operator $h_B(\Delta t)$ is the projector for states occupying region B after the transient time. As such, we recognize eq 2.19 as Miller's quantum reactive flux formula for the thermal rate constant.[6]

Now, to arrive at a formula involving the z factor, we introduce matrix elements in eq 2.19. Standard commutator algebra gives $F = (1/2m)[\delta(q-q^*)p + p\delta(q-q^*)]$, and therefore,

$$\langle q|F|q'\rangle = \frac{1}{2m}\langle q|p|q'\rangle[\delta(q-q^*) + \delta(q'-q^*)] \qquad (2.21)$$

With this representation, eq 2.19 can be written as

$$Q_A k_f = (\hbar/m) \int dq \left[\frac{\partial}{\partial q^*}\rho(q,q^*;\beta)\right]\frac{1}{2i}[\langle q^*|h_B(\Delta t)|q\rangle - \langle q|h_B(\Delta t)|q^*\rangle] \qquad (2.22)$$

or in light of (2.13),

$$k_f = (\hbar/mQ_A) \int dq \, [\partial\rho(q,q^*;\beta)/\partial q^*]z(q^*,q;\Delta t) \qquad (2.23)$$

Equation 2.23 is the alternative expression to which we have referred. An equivalent relation established with integration by parts is

$$k_f = (\hbar/mQ_A) \int dq \, \rho(q,q^*;\beta)[\partial z(q^*,q;\Delta t)/\partial q^*] \qquad (2.23')$$

Equations 2.12 and 2.23 will yield identical results for k_f provided exact evaluations are performed for both the thermal density matrix $\rho(q,q';\beta)$ and the dynamical factor $z(q',q;\Delta t)$. Suppose, however, an approximation is employed when one of these two functions is computed. In that case, the Hamiltonian associated with the thermal density matrix will not commute with that associated with the z factor. As such, the commutation property that allows us to pass from (2.17) to (2.19) would not be satisfied, and eq 2.23 would yield a different k_f than eq 2.12. Therefore, a comparison of rate constants computed from eq 2.12 and 2.23 could be used as a test of the internal consistency of an approximate theory.

III. Model z Factors

The evaluation of the rate constant through either eq 2.12 or 2.23 requires knowledge of the dynamical z factor. In this section we consider its behavior for a few different models.

A. Free Particle. In this case, the dynamics is governed by the Hamiltonian $p^2/2m$, so that

$$\langle q|e^{-iHt/\hbar}|q'\rangle_{free} = (m/iht)^{1/2} \exp[\text{Im } (q-q')^2/2\hbar t] \qquad (3.1)$$

It is then straightforward to show that

$$[z(q,q';\Delta t)]_{free} = -\text{Im}\frac{1}{2\pi}\left\{i \sin\left[\frac{m}{2\hbar\Delta t}(q'^2 - q^2)\right] + \cos\left[\frac{m}{2\hbar\Delta t}(q'^2 - q^2)\right]\right\}\left\{iP\frac{1}{q-q'} + \pi\delta(q-q')\right\} \qquad (3.2)$$

where P denotes Cauchy's principal value. [For notational simplicity, we will generally omit explicit reference to the principal value.] At large Δt we therefore find

(6) Miller, W. H. *J. Chem. Phys.* **1974**, *61*, 1823. Miller, W. H.; Schwartz, S. D.; Tromp, J. W. *J. Chem. Phys.* **1983**, *79*, 4889.

$$z_{free}(q,q';\infty) = \frac{1}{2\pi(q'-q)} \qquad (3.3)$$

Notice that, for free-particle dynamics, large times can literally mean $\Delta t \to \infty$ since, after the transient dynamics, there is no mechanism by which the system can return to the dividing surface.

A suggestive alternative to eq 3.3 is

$$z_{free}(q,q';\infty) = \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar}\theta(p) \sin\left[(q-q')p/\hbar\right] \qquad (3.4)$$

where

$$\theta(p) = 1, \quad p > 0$$
$$= 0, \quad p < 0 \qquad (3.5)$$

In other words, only positive momenta contribute to the free-particle z factor at large times.

It is interesting to note that the z factor is not local. In the semiclassical or stationary phase estimate of $\langle q|h_B(\Delta t)|q'\rangle$, the real part is nonzero for q close to q' only. But the corresponding locality does not occur for the imaginary part as is illustrated explicitly by eq 3.3. On the other hand, as $\beta\hbar^2/m$ becomes small, the thermal density matrix appearing in eq 2.12 or 2.22 does constrain q, q', and q^* to be close together. Indeed

$$\langle q'|e^{-\beta H}|q\rangle = \left\langle \bar{q} + \frac{\Delta q}{2}\middle|e^{-\beta H}\middle|\bar{q} - \frac{\Delta q}{2}\right\rangle$$

