

A purely dynamic theory of the spontaneous dissociation of polyatomic molecules

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In the absence of external fluctuations acting on the atoms, the spontaneous dissociation of molecules is not strictly exponential, but occurs as if there is dynamic chaos and the mean lifetime τ_{av} is quite long. Approximate formulas for τ_{av} are obtained. A very simple model of dynamic dissociation is considered. An empirical dissociation curve is obtained numerically for it and compared with an exponential function. © 1995 American Institute of Physics.

1. INTRODUCTION

The work of Kramer¹ has played a major role in shaping the theory of the spontaneous dissociation of polyatomic molecules. It marked the beginning of the creation of the fluctuation theory of dissociation, in which the equations

$$\dot{x}_\alpha = f_\alpha(x) + \xi_\alpha(t), \quad \alpha = 1, \dots, s \quad (1.1)$$

are taken with the uncorrelated Langevin forces $\xi_\alpha(t)$ as the starting equations (the case of $s=0$ was taken in Ref. 1). Then the fluctuation process $x(t)$ in phase space is Markovian, and dissociation of the molecules reduces to a stochastic escape from a potential well. In this case the Markovian theory of reaching boundaries can be used (see, for example, Ref. 2 and 3), and the exponential character of spontaneous dissociation can easily be explained. The work in this area can be examined by consulting the collection of papers in Ref. 4 (Ref. 2 is also presented there).

One shortcoming of that theory is the fact that the appearance of Langevin forces cannot be regarded as completely substantiated. If they are treated as external random forces acting on a dissociating molecule, its dissociation will not be spontaneous, but caused by the external forces. Under another interpretation of the forces $\xi_\alpha(t)$, the variables $x = (x_1, \dots, x_s)$ represent some of the dynamic variables of the molecule, and the ξ_α depend on other variables. However, when the molecule has a finite number of degrees of freedom, the $\xi_\alpha(t)$ cannot be exactly delta-correlated. In addition, under this interpretation equations for the other variables must be taken into account, and the theory should be much more complicated.

In a purely dynamic theory of spontaneous dissociation we do not consider the speculative random forces, and instead of (1.1) we should use the nonfluctuational dynamic equations

$$\dot{x}_\alpha = f_\alpha(x), \quad \alpha = 1, \dots, 2n. \quad (1.2)$$

Strictly speaking, the dissociation process then loses its exponential character, as will be shown below. At best, it will resemble an exponential function to some extent (a) when there is dynamic chaos in the stable system associated with the initial system and (b) when the lifetime is long or, more precisely, when the inequality $\alpha\tau_{av} \gg 1$, where α is the largest of the Lyapunov exponents of the stable system, holds

with a high degree of confidence. The role of dynamical chaos in the purely dynamical theory of spontaneous dissociation was mentioned in Ref. 5.

The inequality $\alpha\tau_{av} \gg 1$ signifies that although a molecule is unstable, its lifetime is very long, so that the dynamic process in it does not differ much from the dynamical process in an absolutely stable molecule. Thus, we associate an unstable (more precisely, a metastable) molecule with a stable molecule with a somewhat altered potential interaction. It is natural to expect that the more stable is a metastable molecule and the greater is τ_{av} , the smaller is the difference between the distribution function $F(y) = \mathbf{P}[\tau/\tau_{av} > y]$ and the exponential function $\exp(-y)$ (here τ is a random lifetime), if, of course, the initial distribution $w(x, t_0)$ is not degenerate.

Approximate formulas for the mean lifetime will be obtained below.

2. INTERNAL VARIABLES AND REGION IN PHASE SPACE WHERE MOLECULES A AND B ARE CONSIDERED BOUND IN C

Let the molecule C consist of k_3 atoms, whose positions are described by the radius vectors $\mathbf{q}_1^{(3)}, \dots, \mathbf{q}_{k_3}^{(3)}$. Assume that it is most readily capable of spontaneously dissociating into molecules A and B. The atoms of these molecules are located at points $\mathbf{q}_\alpha^{(1)} = \mathbf{q}_\alpha^{(3)}$, for $\alpha = 1, \dots, k_1$, and $\mathbf{q}_\alpha^{(2)} = \mathbf{q}_{k_1+\alpha}^{(3)}$, for $\alpha = 1, \dots, k_2$, respectively ($k_1 + k_2 = k_3$). As in Ref. 5, we introduce the radius vectors of the centers of gravity

$$\mathbf{r}_j = M_j^{-1} \sum_{\alpha=1}^{k_j} m_\alpha^{(j)} \mathbf{q}_\alpha^{(j)} \quad (2.1)$$

