Two-dimensional orientational motion as a multichannel reaction by computer simulation

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The orientational diffusion of a nitrogen molecule N_2 in a three-dimensional crystal of argon atoms is studied by using the reaction coordinate formalism and the Bennett–Chandler approach. To study the two-dimensional orientational diffusion the reaction coordinate formalism has to be generalized to multichannel reactions. The rate coefficient for the motion between the six stable orientational states is determined from correlation function expressions, which include corrections to transition-state theory due to recrossings of free energy barriers. At high temperatures the simulation results are compared with results obtained by standard molecular dynamics methods. At low temperatures the transmission coefficient is computed and the dependence of the plateau value upon the density of the surrounding argon matrix and upon the isotopes, chosen to form the N_2 molecule, is investigated. © *1995 American Institute of Physics.*

I. INTRODUCTION

In the field of condensed matter (chemical-) physics, there is much experimental and theoretical interest in determining the rate constants of transitions between different global or local (meta)-stable states, separated by a free energy barrier much larger than thermal energy. Standard molecular-dynamics (MD) methods are not appropriate to determine these rate constants if the time window of the simulation is in the order (or smaller) of typical relaxation times.

For this reason Bennett[1] and Chandler[2] introduced a nonstandard MD method, able to compute the (fast) dynamics at rare events in condensed phase. A particular way to implement this method, called the blue-moon ensemble,[3] is to constrain the total system at the top of the free energy barrier separating two (meta-) stable states. This is done by constraining a suitable function ξ of the configurational space (the reaction coordinate) to a given value ξ^{TS}. All coordinates are left free to equilibrate while the system is kept at the transition state. At a suitable set of initial times t_i, along the constrained equilibrium trajectory, the constraint is released and new momenta are sampled. Equilibrium rate constants can now be measured with a MD program if the probability density at the transition state is known.

In the Bennett–Chandler approach the equilibration at the transition state and the determination of the probability density at the transition state are worked out in a Monte Carlo (MC) program, whereas the blue-moon ensemble enables one to carry out all the computations by MD.

Up to now, rare event techniques have been applied only to one-channel reactions. Some particular applications are trans-gauche isomerization reactions in liquid butane,[4] chemical reactions[5] of the type $A+BC \rightleftharpoons AB+C$, linear diffusion of vacancies in crystals[6,7] as well as proton[8,9] or electron[10,11] transfer reactions in solutions.

Two-dimensional orientational diffusion cannot be described as a one channel process. If the stable orientations are parallel to the x, y and z axes, the transition of a x-oriented state to a y-oriented state can be direct or it can be obtained by passing through a z-oriented state. Therefore we have to find a formulation of the reaction taking into account all reaction channels.

The aim of the paper is to show how a reaction coordinate for multichannel reactions can be constructed. The focus lies on the application on the reorientation dynamics of a nitrogen molecule N_2 which is embedded in a fcc crystal, composed by point atoms. Once the reaction coordinate has been defined, we derive the phenomenological and the microscopic rate equations. The transmission coefficients, obtained by the rare event technique, are compared at high temperatures to those, obtained by standard MD simulation. At low temperatures the transmission coefficient is computed and the dependence of the plateau value upon the density of the surrounding argon matrix and upon the isotopes, chosen to form the N_2 molecule, are investigated.

II. MULTICHANNEL-REACTION COORDINATE

One of the main problems in the description of activated processes is the definition of an appropriate reaction coordinate ξ. Sometimes the choice of the reaction coordinate is quite obvious. However, even though the reaction coordinate is known, the question arises which value ξ^{TS} corresponds to the transition state, namely at which value of ξ' the free energy $F(T,\xi')$ has a saddle point. $F(T,\xi')$ is defined by

$$F(T,\xi') = -k_B T \ln \int d\Gamma \ e^{-H(\Gamma)/k_B T} \ \delta[\xi(\Gamma)-\xi'],$$

$$(1)$$

with $H(\Gamma)$, the Hamiltonian, a function of all phase space coordinates and δ the Dirac delta function.

