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ON THE ACCURACY OF CLASSICAL TRANSITION STATE THEORY

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Effect of Reaction Path Curvature and Dimensionality
on the Accuracy of Classical Transition State
Theory

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Abstract

Using a simple dynamical approximation based on the reaction path Hamiltonian of Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)], it is shown how reaction path curvature and dimensionality affect the accuracy of classical transition state theory. Also, an explicit expression is obtained for the critical energy up to which classical transition state theory is exact. A variety of implications of these results are discussed.

I. Introduction.

In spite of the many advances in the theory of chemical reaction dynamics over the last twenty years, transition state theory is still the most generally useful and reliable method for determining the rate constants of most non-state-selected (i.e., thermally averaged) bimolecular reactions. There has, moreover, been much progress in recent years in illucidating the dynamical basis of transition state theory and in extending its range of validity by including quantum effects (e.g., tunneling, non-separability of the transition state, etc.) in a variety of more sophisticated ways.¹ Together with high level quantum chemical calculations of the transition state and its necessary properties, these modern versions of transition state theory are providing quantitatively reliable rate constants for a number of simple bimolecular reactions.

One of the key developments which spurred the revival of interest in transition state theory was Pechukas and McLafferty's² work showing that for simple barrier reactions classical transition state theory is exact for at least some range of energies above the barrier height. Classical trajectory calculations for the standard test reaction, $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$, showed³ this critical energy, up to which transition state theory is exact, to be $\sim 0.2-0.4$ eV above the energy of the saddle point (i.e., the transition state) of the potential energy surface. Even more interesting was the observation³ that for energies above this critical energy, i.e., energies for which the transition state (microcanonical) rate constant was too large, the fractional error in transition state theory was much less for the three-dimensional version of the reaction than for the one-dimensional (collinear) version, using

the same potential energy surface for both cases. This seemed to suggest the happy result that transition state theory is more accurate in three-dimensions than in one-dimension.

The original motivation for this paper was to explore this "dimensionality effect" noted above, i.e., to see if on the basis of a simple model one could understand (if it is indeed true) that classical transition state theory is a better approximation the higher the dimensionality (other things being equal). The results of the analysis do indeed show this effect; i.e., at energies above the critical energy E_c (up to which transition state theory is exact) transition state theory deviates less from the correct result the higher the number of degrees of freedom. Furthermore, the simple model that is proposed and developed in the paper provides an estimate of the critical energy E_c in terms of transition state frequencies and reaction path curvature, and shows that E_c is in many cases expected to be approximately independent of dimensionality. Finally, for the canonical (i.e., thermally averaged) rate constant, as opposed to the microcanonical case discussed above, it is seen that the fractional error in transition state theory (i.e., the transmission coefficient) given by the model is actually independent of the dimensionality. This result thus supports the approach suggested (and applied) recently by Bowman et al.⁴ of using the thermal transmission coefficient from an accurate collinear calculation to correct the transition state theory rate constant for the three-dimensional version of the reaction.

Section II describes the approximate model on which the analysis of the paper is based. It utilizes the reaction path Hamiltonian model⁵

of the polyatomic system and includes in an approximate fashion the effect of reaction path curvature on the reaction probability. The calculation is carried out first for the microcanonical (fixed total energy E) case, and implications of the results are discussed in Section III. Section IV considers the canonical (fixed temperature) case and also the modifications of the classical analysis to include quantum mechanical effects.

