Kinetics of conformational transitions in chain molecules

Jeffrey Skolnick* and Eugene Helfand

Bell Laboratories, Murray Hill, New Jersey 07974
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A theory is developed for the rate of conformational transitions (trans—gauche) of bonds in chain molecules, such as alkanes and polymers. This is a multidimensional extension of Kramers' reaction rate theory. Central to the understanding of how changes in the chain's geometry affect transition rate is the determination and examination of the reaction coordinate. The reaction coordinate is a localized mode; i.e., the rotational motion of the transforming bond is accompanied by motion in neighboring bonds, but this motion diminishes with distance. Comparison is made between the calculated rates and those determined by Brownian molecular dynamics simulations.

I. INTRODUCTION

The rotational potential energy of a bond in a polymer generally exhibits several stable states: trans (t), gauche plus (g*), and gauche minus (g—) separated by barriers (Fig. 1). Transitions from state to state, i.e., conformational changes, are an important relaxation mode of motion manifest in numerous physical properties. In this paper we shall discuss the calculation of conformational transition rates and identify some of the major factors controlling these rates.

It has been realized for some time that conformational transitions in polymers must have a special character. Consider a bond near the center of a long chain molecule, and picture a rotational motion taking place about this bond, let us say t—g+. If all other bonds remain fixed at the local minimum of the torsional energy during this transition, the two, long tails attached to the rotating bond would have to undergo a wide swinging motion. Such a motion would be strongly opposed by viscous and inertial forces. In consideration of this, two points of view have arisen about the mechanism of conformational transitions.

The first viewpoint holds that along the chain compensating transitions occur which limit the necessary motion of the tails. The most extreme version of this theory restricts consideration to the so-called type 1 or crankshaft motions wherein several conformational transitions occur close together in space and time, in such a way that there is no net motion of the attached tails. Historically, the first crankshaft considered was the Schatzki crankshaft picture in Fig. 2. Another type 1 motion is the three-bond motion. Every time one has a gauche bond in a chain, that bond and its neighbors on each side form "half a cyclohexane ring" (Fig. 3). A motion in which these bonds flip to the other half of the cyclohexane ring (possible only if one of the new bond positions is not already occupied) clearly leaves the tails in the same position finally that they were in initially.

There is another type of multiple transition, discussed earlier by one of us and called type 2, in which the polymer tails do not have to swing, but they do translate.

Every time there is a trans bond in the chain, the two attached bonds are parallel. If one of these two parallel bonds undergoes a rotation +ϕ while the other rotates −ϕ, then the tails translate but do not rotate (Fig. 4). Considerable motion of this type has been observed in Brownian motion computer simulations of polymers.

The difficulty with the concept of compensating transitions is that they seemingly call for high activation energies because several bonds must be in the activated state almost simultaneously. What is observed experimentally and in the simulations are activation energies of about one barrier height. This is suggestive of independent events (which are also observed in the simulations). The argument which has been advanced in support of this description is that the tails of the molecule do not have to rigidly follow the rotation of the transforming bond, but can lag behind in such a manner as to have each tail eventually "heal" onto its old position. This involves some distortion of the tails but if the distortion is spread over a large number of units the energy involved will not be high.

It is this independent transition viewpoint which will be taken in the present paper. In fact the model we employ gives no consideration to the possibility of cooper-
ative, multiple transitions, although we will find that there is cooperativity of the small displacement motion of several bonds. We will determine the manner and rate at which a bond in a polymer moves over the top of the barrier separating its trans from gauche states. In the most favorable mode of motion the neighboring units move, to a certain extent, but not in rigid rotation of the tails. The amount that the neighboring carbon centers are displaced decreases with distance from the transforming bond. This necessitates a distortion of the tail. It is found, as expected, that the distortion is, to a large extent, in the softest degrees of freedom—bond rotations rather than bond angle bending or bond stretching. This qualitative point of view enables us to understand the results which emerge for the dependence of the transition rate on the conformation of the tails. In this sense, the neighboring bonds’ motions turn out to be evocative of the motions involved in cooperative type 2 transitions. We explain the general matter of the localized collective modes involved in transitions below.

The polymer model we shall employ is delineated in Sec. II. The basic framework for transition rate calculations which we employ is that of Kramers for motion in a high friction medium. The theory is discussed in Sec. III. In Sec. V application is made to a single transforming bond in the center of an otherwise all trans chain of from 4 to 32 carbon centers. Subsequently, the influence of the conformation of the tails attached to the transforming bond is explored in Sec. VI. The general rules and rationalizations of the observed conformational dependence emerge. Average transition rates which agree fairly well with the Brownian simulations of butane, octane, and polymers are calculated in Sec. VII. The concluding discussion highlights implications of this research.

II. MOLECULAR MODEL

For the performance of quantitative calculations we shall use a molecular model, in which there are only interactions along the backbone. No consideration will be given to long-range excluded volume so the model is what is usually called a phantom chain, one that can pass through itself. We believe that this is not a serious approximation because the motions we are considering are quite fast and involve only short segments of the chain in the critical process of passing through the activated state. The potential is the same as that used in the Brownian dynamics simulations so that comparisons can be made.

The molecule is modeled as a chain of \( N-1 \) bonds that connect \( N \) identical vertices, labeled 0 to \( N-1 \). Each vertex represents a carbon atom and its substituents. The bond lengths \( b_i \) (distance from vertex \( i-1 \) to \( i \)) are maintained near a value \( b_0 \) by a potential \( v_b \) harmonic in bond length:

\[
v_b(b_i) = \frac{1}{2} \gamma_b (b_i - b_0)^2,
\]

where \( \gamma_b \) is the bond stretching force constant. The bond angle \( \theta_i \), the angle (acute for tetrahedral bonds, see Fig. 5) between bond vectors \( i-1 \) and \( i \), is kept near a value \( \theta_0 \) by a potential \( v_{\theta} \) of the form

\[
v_{\theta}(\theta_i) = \frac{1}{2} \gamma_{\theta} (\cos \theta_i - \cos \theta_0)^2.
\]

