Kinetics of the self-intersection of macromolecules in the Gaussian-chain model

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The kinetics of intrachain collisions in polymer molecules of arbitrary configuration described in the Gaussian chain approximation are investigated. An accurate exact value of the mean collision time of two reactive segments is found in the limit of a small reaction volume. It is shown that the problem can be reduced to calculating the resistance between two corresponding points in an electrical circuit having the same topology as the molecule under consideration. © *1996 American Institute of Physics.* [S1063-7761(96)01101-3]

1. INTRODUCTION

The description of intramolecular relaxation processes in polymer molecules in a dilute solution, particularly the kinetics of intrachain collisions, is important in the study of numerous physical and chemical processes involving active segments within a polymer chain. The essential point of such processes is that active groups in a macromolecule undergo chemical reactions upon collision, as in the case of intramolecular catalytic or intrachain cross-linking reactions, or energy-transfer processes, as, for example, in the case of luminescence quenching.[1] Hence there is great interest in the problem of the mean collision time of two particular segments in a polymer chain undergoing Brownian motion in a dilute solution.

From the mathematical standpoint the solution of this problem requires an analysis of the Fokker–Planck equation for a system of many particles interacting with one another and with the solvent. In most cases such an analysis is very difficult due to the complexity of these interactions. Nevertheless, it is well known that the statistical properties of a polymer chain in a solution at a certain temperature allow us to identify it with a system of coupled oscillators.[1,2] This so-called Gaussian model, which faithfully describes the equilibrium properties of a macromolecule, can also serve as an approximation for studying its relaxation properties. Here it must be borne in mind that although this model does not provide a satisfactory description of the kinetics of real molecules, since the neglect of such important factors as the hydrodynamic corrections in the kinetic equation results in incorrect scaling for the characteristic relaxation time,[3] it can still serve as a starting point for subsequent systematic consideration of these corrections and as a test for various approximations and numerical methods.

The first attempt to systematically analyze the kinetics of intramolecular collisions and reactions with consideration of all the important factors influencing the kinetic scaling was made by Wilemski and Fixman.[4] After several approximations, they succeeded in obtaining a closed expression for the kinetic constants of intramolecular reactions and the rate of luminescence quenching in the case of a linear polymer chain with active groups located at its ends. The results of Wilemski and Fixman prompted the studies of Sunagawa and Doi,[5–7] in which a linear chain with terminal active groups was considered in the Gaussian approximation and accurate values were found for the kinetic constants of reactions. A comparison of their results with the results in Ref. 4 showed that in the case of a purely Gaussian chain, the approximations used in the latter work give inaccurate values for the kinetic constants when the reaction volume is small compared with the volume occupied by the molecule and predict incorrect behavior for these constants when the reaction volume is increased above a certain level.

The present paper shows how the results in Refs. 5–7 can be generalized to the case of a Gaussian chain of arbitrary configuration. The mean collision time between any two segments is found, and it is shown that the Gaussian approximation makes it possible to compare each macromolecule with an electrical circuit and to reduce the problem of the relative motion of any two segments to the problem of calculating the resistance of that circuit.

2. FORMULATION OF THE PROBLEM

According to the Gaussian model, we must consider the Brownian motion of a system of N particles interacting according to a quadratic law. It is convenient to specify the spatial configuration of such a system with a vector $\mathbf{R}=(X_1,\ldots,x_N;y_1,\ldots,y_N;z_1,\ldots,z_N)^T$, which is constructed from the Cartesian coordinates of the individual particles x_i,y_i, and z_i. The Fokker–Planck equation for such a system has the form

$$\frac{\partial P}{\partial T}=D\left(\frac{\partial}{\partial\mathbf{R}}\right)^2 P+\frac{\partial}{\partial\mathbf{R}}(\mu\kappa\hat{A}\mathbf{R}P). \tag{1}$$

Here $P(\mathbf{R},t)$ is the distribution function in the coordinate space of the entire system, and D is the diffusion coefficient, which is related to the mobility μ by the Einstein relation $D=\mu T$. It is assumed that D and μ are identical for all the particles appearing in the system; $\hat{A}$ is a square positive definite matrix that specifies the interaction energy of the particles,

$$U(\mathbf{R})=\frac{1}{2}\kappa(\mathbf{R},\hat{A}\mathbf{R}), \tag{2}$$

where κ is a coefficient with dimensions of stiffness.

