TABLE II. Bend potential (kcal/mol, relative to collinear energy at same level) for F(3.069 a_0)H(1.43 a_0)H with an $E+(3d\,1f,1p1d)$ basis as a function of bond angle in degrees.

Level \ Angle	175	150	130	120	110	100
Variational[a]	0.04	0.10	0.01	0.05	0.20	0.54
$+Q_D$[b]	0.04	0.08	− 0.14	− 0.20	− 0.17	0.00
SEC[a]	0.04	0.06	− 0.27	− 0.41	− 0.51	− 0.51

[a] Reference 11.
[b] Present.

and SEC estimates, indicating a consistent trend with the collinear results. These calculations give us more confidence in the basic correctness of the trends obtained by the SEC method.

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Activated barrier crossing for many degrees of freedom: Corrections to the low friction Kramers result[a]

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Recent studies of activated barrier crossing of a Brownian particle in a metastable potential have extended Kramers treatment[1] of the low friction regime to an arbitrary number n of strongly coupled degrees of freedom.[2–4] As for a single degree of freedom the rate constant is proportional to the damping rate γ at low γ. Here we evaluate the corrections to this result and show that the rate constant behaves as $\gamma(1-\text{const}\,\gamma^{1/(n+1)}+\cdots)$. As n increases such correction terms become increasingly important and they will substantially diminish the rate constant in a physically accessible low friction regime.

The theory of unimolecular reactions in the gas phase[5] reduces to the weak collision limit for a Brownian particle.[2,4] The probability density $P(E,t)$ for finding a reactant molecule with n strongly coupled degrees of freedom with an energy E is described by an energy diffusion equation[2,4]

$$\frac{\partial P(E,t)}{\partial t}=-\frac{\partial j_E}{\partial E}-k_{\mathrm{RRKM}}(E)P(E,t)\,, \tag{1}$$

where the energy flux is

$$j_E=-D(E)P_{\mathrm{eq}}(E)\,\frac{\partial\,[P(E,t)/P_{\mathrm{eq}}(E)]}{\partial E}\,. \tag{2}$$

For simplicity consider a harmonic density of states and an isotropic Markovian friction kernel with an energy diffusion coefficient $D(E)=\gamma k_B TE$ and an equilibrium distribution function $P_{\mathrm{eq}}(E)\propto E^{n-1}e^{-\beta E}$ with $\beta=1/k_BT$. Nevertheless, our arguments are independent of these assumptions and apply to arbitrary potentials and to non-Markovian friction kernels.

The dissociation rate above the barrier threshold Q is approximated by the RRKM expression[5]

$$k_{\mathrm{RRKM}}(E)=\frac{1}{2\pi}\,\frac{\Pi_i\omega_i^{(0)}}{\Pi_i\omega_i^{(s)}}\left(\frac{E-Q}{E}\right)^{n-1} \tag{3}$$

for $E>Q$ and $k_{\mathrm{RRKM}}(E)=0$ for $E\leqslant Q$. The frequencies of the stable normal modes $\omega_i^{(0)}$ and $\omega_i^{(s)}$ are evaluated in the reactant well and at the saddle point, respectively. Equation (1) describes the activation process of the molecule to an energy $E>Q$ whereupon it dissociates in accordance with RRKM theory.

The overall reaction rate constant is obtained by solving Eq. (1) for the normalized steady state distribution $P_{\mathrm{ss}}(E)$. The rate constant is equal to the constant steady state flux j_E below threshold. At high damping the energy activation is so rapid that $P_{\mathrm{ss}}(E)=P_{\mathrm{eq}}(E)$ above threshold and the flux is obtained by averaging Eq. (3) over $P_{\mathrm{eq}}(E)$, giving the transition state theory[4,5] result for the rate constant[6]

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$$k_{\mathrm{TST}} = \frac{1}{2\pi} \frac{\Pi_i \omega_i^{(0)}}{\Pi_i \omega_i^{(s)}} e^{-\beta Q}. \tag{4}$$