Finally, bond rotation is specified by the torsional angle \( \phi_i \), which is the angle between the plane of bonds \( i-1 \) and \( i \) and the plane of bonds \( i \) and \( i+1 \), taken as zero for trans bonds. Rotational motion is subject to the potential, depicted in Fig. 1, of

\[
v_{\phi}(\phi_i) = \gamma_{\phi} \sum_{n=0}^{N} a_n \cos^n \phi_i,
\]

with \( \theta_0 = 1 \), and

\[
\sum_{n=0}^{N} a_n = 0,
\]

so that the zero of energy is trans. In the calculation of transition rates, interest will center on motions in the neighborhood of the torsional energy minima and the barrier. Therefore, the forms of the rotational potential which will be most needed are the local expansions

\[
v_{\phi}(\phi_i) = \frac{1}{2} \gamma_{\phi} \phi_i^2,
\]
TABLE I. Parameters of the system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta \zeta$</td>
<td>$1.00 \times 10^5$ nm$^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>0.014 kg/mole</td>
</tr>
<tr>
<td>$b_0$</td>
<td>0.153 nm</td>
</tr>
<tr>
<td>$\gamma_b/m$</td>
<td>$2.5 \times 10^3$ J/kg nm$^2$ = ns$^{-2}$</td>
</tr>
<tr>
<td>$\gamma_\theta/m$</td>
<td>$70.53^\circ$</td>
</tr>
<tr>
<td>$\gamma_{\phi}/m$</td>
<td>$1.3 \times 10^4$ J/kg</td>
</tr>
<tr>
<td>$\gamma_{\phi}/m$</td>
<td>$6.634 \times 10^6$ J/kg</td>
</tr>
<tr>
<td>$a_0$</td>
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</tr>
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<tr>
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<td>2.93 kJ/mole</td>
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<tr>
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<td>2.93 kJ/mole</td>
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<td>$E_{\phi}$</td>
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<td>$\phi_\phi$</td>
<td>$\pm 120^\circ$</td>
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<tr>
<td>$\gamma_{\phi}$</td>
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<tr>
<td>$\gamma_{\phi}$</td>
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</tr>
<tr>
<td>$\gamma_{\phi}$</td>
<td>$7.530 \times 10^6$ J/kg</td>
</tr>
</tbody>
</table>

*These parameters fundamentally define the Ryckaert–Bellemans potential (Ref. 12). Derived parameters are given with extra figures.

might affect the quantitative results, and how polymer motions are best described near the activated state. Our understanding of these matters will be enhanced by having a physical description of the reaction rate theory.

It will be useful to begin by heuristically$^9$ describing the rate theory for a one-dimensional, one-particle process, following the Kramers' picture of reaction rate theory.$^{10}$ Consider an ensemble of systems which are one particle (any one degree of freedom) moving in a potential, as depicted in Fig. 6. In the neighborhood of the minimum near $x_A$ let the potential be

$$V(x) = \frac{1}{2} \gamma_A (x - x_A)^2,$$

while near the barrier let it be

$$V(x) = E^* - \frac{1}{2} \gamma^*(x - x^*)^2.$$

In order to study a steady state passage over the barrier, we imagine that systems are withdrawn from the ensemble when the particles reach large positive $x$ and the ensemble is renormalized. An estimate of the reaction rate is given by the current over the barrier. If the particle is moving in a high friction fluid, then the motion is diffusive and the current is given by

$$j = -D \frac{dn}{dx}.$$

$D$ is the diffusion constant, $k_BT/\zeta$, with $\zeta$ the friction constant. Across the barrier the density $n$ falls from its equilibrium value

$$n^* = n_A \exp(-E^*/k_BT),$$

to zero in a distance $d^*$, so that $-dn/dx$ in Eq. (3.3) can be replaced by $(n^* - 0)/d^*$. Here $n_A$ is the density near the bottom of the well which is one over some distance: $n_A = 1/d_A$. In turn, $d_A$ can be taken as the configurational partition function near the well at $A$:

$$d_A = \left( \frac{2\pi k_BT}{\gamma_A} \right)^{1/2} \left( \frac{2\pi k_BT}{\gamma_A} \right)^{1/2}.$$

This potential is the same one which has been used in Brownian dynamics simulations.$^6$ For numerical calculations and comparison the parameters listed in Table I are employed.

The potential is suggestive of the simplest linear polymer, polyethylene, and is useful for understanding general principles. Models of more complex macromolecules are now under consideration.

III. RATE THEORY

In this section we will try to do more than just derive the formulas to be used for the transition rate calculations. We will attempt to bring out the features that are important in the rate calculation, what approximations are made, the extent to which the approximations

![Reaction Coordinate](https://via.placeholder.com/150)

FIG. 6. Potential along a reaction coordinate. In the reaction under consideration a particle initially located near $A$ goes over the barrier at $B$, and is regarded as eventually falling into a sink at $-\infty$ in the Kramers theory.


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We now generalize these arguments for many degrees of freedom. Although the description is specialized to the polymer system of Sec. II, the formulas clearly have wider applicability. It is useful to picture the total potential in the 3N-dimensional space of all the carbon centers' Cartesian coordinates. We have depicted this in Fig. 7 in a way which may be regarded either as schematic or as a typical two-dimensional projection of the potential's level diagram. The stable conformations appear as minima or wells, and the lowest energy passes from state to state go through saddle points which are the centers of the activated states. (Strictly speaking the passes are not saddle points in the full 3N-dimensional space defining the molecule's state because of the six translational and rotational degrees of freedom upon which the potential does not depend. The saddle point description applies to the 3N-6 internal degrees of freedom. We will return to this nontrivial point in Appendix B.)

Interest will center on going from one minimum to another, representing two different conformational states of one of the bonds, all other bonds staying in the same conformational state. We know that these two minima are actually very far apart in the multidimensional space because to get from one of these states to the other requires a long swinging motion of the tails. However, we need not concern ourselves with actually arriving at the minima. The rate is determined by the current through a plane containing the saddle point and sensibly dividing the space into two conformational states. In the spirit of Kramers, we can say that far from this plane equilibrium is achieved on one side, and the distribution has zero weight on the other. In the present case this can not be strictly true because there are some modes of motion of the polymer which have relaxation times of the same order or longer than the inverse of the reaction rate. Therefore memory is retained of the position of the states from which they came. The modes with such long decay times are longer wavelength modes (distortions spread over many units) and therefore do not contribute strongly to the energy. We will make the assumption that the extra contribution of these distortions to the activation energy or other aspects of the rate can be neglected. In the presence of such long time modes, it is difficult to define transition rate unambiguously, but the difference between definitions should be quantitatively small.)

It will be further assumed that the reaction paths are distributed in an equilibrium fashion about the path of steepest descent through the saddle point. Thus the calculation is very much like a one-dimensional rate calculation along the reaction coordinate. The added features are that: (1) the reaction coordinate must be determined as the path of steepest descent, and (2) the probability density of being near the barrier must be calculated in terms of free energy of activation, including the entropy of activation, which describes how broad the distribution is near the saddle point orthogonal to the reaction coordinate. According to statistical mechanics the free energy difference is obtained by taking the ratio of the partition function at the saddle point to the initial state partition function which comes pre-
dominantly from the region near the bottom of the well. Again, all of this can be made to emerge from an extension of Kramers’ method for obtaining a solution of the multidimensional Fokker–Planck equation, or by Blomberg’s extension of the Kramers’ current conservation argument to the multidimensional space. Since these methods are explained elsewhere, we can content ourselves with the heuristic argument here.