An illustrative simple example of the construction of the reaction coordinate is the case of adiabatic proton transfer in
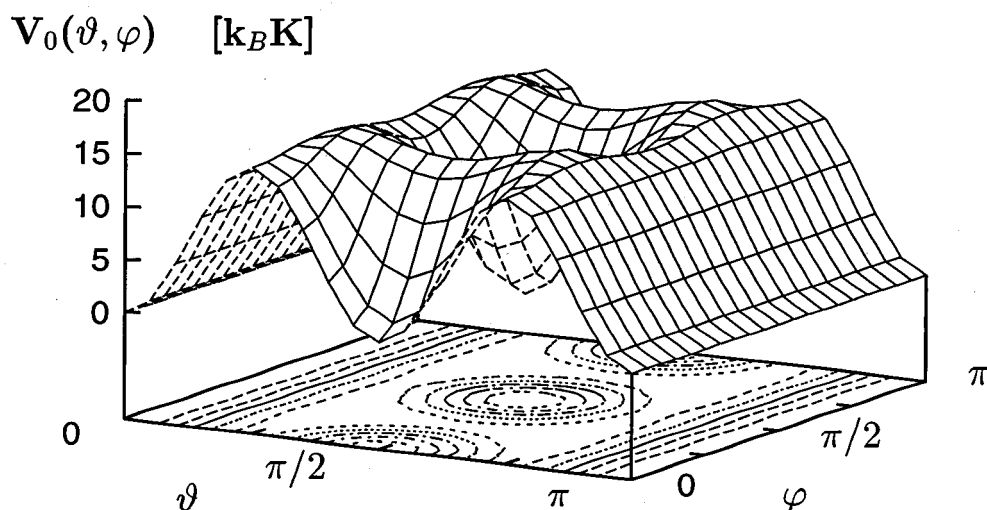
$$\mathbf{V}_0(\vartheta, \varphi) \quad [\mathbf{k}_B\mathbf{K}]$$

FIG. 1. Minimal total potential V_0 (in units of Kelvin) for fixed orientations, defined by the angles ϑ and φ.

a linear molecule (whose orientation defines the z axes), where a suitable choice of ξ is the quantum mechanical expectation value of the protons z operator for a given configuration of the solvent molecules.[8] In the case of homonuclear molecules $\xi^{TS}=0$, due to inversional symmetry, while for heteronuclear molecules ξ^{TS} would have to be determined numerically by an estimation of the probability density $p(\xi)$, which, in statistical mechanics, is given by

$$p(\xi) = e^{-\beta[F(T,\xi)]} \Big/ \int d\xi' e^{-\beta[F(T,\xi')]}. \tag{2}$$

The value of ξ, where $p(\xi)$ has a minimum correspond to the value of ξ^{TS}. For an efficient way to compute $F(T,\xi)$ see Ref. 2 for the Bennett–Chandler approach and Refs. 3, 12 for the blue-moon ensemble.

In the case of two-dimensional orientational diffusion the reaction coordinate should be closely related to the angles ϑ and φ, describing the orientation of the rotator impurity. To fix the ideas we choose the same model of a recent Monte Carlo study,[13] where the orientational degrees of freedom had been treated in a classical and quantum mechanical way. The preferred orientations of the molecule have been detected for $\vartheta=\pi/2$ with $\varphi=0$, π, for $\vartheta=\pi/2$ with $\varphi=\pi/2$, $3\pi/2$, and for $\vartheta=0$, π. Hence, the states will be classified as x, y, and z oriented states and the orientational diffusion will be described by a multichannel process. We do not distinguish between $+x$ and $-x$ oriented states, because of the inversional symmetry of the nitrogen molecule. Thus the number of stable states to be taken into account is automatically reduced from six to three.

The first step in finding the reaction coordinate—in this case a function of ϑ and φ—is to find the saddlepoint or better the saddlelines of the free energy surface. In general, this has to be done numerically. In our case, it is sufficient to take advantage of the cubic symmetry. The transition lines can be only at $x^2=y^2$, $z^2=x^2$, and $y^2=z^2$, whereby x, y, and z are the Cartesian components of the normalized vector, indicating the direction of the molecule. In order to demonstrate the cubic symmetry, we plot the total potential V_0 as a

function of ϑ and φ in Fig. 1, whereby the translational coordinates are chosen such that the total potential energy is minimized. Note, that at low temperatures $V_0(\vartheta,\varphi)$ is closely related to the free energy $F(T,\vartheta,\varphi)$, because the integration over the translational degrees of freedom reduces to Gaussian integrals. In Fig. 1, it can be seen, that one barrier is located at $\varphi=\pi/4$, in other words it is located at $x^2=y^2$.