($M_j = \sum_\alpha m_\alpha^{(j)}$) and the internal coordinates

$$\mathbf{q}_{j\sigma} = \mathbf{q}_\sigma^{(j)} - \mathbf{q}_1^{(j)}, \quad \sigma = 2, \dots, k_j \quad (2.2)$$

of the j th molecule. This transformation of (2.1) and (2.2), which has a unit Jacobian, induces a transformation of the momenta

$$\mathbf{P}_j = \sum_{\alpha=1}^{k_j} \mathbf{p}_\alpha^{(j)}, \quad \mathbf{p}_{j\sigma} = \mathbf{p}_\sigma^{(j)} - m_\sigma^{(j)} \mathbf{P}_j / M_j. \quad (2.3)$$

It is obvious that in this case

$$\mathbf{r}_3 = (M_1 \mathbf{r}_1 + M_2 \mathbf{r}_2) / M_3, \quad \mathbf{P}_3 = \mathbf{P}_1 + \mathbf{P}_2.$$

As in Ref. 5, we use the notation

$$\mathbf{r}'_2 = \mathbf{r}_{21} \equiv \mathbf{r}_2 - \mathbf{r}_1, \quad \mathbf{P}'_2 = (M_1 \mathbf{P}_2 - M_2 \mathbf{P}_1) M_3.$$

The variables $x^{(j)} = (\mathbf{q}_{j2}, \mathbf{p}_{j2}, \dots, \mathbf{q}_{jk_j}, \mathbf{p}_{jk_j})$ are internal variables of the j th molecule. Here the variables $\tilde{x}^{(3)} = (\mathbf{r}_{21}, \mathbf{P}'_2, x^{(1)}, x^{(2)})$ are equivalent to the variables $x^{(3)}$, since the Jacobian of the transformations $x^{(3)} \leftrightarrow \tilde{x}^{(3)}$ is equal to unity. Any of these sets can be taken as the internal dynamical variables x of molecule C. The number of these variables is $2n = 6(k_3 - 1)$. It is significant that Eqs. (2.1)–(2.3) are valid both when A and B are joined in C and when A and B are isolated.

In the transformation from the variables $(\mathbf{q}_1^{(3)}, \mathbf{p}_1^{(3)}, \dots, \mathbf{q}_{k_3}^{(3)}, \mathbf{p}_{k_3}^{(3)})$ to the internal and external variables of molecule C, the Hamiltonian

$$H_3 = \sum_{\alpha=1}^{k_3} (2m_\alpha^{(3)})^{-1} |\mathbf{p}_\alpha^{(3)}|^2 + U(\mathbf{q}_{32}, \dots, \mathbf{q}_{3k_3}) \quad (2.4)$$

is transformed into the sum of the external Hamiltonian $H_3^{\text{ex}} = P_3^2 / (2M_3)$ and the internal Hamiltonian

$$H_3^{\text{in}} = \sum_{\sigma=2}^{k_3} \frac{1}{2m_\sigma^{(3)}} p_{3\sigma}^2 + \frac{1}{2m_1^{(3)}} \left| \sum_{\sigma=2}^{k_3} \mathbf{p}_{3\sigma} \right|^2 + U, \quad (2.5)$$

which depends on the internal variables. For brevity, the kinetic energy appearing therein can be written in the form

$$T = \frac{1}{2} M_{kl}^{-1} p^k p^l.$$

Here and in the following, summation over repeated indices is understood and $(\mathbf{p}_{32}, \dots, \mathbf{p}_{3k_3})$ is denoted by (p^1, \dots, p^n) . Similarly, the internal coordinates of molecule C will be denoted below by q_1, \dots, q_n .

Molecule C does not dissociate at once, but exists for a fairly long time in a metastable state. For this reason the region of phase space corresponding to the existence of molecule C in the still undissociated state is surrounded by a potential barrier, which cannot be overcome for a long time. This is represented by the potential energy U in (2.4) and (2.5).

We assume first that the barrier indicated has slopes on both sides of the "water parting" W , which is defined in the appendix and forms a closed hypersurface. It is simplest to consider molecule C undissociated, if the coordinates \mathbf{q} correspond to a point within W , and the momenta are arbitrary. This is one of the definitions of the region R of the states of molecule C which have not dissociated into A and B.

The region R can be defined more precisely. From the energy conservation law $dT = -dU$, which is consistent with Hamilton's equations, we obtain

$$\dot{T} = -\dot{U} = -\frac{\partial U}{\partial q_k} \dot{q}_k,$$

i.e.,

$$T = -\frac{\partial U}{\partial q_k} M_{kl}^{-1} p^l,$$

since $\dot{q}_k = M_{kl}^{-1} p^l$. The points in phase space where the decrease in potential energy ends would naturally be assumed to belong to the boundary Γ of the region R , because the increase in T occurs beyond it (this increase is interpreted as proof that the potential barrier has been successfully overcome). Under such a definition the boundary Γ is defined by the equation

$$\frac{\partial U(q)}{\partial q_k} M_{kl}^{-1} p^l = 0. \quad (2.6)$$

It is assumed that for each vector $\mathbf{p} = (p^1, \dots, p^n)$ this equation defines a closed hypersurface $A(\mathbf{p})$ in an n -dimensional coordinate space. It is clear that the following symmetry property exists for each of the two definitions of the region R indicated: the point $(q_1, -p^1, \dots, q_n, -p^n)$ belongs to Γ , if the point $(q_1, p^1, \dots, q_n, p^n)$ belongs to Γ .