II. Theory; The Microcanonical Case.

The quantity of interest here is $N(E)$, the microcanonical average of the reactive flux through a surface which divides reactants from products, and within classical mechanics it is given by^{1,6}

$$N(E) = 2\pi\hbar h^{-F} \int d\mathbf{p} \int d\mathbf{q} \delta(E-H) \delta(s)\dot{s} \chi_r(\mathbf{p},\mathbf{q}) \quad (2.1)$$

where F is the number of degrees of freedom of the complete molecular system, $(\mathbf{p},\mathbf{q}) \equiv (p_k, q_k)$, $k=1, \dots, F$ is any set of canonical coordinates and momenta, H is the classical Hamiltonian, s the reaction coordinate ($s=0$ defines the dividing surface separating reactants and products), \dot{s} its time derivative, and χ_r is the characteristic function for reaction. The characteristic function $\chi_r(\mathbf{p},\mathbf{q}) = 1$ if the trajectory determined by the phase point (\mathbf{p},\mathbf{q}) evolved in the infinite past from reactants, and is 0 otherwise. To evaluate this expression it is in general necessary to compute classical trajectories to determine when χ_r is 0 or 1. The thermally averaged rate constant, to be considered more specifically in Section IV, is given in terms of $N(E)$ by

$$k(T) = (2\pi\hbar Q_0)^{-1} \int_0^\infty dE N(E) \exp(-E/kT) \quad (2.2)$$

where Q_0 is the partition function (per unit volume) for reactants.

Approximations to $N(E)$ correspond to making approximations to the characteristic function χ_r . Transition state theory, for example, corresponds to the approximation

$$\chi_r(\underline{p}, \underline{q}) \rightarrow h(\dot{s}) \quad , \quad (2.3)$$

where h is the step function

$$h(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}$$

but in the present analysis we wish to do better than this. For this purpose the reaction path Hamiltonian as formulated by Miller, Handy and Adams⁴ is used to characterize the molecular system,

$$H(p_s, s, \underline{n}, \underline{q}) = \sum_{k=1}^{F-1} h \omega_k(s) (n_k + \frac{1}{2}) + V_0(s) + \frac{\frac{1}{2} [p_s - \sum_{k,k'=1}^{F-1} B_{k,k'}(s) \sqrt{(2n_k+1)(2n_{k'}+1)\omega_{k'}(s)/\omega_k(s)} \sin q_k \cos q_{k'}]^2}{[1 + \sum_{k=1}^{F-1} B_{k,F}(s) \sqrt{(2n_k+1)/\omega_k(s)} \sin q_k]^2} \quad (2.4)$$

where s is the (mass-weighted) distance along the reaction path, p_s its conjugate momentum, and $(\underline{n}, \underline{q})$ the action-angle variables for normal mode vibrations orthogonal to the reaction path. $\{\omega_k(s)\}$ are the local harmonic frequencies for these modes, and $V_0(s)$ is the potential energy surface along the reaction path. (Rotation is being ignored in the present analysis.) The functions $B_{k,k'}(s)$ are coriolis-like coupling elements which couple vibrational mode k and k' , and $B_{k,F}(s)$ are curvature-coupling elements which couple mode k to the reaction coordinate (labeled as mode F).

To evaluate the phase space integral in Eq. (2.1) it is clearly convenient to take the reaction path variables (p_s, s) , (n_k, q_k) , $k=1, \dots, F-1$, as the canonical variables. Because of the two delta functions in the integrand of Eq. (2.1), two integrations can be carried out, and the obvious ones are the integral over s and the one over p_s . Since

$$\dot{s} = \frac{\partial H}{\partial p_s} \quad , \quad (2.5)$$

it is straight-forward to show that integration over these two variables gives

$$N(E) = (2\pi\hbar)^{-(F-1)} \int_{-\frac{1}{2}}^{\infty} dn \int_0^{2\pi} dq \quad h[E - V_{\tilde{n}}(0)] [\text{Sign}(\dot{s}_+) \chi_{\tilde{r}}^+(n, q) + \text{Sign}(\dot{s}_-) \chi_{\tilde{r}}^-(n, q)] \quad , \quad (2.6)$$

where

$$V_{\tilde{n}}(s) = V_0(s) + \sum_{k=1}^{F-1} \hbar \omega_k(s) \left(n_k + \frac{1}{2} \right) \quad , \quad (2.7)$$