The potential function in the two regions of importance is:

$$V(r) = E^* + \frac{1}{2} \sum_{i,j=1}^{3N} W_{ij} (x_i - x_i^0)(x_j - x_j^0),$$

(3.9)

and near the initial state well,

$$V(r) = \frac{1}{2} \sum_{i,j=1}^{3N} V_{ij} (x_i - x_i^0)(x_j - x_j^0).$$

(3.10)

(Explicit expressions for $V$ and $W$ are given in Appendix A.) The $W$ matrix has one negative eigenvalue, $\lambda$, with eigenvector $\mathbf{p}^*$ which points in the direction of steepest descent. The collective motion which $\mathbf{p}^*$ represents will be discussed extensively below. At this point it is only important to note that it is a localized mode, which means that its three-dimensional components, $p_n^*$, grow smaller as $i$ gets further from the transforming bond. The curvature along the reaction coordinate is $\lambda$ (which thus plays the role of the one-dimensional quantity $-\gamma$). The characteristic distance is

$$a^* = \left(-2\pi k_B T / \lambda\right)^{1/2}.$$  

(3.11)

Let us define a classical configurational partition function $Q^*$ for displacements orthogonal to the reaction coordinate at the saddle point. Also define a partition function for the initial state as if the potential, Eq. (3.10), held everywhere. Then the density $n^*$ at the barrier can be approximated as

$$n^* = Q^*/Q_A.$$  

(3.12)

$$Q_A = 8\pi^2 \Omega \left(\frac{\det(\mathbf{1})}{m^3}\right)^{1/2} N^{3/2} (2\pi k_B T)^{(3N-6)/2} \det(\mathbf{V})^{1/2}.$$  

(3.13)

This is obtained from the integral of $\exp(-V/k_BT)$ by converting to internal coordinates, center of mass coordinates, and Euler angles to describe orientation. The determinant of the inertial tensor over $m^3$ enters from the Jacobian of the transformation. The factor $8\pi^2 \Omega$, where $\Omega$ is the volume, comes from the center and center of mass integration. The rest of Eq. (3.13) is from the integration over internal degrees of freedom (which we assume can be treated classically). $\mathbf{V}$ is a $3N-6$ degree matrix obtained by eliminating the translational and rotational quantities. The determinant, $\det(\mathbf{V})$, is equal to the product of the nonzero eigenvalues of $\mathbf{V}$. [Equation (3.13) may be recognized as the full partition function of a polyatomic molecule divided by the momentum partition function for $3N$ Cartesian degrees of freedom.]

The partition function $Q^*$ is

$$Q^* = 8\pi^2 \Omega \left(\frac{\det(\mathbf{1})}{m^3}\right)^{1/2} N^{3/2} (2\pi k_B T)^{(3N-6)/2} \det(\mathbf{W})^{1/2} \exp\left(-\frac{E^*}{k_B T}\right).$$  

(3.14)

where $\mathbf{W}$ is the potential matrix for an expression of the potential in which not only have 6 variables been eliminated by the six linear conditions expressing no translation and rotation, but also an additional variable is eliminated by the condition that the motion be orthogonal to the reaction coordinate. It is convenient not to eliminate this variable from the determinant, but to write

$$\det(\mathbf{W})^1 = \det(\mathbf{W})/\lambda,$$

(3.15)

where $\mathbf{W}$ is the determinant including all the internal degrees of freedom. Essentially we have merely multiplied and divided by $\lambda$.

Thus an expression for the transition rate in the high friction limit is

$$k = \frac{1}{2\pi h} \left| \left| \frac{\det(\mathbf{1})^{1/2}}{\det(\mathbf{W})} \right| \right| \det(\mathbf{V})^{1/2} \exp\left(-\frac{E^*}{k_B T}\right).$$  

(3.16)

Extension to intermediate friction is possible. Although the above derivation is heuristic, this is essentially the result which Blomberg obtained. For his model he did not have to consider the effect of the overall rotational or translational degrees of freedom because he fixed the molecule’s ends. We shall find that for a class of separable potentials, which are the type which we shall consider, great simplification of the rate expression can be achieved.

IV. SIMPLIFICATION OF THE RATE EXPRESSION AND DETERMINATION OF THE REACTION COORDINATE

For the separable potential of Eq. (2.8), rather than transforming to internal, center of mass, and rotational variables, there is a simpler way of performing the evaluation of the partition functions $Q_A$ and $Q^*$. One goes to relative variables. Let $r_i, i = 0, \ldots, N-1$, be the position of carbon center $i$, and $b_i = r_i - r_{i-1}, i = 1, \ldots, N-1$, be the bond vectors. One can employ the bond vectors as integration variables and complete the set with $r_0$. Furthermore the variables $b_i, \theta_i, \phi_i$ are polar coordinates for the $b_i$ integration. The unspecified $\theta_i$ and $\phi_i$ are selected relative to an arbitrary orientation, and integration over these and over $r_0$ gives $8\pi^2 \Omega$. The potential is separable in the remaining variables, so that the partition function $Q_A$ is factorizable. $Q^*$ is not quite factorizable because the integration along the reaction coordinate, a collective mode, is omitted. If the omitted variable represented a stable mode, the integration could be restored and the difference accounted for by dividing the product of the frequencies of the included modes by that of the omitted mode. By an analytic continuation argument, detailed in Appendix B, the result goes through for an unstable omitted mode. The result is that $Q^*$ can be written as

$$Q^* = (2\pi k_BT)^{1/2} Q^0 |\lambda|^{1/2} \exp(-E^*/k_BT),$$

where $Q^0$ involves a product of factors, one for each de-
tion of steepest descent from the saddle point, given by
the eigenvector of the interaction matrix \( W \), correspond-
ing to the negative eigenvalue. The question of what the
reaction coordinate is physically can be thought of in
the following terms. Consider the system located at the
saddle point of the potential in the multidimensional
space. The problem is to determine what overall motion
in this space will lead to the greatest decrease of energy
for a given amount of motion. The net amount of motion
to be considered is

\[
\sum_{i=1}^{N} |\Delta \rho_i| = \hbar^2 |\Delta s|^3, \tag{4.3}
\]

where \( \Delta \rho_i \) is the displacement of the \( i \)th carbon center
and \( \Delta s \) is an arbitrarily fixed constant. Let us consider
some possible motions. First picture the motion in
which the transforming bond rotates and the tails rigidly
follow this rotation by swinging. True, this lowers the
energy because the transforming bond's energy moves
down from the torsional barrier, and in this motion
there is no rise in energy associated with distortion of
any other degree of freedom. However, in any such
motion the tails must undergo considerable movement,
so that for Eq. (4.3) to be satisfied very little rotational
movement of the transforming bond can occur. It fol-
lows that there is only a small decrease in energy. On
the other hand, by moving only the two centers adjacent
to the transforming bond a larger decrease in the tor-
sional potential can be achieved, but it is accompanied
by a large increase of energy due to distortion of neigh-
boring degrees of freedom.