Cases in which the potential barrier has only one slope, i.e., the water parting is at an infinite distance, are also possible. An example of such a case is provided by the potential energy defined by pairwise interactions

$$U = \sum_{\substack{\alpha, \beta=1, \\ \alpha < \beta}}^{k_3} \Phi(|\mathbf{q}_\alpha^{(3)} - \mathbf{q}_\beta^{(3)}|)$$

with an ordinary form of $\Phi(\mathbf{r})$, say, the Lennard–Jones potential, which increases monotonically with increasing r after a certain value r_1 . Therefore, the energy U increases as one fixed configuration of atoms moves away from another fixed configuration of atoms, if the distance between them is not excessively small.

In the absence of a closed water parting, i.e., in the absence of a "slope" on the outside, the region R of states of molecule C can be defined, as in Ref. 5, by the inequality

$$r_{21} \leq r_0. \quad (2.7)$$

Here $r_{21} = |\mathbf{r}_{21}|$, and r_0 is a value which satisfies the conditions

$$r_{\text{int}} \ll r_0 \ll v^{1/3}, \quad (2.8)$$

where $v = V/N$ and r_{int} is the interaction radius of the atoms. Of course, some arbitrariness is allowed here, since r_0 is not uniquely defined by the inequalities (2.8). Under the definition (2.7) the boundary hypersurface Γ in the $2n$ -dimensional phase space is the set of points where $r_{21} = r_0$, and the other variables \mathbf{P}'_2 , x_1 , and x_2 are arbitrary.

Let $c^\alpha(x)$ be the vector of the normal to Γ at the point x . It is defined as follows: if x and $x + \delta x$ belong to Γ , to within terms of higher order in δx we have $c^\alpha(x) \delta x_\alpha = 0$. The vector c^α is the vector of an external normal, if $c^\alpha(x) \delta x_\alpha \geq 0$ holds at the point $x + \delta x$ lying outside Γ and R and if $x \in \Gamma$.

Under either of the definitions of R described, the hypersurface Γ can be represented as the union of two subsurfaces Γ_+ and Γ_- . The outlet subsurface Γ_- is defined by the additional condition

$$f_\alpha(x) c^\alpha(x) > 0,$$

and the inlet subsurface is defined by the condition

$$f_\alpha(x) c^\alpha(x) < 0$$

(points satisfying $f_\alpha c^\alpha = 0$ can be assigned to either of the subsurfaces).

Owing to the motion of points in the phase space, a probability flux $g_\alpha(x) = f_\alpha(x)w(x)$ appears in it. The total flux through the boundary

$$G = \int_{\Gamma_-} w(x) f_\alpha(x) d\Gamma^\alpha(x) \quad (2.9)$$

is simply the probability that the image point leaves R in a unit of time. The vector $d\Gamma^\alpha$ of the area of an element of the hypersurface is collinear to the vector of the external normal c^α . If that element coincides with the parallelepiped constructed on the basis of the infinitesimal vectors $\delta x_\alpha^{(1)}, \dots, \delta x_\alpha^{(n-1)}$ lying in Γ , then

$$d\Gamma^\alpha(x) = e^{\alpha\beta\dots\omega} \delta x_\beta^{(1)} \dots \delta x_\omega^{(n-1)}.$$

Here the tensor $e^{\alpha\dots\omega}$ is equal to $\varepsilon^{\alpha\dots\omega}$ or $-\varepsilon^{\alpha\dots\omega}$, $\varepsilon^{\alpha\dots\omega}$ being the completely antisymmetric tensor whose nonzero elements are equal to 1 or -1 . The sign of $\varepsilon^{\alpha\dots\omega}$ is taken so that the vector $d\Gamma^\alpha$ is aligned in the same direction as the vector of the external normal. In particular, if we take the infinitesimal vectors

$$\delta x_\alpha^{(i)} = (\delta_{\alpha,i+1} - c_{i+1} \delta_{\alpha 1} / c_1) dx_{i+1},$$

we have

$$f_\alpha d\Gamma^\alpha = f_\alpha c^\alpha |c^1|^{-1} dx_2 dx_3 \dots dx_{2n}$$