and where + and - refer to the two possible values of p_s , and thus \dot{s} , that are determined by energy conservation at $s=0$,

$$H(p_s, s=0, \tilde{n}, \tilde{q}) = E \quad . \quad (2.8)$$

With the reaction path Hamiltonian, Eq. (2.4), and Eqs. (2.5) and (2.8), one finds

$$\dot{s}_{\pm} = \pm \sqrt{2[E - V_{\tilde{n}}(0)]/[1 + \Sigma(0)]} \quad (2.9)$$

where

$$\Sigma(s) = \sum_{k=1}^{F-1} B_{k,F}(s) \sqrt{(2n_k+1)/\omega_k(s)} \sin q_k \quad (2.10)$$

Equation (2.6) is still exact (at least within the reaction path Hamiltonian model of the molecular system) as it stands, but we now introduce assumptions about χ_r in order to be able to proceed further (without requiring a trajectory calculation). First, it is assumed that trajectories which emanate from regions of the transition state (i.e., values of \tilde{n}, q and $s=0$) for which

$$1 + \Sigma(0) > 0 \quad , \quad (2.11a)$$

have come directly from reactants (and proceed directly to products).

Since for all values of s energy conservation gives

$$\dot{s} = \pm \sqrt{2[E - V_{\tilde{n}}(s)]/[1 + \Sigma(s)]} \quad ,$$

this is equivalent to the assumption that $1 + \Sigma(s) > 0$ for all values of s along such a trajectory, i.e., that \dot{s} does not change sign. Since the transition state (i.e., $s=0$) is typically the region of largest curvature (i.e., largest values of $\{B_{k,F}(s)\}$) and since $\Sigma(s) \rightarrow 0$ as $s \rightarrow \pm\infty$, it seems like a reasonable approximation to assume that if $1 + \Sigma(s)$ begins positive at $s=0$ that it will remain positive as $s \rightarrow +\infty$ and $-\infty$. With this approximation one thus has

$$\begin{aligned} \text{Sign } (\dot{s}_+) \chi_r^+ &= +1 \\ \chi_r^- &= 0 \end{aligned} \quad (2.11b)$$

for values of $(\underline{n}, \underline{q})$ for which Eq. (2.11a) is satisfied.

Trajectories which emanate from regions of the transition state for which

$$1 + \Sigma(0) < 0 \quad (2.12a)$$

are more complicated to deal with. Since $\Sigma(s) \rightarrow 0$ as $s \rightarrow +\infty$ and $-\infty$, it must be that $1 + \Sigma(s)$ goes through (at least one) zero for $s > 0$ and also for $s < 0$, and thus that \dot{s} has sign changes for $s > 0$ and $s < 0$. It thus seems reasonable to assume that such trajectories correspond to some sort of collision complex. For a long-lived collision complex one would expect it to be equally likely that the trajectory has come from reactants if $\dot{s} < 0$ at $s = 0$ (which is \dot{s}_+) or if $\dot{s} > 0$ at $s = 0$ (which is \dot{s}_-). This implies the assumption that on the average

$$\langle \text{Sign } (\dot{s}_+) \chi_r^+ \rangle + \langle \text{Sign } (\dot{s}_-) \chi_r^- \rangle \approx 0 \quad , \quad (2.12b)$$

so that such trajectories would not contribute to Eq. (2.6). Other somewhat more sophisticated approximations are possible in this case, but none that we have thought of influence the outcome significantly.

Combining the assumptions in Eqs. (2.11) and (2.12), the approximation arrived at for Eq. (2.6) is

$$N(E) = (2\pi\hbar)^{-(F-1)} \int_{-\frac{1}{2}}^{\infty} d\underline{n} \int_0^{2\pi} d\underline{q} \ h[E - V_{\underline{n}}(0)] \ h[1 + \Sigma(0)] \quad , \quad (2.13)$$

with $\Sigma(s)$ defined by Eq. (2.10). It is clear that if one makes a zero-curvature approximation, then $\Sigma(0) \rightarrow 0$ and Eq. (2.13) becomes ordinary transition state theory. Equation (2.13) thus incorporates (approximately) the effects of reaction path curvature into transition state theory. (It may also be interesting to note that the requirement expressed by Eq. (2.13), namely that $1 + \Sigma(0) \geq 0$, is also equivalent to restricting the phase space integral to the single-valued region⁷ of the reaction path coordinates at $s=0$.)