Now the three stable states can be defined. It is convenient to call a state

$$x \text{ oriented} \quad \text{if}: \quad x^2>y^2 \quad \text{and} \quad x^2>z^2,$$
$$y \text{ oriented} \quad \text{if}: \quad y^2>z^2 \quad \text{and} \quad y^2>x^2, \tag{3}$$
$$z \text{ oriented} \quad \text{if}: \quad z^2>x^2 \quad \text{and} \quad z^2>y^2.$$

With this in mind, it is furthermore possible to define a function $\tilde{\xi}$ describing direct transitions. This function is only an intermediate step toward producing one scalar reaction coordinate. Keeping in mind, that the xy transition across the line $x^2=y^2$ has to fulfill $z^2<x^2$ and $z^2<y^2$ a suitable choice of $\tilde{\xi}$ is

$$\tilde{\xi} = \begin{cases} x^2-y^2 & \text{for } z^2<x^2 \text{ and } z^2<y^2, \\ y^2-z^2 & \text{for } x^2<y^2 \text{ and } x^2<z^2, \\ z^2-x^2 & \text{for } y^2<z^2 \text{ and } y^2<x^2, \end{cases} \tag{4}$$

which represent the xy, yz, and zx transitions respectively in the same interval $(-1,1)$. Now, to disentangle the range of values representing the three transitions, let us simply introduce suitable constants $\xi_{xy}^{\#}$, $\xi_{yz}^{\#}$, and $\xi_{zx}^{\#}$. By choosing

$$\xi_{xy}^{\#}=0, \xi_{yz}^{\#}=-2, \xi_{zx}^{\#}=2 \tag{5}$$

and

$$\xi = \begin{cases} \xi_{xy}^{\#}+x^2-y^2 & \text{for } z^2<x^2 \text{ and } z^2<y^2, \\ \xi_{yz}^{\#}+y^2-z^2 & \text{for } x^2<y^2 \text{ and } x^2<z^2, \\ \xi_{zx}^{\#}+z^2-x^2 & \text{for } y^2<z^2 \text{ and } y^2<x^2, \end{cases} \tag{6}$$

one is now able to characterize the orientational state of the system by the value of the function ξ. The scalar reaction

coordinate ξ, which describes uniquely the oriented state of the system, can now be written in compact form as

$$\xi = (\xi_{xy}^\sharp + x^2 - y^2)\,\theta(x^2 - z^2)\,\theta(y^2 - z^2) + (\xi_{yz}^\sharp + y^2 - z^2)$$
$$\times \theta(y^2 - x^2)\,\theta(z^2 - x^2) + (\xi_{zx}^\sharp + z^2 - x^2)\,\theta(z^2 - y^2)$$
$$\times \theta(x^2 - y^2), \qquad (7)$$

with $\theta(\bullet)$ the Heaviside step function.

ξ is a function, that maps the sphere on a line in the following manner: If $\xi = 0$ the system is on the x-y transition line, for $0 < \xi < 2$ it is in an x-oriented state, for $-2 < \xi < 0$ a y-oriented state is found, and so on. According to these remarks, the probabilities c_x, c_y, and c_z, that the system is either in a x, y, or z oriented state, have to be written as

$$c_x = \langle \theta_x \rangle \quad \text{with} \quad \theta_x = \theta(\xi)\,\theta(2 - \xi),$$
$$c_y = \langle \theta_y \rangle \quad \text{with} \quad \theta_y = \theta(2 + \xi)\,\theta(-\xi), \qquad (8)$$
$$c_z = \langle \theta_z \rangle \quad \text{with} \quad \theta_z = \theta(\xi - 2) + \theta(-\xi - 2),$$

where $\langle \bullet \rangle$ denotes a thermodynamical averaging according to the relevant ensemble and where $i = 1,2,3$ can be used instead of x,y,z so that $\Sigma_i c_i = 1$.