($dx_2 \dots dx_{2n} = dq_2 \dots dq_n dp^1 \dots dp^n$). In the case (2.6) it is not difficult to obtain

$$c^j = -p^k M_{kl}^{-1} \frac{\partial^2 U}{\partial q_l \partial q_j}, \quad c^{n+j} = M_{jl}^{-1} \frac{\partial U}{\partial q_l},$$

$$j = 1, \dots, n.$$

For the region R defined by the water parting W , we have $c^j = b^j(q)$, $c^{n+j} = 0$, where $b^j(q)$ is the vector of an external normal to W (see Appendix). Here we have

$$f_l d\Gamma^\alpha = \sum_{j=1}^n \dot{q}_j dW^j.$$

3. STABLE MOLECULE WITH WHICH THE METASTABLE MOLECULE C IS COMPARED

If we place an ideally reflecting wall on the boundary hypersurface Γ , i.e., if we supplement the Hamiltonian (2.5) with the potential energy

$$U_0 = \begin{cases} 0 & \text{in } R, \\ \infty & \text{outside } R, \end{cases}$$

the molecule becomes completely stable. Let us consider the stationary distribution corresponding to it. Before the external dynamic variables were eliminated, the following single-valued motion integrals existed: the momentum \mathbf{P}_3 of the center of mass, the energy H_3 , and the angular momentum. Elimination of the momentum \mathbf{P}_3 from the treatment means that thereafter we have, as it were, $\mathbf{P}_3 = 0$. In fact Eq. (2.5) is consistent with the equalities

$$\mathbf{p}_1^{(3)} = - \sum_{\sigma=2}^{k_3} \mathbf{p}_{3\sigma}, \quad \mathbf{p}_2^{(3)} = \mathbf{p}_{32}, \dots, \mathbf{p}_{k_3}^{(3)} = \mathbf{p}_{3k_3}.$$

Therefore, the only constants of motion remaining after the transition to the internal variables are H_3^{in} and the angular momentum

$$\mathbf{M}(x) = \sum_{\sigma=2}^{k_3} [(\mathbf{q}_\sigma^{(3)} - \mathbf{r}_3), \mathbf{p}_{3\sigma}] - \left[(\mathbf{q}_1^{(3)} - \mathbf{r}_3), \sum_{\sigma=2}^{k_3} \mathbf{p}_{3\sigma} \right],$$

the $\mathbf{q}_\alpha^{(3)} - \mathbf{r}_3$ being expressed in terms of $\mathbf{q}_{32}, \dots, \mathbf{q}_{3k_3}$.

Therefore, the stationary distribution has the form

$$w_{\text{st}}(x) = C \delta(H_3^{\text{in}}(x) - E) \delta_3(\mathbf{M}(x) - \mathbf{m}).$$

Next, the three-dimensional coordinate system can be rotated into an orientation in which the vector \mathbf{m} has the form $(0, 0, |\mathbf{m}|)$ or, say, $(|\mathbf{m}|, 0, 0)$. Therefore, we can also consider the stationary distribution

$$w_{\text{st}}(x) = C \delta(H_3^{\text{in}}(x) - E) \delta(M_1(x)) \delta(M_2(x)) \delta(M_3(x) - m),$$

which depends on two parameters, E and $m = |\mathbf{m}|$.

4. MEAN LIFETIME ACCORDING TO THE DYNAMICAL THEORY

Equations (1.2), which are simply Hamilton's equations, correspond to the Liouville equation

$$\dot{w}_t(x) = - \frac{\partial}{\partial x_\alpha} [f_\alpha(x) w_t] = - f_\alpha(x) \frac{\partial w_t}{\partial x_\alpha} \quad (4.1)$$

for the probability density $w_t(x)$ in the phase space. Here the summation is understood to extend from 1 to $2n$.

The solution of Eqs. (1.2) under the initial conditions $x(t_0) = x^0$ (outside this section we shall set $t_0 = 0$) can, in principle, be written in the form

$$x_\alpha(t) = G_\alpha(x^0, t - t_0), \quad (4.2)$$

where G_1, \dots, G_{2n} are the corresponding functions. They have the property $G_\alpha(x^0, 0) = x^0$. If the initial distribution $w_{t_0}(x) = w_0(x)$ is chosen, the solution of Eq. (4.1) can be written in the form

$$w_t(x) = w_0(G(x, t_0 - t)). \quad (4.3)$$

If we integrate $w_t(x)$ with respect to x within the region R , we obtain the probability

$$P[\tau > t - t_0] = W_t = \int_R w_t(x) dx \quad (4.4)$$

that molecule C has not yet dissociated at the time t , i.e., that its lifetime τ is greater than $t - t_0$. It is clear that to obtain the probability density $p(\tau)$ of the random lifetime τ it is sufficient to differentiate (4.4) with respect to t and to reverse the sign:

$$p(\tau) = - \dot{W}_{t_0+\tau} = - \int_R \dot{w}_{t_0+\tau}(x) dx. \quad (4.5)$$