The result obtained from Eq. (2.13) is most conveniently expressed by giving the transmission coefficient κ , the ratio of $N(E)$ to the usual transition state theory (i.e., zero curvature) approximation to it.

Thus $\kappa(E)$ is defined by

$$N(E) = \kappa(E) N_{\text{TST}}(E) \quad , \quad (2.14)$$

where N_{TST} is the usual microcanonical transition state theory expression

$$N_{\text{TST}}(E) = (E - V_0)^{F-1} / [(F-1)! \prod_{k=1}^{F-1} \hbar \omega_k^\ddagger] \quad , \quad (2.15)$$

with $\omega_k^\ddagger \equiv \omega_k(0)$ and $V_0 \equiv V_0(0)$. Carrying out the integrals in Eq. (2.13) gives the transmission coefficient as

$$\kappa(E) = 1 \quad , \quad E \leq E_c \quad (2.16)$$

$$= 1 - (2\pi)^{-1} \int_1^R dx \frac{(1-x/R)^{F-1}}{x\sqrt{x-1}} \quad , \quad E > E_c$$

where $R = (E - V_0) / (E_c - V_0)$ and E_c , the critical energy up to which

transition state theory is exact (i.e., $\kappa=1$), is given by

$$E_c = V_0 + \frac{1}{2} \left[\sum_{k=1}^{F-1} B_{k,F}(0)^2 / \omega_k(0)^2 \right]^{-1} \quad (2.17)$$

The one remaining integral in Eq. (2.16) can also be carried out, to give κ explicitly as

$$\begin{aligned} \kappa(E) = & 1 - \pi^{-1} \left[\tan^{-1}(\sqrt{R-1}) \right. \\ & \left. + \sum_{k=1}^{F-1} \binom{F-1}{k} \left(\frac{-1}{R}\right)^k \sum_{\ell=0}^{k-1} \binom{k-1}{\ell} \frac{(R-1)^{\ell + \frac{1}{2}}}{2\ell+1} \right] \quad (2.18) \end{aligned}$$

Equations (2.14)-(2.18) are the basic results of the present model, the implications of which the remainder of the paper explores.

III. Discussion.

Consider first the expression for the critical energy E_c , Eq. (2.17). It behaves qualitatively correctly in that if there is no curvature ($B_{k,F} \rightarrow 0$), then $E_c \rightarrow \infty$; i.e., if the reaction path is straight, transition state theory is correct for all energies. Conversely, the larger the curvature coupling elements, the lower E_c .

Consider also the example of an atom-diatom reaction, $A + BC \rightarrow AB + C$, for which the reaction path is collinear. This means that $B_{k,F}(s) = 0$ for modes k that are bending modes, which in turn implies that E_c is the same for the collinear reaction as for the three-dimensional version of the same reaction. This is indeed what is observed³ empirically for the collinear/three-dimensional versions of the $H + H_2$ reaction on the Porter-Karplus potential surface. In general, Eq. (2.17) shows that only modes k which the curvature couples significantly to the reaction coordinate (i.e., for which $B_{k,F}$ are significant) contribute to determining E_c .

One can give Eq. (2.17) a semi-quantitative check via the $H + H_2$ reaction on the Porter-Karplus surface. The only ambiguous aspect is that the saddle point on this surface is not the point of maximum curvature, and Eq. (2.17) gives a value of ~ 2 eV above the barrier height, much too large. If rather one evaluates the expression at the point of maximum curvature ($s \approx 8$ mass-weighted atomic units--see Figure 4 of reference 5), then one obtains $E_c \approx 0.3$ eV above the barrier height, in excellent agreement with the empirically observed³ value.