$$\sim \rho_{free}(0,\Delta q;\beta) \exp[-\beta V(\bar{q})] \qquad (3.6)$$

Here, $\Delta q = q' - q$, and $\bar{q} = (q + q')/2$, and $V(q)$ is the potential energy. The free particle density matrix is a Gaussian of width $\Delta q \approx (\beta\hbar^2/m)^{1/2}$. If we combine the classical limit, eq 3.6, with the free-particle z factor, eq 3.4, a short calculation beginning with either eq 2.23 or 2.12 yields

$$Q_A k_f \sim \exp[-\beta V(q^*)] \int \frac{dp}{2\pi\hbar}\phi(p)(p/m)\theta(p)$$

$$= (k_B T/h) \exp[-\beta V(q^*)] \qquad (3.7)$$

where $\phi(p) = \exp(-\beta p^2/2m)$ is the unnormalized Maxwell-Boltzmann distribution. Equation 3.7 is the classical transition-state theory rate constant. More will be said about the classical limit in part C below.

B. Parabolic Barrier. In this case, we compute the z factor with the potential energy

$$V_{pb}(q) = V_0 - \frac{1}{2}m\omega_b^2(q - q^*)^2 \qquad (3.8)$$

For notational convenience, take $q^* = 0$. Then

$$\langle q|e^{-iHt/\hbar}|q'\rangle = [m\omega_b/2\pi i\hbar \sinh (\omega_b t)]^{1/2} \exp\{i[m\omega_b/2\hbar \times \sinh (\omega_b t)][(q^2 - q'^2) \cosh (\omega_b t) - 2qq'] - iV_0 t/\hbar\} \qquad (3.9)$$

As a result

$$[z(q,q';\Delta t)]_{pb} = -\text{Im} \int_0^{\infty} dq'' \, [m\omega_b/2\pi\hbar \sinh (\omega_b\Delta t)] \times \exp\{-i[m\omega_b/2\hbar \sinh (\omega_b\Delta t)][(q^2 - q''^2) \cosh (\omega_b\Delta t) + 2q''(q'-q)]\} \qquad (3.10)$$

which in a large Δt limit gives

$$z_{pb}(q,q';\infty) = \frac{1}{2\pi}\frac{1}{(q'-q)} \cos\left[\frac{m\omega_b}{2\hbar}(q^2 - q'^2)\right] \qquad (3.11)$$

Once again, the z factor is nonlocal. Recall that in the rate constant formula, eq 2.12, q is on one side of the barrier, $q^* = 0$, and q' is on the other side. When k_f is computed, the effect of the cosine factor in eq 3.11 is to emphasize configurations where $q = -q'$.

The thermal density matrix for the parabolic barrier is obtained from eq 3.9 by replacing t with $-i\beta\hbar$. The matrix element for this mechanically unstable system exists only for $\beta\hbar\omega_b < \pi$.

Within this high-temperature regime, we can combine the thermal density matrix with eq 3.11 and 2.23 to give

$$[Q_A \exp(\beta V_0) k_f]_{\text{high } T} = (\hbar/m) \int_{-\infty}^{\infty} dq \, \frac{1}{2\pi q} \cos\left(\frac{m\omega_b}{2\hbar} q^2\right) \times$$

$$\left[\frac{m\omega_b}{2\hbar \sin (\beta\hbar\omega_b)}\right]^{3/2} (2q/\pi^{1/2}) \exp\left[\frac{-m\omega_b}{2\hbar} q^2 \cot (\beta\hbar\omega_b)\right]$$

$$= (k_B T/h)\frac{\beta\hbar\omega_b/2}{\sin (\beta\hbar\omega_b/2)} \qquad (3.12)$$

This result—and its multidimensional generalization[7]—is is the standard tunneling correction factor to classical transition-state theory. Unfortunately, its utility is limited to high temperatures. It exhibits an unphysical divergence as $\beta\hbar\omega_b \to 2\pi$ due to the unacceptable statistical thermodynamics of the parabolic behavior, and its derivation requires $\beta\hbar\omega_b < \pi$.

There is an interesting bound that follows from the positivity of the thermal density matrix and the fact that the z factors for the free particle and parabolic barrier differ by a cosine. In particular,

$$\int_{q^*}^{\infty} dq' \int_{-\infty}^{q^*} dq \, \rho(q',q;\beta) \, z_{pb}(q,q';\infty) \leq$$

$$\int_{q^*}^{\infty} dq' \int_{-\infty}^{q^*} dq \, \rho(q',q;\beta) \, z_{free}(q,q';\infty) \qquad (3.13)$$

Hence, the rate constant computed with the free-particle z factor will always be greater than that computed with the parabolic barrier z factor. The divergence of k_f given in eq 3.12 is due to the parabolic barrier density matrix, $\rho_{pb}(q,q';\beta)$, and *not* the z factor, $z_{pb}(q,q';\infty)$. A reasonable speculation is that the replacement of $z(q,q';\Delta t)$ with $z_{free}(q,q';\Delta t)$ will in general yield an upper bound to k_f, but we have only empirical evidence and no rigorous proof.