Hence we find the mean lifetime

$$M \equiv \langle \tau \rangle = - \int_0^\infty \tau \dot{W}_{t_0+\tau} d\tau = \int_0^\infty W_{t_0+\tau} d\tau. \quad (4.6)$$

We now set $w_0(x) = \delta(x - x^0)$ in (4.3). The corresponding solution

$$w_t(x) = \delta(G(x, t_0 - t) - x^0) = \delta(x - G(x^0, t - t_0))$$

satisfies not only Eq. (4.1), but also the adjoint differential equation

$$\frac{\partial w_t(x)}{\partial t} = - \frac{\partial w_t(x)}{\partial t_0} = f_\alpha(x^0) \frac{\partial w_t}{\partial x_\alpha}, \quad (4.7)$$

which is a nonfluctuational special case of Kolmogorov's first equation like (4.39) from Ref. 3. If we integrate (4.7) with respect to x within R and take into account Eq. (4.4), we obtain $\dot{W}_t = f_\alpha(x^0) \partial W_t / \partial x_\alpha^0$. Integration of this relation with respect to t from t_0 to ∞ gives the following equation for M as a function of the initial point:

$$f_\alpha(x^0) \frac{\partial M(x^0)}{\partial x_\alpha^0} = -1. \quad (4.8)$$

Here (4.6) has been taken into account. This is a nonfluctuational case of the Pontryagin-Andronov-Vitt equation from Ref. 2 [the equation coming after (V)]. The boundary condition for it is $M(x^0) = 0$ when $x^0 \in \Gamma_-$. Knowing the function $M(x^0)$ and the initial distribution $w_0(x)$, we have an exact equation for the mean lifetime

$$\tau_{av} = \int M(x^0) w_0(x^0) dx^0. \quad (4.9)$$

Since the characteristics of Eq. (4.8) are the same as those of Eq. (4.1) and are specified by Eqs. (1.2), the general formal solution of $M(x^0)$ is written in terms of the former functions $G_\alpha(x, t - t_0)$ appearing in (4.2):

$$F[G_1(x^0, M), \dots, G_{2n}(x^0, M)] = 0,$$

where F is an arbitrary function determined from the boundary condition. If the outlet hypersurface Γ_- is assigned by the equation $\varphi_-(x_1, \dots, x_{2n}) = 0$, then after the function F is defined, we have

$$\varphi_-(G_1(x^0, M), \dots, G_{2n}(x^0, M)) = 0,$$

which implicitly determines $M(x^0)$.

The dependence of the mean lifetime (4.9) on the initial distribution can be eliminated by the following nonrigorous argument. We assume that

$$w_0(x) = \text{const} \begin{cases} 1 & \text{when } x \in A, \\ 0 & \text{when } x \notin A, \end{cases}$$

where $A \subset R$ is a certain subregion having a nonzero measure

$$\int_A w_{st}(x) dx > 0.$$

Then, owing to the existence of dynamic chaos during a time several times greater than α (where α is a Lyapunov exponent) the distribution (4.3) "becomes similar" to $w_{st}(x)$, if a reflecting wall is erected on the boundary hypersurface. When there is no reflecting wall, but $\alpha \tau_{av} \gg 1$ holds, the process of reaching the boundary can be conceived as two alternately occurring processes: a relatively rapid process of establishing the stationary distribution $w_{st}(x)$ and a very slow

process of reaching the boundary under the original distribution $w_{st}(x)$. Therefore, in (4.9) we can replace $w_0(x^0)$ by $w_{st}(x^0)$ and obtain

$$\tau_{av} \approx \int M(x^0) w_{st}(x^0) dx^0.$$

If exponential dissociation were possible, the solution

$$w_t(x) = e^{-\gamma(t-t_0)} w_*(x) \quad (4.10)$$

($\int w_*(x) dx = 1$) of Eq. (4.1) with a zero boundary condition on the inlet hypersurface Γ_+ would exist. Plugging (4.10) into (4.1) gives

$$f_\alpha(x) \frac{\partial w_*(x)}{\partial x_\alpha} = \gamma w_*(x) \quad (4.11)$$

with the boundary condition $w_*(x) = 0$ when $x \in \Gamma_+$. An analysis shows that only the zero solution $w_*(x) \equiv 0$ of Eq. (4.11) is possible with this equation.

In fact, the general solution of Eq. (4.11) has the form

$$F(G_1(x, -\gamma^{-1} \ln w_*), \dots, G_{2n}(x, -\gamma^{-1} \ln w_*)) = 0,$$

where F is an arbitrary function. It cannot be determined from the boundary condition $w_*(x) = 0$ when $x \in \Gamma_+$ holds [i.e., when we have $\varphi_+(x_1, \dots, x_{2n}) = 0$], suggesting that strictly exponential dissociation is impossible.