The path of steepest descent is a compromise between
the former, long-range motion and the latter, extreme-
short-range motion; viz., the reaction coordinate is a
localized mode with motion of the carbon centers falling
off with distance from the transforming bond (in an in-
finitie chain). Such a localized mode takes a quite simple
form in the case of the one-dimensional transition
chain. It has been quantitatively described previously.5
We will discuss the localized modes and their relation
to \( \lambda \) for various molecular chains as a function of length
and conformation in Sec. V–VI.

V. RATE OF TRANSITION OF THE CENTRAL
BOND OF AN ALL TRANS CHAIN

We shall examine the transition rate for the \( t \rightarrow g^* \)
transition of the central bond of chains with all other
bonds in the trans state. Except for a few cases, noted
explicitly below, all rates reported are for a tempera-
ture such that the torsional barrier height is \( 4k_B T \) (i.e.,
\( T = 372 \) °K). In Fig. 8 is plotted the transition rate vs.
chain length \( N \). The rate decreases for increasing
length because for a fixed motion, \( \Delta s \), the multidimen-
sion space is composed less of central bond rotation as
the chain grows longer.

Particularly for small \( N \), it is apparent that adding a
carbon center to make an even number in the tail has
more of a rate inhibiting effect than adding an odd num-
ber. That is because each even numbered carbon is at
an increased distance from the axis of rotation of the
transforming bond compared with the previous center.
TABLE II. Localized mode for an all trans initial state, sixteen vertex chain.

<table>
<thead>
<tr>
<th>j</th>
<th>$D_{s,i}$, $i=8+j$</th>
<th>$D_{s,i}$, $i=8+j$ or $7-j$</th>
<th>$D_{s,i}$, $i=8+j$</th>
<th>$b_{s,i}p_{s,i}^*$, $i=8+j$ or $7-j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.57</td>
<td>-0.13</td>
<td>0.018</td>
<td>0.073</td>
</tr>
<tr>
<td>1</td>
<td>0.19</td>
<td>0.052</td>
<td>0.0085</td>
<td>0.039</td>
</tr>
<tr>
<td>2</td>
<td>-0.31</td>
<td>-0.059</td>
<td>0.015</td>
<td>0.019</td>
</tr>
<tr>
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<td>0.045</td>
<td>0.0073</td>
<td>0.0050</td>
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<td>0.0080</td>
<td>0.014</td>
</tr>
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</tr>
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<td>0.022</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.0013</td>
<td></td>
<td>0.017</td>
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</table>

(as is shown in Fig. 9). This illustrates an important geometric factor in the way that the rate is affected by the state of the tail.

The rates given in Fig. 8 can be reasonably fit with the curve

$$k = 4.19 + 10.4 \exp(-N/6.72) \text{ ns}^{-1},$$ (5.1)

indicating that the rate for a bond in an all trans macromolecule would be $4.19 \text{ ns}^{-1}$ and that only a 2\% decrease of rate will occur beyond $N=32$ (16 vertices per tail).

A further understanding of the effect of the tail can be achieved by examining the localized mode which is the reaction coordinate. For illustrative purposes, the results for $N=16$ are presented in Table II. It is convenient to view the localized mode in terms of changes of the torsional angles, bond angles, and bond lengths. (The relation between these variables and Cartesian vertex displacements is given in Appendix C.) For a total motion $ds$, as defined by Eq. (4.3), we will write for the change of bond length of bond $i$

$$\frac{db_i}{b_0} = D_{s,i} ds,$$ (5.2)

for the change of bond angle at vertex $i$

$$\frac{d\theta_i}{\theta_0} = D_{s,i} ds \text{ (rad)},$$ (5.3)

and for the change of torsional angle of bond $i$

$$\frac{d\phi_i}{\phi_0} = D_{s,i} ds \text{ (rad)}. $$ (5.4)

The distance of motion of the $i$th carbon is also of interest.

The following observations can be made. (1) The largest distortions in the localized mode are of the soft torsional angles. However, a localized mode can not be constructed without some bond length and angle distortion. We will return to this point in a future work. (2) The torsion in bonds an even number from the transforming bond (these bonds are parallel to the central bond) is greater than in the odd neighboring bonds, although the latter's torsion is not negligible. (3) The even rotations are of opposite sign to that of the central bond, which is the simplest manifestation of the minimization of motion of the tails. (4) The above rules may be broken near the chain ends for finite chains.

VI. EFFECT OF POLYMER CONFORMATION ON TRANSITION RATE

We next study the effect of the conformations of the tails on the transition rate. A systematic study is only practical for short chains, so in this section we report results for $N=6, 8, 12,$ and 16. The rates of $t-g^*$ transition of the central bond with various tail conformations are reported in Tables III–VI.

Several general conclusions can be drawn.

(1) If gauche bonds are located only in positions even to the central bond, then the rate of transition is close to that of the all trans chain, perhaps higher. This is because the even bonds are still all parallel to the central bond, as can be seen in Figs. 9 and 10, for instance. Thus a great deal of the distortion which diminishes the displacements far from the center can be taken up in bond rotation.

(2) As illustrated in Fig. 10, gauche bonds in even positions relative to the transforming bond can bring the centers closer to the axis of torsional rotation relative to an all trans chain. This decreases the displacement of tail units for a given rotation, accounting for an increased transition rate.

(3) On the other hand, gauche bonds as odd neighbors to the central bond turn the tail in such a way as to stiffen the tail toward the distortion needed to localized the mode (cf. Fig. 11). The tail then has a more rigid character so that a unit 3N-dimensional motion has a smaller component of central bond torsion. This is evident in the normalized reaction coordinate for the transition.