Below threshold ($E \leqslant Q$) the general steady state solution of Eq. (1) is

$$h(E) = j_E \int_E^Q dE \frac{1}{P_{\mathrm{eq}}(E) D(E)} + C_1, \tag{5}$$

where $h(E) = P_{\mathrm{ss}}(E)/P_{\mathrm{eq}}(E)$ and C_1 is an unknown constant. Unfortunately above threshold ($E > Q$) Eq. (1) cannot be solved in general. However, the low friction limit can be analyzed easily. Since particles above the threshold disappear with a finite dissociation rate, the threshold becomes an absorbing boundary in this limit, i.e., $C_1 = 0$. For high barriers[7] the rate constant in the low fiction limit becomes[2–4]

$$k_{\mathrm{low}} = \gamma \frac{(\beta Q)^n}{(n-1)!} e^{-\beta Q}. \tag{6}$$

However we can solve Eq. (1) for $E > Q$ at low damping more carefully. In the steady state, for high barriers, Eq. (1) simplifies to

$$z \frac{d}{dx} \left[e^{-x} \frac{dh(x)}{dx} \right] = \frac{x^{n-1}}{(n-1)!} e^{-x} h(x), \tag{7}$$

where $x = \beta(E - Q)$ and

$$z = \frac{k_{\mathrm{low}}}{k_{\mathrm{TST}}}. \tag{8}$$

The substitution $h(x) = \sqrt{x}\, e^{x/2} f(x)$ and $y = [4x^{n+1}/z(n-1)!(n+1)^2]^{1/2}$ transforms Eq. (7) into

$$y^2 \frac{d^2 f}{dy^2} + y \frac{df}{dy} - [(n+1)^{-2} + y^2 + c_n (zy^2)^{2/(n+1)}] f = 0, \tag{9}$$

where c_n is an unimportant numerical constant. Since z vanishes at low γ [cf. Eq. (6)] the z-dependent term in Eq. (9) can be dropped. Up to a proportionality constant C_2 the solution of the resulting equation[8] is a modified Bessel function $K_{1/(n+1)}(y)$. The undetermined constants C_1 and C_2 can be eliminated by matching $h(E)$ and its derivative at $E = Q$. The rate constant becomes[9]

$$\frac{k}{k_{\mathrm{TST}}} = z(1 - a_n z^{1/(n+1)} + \cdots), \tag{10}$$

where

$$a_n = [(n+1)^2 \Gamma(n)]^{1/(n+1)} \Gamma\left(\frac{n+2}{n+1}\right) \Big/ \Gamma\left(\frac{n}{n+1}\right)$$

and $\Gamma(x)$ is the Gamma function.[8] Some values of a_n are given in Table I. Similar analysis can be done for the symmetrical double well problem. Again one obtains Eq. (10) but z has to be replaced by $z/2$.

For a single degree of freedom ($n = 1$) the present unimolecular RRKM theory is essentially equivalent to the original approach to this problem.[10] Both approaches predict that the rate constant behaves as $\gamma(1 - \mathrm{const}\sqrt{\gamma} + \cdots)$ at low γ. Recent work[11] shows that RRKM theory overestimates the coefficient a_1 in Eq. (10). We include the accurate values of a_1 in Table I for comparison.

For n degrees of freedom the rate constant behaves as $\gamma(1 - \mathrm{const}\, \gamma^{1(n+1)} + \cdots)$ at low γ. As for a single degree of freedom[11] we expect small modifications of the numerical coefficients a_n in Eq. (10) for higher n. It would be interesting to investigate possible extensions of this analysis to an arbitrary number of degrees of freedom. As γ is decreased the low friction limit of the rate constant, Eq. (6) will be approached extremely slowly and such corrections become increasingly important for larger n. This has already been clearly recognized in numerical studies of unimolecular rate constants for weak collision models.[12] Such a slow approach[13] to the low collision limit must be included for the interpretation of experimental or simulation data. Otherwise data collected over a limited friction range might lead to errorenous conclusions about the number of strongly coupled vibrational modes.

TABLE I. Numerical coefficients a_n for the corrections to the Kramers low friction result. The second column is the present prediction [Eq. (10)] for n strongly coupled degrees of freedom based on the energy diffusion equation and RRKM theory which is used to approximate the dynamics on the potential surface [cf. Eq. (1)]. This theory predicts equal coefficients for a metastable well and the symmetrical double well. The last two columns show the accurate results for a single degree of freedom (Ref. 11) based on the true dynamics on the potential surface.

n	RRKM theory	Metastable well (Ref. 11)	Double well (Ref. 11)
1	1	0.824	0.683
2	1.372		
3	1.759		
4	2.148		
5	2.536		

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ory sets $\alpha = 1$. Treating α as an adjustable parameter their approach can yield a correct coefficient a_1 in Eq. (10), that is one in agreement with Ref. 11. Unfortunately then $\alpha > 1$ and their approach incorrectly yields a rate constant which is larger than the transition state value in the high friction limit. The improved analysis given in Ref. 11 does not suffer from this drawback.