5. ANOTHER METHOD FOR APPROXIMATE DETERMINATION OF THE MEAN LIFETIME

The present method involves the determination of the first few coefficients of the Taylor expansions

$$p(\tau) = a_1 + a_2 \tau + \frac{1}{2} a_3 \tau^2 + \dots, \quad (5.1)$$

$$W_\tau = 1 - \int_0^\tau p(\tau') d\tau' = 1 - a_1 \tau - \frac{1}{2} a_2 \tau^2 - \frac{1}{6} a_3 \tau^3 - \dots \quad (5.2)$$

or the expansion

$$u(\tau) = -\ln W_\tau = b_1 \tau + \frac{1}{2} b_2 \tau^2 + \dots, \quad (5.3)$$

Clearly, from the equality $u = -\ln W_\tau$ and (5.2) we find

$$b_1 = a_1, \quad b_2 = a_2 + a_1^2, \quad b_3 = a_3 + 3a_1 a_2 + 2a_1^3,$$

.....

To find $\{a_1, \dots, a_r\}$ and then $\{b_1, \dots, b_r\}$, where the choice of the number of terms r in the approximating expansion depends on the treatment accuracy chosen, we use Eq. (4.5), which, owing to (4.1), can be written for $t_0 = 0$ in the form

$$-\dot{W}_\tau = p(\tau) = \int_R \frac{\partial}{\partial x_\alpha} [\omega_\tau f_\alpha] dx.$$

The application of Gauss' equation to the right-hand side gives

$$p(\tau) = \int_{\Gamma_+} w_\tau(x) f_\alpha(x) d\Gamma_\alpha. \quad (5.4)$$

The result coincides with (2.9). The integral over the inlet hypersurface is absent from (5.4), since it is assumed that we have $w_\tau f_\alpha c^\alpha = 0$ for $x \in \Gamma_+$.

To find the coefficients a_1, a_2, \dots we use Eq. (5.4). Differentiating both sides of (5.4) with respect to τ at the zero point j times, as a consequence of (5.1) we find

$$a_j = \int_{\Gamma_-} \left. \frac{\partial^{j-1} w_\tau}{\partial \tau^{j-1}} \right|_{\tau=0} f_\alpha d\Gamma^\alpha. \quad (5.5)$$

Then, using (4.1) several times, we obtain

$$\frac{\partial^2 w_l}{\partial \tau^2} = -f_\beta \frac{\partial^2 w_\tau}{\partial x_\beta \partial \tau} = f_\beta \frac{\partial}{\partial x_\beta} \left[f_\gamma \frac{\partial w_\tau}{\partial x_\gamma} \right] \quad (5.6)$$

etc. Choosing $w_{st}(x)$ as the initial distribution, from (5.5) and (5.6) we obtain

$$a_1 = \int_{\Gamma_-} w_{st}(x) f_\alpha d\Gamma^\alpha, \quad a_2 = - \int_{\Gamma_-} \frac{\partial w_{st}}{\partial x_\beta} f_\beta f_\alpha d\Gamma^\alpha, \quad (5.7)$$

$$a_3 = \int_{\Gamma_-} \frac{\partial}{\partial x_\beta} \left[\frac{\partial w_{st}}{\partial x_\gamma} f_\gamma \right] f_\beta f_\alpha d\Gamma^\alpha, \dots$$

In a very rough (first) approximation we take into account only one term of expansion (5.3), i.e., the term with $b_1 = a_1$. This gives

$$P[\tau > t] = e^{-b_1 t},$$

i.e., in this approximation

$$\tau_{av} = 1/b_1 = 1/a_1. \quad (5.8)$$

In a more exact treatment, in which $r > 1$ holds, we identify $W_\tau = \int_{\tau}^{\infty} p(\tau') d\tau'$ with the function

$$\varphi_r(\tau) = \exp \left[- \sum_{i=1}^r \frac{1}{i!} b_i \tau^i \right].$$

Then $\gamma = 1/\tau_{av}$ can be determined by minimizing the integral

$$J(\gamma) = \int_0^\infty [\varphi_r(\tau) - e^{-\gamma\tau}]^2 d\tau.$$

The condition for an extremum $dJ(\gamma)/d\gamma = 0$ takes the form

$$\int_0^\infty \varphi_r(\tau_{av}\sigma) e^{-\sigma} \sigma d\sigma = \frac{1}{4}. \quad (5.9)$$

It is expedient to determine $\tau_{av} = 1/\gamma$ from it numerically.