Let us clarify the origin of the potential (2). We consider a long linear macromolecule in the model of a freely articulated chain, i.e, a sequence of identical rigid segments joined by ball-and-socket joints. We consider the vector joining the ends of the molecule. According to the central limit theorem, in a state of statistical equilibrium the probability density that this vector equals **R** is

$$P_N(\mathbf{R})=(2\pi N l^2/3)^{-3/2}\exp(-3\mathbf{R}^2/2Nl^2),$$

where l is the segment length and N is the number of segments.

The distribution function $P_N(\mathbf{R})$ coincides with the Boltzmann distribution function for a harmonic oscillator with stiffness $3T/Nl^2$. Hence it is seen that a long polymer chain in a state of thermodynamic equilibrium can be represented as a harmonic oscillator. It is clear that a macromolecule of arbitrary topology can be represented as a system of oscillators (of course, the macromolecule must consist of long subunits so that the Gaussian distribution is satisfied to sufficient accuracy). This model was first proposed and used to analyze the kinetics of macromolecules in a dilute solution by Kargin and Slonimskiĭ in 1948.[1] We note that the model under consideration actually describes a far broader class of polymer chains.[1,3]

We choose any pair of particles with the indices k and m. If these particles approach each other within a distance smaller than a certain value q, we assume that a collision has occurred between them. Our goal is to investigate the relative motion of these particles and to find their mean collision time in the case in which the system as a whole is in a state of thermodynamic equilibrium.

3. PAIRWISE CORRELATION FUNCTION

In (1) we perform the orthogonal coordinate transformation $\mathbf{R}=\hat{\Lambda}\mathbf{Y}$, that diagonalizes the matrix $\hat{A}$. In the new variables the solution of Eq. (1) for the initial conditions

$$P|_{t=0}=\delta[\mathbf{Y}-\mathbf{Y}(0)]$$

has the form

$$P(\mathbf{Y},t)=\prod_{n=1}^{3N} P_n(Y_n,t), \tag{3}$$

where

$$P_n(Y_n,t)=\left(\frac{\kappa\mu a_n}{2\pi D[1-\exp(-2\mu\kappa a_n t)]}\right)^{1/2} \times\exp\left(-\frac{a_n\mu\kappa[Y_n-Y_n(0)\exp(-\mu\kappa a_n t)]^2}{2D[1-\exp(-2\mu\kappa a_n t)]}\right). \tag{4}$$

Here a_n denotes the eigenvalues of $\hat{A}$, and Y_n denotes the components of the vector **Y**. If the system has translational symmetry, three of the eigenvalues a_n appearing in Eq. (4) are equal to zero. However, Eq. (4) then remains valid, if it is taken in the sense of the limiting transition when the respective eigenvalues tend to zero.

We now calculate the pairwise correlation function $P_{km}(\mathbf{r}_{km},t)$ for the particles numbered k and m (in the case of a spatially homogeneous system it depends only on the difference between the coordinates of the particles $\mathbf{r}_{km}$). By definition, we have

$$P_{km}(\mathbf{r}_{km},t)=\int\dots\int P(\mathbf{R},t\,\delta(\mathbf{r}_k-\mathbf{r}_m-\mathbf{r}_{km})d\mathbf{r}_1\dots d\mathbf{r}_n. \tag{5}$$

The difference between the coordinates of the individual particles appearing in (5) $\mathbf{r}_k-\mathbf{r}_m$ can be expressed in terms of the vector **R**:

$$\mathbf{r}=\hat{F}^{km}\mathbf{R},$$

where the matrix $\hat{F}^{km}$ has the form

$$(\hat{F}^{km})_{ij}=\delta_{ik}-\delta_{jm}, \quad i=1,\dots,3; \quad j=1,\dots,3N. \tag{6}$$