**TABLE III. Rate of the central $t-g^*$ transition in a six vertex chain for $E^*/k_B T=4$.**

<table>
<thead>
<tr>
<th>Initial state conformation</th>
<th>Rate (ns$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$tt$</td>
<td>16.05</td>
</tr>
<tr>
<td>$g^*tt$</td>
<td>12.56</td>
</tr>
<tr>
<td>$g^*t$</td>
<td>10.81</td>
</tr>
<tr>
<td>$g^<em>tg^</em>$</td>
<td>5.04</td>
</tr>
<tr>
<td>$g^<em>g^</em>$</td>
<td>5.87</td>
</tr>
<tr>
<td>$g^<em>g^</em>$</td>
<td>4.36</td>
</tr>
</tbody>
</table>

FIG. 9. Central bond (darkened) at the $tg^*$ barrier (60°) with an otherwise all trans chain.
FIG. 10. Central bond at the \( \tau g^* \) barrier. All odd neighbors of the central bond are \( \text{trans} \), but some even neighbors are \( \text{gauche} \). This brings units of the chain in closer to an axis defined by the central bond. Note that all even neighbor bonds of the central bond are parallel to it and can be effectively used in the localized mode.

Initial state \( \text{llll}^* \text{tg}^* \text{llll} \) given in Table VII. Note the nearly threefold decrease in the central bond's torsion as compared to the all \( \text{trans} \) chain of Table II, and an even greater decrease in the second neighbors' torsions (which are now of the same sign). The distortion of the bond angles, however, is increased. The greater rigidity of the tail is manifest in the increased displacement of the end unit.

(4) When only one of the odd neighbors is \( \text{gauche} \), as in Table VIII, the motion over the barrier is shifted away from the more rigid tail, and the rate is diminished nearly as greatly as from the all \( \text{trans} \) value.

(5) From the rate tables we also see, as expected, that the further the odd \( \text{gauche} \) neighbor is from the central bond, the less its effect on the rate is.

(6) If there is more than one \( \text{gauche} \) in the tail, the dominant effect on the rate if exerted by the one closest to the central bond. Additionally, the \( \text{gauche} \) bond do have a tendency to bring neighboring units closer to the axis of rotation, or move them away. This has a geometric effect as discussed under point (2).

VII. COMPARISON OF CALCULATED RATES WITH COMPUTER SIMULATIONS

So far we have presented transition rates from specified initial states. In order to compare these results with the recent simulations of Helfand, Wasserman, and Weber we must obtain an average rate, i.e., a rate weighted by the probability of the conformation of the tail:

\[
\bar{k} = \sum_{\text{conf}} \rho_{\text{conf}} k_{\text{conf}}
\]

(7.1)

where \( \rho_{\text{conf}} \) is the equilibrium probability of observing a particular conformation of the tails, and \( k_{\text{conf}} \) is the corresponding rate for that central bond to undergo \( \tau \rightarrow g^* \).

In the case of butane only the central bond has a conformational state. A Brownian dynamics simulation gives a transition rate of 29.3 \( \text{ns}^{-1} \) for \( E^* = 3.5 \ k_B T \). The present theory gives a rate of 30.0 \( \text{ns}^{-1} \), in very close agreement.

Brownian simulations have now been performed for octane for \( E^* = 3.5 \ k_B T \). The observed rates of the three different bonds are contrasted in Table IX with the calculated rates averaged over conformations. Again the agreement is good.

In order to compare the present theory with the polymer simulations we have studied the rates for chains of 28 carbon centers. Even for these finite chains a systematic study of the \( 3 \times 10^{14} \) conformations is prohibitive, so we have resorted to the following approach. The

\[
\text{TABLE IV. Rate of the central } \tau \rightarrow g^*\text{ transition in an eight vertex chain for } E^*/k_B T = 4. \text{ This list does not include all tail conformations.}
\]

<table>
<thead>
<tr>
<th>Initial state conformation</th>
<th>Rate (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tt)(tt)</td>
<td>7.29</td>
</tr>
<tr>
<td>(g't)(tt)</td>
<td>9.05</td>
</tr>
<tr>
<td>(g't)(tt)(tt)</td>
<td>7.69</td>
</tr>
<tr>
<td>(tg')(tt)</td>
<td>5.83</td>
</tr>
<tr>
<td>(tg')(tt)(tt)</td>
<td>4.83</td>
</tr>
<tr>
<td>(tg')(g't)</td>
<td>2.60</td>
</tr>
<tr>
<td>(tg')(tg')(tt)</td>
<td>2.12</td>
</tr>
<tr>
<td>(tg')(tg')(g't)</td>
<td>1.80</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(tt)</td>
<td>9.83</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(g't)</td>
<td>8.24</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(tg')(tt)</td>
<td>2.40</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(tg')(g't)</td>
<td>3.39</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(tg')(tg')(tt)</td>
<td>3.58</td>
</tr>
<tr>
<td>(tg')(tg')(tg')(tg')(tg')(g't)</td>
<td>3.70</td>
</tr>
</tbody>
</table>

\[
\text{TABLE V. Rate of the central } \tau \rightarrow g^*\text{ transition in a twelve vertex chain for } E^*/k_B T = 4. \text{ This list does not include all possible tail conformations.}
\]

<table>
<thead>
<tr>
<th>Initial state conformation</th>
<th>Rate (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tttt)</td>
<td>5.52</td>
</tr>
<tr>
<td>(g'tt)(tttt)</td>
<td>5.47</td>
</tr>
<tr>
<td>(g'tt)(tttt)(tttt)</td>
<td>5.15</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)</td>
<td>3.92</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)(tttt)</td>
<td>4.08</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)(tttt)(tttt)</td>
<td>7.18</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)(tttt)(tttt)(tttt)</td>
<td>5.40</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)(tttt)(tttt)(tttt)(tttt)</td>
<td>4.37</td>
</tr>
<tr>
<td>(tg')(tttt)(tttt)(tttt)(tttt)(tttt)(tttt)(tttt)</td>
<td>5.18</td>
</tr>
</tbody>
</table>