6. SIMPLE HAMILTONIAN MODEL OF DYNAMIC DISSOCIATION; COMPARISON WITH RESULTS OF THE NUMERICAL CALCULATION

Two-dimensional motion, i.e., motion in a plane, is considered in the simplest dynamical model of a polyatomic molecule. All the atoms apart from the subject atom are assumed to be stationary. If the interaction between the atoms is reduced to the repulsion between rigid spheres, the specified atom can be considered a mass point, and the radii of the other atoms are increased accordingly. The attraction of the atoms is replaced by a condition of nondeparture (in the case of a stable molecule) from a square with a side l .

It is simpler to assume that there is only one stationary atom with an effective radius r_1 apart from the mobile subject atom (Fig. 1). Finally, for simplicity we assume that a

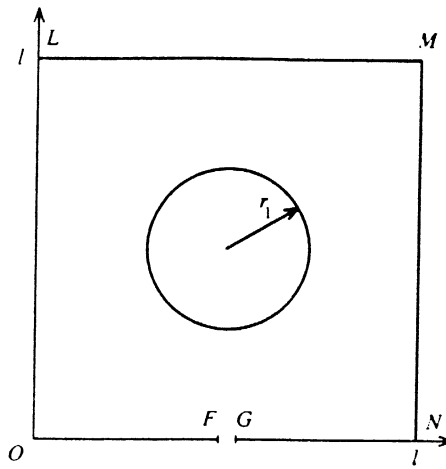


FIG. 1. Square with a cut-out circle as the region where the particle moves.

periodic continuation is carried out beyond the lateral walls OL and NM , i.e., the square is bent into a cylinder by identifying the segment OL with NM . The molecule is unstable if the mobile mass point can escape through the opening FG with a length of l_0 , which symbolizes dissociation.

In the model under discussion there are two coordinates and two components of the momentum vector. Owing to the energy conservation law, reflection from segments LM , OF , and CN , as well as the circle, takes place according to the law of elastic impact, so that the magnitude of the momentum or the velocity is conserved. Therefore, we can consider motion in a three-dimensional space with the coordinates q_1, q_2 , and φ , where $\varphi \in [0, 2\pi]$ is the angle indicating the direction of the velocity vector $\mathbf{v} = (v_0 \cos \varphi, v_0 \sin \varphi)$.

In the case of a stable molecule there is dynamical chaos in the system under consideration. The stationary distribution is described by the expression

$$w_{st}(\mathbf{q}, \varphi) = \begin{cases} \frac{1}{2} \pi^{-1} (J^2 - \pi r_1^2)^{-1} & \text{in } R, \\ 0 & \text{outside } R, \end{cases} \quad (6.1)$$

where R is the direct product of the area of the interior of the square (minus the area of the interior of the circle) and the interval $[0, 2\pi]$. Equation (6.1) follows from the microcanonical distribution

$$w_{st}(\mathbf{q}, \mathbf{p}) = C_0 \delta(\frac{1}{2} p^2 - \frac{1}{2} p_0^2) = C_0 p_0^{-1} \delta(p - p_0),$$

which indicates that the distribution in R should be uniform.

When the opening FC (Fig. 1) is sufficiently small, the lifetime of the "molecule" is large and is specified approximately by means of (5.8) and (5.7), i.e.,

$$\tau_{av}^{-1} = w_{st} l_0 \int_{\pi}^{2\pi} \nu \nu d\varphi,$$

where $\nu = (0, -1)$. Therefore, when (6.1) is taken into account, we have

$$\tau_{av} = \pi (l^2 - \pi r_1^2) / (l_0 v_0). \quad (6.2)$$

The dissociation process in this model and its closeness to exponential dissociation were calculated numerically by O.

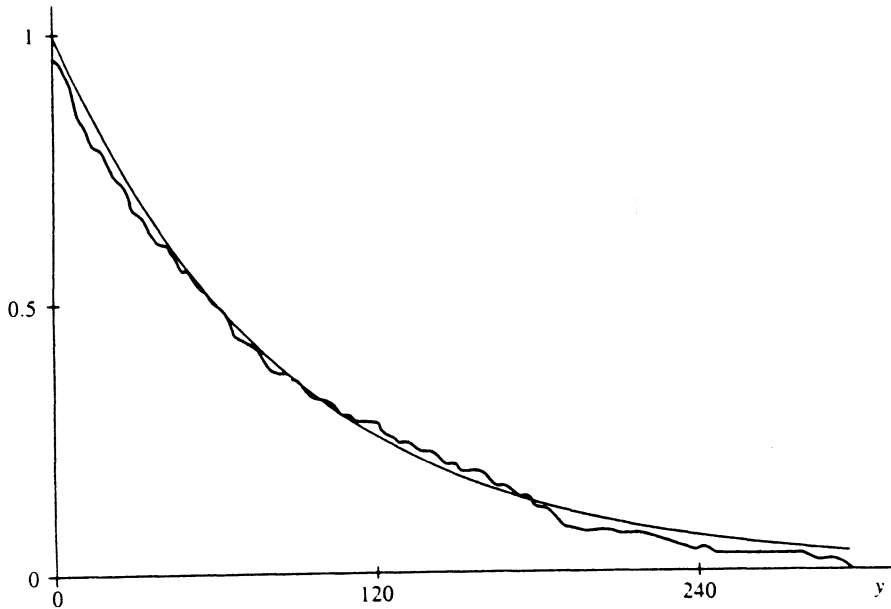


FIG. 2. Empirical dissociation curve and exponential function ($y = v_0 \tau / l$).