C. Semiclassical Estimate. Here we derive a semiclassical expression for the z factor of a general one-dimensional model in which the potential energy, $V(q)$, has a barrier of height V_0 at $q = 0$.

The coordinate space representation of the population operator in eq 2.13 can be written as a path integral, given by

$$\langle q|h_B(\Delta t)|q'\rangle = \int_{-\infty}^{\infty} dq'' \, h_B(q'') \int \mathcal{D}q_1(t) \int \mathcal{D}q_2(t) e^{i[S_1-S_2]/\hbar} \qquad (3.14)$$

where the paths $q_1(t)$ and $q_2(t)$ start at q' and q, respectively, and end at q''. The action difference $S_1 - S_2$ is given by

$$S_1 - S_2 = \int_0^{\Delta t} dt \left\{ \frac{m}{2}[\dot{q}_1(t)^2 - \dot{q}_2(t)^2] - V[q_1(t)] + V[q_2(t)]\right\} \qquad (3.15)$$

In the semiclassical ($\hbar \to 0$) limit, there may be several classical trajectories for the coordinates q_1 and q_2 which give the stationary-phase contributions to the path integrals in eq 5.1. For any one of these classical paths between q_1 and q_2, we can expand all other paths about the classical one. With that idea in mind, the general paths in eq 3.14 are written as $q_i(t) = q_i^{cl}(t) + \delta q_i(t)$, where $\delta q_i(t)$ is a fluctuation away from a chosen classical path $q_i^{cl}(t)$. The variables $\delta q_i(t)$ obey the boundary conditions $\delta q_i(0) = \delta q_i(\Delta t) = 0$. Upon inserting this representation of the paths into eq 3.15, integrating by parts, and applying the boundary conditions, one obtains

$$S_1 - S_2 = \int_0^{\Delta t} dt \left\{ \frac{m}{2}[\dot{q}_1^{cl}(t)^2 - \dot{q}_2^{cl}(t)^2] - V[q_1^{cl}(t) + \delta q_1(t)] + V[q_2^{cl}(t) + \delta q_2(t)] + \frac{m}{2}[\delta\dot{q}_1(t)^2 - \delta\dot{q}_2(t)^2] - m[\delta q_1(t)\ddot{q}_1^{cl}(t) - \delta q_2(t)\ddot{q}_2^{cl}(t)]\right\} \qquad (3.16)$$

(7) Wolynes, P. G. *Phys. Rev. Lett.* **1981,** *47,* 968. Pollak, E. *Chem. Phys. Lett.* **1986,** *127,* 178.

If $\hbar$ is small enough, the important path fluctuations $\delta q_i(t)$ will be small enough to allow for a series expansion of $V[q_i^{cl}(t) + \delta q_i(t)]$ through second order in $\delta q_i(t)$, and eq 3.16 may be approximated by

$$S_1 - S_2 \approx$$
$$\int_0^{\Delta t} dt \left\{ \frac{m}{2}[\dot{q}_1^{cl}(t)^2 - \dot{q}_2^{cl}(t)^2] - V[q_1^{cl}(t)] + V[q_2^{cl}(t)]\right\} +$$
$$\int_0^{\Delta t} dt \left\{ \frac{m}{2}[\delta\dot{q}_1(t)^2 - \delta\dot{q}_2(t)^2] - \frac{1}{2}V''[q_1^{cl}(t)] \, \delta q_1(t)^2 + \right.$$
$$\frac{1}{2}V''[q_2^{cl}(t)]\delta q_2(t)^2 \left.\right\} - \int_0^{\Delta t} dt \, \delta q_1(t)\{m\ddot{q}_1^{cl}(t) + V'[q_1^{cl}(t)]\} +$$
$$\int_0^{\Delta t} dt \, \delta q_2(t)\{m\ddot{q}_2^{cl}(t) + V'[q_2^{cl}(t)]\} \qquad (3.17)$$

This expression may be considerably simplified because the expressions in braces in the last two terms satisfy the classical Euler-Lagrange equations and are identically zero for all values of t. Furthermore, for Δt large, the dominant classical trajectories are those with just enough energy to surmount the barrier, and therefore for most times, $q_i^{cl}(t)$ will be close to the barrier top. As a result, the second derivatives of the potential appearing in the second term of eq 3.17 may be replaced by $V''(0)$. The Gaussian path integrals over $\delta q_i(t)$ may then be performed to give the result

$$\langle q|h_B(\Delta t)|q'\rangle \approx \frac{m\omega_b}{2\pi\hbar \, \sinh (\omega_b\Delta t)} \int_{-\infty}^{\infty} dq'' \, h_B(q'') \times$$
$$\exp\{i[S_1^{cl}(q',q'';\Delta t) - S_2^{cl}(q,q'';\Delta t)]/\hbar\} \qquad (3.18)$$

where the S_i^{cl}'s are the classical actions for the trajectories $q_i^{cl}(t)$ and ω_b is the barrier frequency. The imaginary part of (3.18) is the semiclassical z factor. Since the sine function is zero for zero argument, it is clear that the semiclassical z factor is nonlocal in character.