Using such a representation for the vector $\mathbf{r_k}-\mathbf{r}_m$, we rewrite (5) in normal coordinates:

$$P_{km}(\mathbf{r}_{km},t) =\int\dots\int P(\hat{\Lambda}\mathbf{Y},t)\,\delta(\hat{F}^{km}\hat{\Lambda}\mathbf{Y}-\mathbf{r}_{km})dY_1\dots dY_{3N}. \tag{7}$$

For convenience in the ensuing calculations, we introduce the matrix functions $\hat{L}$ and $\hat{N}$:

$$\hat{L}=\sqrt{1-\exp(-2\mu\kappa\hat{A}t)}, \quad \hat{N}=\exp(-\mu\kappa\hat{A}t). \tag{8}$$

In (7) we perform the replacement of variables

$$\hat{L}\mathbf{X}=\mathbf{Y}-\hat{N}\mathbf{Y}(0). \tag{9}$$

Then in the new variables with consideration of (4) and (5) we have

$$P_{km}(\mathbf{r}_{km},t)=\int\dots\int g(\mathbf{X})\,\delta(\hat{F}^{km}\hat{\Lambda}\hat{L}\mathbf{X}+\hat{F}^{km}\hat{\Lambda}\hat{N}\mathbf{Y}(0) -\mathbf{r}_{km})dX_1\dots dX_{3N}, \tag{10}$$

where

$$g(\mathbf{X})=\prod_{n=1}^{3N}\left(\frac{\mu\kappa a_n}{2\pi D}\right)^{1/2}\exp\left(-\frac{\mu\kappa a_n X_n^2}{2D}\right).$$

Such an integral can be calculated using the formula[8]

$$\int\dots\int F\left(\sum_{j=1}^{k} b_j x_j\right)\exp\left(-\sum_{i,j=1}^{k} g_{ij}x_j x_i\right)dx_1\dots dx_k =\frac{\pi^{(k-1)/2}}{(c^2\det\hat{G})^{1/2}}\int F(u)\exp\left(-\frac{\mu^2}{c^2}\right)du, \tag{11}$$

where

$$\hat{G}=(g_{jk}), \quad c^2=\sum_{j,k}\bar{g}_{jk}b_j b_k, \quad (\bar{g}_{jk})=\hat{G}^{-1}.$$

Due to the equivalence of the x,y, and z directions, the matrices $\hat{A}$ and $\hat{\Lambda}$ have a block structure, owing to which the integral (10) can be factored and reduced to (11). Ultimately we obtain

$$P_{km}(\mathbf{r}_{km},t)=\frac{1}{\pi^{3/2}C_{km}^{3}}\times\exp\left\{-\frac{[\mathbf{r}_{km}-\hat{F}^{km}\exp(-\mu\kappa\hat{A}t)\mathbf{R}(0)]^{2}}{C_{km}^{2}}\right\},\tag{12}$$

where

$$C_{km}^{2}(t)=\sum_{n}\frac{2D}{\mu\kappa}[1-\exp(-2\mu\kappa a_{n}t)]\frac{(\lambda_{kn}-\lambda_{mn})^{2}}{a_{n}},\tag{13}$$

λ_{ij} denotes the elements of $\hat{\Lambda}$, and the summation is carried out over the n which corresponds to the zero eigenvalues of one block of $\hat{A}$.