TABLE VI. Rate of central $t \rightarrow g$ transition in a sixteen vertex chain for $E^*/k_BT = 4$. Not all conformations are included.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Rate (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tttttt)(tttttt)</td>
<td>5.06</td>
</tr>
<tr>
<td>(gg'ttttttttttttt)</td>
<td>4.67</td>
</tr>
<tr>
<td>(gg'hhhhhhhhhhhh)</td>
<td>4.61</td>
</tr>
<tr>
<td>(gg'ttttttttttttt)</td>
<td>4.07</td>
</tr>
<tr>
<td>(gg'ttttttttttttt)</td>
<td>4.24</td>
</tr>
<tr>
<td>(gg'ttttttttttttt)</td>
<td>4.71</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.32</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.48</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.57</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>6.54</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>6.82</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.87</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>2.81</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.60</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.24</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.36</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>6.65</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>5.57</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.82</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>1.12</td>
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<tr>
<td>(tttt'tttttttttt)</td>
<td>1.22</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>1.13</td>
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<tr>
<td>(tttt'tttttttttt)</td>
<td>4.18</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.88</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>2.70</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.01</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.26</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.13</td>
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<tr>
<td>(tttt'tttttttttt)</td>
<td>1.19</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>1.27</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>6.00</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.73</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.64</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.26</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>4.42</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>3.29</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>1.15</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>1.17</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.75</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.54</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.66</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>0.75</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>5.67</td>
</tr>
<tr>
<td>(tttt'tttttttttt)</td>
<td>5.36</td>
</tr>
</tbody>
</table>

The Brownian dynamics simulation rate$^5$ of $k = 4.6$ ns$^{-1}$. The faster transition rate for the polymer simulation may reflect the cooperativity between conformational transitions, absent in the present calculation. Cooperative transitions can greatly decrease the amount of motion allowed with no net energy cost. Furthermore, if one transition induces another as a cooperative pair then the net rate is increased. This observation is consistent with the excellent agreement of the calculated and simulated rate for butane, where no cooperativity can occur. In the case of octane only a small amount of cooperativity is observed and agreement is still good.

VIII. OBSERVATIONS AND CONCLUSIONS

Central to the current research is the assumption that standard reaction rate theory provides a consistent and plausible description of the mechanism of polymer conformational transitions. That is to say, the presence of modes with long correlation times in the polymer does not appreciably affect the rate of conformational transitions. The transition rate then depends only on the single barrier height $E^*$, the torsional force constants of the bond undergoing transition, and the negative eigenvalue $\lambda$, which represents the curvature in the direction of the reaction coordinate. The effects of polymer geometry, i.e., conformation and length of the tails, enter through $\lambda$ only and are manifest in the associated localized mode. We emphasize that because the reaction coordinate is a localized mode the rates are finite even for an infinite polymer and are influenced only by fairly local conditions. This makes the theory reasonably easy to apply for the purposes of making either quantitative or qualitative predictions. Once one has obtained a rate for all trans tails one can examine a model with another tail conformation and, on the basis of the degree to which the central bond's rotations can be taken up in neighbor counter rotations and the distance of near neighbors from the rotation axis, one can make reasonable estimates of the relative transition rates.

An observation about the temperature dependence of the reaction rate is important. The rate is fairly sensitive to having trans bonds as odd neighbors, especially in the first and third position. Consider a molecule with the trans state energetically favored. As the temperature falls the activation energy factor, $\exp(-E^*/k_BT)$, falls, but the prefactor may be speeded up by the in-

dominant influence on the rate is exerted by the four nearest rotational states on each side of the central bond. Hence we systematically ran through all the conformations of the first two bonds on both sides, using proper equilibrium weights. The states of the next two bonds on each side were varied statistically. For the remainder of the tails we employed in every case the same representative conformation, $tg'tg' ttg'$ on the left, and $tg'tg' g' ttt$ on the right. Thus, in all, we sampled 81 conformations.

With a temperature of $T = 372^\circ K (E^*/k_BT = 4)$ an average rate of $k = 1.66$ ns$^{-1}$ was found, to be contrasted with

TABLE VII. Localized mode for (tttttt'g')(tttttt) initial state, sixteen vertex chain.

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$D_{ij}$</th>
<th>$D_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j = i + 8$</td>
<td>$i = 8 + j$</td>
<td>$i = 8 + j$</td>
</tr>
<tr>
<td>0</td>
<td>0.0035</td>
<td>0.055</td>
</tr>
<tr>
<td>1</td>
<td>0.057</td>
<td>0.0035</td>
</tr>
<tr>
<td>2</td>
<td>0.038</td>
<td>0.057</td>
</tr>
<tr>
<td>3</td>
<td>0.032</td>
<td>0.0035</td>
</tr>
<tr>
<td>4</td>
<td>0.032</td>
<td>0.0035</td>
</tr>
<tr>
<td>5</td>
<td>0.032</td>
<td>0.0035</td>
</tr>
<tr>
<td>6</td>
<td>0.032</td>
<td>0.0035</td>
</tr>
<tr>
<td>7</td>
<td>0.032</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
crease in the number of trans bonds. The result may be an effective activation energy less than a barrier height.

In conclusion, we feel that a framework has been provided for discussing important aspects of the rate of conformational transition rates, although we recognize that for chains our understanding will not be complete until cooperative transition phenomena can be described.

It is our intention to apply the theory to more complex polymers than those treated here.

ACKNOWLEDGMENT

We thank Mrs. Z. R. Wasserman for her assistance in preparing the figures.

APPENDIX A: HARMONIC APPROXIMATION TO THE POTENTIAL ENERGY

Consider that one of the stationary points (minima or saddle points) of the potential energy corresponds to a vector in the $3N$-dimensional space $r^{(0)}$. Let a displacement from $r^{(0)}$ be represented by $p$ with three-dimensional components $(\rho_1, \rho_2, \ldots, \rho_N)$ and $3N$-dimensional components $(\rho_{i1}, \rho_{i2}, \rho_{i3}, \rho_{i4}, \ldots, \rho_{iN})$. The objective of this Appendix will be to expand the potential of Sec. II to terms quadratic in components of $p$.

The bond stretching potential

$$ v_s(b_i) = \frac{1}{2}(b_i - b_0)^2 $$

(2.1)

is easiest to handle. Note that

$$ b_i = b_0 e_i + \rho_i - \rho_{i-1} $$

(A1)

where $e_i$ is a unit vector along the unperturbed bond $i$. Thus, to first order

$$ b_i = b_0 e_i + e_i \cdot (\rho_i - \rho_{i-1}) $$

(A2)

and this is all that is needed to get $v_s$ correct to second order. The total bond stretching potential is

$$ v_s = \frac{1}{2} \sum_{i=1}^{n} (e_i \cdot (\rho_i - \rho_{i-1}))^2 $$

(A3)

The object is to put this in the form of a $V$ or $W$ matrix, as in Eq. (3.9) or (3.10). It is necessary to define a coordinate system in which to express $e_i$. We have used the single coordinate system defined at vertex zero and have transformed all unit bond vectors into this coordinate system by means of rotation matrices [discussed in Flory’s Appendix B (Ref. 11)]. Then one must assign the coefficient of $\rho_i \rho_{ij}$ in Eq. (A3) to the $(ij;ji)$ box of the matrix (best regarded as composed of $3 \times 3$ blocks).