In the general case, the classical actions S_i^{cl} in eq 3.18 are complicated functions of the integration variable q'', presumably requiring a numerical analysis. The function can be treated in an approximate fashion analytically, however, by expanding the actions through first order about $q'' = 0$. Such an approximation allows the integral over q'' to be performed explicitly, giving

$$\text{Im } \{\langle q|h_B(\Delta t)|q'\rangle\} \approx$$
$$\frac{m\omega_b}{2\pi\hbar \, \sinh (\omega_b\Delta t)} \, \frac{\cos \{[S_1^{cl}(q',0;\Delta t) - S_2^{cl}(q,0;\Delta t)]/\hbar\}}{(\partial\Delta S/\partial q'')|_{q''=0}} \qquad (3.19)$$

where ΔS is the difference in classical actions. If the first derivative of ΔS in eq 3.19 is also approximated by expanding it to lowest order in q and q' about $q = q' = 0$, an approximate analytical semiclassical z factor is obtained:

$$[z(q,q';\Delta t)]_{sc} \approx \frac{1}{2\pi(q'-q)} \cos \left\{ \frac{(2m)^{1/2}}{\hbar} \int_0^{q'} dq_1 \, |[V_0 - V(q_1)]^{1/2}| - \frac{(2m)^{1/2}}{\hbar} \int_q^0 dq_2 \, |[V_0 - V(q_2)]^{1/2}|\right\}, \quad \Delta t \text{ large} \qquad (3.20)$$

The barrier energy, V_0, appears in this formula because the long-time paths are those with energy equal to V_0. In view of eq 3.11, we see that this semiclassical z factor is exact for the case of a parabolic barrier. Further, the semiclassical z factor is nonlocal in the variables q and q'.

In the classical $\hbar\beta \to 0$ limit of the rate expression, eq 2.12, q and q' are generally close together since $\rho(q,q';\beta)$ becomes local in that limit [see eq 3.6]. Therefore, over the relevant range of integration, the argument of the cosine in eq 3.20 is approximately zero, and the z factor is effectively the same as the free-particle z factor, eq 3.3. The classical transition-state theory rate constant is thus obtained from the same line of reasoning as that following eq 3.6.
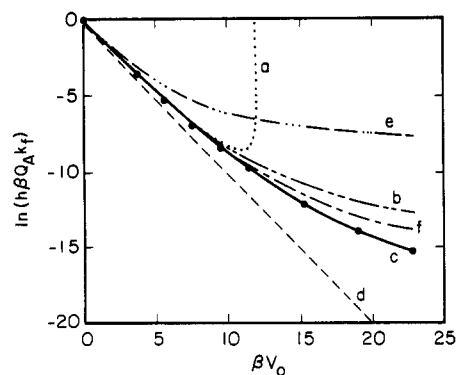
Figure 3. Arrhenius plot of the rate constant for a symmetric Eckart barrier. The parameters are $\alpha = 12$, $u = 2$–12. The straight dashed line (d) is the classical result (classical transition-state theory). The solid line and circles (c) are the exact rate constants (from Johnston, ref 8). Our numerical results use eq 2.12 combined with approximate z factors. The dashed line (f) is for the semiclassical z factor [eq 3.20], the dashed line (b) is for the parabolic barrier z factor [eq 3.11], and the dashed-dotted line (e) is for the free-particle z factor [eq 3.3]. The dotted line (a) is the standard parabolic barrier formula, eq 3.12.

IV. Calculation of k_f with Approximate z factors

In this section we study whether reasonable estimates of the quantum rate constant can be made with approximations to the z factor. In particular, we adopt the z factors derived in the previous section and use them to compute the rate constant for a less trivial model, the Eckart barrier for which Johnston has reported[8] the exact numerical values of k_f. We make no approximations with regard to the thermal density matrix. In this sense, the calculations we report here are in the spirit of classical transition-state theory. We use the comparison of our approximate calculations with the exact results to judge the feasibility of our approach.