Let us investigate the asymptotic behavior of P_{km} in the limits $t\rightarrow 0$ and $t\rightarrow\infty$. We first show that despite the fact that $\hat{A}$ has three zero eigenvalues, $\hat{F}^{km}\exp(-\mu\kappa\hat{A}t)\mathbf{R}(0)\rightarrow 0$ when $t\rightarrow\infty$. In fact, all the eigenvalues of $\hat{A}$ are nonnegative. The three zero eigenvalues correspond to the translational symmetry of the system as a whole. We expand $\mathbf{R}(0)$ in the eigenvectors $\mathbf{B}_n$ of $\hat{A}$:

$$\hat{F}^{km}\exp(-\mu\kappa\hat{A}t)\sum_{n=1}^{3N}\beta_{n}\mathbf{B}_{n}$$

$$=\hat{F}_{km}\sum_{n=1}^{3N}\beta_{n}\exp(-\mu\kappa a_{n}t)\mathbf{B}_{n}.$$

When $t\rightarrow\infty$, only the vectors that correspond to the zero eigenvalues a_n of the matrix are retained in this sum, but such vectors have the structure

$$\mathbf{B}=(x,\dots,x;y,\dots,y;z,\dots,z)^{T}$$

and vanish under the action of the matrix $\hat{F}^{km}$. Utilizing this fact, we proceed to the limit $t\rightarrow\infty$ in (12):

$$P_{km}(\mathbf{r}_{km},\infty)=\frac{1}{\pi^{3/2}C_{km}^{3}(\infty)}\exp\left(-\frac{\mathbf{r}_{km}^{2}}{C_{km}^{2}(\infty)}\right).\tag{14}$$

This distribution function coincides, as it should, with the equilibrium distribution function of a harmonic oscillator with stiffness

$$\kappa_{km}=\frac{2T}{C_{km}^{2}(\infty)}=\kappa\left(\sum_{n}\frac{(\lambda_{kn}-\lambda_{km})^{2}}{a_{n}}\right)^{-1}.\tag{15}$$

On the other hand, letting t go to zero in (13), we find

$$C_{km}^{2}(t)\approx\sum_{n}4Dt(\lambda_{kn}-\lambda_{mn})^{2}=4D_{km}t,\tag{16}$$

where μ_{km} and D_{km} must be construed as the effective mobility and diffusion coefficient for the pair consisting of particles k and m. Opening the parentheses in (16) and utilizing the orthogonality of $\hat{\Lambda}$, we easily see that

$$D_{km}=2D.$$

Taking into account the Einstein relation for D_{km} and μ_{km}, we ultimately obtain

$$D_{km}=2D,\quad \mu_{km}=2\mu.\tag{17}$$

Thus, at times which significantly exceed the relaxation time of the molecule as a whole, the relative motion of any two particles appearing in the system can be represented as the motion of a harmonic oscillator with the parameters specified by (15) and (17).

4. MEAN COLLISION TIME OF PARTICLES

Since the relative motion of two particles can be reduced to the motion of a single harmonic oscillator with a radius vector coinciding with the vector $\mathbf{r}_{km}$, the problem of the mean collision time of the particles can be reduced to the problem of the determining when the oscillator reaches the surface of a sphere of radius q located at the origin of coordinates. (We recall that if two particles approach each other at a distance q, it is assumed that a collision occurs between them.) The mean time to reach this surface τ can be obtained directly as a solution of the Pontryagin equation[9]

$$D_{km}\nabla^{2}\tau-\mu_{km}\kappa_{km}\mathbf{r}\frac{\partial\tau}{\partial\mathbf{r}}=-1\tag{18}$$

under the boundary conditions[10]

$$\tau\,|_{|\mathbf{r}|=q}=0,\quad \left.\frac{\partial\tau}{\partial r}\right|_{|\mathbf{r}|=\infty}=0.$$

Passing to spherical coordinates in (18) and taking into account relation (17), we obtain

$$2D\frac{d^{2}\tau}{dr^{2}}+\left(\frac{4D}{r}-2\mu\kappa_{km}r\right)\frac{d\tau}{dr}=-1.\tag{19}$$

The solution of (19) under the present boundary conditions has the form

$$\tau(r)=\frac{1}{\mu\kappa_{km}}\int_{q/L}^{r/L}d\nu\left[\int_{\nu}^{\infty}dy\,y^{2}\exp(-y^{2})\right]\frac{\exp(\nu^{2})}{\nu^{2}},\tag{20}$$

where $L=\sqrt{2D/\kappa_{km}\mu}$. [We recall that $\tau(r)$ is the mean time for a particle located at a distance r from the center of the sphere at $t=0$ to reach its surface.]