Now consider the limit of $\kappa(E)$ for E only slightly above the critical energy. From Eq. (2.16) (most easily) one finds

$$\kappa(E) = 1 - c_F \left(\frac{E-E_c}{E_c-V_0} \right)^{F-\frac{1}{2}}, \quad (3.1)$$

where

$$c_F = \frac{\Gamma(F)}{2\Gamma(\frac{1}{2})\Gamma(F+\frac{1}{2})}$$

$$\approx \frac{1}{2}(\pi F)^{-1/2} \quad \text{for large } F \quad (3.2)$$

This displays the dimensionality effect mentioned in the Introduction, i.e.,

$$\kappa(E)-1 \sim -(E-E_c)^{F-\frac{1}{2}},$$

for $E-E_c$ small; the larger F the more gradually $\kappa(E)$ differs from unity for $E > E_c$.

It is also easy to show that the high energy limit of $\kappa(E)$ is

$$\lim_{E \rightarrow \infty} \kappa(E) = \frac{1}{2} \quad (3.3)$$

This limit can also be thought of as the large curvature limit for fixed energy, and in this sense is actually the correct limit. Thus consider the family of atom-diatom reactions of the heavy-light-heavy variety, e.g.,



which have very sharply curved reaction paths (in the proper scaled/skewed

coordinates). They are in many respects similar to symmetric charge transfer reactions, and for energies above the barrier the reaction probability behaves as⁸

$$P(E) \approx \sin^2[\Delta\eta(E)] \quad ,$$

where $\Delta\eta$ is a phase shift difference. The only relevant point for present considerations is that the energy-averaged reaction probability is $\sim \frac{1}{2}$! (One should not make too much of this perhaps coincidental agreement, however; the assumptions contained in Eqs. (2.11)-(2.12) are probably too crude to believe the high curvature limit in detail.)

Finally, Figure 1 shows $\kappa(E)$ as a function of the energy relative to the critical energy (both relative to $V_0(0)$ as zero of energy) for several values of F . $F=2$ is the lowest possible value, corresponding to a collinear atom-diatom reaction. This figure shows more explicitly the effect of dimensionality on κ and how relatively slowly it approaches its infinite energy limit of $\frac{1}{2}$.

IV. The Canonical Case.

The quantity of perhaps more interest than $N(E)$ is the thermal rate constant $k(T)$, which is given in terms of $N(E)$ by Eq. (2.2). By using the integral representation of $\kappa(E)$ in Eq. (2.16) it is not hard to show that one obtains

$$k(T) = \kappa(T) k_{\text{TST}}(T) \quad , \quad (4.1)$$

where k_{TST} is the standard (i.e., zero curvature) transition state expression,

$$k_{\text{TST}}(T) = \frac{kT}{h} \exp(-V_0/kT) \left[\prod_{k=1}^{F-1} \frac{kT}{h\omega_k} \right] / Q_0 \quad , \quad (4.2)$$

with the effective thermal transmission coefficient $\kappa(T)$ given by

$$\kappa(T) = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left[\sqrt{(E_c - V_0)/kT} \right] \quad . \quad (4.3)$$

Within the present model, therefore, the effective thermal transmission coefficient $\kappa(T)$ - [Eq. (4.3)] depends on the dimensionality of the system only through the critical energy E_c . As noted in Section III, though, E_c is expected to be often approximately independent of the dimensionality, and to the extent that this is true $\kappa(T)$ is thus independent of the dimensionality. As noted in the Introduction, this idea of the independence of $\kappa(T)$ to dimensionality has been assumed and applied with some success recently by Bowman et al.⁴