The symmetric Eckart barrier is

$$V(q) = V_0 \operatorname{sech}^2 (q/a_0) \tag{4.1}$$

Results for this system are characterized by the two parameters

$$\alpha = 2\pi V_0 / \hbar \omega_b \tag{4.2}$$

$$u = \beta \hbar \omega_b \tag{4.3}$$

where $\omega_b^2 = 2V_0/ma_0^2$, m being the mass of the quantum particle. We have studied this system for various choices of these parameters. Representative results for $\alpha = 12$ with u ranging from 2 to 12 are illustrated in Figure 3. We plot $\ln (\beta h Q_A k_f)$ as a function of βV_0, and the classical result is

$$\ln (\beta h Q_A k_f)_{cl} = -\beta V_0 \tag{4.4}$$

Hence, the deviations from the straight line of slope -1 are the results of quantum mechanics.

The approximate results shown in Figure 3 were computed according to eq 2.12

$$Q_A k_f \approx (4\pi/\beta h) \int_{-\infty}^{0} dq \int_{0}^{\infty} dq' \, \rho(q',q;\beta) \, z_{app}(q,q') \tag{4.5}$$

where $z_{app}(q,q')$ is the approximate z factor taken from either eq 3.3 (the free-particle model), or eq 3.11 (the parabolic barrier model), or eq 3.20 (the analytical approximation to the semiclassical model). The barrier frequency, ω_b, in those equations is taken to be that frequency for the Eckart barrier at its maximum. The thermal density matrix was computed by direct matrix multiplication[9]

$$\rho(q_1,q_P;\beta) = \sum_{q_2,q_3,\cdots q_{P-1}} \prod_{i=2}^{P-1} \rho_{free}(q_i,q_{i+1};\beta/P) \exp[-(\beta/P)V(q_i)] \tag{4.6}$$
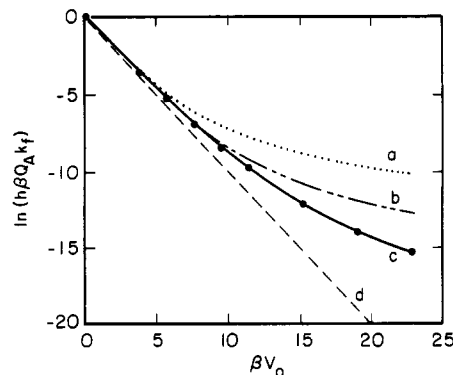
Figure 4. Arrhenius plot of the rate constant for the symmetry Eckart barrier studied in Figure 3. The dashed curve (b) corresponds to eq 2.12 with the z factor approximated with eq 3.11. The dotted curve (a) corresponds to eq 2.23 with the z factor approximated with eq 3.11. The circles and solid line (c) are the exact results, and the straight dashed line (d) is the classical transition-state theory.

where the value of P and the size and number of spatial grid points were adjusted until satisfactory convergence was attained. The remaining integrations over q and q' in eq 4.5 were performed as a two-dimensional quadrature.

Figure 3 also shows the characteristic divergence obtained if the parabolic barrier model is used for *both* the z factor *and* the thermal density matrix, i.e., eq 3.12. No such divergence occurs if the exact thermal density matrix is employed.

In section II, we showed that k_f computed from eq 2.12 will be the same as that computed from eq 2.23 provided the exact z factor is employed. We suggested that a comparison between the the two methods of computation should provide an a priori measure of the errors introduced by an approximate z factor. The apparent correctness of this idea is illustrated in Figure 4. We show there representative results comparing the rate constants obtained from eq 2.12 and 2.23 when in both cases the z factor is estimated from the parabolic barrier formula, eq 3.11.

V. Discussion

The results illustrated in Figures 3 and 4 are encouraging since they suggest that reasonable estimates of a rate constant can be obtained without detailed real time dynamical considerations. The required thermal calculation by, e.g., Monte Carlo integration is a far simpler numerical task than the exact evaluation $z(q,q';\Delta t)$. The latter requires the analysis of phase oscillations, a generally difficult numerical task. A few important issues remain to be resolved, however, if the present analysis is to become generally useful for treating realistic systems.

First, this paper omits any systematic method for creating or adjusting model z factors to best represent the effects of the exact z factor—something akin to variational transition-sate theory used so successfully in classical theory.[10] The importance of this issue is appreciated for systems as simple as a one-dimensional but asymmetric Eckart barrier. One might expect that a reasonable approximation would again be eq 4.5 with, for example, the parabolic barrier placed at the maximum of the asymmetric Eckart potential, and with the curvature of the model potential also coinciding with that of the Eckart potential at its maximum. At low temperatures, however, this choice of parabolic barrier is rather arbitrary since $\rho(q,q';\beta)$ is then highly nonlocal as is the z factor too. In fact, when we apply this "reasonable" but arbitrary approximation to a highly asymmetric Eckart barrier at very low temperatures, the calculation gives the totally unacceptable prediction of negative "rates". Clearly, a physically motivated procedure is needed to correct this deficiency.

(8) Johnston, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966; p 44.

(9) Thirumalai, D.; Bruskin, E. J.; Berne, B. J. *J. Chem. Phys.* **1983**, *79*, 5063.