To find the mean collision time of a pair of particles with the indices k and m, the expression (20) must be averaged over the equilibrium distribution (14). If the parameter L, which equals the thermal rms amplitude of the oscillator up to a multiplicative factor, is much greater than q, the integral in (20) is easily calculated with consideration of its divergence in the lower limit. Expanding (20) in L/q and taking into account the relation (15), we obtain the time sought,

$$\tau_{km}=\frac{\sqrt{2\pi}}{4}\frac{T^{1/2}}{q\mu\kappa^{3/2}}\left(\sum_{a_{n}\neq 0}\frac{(\lambda_{kn}-\lambda_{mn})^{2}}{a_{n}}\right)^{3/2}.\tag{21}$$

5. RESULTS AND DISCUSSION

Although (15) and (17) represent the desired characteristics of the relative motion of particular particles, the use of (15) is not convenient for analyzing specific cases, since it requires diagonalization of $\hat{\Lambda}$ and summation of the series appearing in (15), which does not have a clear physical meaning. Therefore, to investigate concrete problems we reformulate the answer obtained. First of all, utilizing the identity

$$(\hat{A}^{-1})_{km}=\sum_n \lambda_{kn}\frac{1}{a_n}\lambda_{mn},$$

we rewrite (15) in the form

$$\kappa_{km}=\frac{\kappa}{(\hat{A}^{-1})_{kk}+(\hat{A}^{-1})_{mm}-2(\hat{A}^{-1})_{km}}. \tag{22}$$

Let the system consist of N particles joined in pairs by springs with stiffness K_{km} for particles k and m. Then the potential energy of the system equals

$$U=\frac{1}{2}\sum_{i,j=1}^{N} K_{ij}(\mathbf{r}_i-\mathbf{r}_j)^2, \tag{23}$$

which gives the following expressions for $\hat{A}$:

$$(\hat{A})_{km}=\frac{K_{km}}{\kappa},\quad k\neq m;\quad (\hat{A})_{km}=-\frac{1}{\kappa}\sum_{j\neq k} K_{jk},\quad k=m. \tag{24}$$

Now it is not difficult to show that κ_{km} equals the ohmic resistance between points k and m of an electrical circuit (this circuit, like the original molecule, does not necessarily have a linear topology) composed of resistors with the resistance

$$R_{ij}=\frac{1}{K_{ij}}, \tag{25}$$

which connect the ith and jth points of the circuit. In fact, Kirchhoff's equations for such a circuit would have the form

$$\sum_i \frac{\phi_i-\phi_j}{R_{ij}}=-\delta_{jk}I_k-\delta_{jm}I_m, \tag{26}$$

where ϕ_i is the potential of the ith point and I_k is the current flowing in the kth point. Using (24) and (25), we rewrite (26) in the form

$$\kappa\sum_i (\hat{A})_{ji}\phi_i=-\delta_{jk}I_k-\delta_{jm}I_m. \tag{27}$$

To calculate the resistance ρ_{km} between points k and m, in (27) we set $I_k=-I_m=I$, and we find the potentials of these points from (27):

$$\phi_k=\frac{I}{\kappa}[(\hat{A}^{-1})_{km}-(\hat{A}^{-1})_{kk}],$$

$$\phi_m=\frac{I}{\kappa}[(\hat{A}^{-1}]_{mm}-(\hat{A}^{-1}]_{km}), \tag{28}$$

whence we directly obtain

$$\rho_{km}=\frac{1}{\kappa}[(\hat{A}^{-1})_{kk}+(\hat{A}^{-1})_{mm}-2(\hat{A}^{-1})_{km}]=\frac{1}{\kappa_{km}}. \tag{29}$$

The result (29) has a clear physical meaning. In fact, when two or more oscillators of different stiffness are joined, their inverse stiffnesses are summed according to the same law as are the resistances in an electrical circuit.