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[13] Another reason why the rate constant might approach the low collision limit extremely slowly could be due to weak coupling between the vibrational modes. For a damping rate γ larger than the rate of energy exchange between the vibrational modes, the reaction rate constant will be approximately given by Eq. (6) with $n = 1$. For a discussion see J. E. Straub and B. J. Berne, J. Chem. Phys. **85**, 2999 (1986); M. Borkovec, J. E. Straub, and B. J. Berne, *ibid.* **85**, 146 (1986).

COMMENTS

Comment on "A critique of the Brownian approximation to the generalized Langevin equation in lattice dynamics"

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In a recent publication, Diestler and Riley (DR)[1] have examined the use of the Brownian approximation (BA) in describing the motion of a subset of particles (termed the primary zone, and denoted P) in a harmonic lattice. These authors found that the Brownian theory admitted the possibility of undamped modes in P; they thereby concluded that the BA gave rise to results that were not physically meaningful, and suggested that it might, therefore, also engender other spurious effects.

While DR were correct in pointing out the existence of undamped modes, their subsequent conclusions about the validity of the BA are misleading for two reasons: (i) the undamped modes are a *real* effect, being a consequence of time-reversal symmetry, and (ii) the method used by DR is invalid when the lattice response function is nonanalytic about $\omega = 0$, as will be shown to occur for the Rosenstock–Newell model. What the results of DR can be used to illustrate is the inherently nondissipative nature of the zero frequency limit (ZFL), and therefore that the conventionally accepted equivalence between the ZFL and BA is inappropriate.

For any finite classical lattice that interacts through a purely position dependent potential, the existence of undamped modes follows immediately from Poincaré's theorem.[2] According to this theorem, any such system will eventually return arbitrarily close to its initial phase point. Since such quasiperiodicity is inconsistent with the irreversible loss of energy from any region of the lattice, one must conclude that any model of a finite lattice that is based upon the exact equations of motion must exhibit undamped modes. For infinite lattices, the situation is not transparent, since the proof of Poincaré's theorem assumes that the lattice has finite extent. If the ZFL is taken first, then the undamped modes will remain as one arbitrarily increases the lattice, thus implying that the undamped modes in this infinite lattice limit (ILL) are a real effect. On the other hand, if (following DR) the ILL is taken before the ZFL, then one can no longer apply Poincaré's theorem and the undamped modes are not obvious. However, this is precisely the case for which DR proved the existence of undamped modes. Thus changing the order in which the double limit is attained does not alter the final result, suggesting that the underlying physics is the same in both bases, and therefore that undamped modes in the ZFL motion of infinite lattices are a direct consequence of Poincaré's theorem.

In its essence, the above discussion is far from new, being just another manifestation of the problem of how to reconcile microscopic reversibility with macroscopic irreversibility.[2] Traditionally this paradox has been resolved by recognizing that the period of a Poincaré cycle is immensely long, and therefore of no physical significance in any chemical system. Thus, in practice, one can consider a very long but finite time, for which the paradox does not arise. However, such a procedure also implies that the frequencies dealt with are constrained to be nonvanishing, and thus precludes the consideration of a ZFL. Hence, the ZFL is the one situation for which the quasiperiodic nature of stable lattices cannot be ignored. In this sense DR were correct in ascribing origin of the undamped modes to the localization of the P motion about zero frequency.

One conclusion to be drawn from these comments is that the physically useful domain in which to examine the BA is at low, rather than zero, frequencies (i.e., long, but finite time scales—note that the BA is still meaningful for finite times); however for these conditions the method of DR leads to difficulties. In the first place, the method is based on a Taylor series expansion of the friction kernel, $\tilde{\theta}_{pp}(\omega)$, about $\omega = 0$ and should therefore break down for nonanalytic $\tilde{\theta}_{pp}(\omega)$; such nonanalytic behavior has been found before in transport coefficients,[3–5] and will be shown

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