(10) For a review, see: Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985.

Presumably, a physical criterion for adjusting the model used in an approximate z factor will also provide an indication of appropriate models for the dynamics of high-dimensional systems. If a separable model is used for the z factor, the formula for the rate constant is then eq 4.5 with the reduced thermal density matrix

$$\rho(q',q;\beta) = \int dR \ \langle q',R|e^{-\beta H}|q,R\rangle \tag{5.1}$$

where R denotes all variables other than that identified as the reaction coordinate in the separable model. In other words, when a separable dynamical model is adopted for the z factor, the problem of computing the rate constant is then diagonal in all variables except the reaction coordinate.

Perhaps the principal qualitative feature of the z factor is its nonlocal character. It suggests the favorable geometry of paths contributing to the rate constant are approximately rings with centroids at or near the barrier since other arrangements lead to rapid oscillatory weights. This favorable geometry is precisely that of the instanton paths[11] first introduced by Miller in a semiclassical version of quantum transition-state theory.[12] It is also the geometry suggested by Gillan in his formulation of quantum rate theory.[13] Gillan's requirement that the "center of gravity" of an imaginary time path be located at the transition state is roughly equivalent to the instantonic path (periodic orbit on the upside down potential energy surface). Inspection of his rules for prefactors, however, shows that Gillan's formulation fails to capture the correct high-temperature transition-state theory limit. Miller's version, on the other hand, is manifestly classical transition-state theory for small $\beta\hbar$. In this context, it is also worth stressing that the computation of k_f is *not* primarily the computation of the *local* density at the barrier top, $\rho(q^*) = \rho(q^*,q^*;\beta)$. This local object at low temperatures is dominated by paths that do not pass from one stable state to the other. In Miller's theory and also Gillan's proposal, one discards these contributions and considers only the instantonic circuits that pass between A and B. This geometry is evidently correct as indicated by the favorable geometry of our analysis herein.

It may be possible to derive a more precise connection between an approximate nonlocal z factor and Miller's algorithm for computing quantum rate constants. That connection would suggest a sampling method by which the exact z factor could be computed from a Monte Carlo procedure directed by the approximate model. We believe that the connection might also provide the physical criterion alluded to at the beginning of this discussion.

Appendix

We discuss here the z-factors for cases of multidimensional systems.

A. Two Localized States Coupled to a Bath. As one illustration, consider a reaction coordinate r coupled to a bath of other variables which we denote by R. Further, imagine that r is primarily confined to one of two localized regions A or B. The two different wave functions, $\Psi_A(r) = \langle r|A\rangle$ and $\Psi_B(r) = \langle r|B\rangle$, are highly localized in the two different regions of space. The projectors $|A\rangle\langle A|$ and $|B\rangle\langle B|$ serve as the population operators h_A and h_B, respectively. The Hamiltonian for this system is

$$H = |A\rangle H_A\langle A| + |B\rangle H_B\langle B| + V(|A\rangle\langle B| + |B\rangle\langle A|) \tag{A.1}$$

where H_A, H_B, and V depend upon the bath variables. The energetically favorable configurations of region A are well sep-

arated from those of region B. Therefore, the coupling of the two states, V, is small in some sense.

As a concrete example, this model can correspond to a charge transfer or mixed valence system.[14] States $|A\rangle$ and $|B\rangle$ then denote two localized redox states. The variable r is the position of an electron which jumps from the site A to site B, and R stands for the configurations of the nuclei. The so-called "diabatic" Hamiltonian in the charge-transfer example is (A.1) with the coupling, V, set to zero. In the Condon approximation, V would be taken to be independent of R, though we do not utilize this simplification in what follows.

The rate constant for A to B transitions is given, for example, by eq 2.16. Upon repeated insertion of the completeness relationship in the mixed coordinate/state space representation

$$1 = \sum_{i=A}^{B} \int dR \ |i,R\rangle\langle i,R| \tag{A.2}$$

one finds

$$Q_A k_f =$$
$$\frac{2}{\beta\hbar} \int dR \int dR' \ \langle B,R'|e^{-\beta H}|A,R\rangle \ \mathrm{Im} \ \{\langle A,R|h_B(\Delta t)|B,R'\rangle\} \tag{A.3}$$

The z factor is therefore

$$z(A,R;B,R') = \mathrm{Im} \ \{\langle B,R|e^{iH\Delta t/\hbar}h_B e^{-iH\Delta t/\hbar}|A,R'\rangle\} \tag{A.4}$$

In the full coordinate representation

$$z(A,R;B,R') = \int dr \int dr' \ \Psi_A(r) \ \Psi_B(r') \ z(r,R;r',R') \tag{A.5}$$

Once again, we see that the z factor is nonlocal with the largest contributions to the integrals over r and r' coming primarily from the energetically favorable configurations for regions A and B, respectively.