Let us consider several concrete examples that illustrate the results presented above. We being with the thoroughly studied case of a linear chain consisting of segments with an effective thermodynamic stiffness κ. Using the electrical analogy and the fact that the resistance of a linear electrical circuit increases linearly with the distance between two of its points, on the basis of (21) we obtain the familiar scaling result[5]

$$\tau_{km}\sim|k-m|^{3/2}.$$

The case of a two-dimensional lattice is somewhat more complicated. Employment of the electrical analogy requires a calculation of the Green's function of the finite-difference Laplace equation describing current transfer to calculate the resistance between two arbitrary points of a square lattice. It is not difficult to show that this problem reduces to the problem of the Brownian motion of a particle on a square lattice. The resistance between the points with coordinates (0,0) and (p,q) is given by the following expression[11] (it is assumed that the resistance between two neighboring sites equals unity):

$$R_{pq,00}=\frac{1}{2(2\pi)^2}\int_{-\pi}^{\pi}\int_{-\pi}^{+\pi}\frac{1-\cos(p\theta_1)\cos(q\theta_2)}{1-(1/2)(\cos\theta_1+\cos\theta_2)}d\theta_1 d\theta_2. \tag{30}$$

The quantity $R_{pq,00}$ coincides with the sum appearing in Eq. (15). When p and q are large, the asymptote of the integral (30) has the form

$$R_{pq,00}\simeq\frac{1}{\pi}\ln\sqrt{p^2+q^2}+C_1. \tag{31}$$

The numerical value of C_1 equals 0.5146.

We use L and l to denote the distance between two nearest-neighbor sites of a square lattice and the length of an elementary segment (see Sec. 2), respectively. Then the effective thermodynamic stiffness κ of a polymer joining two neighboring sties is $3T/Ll$. Using Eq. (21), we find that the mean collision time of sites with coordinates (0,0) and (p,q) is

$$\tau_{pq,00}=\frac{\sqrt{2\pi}}{4}\frac{T^{1/2}}{q\mu\kappa^{3/2}}R_{pq,00}^{3/2}.$$

For large p and q we have

$$\tau_{pq,00}\simeq\frac{1}{(2\sqrt{3})^3\pi}\frac{(Ll)^{3/2}}{qD}\ln^{3/2}(p^2+q^2).$$

In the three-dimensional case we similarly obtain

$$\tau_{pqr,000}\simeq\frac{1}{(2\sqrt{3})^3\pi}\frac{(Ll)^{3/2}}{qD}\left(\frac{2\pi}{3}C-\frac{1}{\sqrt{p^2+q^2+r^2}}\right)^{3/2},$$

where

$$C=\frac{1}{(2\pi)^3}\int\int_{-\pi}^{+\pi}\int\frac{d\theta_1 d\theta_2 d\theta_3}{1-(1/3)(\cos\theta_1+\cos\theta_2+\cos\theta_3)}.$$

The numerical value of C is 1.5164 (Ref. 11).

Of course, the same result is obtained for the resistance between two distant contacts of unit radius on a uniform conducting plane with surface conductivity $\sigma=1$, i.e., the continuum approximation can be used at large distances. Thus, in the two-dimensional case, for the mean collision time we obtain the logarithmic asymptote

$$\tau_{pq,00}\sim\ln^{3/2}(p^2+q^2). \tag{32}$$

In the case of a three-dimensional cubic lattice composed of subchains of identical length, in analogy to the preceding example, for large p, q, and r we obtain

$$\tau_{pqr,000}\sim\left(\text{const}-\frac{1}{\sqrt{p^2+q^2+r^2}}\right)^{3/2}, \tag{33}$$

However, it must be taken into account that topological constraints are crucial in the three-dimensional case and that, therefore, the model employed provides a faithful description only for closely positioned sites.