A. Chichigina for the values $r_1/l=0.2$ and $l_0/l=0.034$. A uniform distribution in the region $0.45 < q_1/l < 0.6$, $0.73 < q_2/l < 0.76$, $0 < \varphi < 2\pi$ was chosen as the initial distribution. The initial values of the dynamical variables q_1 , q_2 , and φ were determined in this region using a table of random numbers.

The empirical distribution function $F_N(y) = P[\tau/\tau_{av} > y]$ for the lifetime was obtained for N trajectories. It was approximated by the exponential function $\exp(-y)$ using Eq. (5.9), where φ_r must be replaced by F_N . The distribution function and the approximating exponential function for $N=200$ are shown in Fig. 2. The exponential function corresponds to $v_0 \tau'_{av}/l = 88$. The empirical mean lifetime τ''_{av} , which was obtained directly as the arithmetic mean lifetime, was $v_0 \tau''_{av}/l = 84$, while Eq. (6.2) gives the value $v_0 \tau'''_{av}/l = 80.8$.

It can be assumed that the relative disparity between the values obtained will be smaller when the length of the opening l_0 is smaller; however, the influence of the discretization noise in the computer calculation increases in that case due to the increase in the lifetime.

In conclusion, it should be noted that this investigation was financially supported in part by Grant ND13000 of the International Science Foundation.

APPENDIX A:

Concept of a water parting for a potential-energy hypersurface

Both with the set of internal variables $x = x^{(3)}$ and with the set $x = \tilde{x}^{(3)}$, the internal Hamiltonian H^m of a molecule can be written as

$$H_3^m = \frac{1}{2} M_{kl}^{-1} p^k p^l + U(q_1, \dots, q_n) = T + U.$$

The Lagrangian corresponding to this Hamiltonian is

$$L = \frac{1}{2} M^{kl} \dot{q}_k \dot{q}_l - U. \quad (A1)$$

Let $\hat{M}^{1/2}$ be a positive definite root of the positive definite matrix $\hat{M} = ||M^{kl}||$. If we introduce the new variables $y_i = (\hat{M}^{1/2})_{ij} q_j$, the Lagrangian (A1) and the Hamiltonian take the form

$$L = \frac{1}{2} \sum_i \dot{y}_i^2 - U_1(y), \quad H = \frac{1}{2} \sum_i \pi_i^2 + U_1(y),$$

where $\pi_i = \dot{y}_i$ is the momentum conjugate to y . The multidimensional graph of the function $U_1(y_1, \dots, y_n)$ in $(n+1)$ -dimensional space can be interpreted as the "relief" of an n -dimensional surface in analogy to the relief of a two-dimensional surface. We call the curve whose parametric representation $y(\lambda)$ satisfies the equation

$$\frac{dy_i(\lambda)}{d\lambda} = - \left. \frac{\partial U_1(y)}{\partial y_i} \right|_{y=y(\lambda)} \quad (A2)$$

the path of steepest descent. If we go over from y_1, \dots, y_n to the original variables q_1, \dots, q_n , Eq. (A2) takes the form

$$\frac{dq_k(\lambda)}{d\lambda} = M_{kl}^{-1} \left. \frac{\partial U}{\partial q_l} \right|_{q=q(\lambda)}.$$

The paths of steepest descent end either at a minimum point (which may be local) of the potential U or at a saddle point (there are very few such lines), or they may go on to infinity. If there are lines of descent of different types, an $(n-1)$ -dimensional surface, i.e., a separatrix W , which separates the lines ending at a minimum from the lines going on to infinity can, in principle, be drawn. This separatrix is the water parting of the multidimensional relief just cited. If the surface has several water partings, we are interested only in the outer water parting having the form of a closed surface which includes all the minima not lying at infinity.

We introduce the vector of the normal $b^k(q)$ to W at the point q . This means that $b^k(q) \delta q_k = 0$ holds to within terms of higher order in δq_k , if both q and $q + \delta q$ belong to W .

The paths of steepest descent cannot intersect W , enter W , or leave W , i.e., some paths lie entirely in W . Therefore, the condition $b^k dq_k(\lambda)/d\lambda = 0$ or $b^k M_{kl}^{-1} \partial U / \partial q_l = 0$ holds when $q \in W$.

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