For very small V, the propagators in eq A.4 can be expanded perturbatively as

$$e^{\pm iHt/\hbar} = e^{\pm iH_0 t/\hbar} \pm$$
$$(i/\hbar) \int_0^t dt' \ e^{\pm iH_0(t-t')/\hbar} V(|A\rangle\langle B| + |B\rangle\langle A|)e^{\pm iH_0 t'/\hbar} + \ldots \tag{A.6}$$

where H_0 is the Hamiltonian (A.1) with $V = 0$. A similar expansion can be used for the thermal density operator, $\exp(-\beta H)$. By retaining only those terms to lowest order in V, eq A.3 gives

$$Q_A k_f = (2/\hbar^2) \ \mathrm{Re} \ \left\{ \frac{1}{(\beta\hbar)} \int_0^{\beta\hbar} \times \right.$$
$$\left. \int_0^t d\tau \int_0^{\Delta t} dt \ \mathrm{Tr} \ e^{-\beta H_A}(e^{\tau H_A/\hbar} V e^{-\tau H_B/\hbar})(e^{itH_B/\hbar} V e^{-itH_A/\hbar}) \right\} \tag{A.7}$$

The τ integration, which arises from the perturbation expansion of the density operator, is inconsequential as can be shown by expressing the trace in terms of the eigenstates of H_0. In particular, for large enough Δt, eq A.7 gives

$$Q_A k_f = (1/\hbar^2) \int_{-\infty}^{\infty} dt \ \mathrm{Tr} \ e^{-\beta H_A} V_{AB}(0) \ V_{BA}(t)$$
$$= (2\pi/\hbar)\sum_{\alpha,\gamma} e^{-\beta E_{A\alpha}}|\langle\alpha,A|V|\gamma,B\rangle|^2 \delta(E_{A\alpha}-E_{B\gamma}) \tag{A.8}$$

where $V_{BA}(t)$ is an abbreviation for the operator $\exp(itH_B/\hbar)V \exp(-itH_A/\hbar)$, $|\alpha,A\rangle$ and $|\gamma,B\rangle$ are eigenstate vectors for the dynamical operators R when r is in the A and B regions, respectively, the eigen energies corresponding to these state vectors

(11) Coleman, S. In *The Whys of Subnuclear Physics*; Zichichi, A., Ed.; Plenum: New York, 1979.
(12) Miller, W. H. *J. Chem. Phys.* **1975**, *62*, 1899.
(13) Gillan, M. J. *J. Phys. C: Solid State Phys.* **1987**, *20*, 3621.

(14) Ulstrup, J. *Charge Transfer Processes in Condensed Media*; Springer-Verlag: New York, 1979.

are $E_{A\alpha}$ and $E_{B\gamma}$, and eq A.8 is the standard golden rule formula for a rate constant.[14,15]

B. Adiabatic Separation of Variables. In this example we imagine $q = (r,R)$ where the reaction coordinate r is a fast variable influenced adiabatically by the remaining variables which we denote by R. The adiabatic states are $|R\rangle \otimes |n;R\rangle$, where $\langle r|n;R\rangle$ is the nth energy eigenfunction for r parametrized by R. The expectation values of the population operators in those states are

$$h_A^{(n)}(R) = \int dr \ \Psi_n^*(r;R) \ h_A(r) \ \Psi_n(r;R)$$

$$= 1 - h_B^{(n)}(R) \qquad (B.1)$$

From eq 2.12, therefore, the rate constant for A → B transitions within the nth adiabatic state is

$$Q_A^{(n)} k_f^{(n)} = (2/\beta\hbar) \int dR \int dR' \ \rho_n(R,R';\beta) \ h_A^{(n)}(R) \ h_B^{(n)}(R') \times$$
$$\text{Im} \ \langle R|e^{iH_n\Delta t/\hbar} h_B^{(n)} e^{-iH_n\Delta t/\hbar}|R'\rangle \qquad (B.2)$$

where H_n is the nth adiabatic state Hamiltonian operating on R, $\rho_n(\beta) = \exp(-\beta H_n)$, and $Q_A^{(n)} = \int dR \ \rho_n(R,R;\beta) h_A^{(n)}(R)$.

A semiclassical approximation to the matrix element in eq B.2 is given by the Weyl correspondence rule,[16]

$$\langle R|e^{iH_n\Delta t/\hbar} h_B^{(n)} e^{-iH_n\Delta t/\hbar}|R'\rangle \approx$$
$$\int_{-\infty}^{\infty} \frac{dP}{2\pi\hbar} e^{iP(R-R')/\hbar} h_B^{(n)}[\Delta t;P,(R+R')/2] \qquad (B.3)$$

where $h_B^{(n)}[t,P,\bar{R}]$ denotes the population as a function of time for a classical system evolving with Hamiltonian H_n where the initial phase space point is the momentum and conjugate coordinate P and $\bar{R}$, respectively. [For notational convenience, eq B.3 is written as if R were one dimensional; multidimensional generalizations are obvious.] Hence, the z factor for this case is

$$z^{(n)}(R,R';\Delta t) \approx \int_{-\infty}^{\infty} \frac{dP}{2\pi\hbar} \sin \ [P(R-R')/\hbar] h_B^{(n)}[\Delta t;P,\bar{R}]$$
$$(B.4)$$

where $\bar{R} = (R' + R)/2$.