$$ v_s(\theta_i) = \frac{1}{2} \sum_{i} \cos \theta_i \cos \theta_i $$

(A4)

The potential can be expanded by noting that

$$ \theta_i = \theta_{i-1} e_i \cdot \theta_{i-1} / |\theta_{i-1}| $$

(A5)

and using, to first order,

$$ \theta_i = \theta_{i-1} + \sum_{j=1}^{n-1} (\theta_j \cos \theta_j) \cdot (\rho_j - \rho_{j-1}) $$

(A6)

The only two nonzero terms in this sum are

$$ v_n \cos \theta_i = g_i b_i (e_i \cdot \theta_i) / b_0 $$

(A7)

$$ v_{n+1} \cos \theta_i = h_i b_i (e_i \cdot \theta_i) / b_0 $$

(A8)

The total bond angle bending potential is

$$ v_s = \frac{1}{2} \sum_{i=1}^{n} (\theta_i \cos \theta_i) $$

(A9)

and again the task of a computer routine is to pick out the coefficient of $\rho_{i1} \rho_{i1}$ and assign it to the correct box.

The harmonic approximation to the torsional potential $v_T(\phi_i)$ is somewhat more intricate to develop. The explicit form of $v_T$ has been given by Eq. (2.3). Here we need merely write

$$ v_T(\phi_i) = w(\cos \phi_i) $$

(A10)

and note that

$$ \cos \phi_i = (b_{i-1} \cdot b_i) / |b_{i-1}| \cdot |b_i| - \cos \theta_i \cos \theta_i $$

$$ \sin \phi_i = \sin \theta_i $$

(A11)

Suppose that $\phi_{10}$ is the location of the extremum of $v_s$ about which the expansion is to be made. The trans

| Location of | Calculated | Simulation |
| transforming | rotational | rate | rate |
| angle, $\phi_i$; $i$ | | (ns⁻¹) | (ns⁻¹) |
| 2 or 6 | 18.5 | 20.7 |
| 3 or 5 | 13.7 | 13.3 |
| 4 | 9.8 | 12.7 |

case, \( \phi_{i0} = 0 \), and non\(\tau\) case must be treated separately.

If \( \phi_{i0} \neq 0 \) then \( w \) can be expanded in Taylor series in \( \cos \phi_i - \cos \phi_{i0} \):

\[
w(\cos \phi_i - \cos \phi_{i0}) = w_{i0} + \frac{1}{2} w_{i0}^2 (\cos \phi_i - \cos \phi_{i0})^2 ,
\]

where \( w_{i0} \) and \( w_{i0}' \) are the functions evaluated at \( \phi_i = \phi_{i0} \). As in the previous cases a linear expansion of \( \cos \phi_i \) in components of \( \rho \) is called for:

\[
\cos \phi_i = \phi_{i0} + \sum_{j=1}^{N-1} (\nabla_{j} \phi_{i0}) \cdot (\rho_{j} - \rho_{j0}) .
\]

There are three nonvanishing gradients for general \( j \):

\[
\nabla_{j} \cos \phi,i = \frac{-O_{j}}{b_{j0} \sin \theta_{0}} = \frac{-\cos \phi_{i0} (1 - \cos \phi_{i0})}{b_{j0} \sin \theta_{0}} \cdot \left( e_{i,j-1} - 2 \cos \theta_{0} e_{i,j} + e_{i,j+1} \right),
\]

\[
\nabla_{x+1} \cos \phi,i = \frac{F_{j}}{b_{j0} \sin \theta_{0}} = \frac{1}{b_{j0} \sin \theta_{0}} \times \left[ -\cos \phi_{i0} e_{i,j+1} - \cos \theta_{0} (1 - \cos \phi_{i0}) e_{i,j} + e_{i,j+1} \right],
\]

\[
\nabla_{x+1} \cos \phi,i = \frac{e_{i,j+1} - \cos \theta_{0} (1 - \cos \phi_{i0}) e_{i,j} - \cos \theta_{0} e_{i,j+1} \right].
\]

Thus we can write

\[
v'(\phi_{i0}) = w_{i0} + \frac{w_{i0}^{'}}{2b_{j0} \sin \theta_{0}} \times \left[ (\rho_{x+1} - \rho_{x-1} - \rho_{x}) + O_{j} \cdot (\rho_{x+1} - \rho_{x-1}) + F_{j} \cdot (\rho_{x+1} - \rho_{x}) \right] \cdot (\phi_{i0} \neq 0).
\]

At the \( \tau \) position, however, \( dv/d\cos \phi_{i0} \) does not have to vanish because \( d\cos \phi_i / d\phi_{i0} \) does. Thus one can write

\[
v'(\phi_{i0}) = w_{i0} + \frac{w_{i0}^{'}}{2} \sin \theta_{0} \cdot (\phi_{i0} = 0).
\]

As the starting point for a linear expansion of \( \phi_i \) in the Cartesian displacements it is convenient to use

\[
\sin \phi_{i0} = \left( e_{i+1} \times e_{i} \right) \cdot (e_{i} \times e_{i+1}) / \sin \theta_{0} \cdot \sin \theta_{0} .
\]

Then one can show, by inserting Eq. (A1) in Eq. (A19) and retaining lowest order terms, that near \( \tau \)

\[
\phi_i = \phi_{i0} + \frac{f_{j}}{b_{j0} \sin \theta_{0}} \cdot (\rho_{x+1} - \rho_{x-1} - \rho_{x} + \rho_{x+1}) ,
\]

\[
f_{j} = e_{i,j} \cdot \sin \theta_{0} ,
\]

where \( f_{j} \) is the \( \tau \) well conformation of \( i \). Use has been made of the fact that for bond \( i \) \( e_{i} \) is always \( e_{i+1} \).

Insertion of Eq. (A20) into the potential expansion, Eq. (A18), yields the quadratic form which may be used to identify the interaction matrix.