A final point has to do with quantization of the classical expressions discussed throughout the paper. This is accomplished at the most elementary level (i.e., neglecting tunneling) by replacing the integrals over the action variables n , e.g., in Eqs. (2.6) and (2.13), by sums over integer values:

$$\int_{-\frac{\infty}{2}}^{\infty} \frac{dn}{2} \rightarrow \sum_{n=0}^{\infty} \quad . \quad (4.4)$$

This modification unfortunately makes it more difficult to carry out the remaining integrals over the angle variables. For the canonical case, for example, Eq. (4.4) (together with Eqs. (2.2) and (2.13)) leads to

$$k(T) = \frac{kT}{h} \exp(-V_0/kT) \left[\sum_{\tilde{n}=0}^{\infty} \kappa_{\tilde{n}} \exp[-\hbar \tilde{\omega}^{\ddagger} \cdot (\tilde{n} + \frac{1}{2})/kT] \right] / Q_0, \quad (4.5a)$$

where

$$\kappa_{\tilde{n}} = (2\pi)^{-(F-1)} \int_0^{2\pi} dq \, h[1 + \sum_{k=1}^{F-1} B_{k,F}(0) \sqrt{(2n_k+1)/\omega_k^{\ddagger}} \sin q_k] \quad (4.5b)$$

By use of the following integral representation for the step-function,

$$h(x) = \lim_{\epsilon \rightarrow 0} (2\pi i)^{-1} \int_{-\infty}^{\infty} dz \frac{e^{ixz}}{z-i\epsilon}$$

Eq. (2.5b) for $\kappa_{\tilde{n}}$ can be simplified to

$$\kappa_{\tilde{n}} = (2\pi i)^{-1} \int_{-\infty}^{\infty} dz \frac{e^{iz}}{z-i\epsilon} \prod_{k=1}^{F-1} J_0[z B_{k,F}(0) \sqrt{(2n_k+1)/\omega_k^{\ddagger}}] \quad (4.6)$$

No further progress can be made in general, but if the coupling elements are small enough for one to approximate the Bessel functions as

$$J_0(y) \approx e^{-y^2/4}$$

then Eq. (4.6) can be evaluated to give

$$\kappa_{\tilde{n}} = \text{erf} \left\{ \left[\sum_{k=1}^{F-1} B_{k,F}(0)^2 \left(\frac{2n_k+1}{\omega_k^{\ddagger}} \right)^{-1/2} \right] \right\} \quad (4.7)$$

Equation (4.7) certainly shows the correct trend: if all $B_{k,F}$'s $\rightarrow 0$, then $\kappa_n \rightarrow 1$ and Eq. (4.5a) gives ordinary (quantized) transition state theory; for $B_{k,F}$ very large $\kappa_n \rightarrow \frac{1}{2}$, the correct limit within the model considered in this paper.

V. Concluding Remarks.

The point of this paper has been to show how a relatively simple dynamical approximation, based on the reaction path Hamiltonian of Miller, Handy and Adams, is able to describe the effect of reaction path curvature and the effect of dimensionality on classical transition state theory. The proposed model only describes these effects approximately, of course, but the discussion in Section III shows that it is at least capable of describing some of these effects correctly. It is interesting to see, for example, that dimensionality effects in the microcanonical transmission coefficient $\kappa(E)$ are not inconsistent with the lack of such effects in the thermal transmission coefficient $\kappa(T)$.