In conclusion, using the continuum approximation, we find the mean collision time of two segments of a hypothetical macromolecule that is topologically equivalent to a sphere. For this purpose we calculate the Green's function for current transfer on a sphere. Assuming that the radius of the sphere is equal to unity and using an expansion in spherical harmonics, we obtain

$$\begin{aligned}G(\mathbf{n},\mathbf{n}_1)&=\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\frac{Y_{lm}^{*}(\mathbf{n})Y_{lm}(\mathbf{n}_1)}{l(l+1)}\\&=\frac{1}{4\pi}\sum_{l=1}^{\infty}\left(\frac{P_l(\cos\theta)}{l+1}+\frac{P_l(\cos\theta)}{l}\right)+\text{const},\end{aligned} \tag{34}$$

where $\mathbf{n}$ and $\mathbf{n}_1$ are unit vectors directed from the center of the sphere to the point where the current is supplied and the point where the potential is measured, respectively, and θ is the angle between $\mathbf{n}$ and $\mathbf{n}_1$. The sum appearing in (34) is calculated using the generating function for Legendre polynomials

$$\frac{1}{|\mathbf{R}-\mathbf{n}|}=\sum_{l=0}^{\infty}R^{l+1}P_l(\cos\theta). \tag{35}$$

In fact, on the basis of (35) it is not difficult to see that

$$\begin{aligned}G(\mathbf{n},\mathbf{n}_1)&=\frac{1}{4\pi}\left(\int_0^1\frac{1}{|\mathbf{R}-\mathbf{n}|}dR+\int_0^1\frac{1}{|\mathbf{R}-\mathbf{n}|}\frac{1}{R}dR\right)+C\\&=\frac{1}{4\pi}\ln(1-\cos\theta)+\text{const}.\end{aligned} \tag{36}$$

For the resistance this gives

$$R=\frac{1}{2\pi}\ln(1-\cos\theta)+\text{const}, \tag{37}$$

and for the mean collision time we obtain

$$\tau\sim[\ln(1-\cos\theta)+\text{const}]^{3/2}. \tag{38}$$

If the local structure of the lattice forming a spherical molecule is square, the value of the constant appearing in (38) can be found from a comparison with Eq. (31), which was obtained for a flat square lattice in the case of small θ. In fact, introducing the angular dimension of the unit cell of the square lattice θ_0 and expanding (38) in small θ, we obtain

$$\tau\sim[\ln(1-\cos\theta)+2\ln\theta_0+C_2]^{3/2},$$

where $C_2=\ln 2+2\pi C_1=3.9264$.

It must be understood that the continuum approximation is valid, in principle, only when θ significantly exceeds the unit-cell parameter of the lattice forming the sphere. However, the result presented above probably remains valid for values of θ comparable to θ_0, since the numerical calculation shows that Eq. (31) holds to within several percent up to p, $q=1$.

6. CONCLUSIONS

Thus, we have shown that the calculation of the mean collision time of two reactive groups requires:

(1) dividing the molecule into segments consisting of a large number of groups and assigning a stiffness K_{km} that is inversely proportional to its length[3] to each segment;

(2) calculating the resistance r_{km} between sites k and m after replacing the oscillators joining sites i and j with stiffness K_{ij} by resistors with resistance $R_{ij}=1/K_{ij}$;

(3) calculating the collision time from Eq. (21) under the assumption $\kappa_{km}=1/r_{km}$.

Let us discuss the conditions for applicability of the results. It is easily seen that the only restriction in the calculation of the mean collision time is that the reaction volume be small. However, the problem can be formulated differently: to calculate the time of the first collision between two specific segments for a certain specified initial distribution. In this case there are additional restrictions: the relaxation time of the system to a Boltzmann distribution T_{rel} must be much smaller than T_q; T_{rel} can be evaluated from Eq. (12) in the case of a pairwise correlation function. At times t greater than $1/\mu\kappa a_{\min}$, where $a_{\min}$ is the smallest nonzero eigenvalue of $\hat{A}$, it can be assumed that the system is in thermodynamic equilibrium. The results of the present work can be used to calculate the kinetic constants of reactions by applying them directly to the results of Refs. 5–7. However, the restrictions indicated above must be borne in mind when the reaction is barrierless and a collision between active groups invariably results in a reaction.

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