APPENDIX B: PARTITION FUNCTION IN THE WELL AND AT THE SADDLE POINT

In the rate calculation, one is called upon to evaluate partition functions: \( Q_{i} \) in the initial state well and \( Q^{*} \) for degrees of freedom orthogonal to the reaction coordinate at the saddle point. As mentioned in the text such partition functions may be determined by transformation to internal degrees of freedom, center of mass variables, and Euler angles for the molecule's orientation. However, for a molecule with a separable potential of the form of Eq. (2.8), there is a simpler way to proceed. Consider the partition function in the initial well. To within terms that go like \( \exp(-E^*/k_{B}T) \) we can extend the potential appropriate near the bottom of the well to more removed positions in such a way that the potential is high in those regions (e.g., harmonically). The partition function integral is over \( r = r_{0}, r_{1}, ..., r_{N-1} \) and has an integrand which is a product of functions of the variables \( b_{i}, \theta_{i}, \phi_{i} \) individually. Consider the \( r_{x+1} \) integration at fixed \( r_{x}, ..., r_{N-2} \). The variables \( b_{x+1}, \theta_{x+1}, \phi_{x+1} \) are the spherical coordinates locating \( r_{x+1} \) in the coordinate system defined on center \( N-2 \) (cf. Sec. II and Ref. 11). The variables are orthogonal, and the Jacobian of the transformation from Cartesian to spherical coordinates is \( b_{x+1} \sin \theta_{x+2} \). After performing the integration over \( r_{x+1} \) the \( r_{x+2} \) integration is done in spherical coordinates based on the \( N-3 \) coordinate system. This is repeated down the chain, but since the potential does not depend on \( \theta_{i} \) the integrals over these variables gives \( 8\pi \sin \theta \). The result is

\[
Q_{i} = 8\pi^{2} \Omega b_{i}^{N-1} \prod_{i=1} \int_{0}^{\pi/2} d\phi_{i} (2\pi \sin \theta_{i} / k_{B}T),
\]

\[
Q^{*} = \int_{0}^{\pi/2} \frac{d\phi_{i}}{k_{B}T} \sin \theta_{i} ,
\]

\[
= \frac{2\pi \sin \theta_{i}}{k_{B}T} ,
\]

where \( c(i) \) is the conformational state of bond \( i \). The approximate forms are given in order to make contact with small vibration theory as used throughout the paper when working in Cartesian variables.

Next attention must be turned to the evaluation of the partition function \( Q^{*} \). In Sec. III we found that this may be written as

\[
Q^{*} = (2\pi \sin \theta / k_{B}T)^{1/2} \sin \theta^{1/2} \exp(-E^{*}/k_{B}T) ,
\]

\[
Q^{*} = 8\pi^{2} \Omega \left( \frac{\text{det} W_{i}}{m^{3}} \right)^{1/2} \frac{N^{2} / 2}{(2\pi \sin \theta / k_{B}T)^{(3N-6)/2}}
\]

a result obtained by substituting Eq. (3.15) into Eq. (3.14). Clearly, \( Q^{*} \) is not a partition function since \( \text{det} W_{i} \) is negative. However, if the force constant \( -\gamma^{*} \) on the bond at the barrier were to be replaced by \( -\gamma^{*} \) with \( \alpha > \gamma^{*} \), then one would have a partition function, \( Q^{*}(\gamma) \), in fact one completely akin to \( Q_{i} \) which we just evaluated. The only difference would be that for \( i \) the transforming bond, \( q_{i}(\gamma) \) always being the initial
state of this bond) would be replaced by \( q_\alpha (\alpha - \gamma) \). One can now analytically continue \( Q^*(\alpha) \), which has a branch point at \( \alpha = \gamma \), to \( \alpha = 0 \), selecting the phase so as to make \( Q^*/Q^* \) positive. The partition functions for all degrees of freedom except the rotation of the transforming bond are identical so that, using Eq. (8), Eq. (4.1) is obtained.

**APPENDIX C: THE REACTION COORDINATE IN \( b_1, \theta_1, \phi_1 \) COORDINATES**

In Appendix A we described how to set up the potential of the system in the neighborhood of the saddle point as a quadratic form in the Cartesian coordinates of the displacements of the carbon centers. The eigenvector \( \rho^* \) of \( W \) corresponding to eigenvalue \( \lambda \) is the reaction coordinate, and we normalized it so that

\[
\sum_i |\rho_i|^2 = 1.
\]  
(C1)

The values of \( |\rho_i| \) as reported in Tables II, VII, and VIII lend some insight into the nature of the reaction coordinate, but the individual Cartesian components have little significance. Much more insight is gained by examining the stretching, bending, and rotating of the various bonds and angles. The reaction coordinate represents a direction in the \( 2N \)-dimensional space so that the meaningful quantity is the rate of change of the internal variables as one moves in the direction of the reaction coordinate. That rate of change was defined by the \( D_{b_1}, D_{\theta_1}, \) and \( D_{\phi_1} \) of Eqs. (5.2)--(5.4), and now we present the relation between these and the Cartesian \( \rho^* \). Actually, most of the required mathematics was developed in Appendix A.

Using Eq. (A2) one sees that for a motion \( \rho^* b_0 \) the change in bond length can be calculated, so that

\[
D_{b_1} = \frac{(1/b_0) db_1}{ds},
\]  
(C2)

\[
= e_{1i} \cdot (\rho_i^* - \rho_1^*).
\]  
(C3)

Likewise, from Eqs. (A6)–(A8)

\[
D_{\theta_1} = \frac{d\theta_1}{ds},
\]  
(C4)

\[
= (-1/\sin \theta_0) [e_1 \cdot (\rho_1^* - \rho_{1i}^*) + e_i \cdot (\rho_{1i}^* - \rho_i^*)].
\]  
(C5)

The formula to evaluate \( D_{\phi_1} \) depends on whether the saddle point conformation of bond \( i \) is trans or not. For \( \phi_{10} \) not trans, Eqs. (A13)–(A16) tell us that

\[
D_{\phi_1} = \frac{d\phi_1}{ds},
\]  
(C6)

\[
= (-1/\sin^2 \theta_0 \sin \phi_{10}) [e_1 \cdot (\rho_1^* - \rho_{1i}^*) + e_i \cdot (\rho_{1i}^* - \rho_i^*)].
\]  
(C7)

For \( \phi_{10} = 0 \) we turn to Eq. (A20) to show that

\[
D_{\phi_1} = \frac{d\phi_1}{\sin \theta_0},
\]  
(C8)

\[
= (-1/\sin \theta_0) [e_1 \cdot (\rho_1^* - \rho_{1i}^*) + e_i \cdot (\rho_{1i}^* - \rho_i^*)].
\]  
(C9)

References:

11. P. J. Flory, Statistical Mechanics of Chain Molecules (Interscience, New York, 1969), p. 20. The only difference in definitions is that our \( e_{1p}, e_{1p}, e_{1p} \) axes are Flory's \( e_{1p}, e_{1p}, e_{1p} \) axes. With our definition, \( b, \theta, \phi \) are the spherical coordinates as usually defined.