Acknowledgments

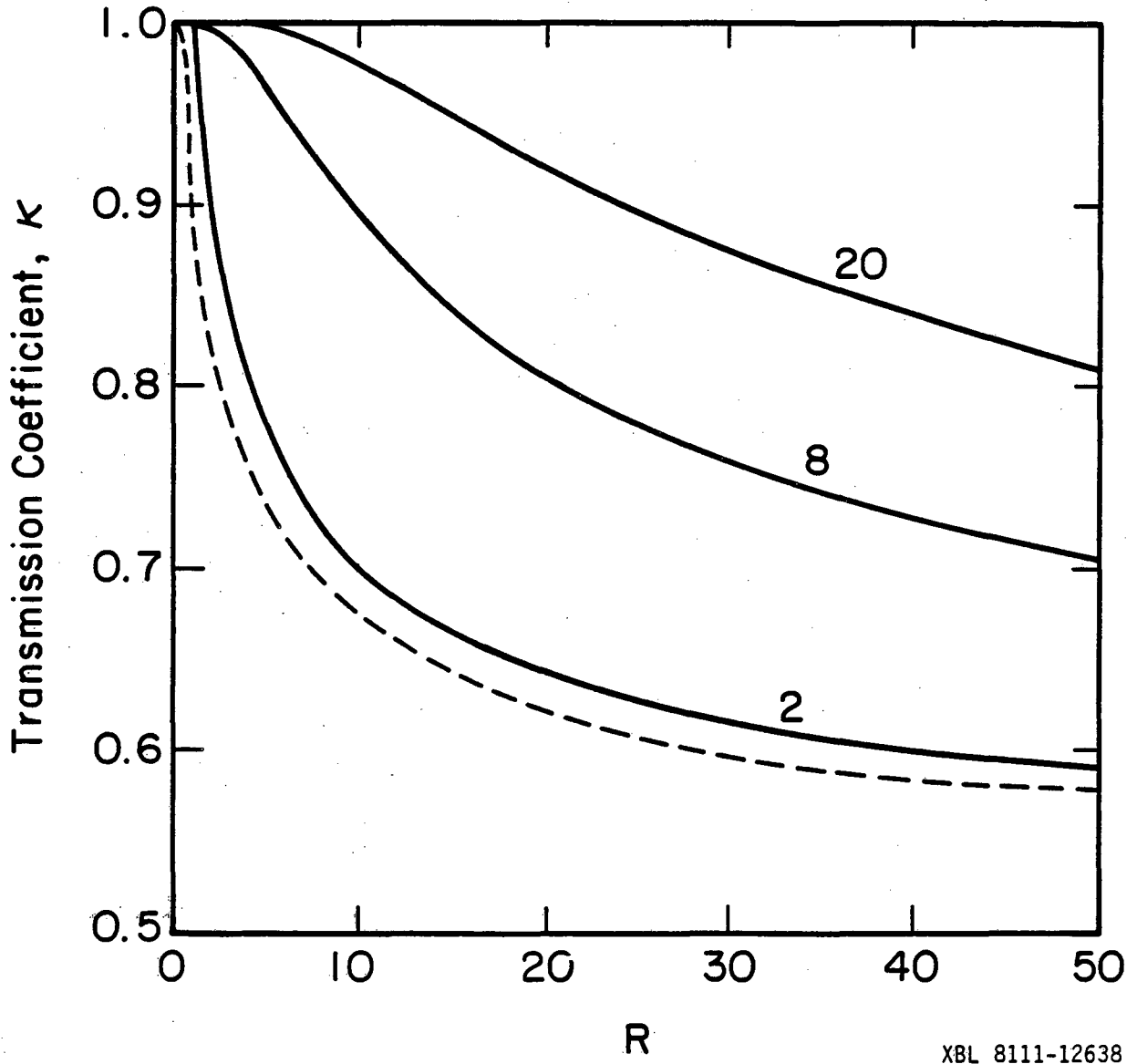
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Figure Caption

The solid curves are the transmission coefficient κ of Eq. (2.18) as a function of the energy parameter $R = (E - E_c) / (E_c - V_0)$ for the cases of $F = 2, 8,$ and 20 degrees of freedom. (V_0 is the barrier height, and E_c the critical energy up to which $\kappa \equiv 1$; thus $\kappa = 1$ for $R \leq 1$.) The broken curve is the canonical (i.e., temperature dependent) transmission coefficient of Eq. (4.3), and for this curve the abscissa $R = kT / (E_c - V_0)$.



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Figure 1

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