In the classical limit, the thermal density matrix in eq B.2 becomes localized with R close to R' since the dispersion of $R - R'$ is $\beta\hbar^2/M$, where M is the mass associated with the variable R. To analyze that limit, we can therefore use

$$\rho_n(R,R';\beta) \approx \rho_{\text{free}}(R-R';\beta) \ \exp[-\beta V_n(\bar{R})] \qquad (B.5)$$

which is asymptotically correct for small β. Here, $V_n(R)$ is the potential energy function for R in the nth adiabatic state, and we have noted that the Gaussian free-particle density matrix is a function of $R - R' \equiv \Delta R$ only. Thus, the classical limit gives

$$Q_A^{(n)} k_f^{(n)} =$$
$$(2/\beta\hbar) \int d\bar{R} \ \frac{1}{2\pi\hbar} \int dP \int d\Delta R \ \exp[-\beta V_n(\bar{R})] \rho_{\text{free}}(\Delta R;\beta) \times$$
$$\sin \ (P\Delta R/\hbar) h_A^{(n)}(\bar{R}+\Delta R/2) \ h_B^{(n)}(\bar{R}-\Delta R/2) \ h_B^{(n)}[\Delta t;P,\bar{R}]$$
$$(B.6)$$

The ΔR integration is facilitated by the expansion

$$h_A^{(n)}(\bar{R}+\Delta R/2) \ h_B^{(n)}(\bar{R}-\Delta R/2) =$$
$$h_A^{(n)}(\bar{R}) \ h_B^{(n)}(\bar{R}) - \frac{\Delta R}{2} \frac{d}{d\bar{R}} h_B^{(n)}(\bar{R}) + O((\Delta R)^2) \quad (B.7)$$

The first term of this expansion inserted into (B.6) gives zero, and the ΔR integration with the second term is evaluated easily to give

$$Q_A^{(n)} k_f^{(n)} = \int dP \int d\bar{R} \ \phi_{MB}(P) \ \exp[-\beta V(\bar{R})](P/M) \times$$
$$\left[\frac{d}{d\bar{R}} h_B^{(n)}(\bar{R})\right] h_B^{(n)}[\Delta t;P,\bar{R}] \quad (B.8)$$

where $\phi_{MB}(P) \propto \exp[-\beta P^2/2M]$ is the normalized Maxwell–Boltzmann distribution.

Equation B.8 is recognized as the well-known classical reactive flux expression[3,4,17] for a rate constant. It should be noted, however, that $h_B^{(n)}(R)$ is a continuous function. While its derivative can be strongly peaked in a small region of R space—the transition region—$dh_B^{(n)}(R)/dR$ is never precisely a delta function. Thus, the right-hand side of (B.8) evaluated in the $\Delta t \to 0^+$ limit gives zero, and it does not produce to the transition-state theory approximation to k_f. The transition-state theory approximation is $h_B^{(n)}[\Delta t;P,\bar{R}]$ replaced by the Heaviside step function, $\theta(P)$. This replacement coincides with a zero time limit of the classical reactive flux correlation function only when one adopts the somewhat *arbitrary* convention of a step function for a population operator. The true rate constant is independent of the precise definition of the population operator provided the operator totally envelops the energetically accessible regions of the stable state. Ambiguities associated with nearly inaccessible regions are irrelevant provided k_f is evaluated exactly by performing the prescribed dynamical calculations.

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(16) Weyl, H. *Z. Phys.* **1927**, *46*, 1. See also: McCoy, N. H. *Proc. Natl. Acad. Sci. U.S.* **1932**, *18*, 674.

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Green–Kubo Relations for Lattice Gas Cellular Automata

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The correlation function description of transport in simple fluids is applied to discrete lattice gas cellular automata. The linearized hydrodynamic equations are derived to Navier–Stokes order and transport coefficients are identified in terms of Green–Kubo time correlation function expressions.

1. Introduction

The use of lattice gas cellular automata as microscopic dynamical models for macroscopic fluid dynamics has been illustrated in many recent applications.[1] Although a primary objective for developing cellular automata was to provide a computational tool for fluid dynamics, they have an additional intrinsic interest at the more microscopic level as well. In many respects, the correspondence between these dynamical models and those for real

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(1) For recent developments see: *Complex Syst.* **1987**, *1*, no. 4.