On the transition lines ξ is not defined at the eight points, where $x^2 = y^2 = z^2$. On the rest of the unity sphere this function is not defined either for the lines $x^2 > y^2 = z^2$ and permutations of this equation. Since a point on a line and a line on a surface have both zero measure, it is sufficient, that ξ is well defined at all other points, in order to get well-defined averages in a computer simulation.

Equation (8) gives an instruction on how to measure the concentrations of the orientational states with the help of the reaction coordinate. Hence the formalism of rate equation for the one channel reactions can now be easily extended to the multichannel case.

III. RATE EQUATIONS

The phenomenological rate equation, which is a linearized version of the master equation, can be written down formally for any multichannel reaction:

$$\dot{c}_i = \sum_{j=1}^{n} K_{ij} c_j \quad \text{with} \quad K_{ij} = -\sum_{l=1}^{n} k_{il}\delta_{ij} + k_{ji}, \qquad (9)$$

with c_i the probability for the system to be in the state i and K_{ij} the (i,j) component of the phenomenological rate constant matrix K. k_{ji} gives the probability, per unit time, that the system goes from j to i, if it is located at j. In the following discussion, the c_i's are assumed to be expressed by the reaction coordinate Eq. (8).

If the system has been perturbated by an external force at times $t < 0$, the initial deviation $\Delta c_i(t=0)$ of $c_i(t)$ with respect to its equilibrium value c_i^{eq} will decay according to

$$\Delta c_{i<n}(t) = \sum_{j=1}^{n-1} (e^{-\tilde{K}t})_{ij}\Delta c_j(0), \qquad (10)$$

where one has to taken into account that $\Sigma_{j=1}^{n}\Delta c_j(t) = 0$.

In a microscopic approach, a Green–Kubo relation[14] can be used to express the dissipative response to external perturbations by spontaneous fluctuations in thermal equilibrium. If the external perturbation H_p, given by $H_p = \Sigma_{j=1}^{n-1}\delta\mu_j\theta_j\theta(-t)$, is switched off at time $t = 0$, than the dissipative response of the system is

$$\Delta c_{i<n}(t) = -\beta\sum_{j=1}^{n-1} \tilde{G}_{ij}(t)\,\delta\mu_j \quad \text{with}$$
$$\tilde{G}_{ij}(t) = \langle \Delta\theta_i(t)\Delta\theta_j(0) \rangle, \qquad (11)$$

where the matrix $\tilde{G}_{ij}(t=0)$ is invertible. All $\delta\mu_j$'s can be expressed by inverting the matrix $\tilde{G}(t)$ at time $t = 0$:

$$\delta\mu_{j<n} = -k_B T\sum_{i=k}^{n-1} \tilde{G}_{jk}^{-1}(0)\Delta c_k(t=0). \qquad (12)$$

Inserting Eq. (12) in Eq. (11) yields:

$$\Delta c_{i<n}(t) = \sum_{j=1}^{n-1}\sum_{k=1}^{n-1} \tilde{G}_{ij}(t)\tilde{G}_{ij}^{-1}(0)\Delta c_k(0). \qquad (13)$$

Remember that $\Delta c_n(t)$ is given by $1 - \Sigma_{i=1}^{n-1}\Delta c_i(t)$, so that the dissipative response is completely described by Eq. (13).

Equation (13) already tells us, how to compute the phenomenological rate constant matrix $\tilde{K}$, defined in Eq. (10), by standard MD simulation. If the motion is activated, then a time scale separation between the relaxation processes and other internal degrees of freedom exists, and the phenomenological $\tilde{K}_{ij}$'s are given by the plateau values of the time derivatives (with opposite sign) of Eq. (13) by:[2,15]

$$\tilde{K}_{ij}(t) = -\frac{\partial}{\partial t}\sum_{k=1}^{n-1} \tilde{G}_{ik}(t)\tilde{G}_{kj}^{-1}(0), \qquad (14)$$

or else, performing the time derivative, by

$$\tilde{K}_{ij}(t) = \sum_{k=1}^{n-1} \langle \Delta\theta_i(t)\Delta\dot{\theta}_k(0) \rangle\tilde{G}_{kj}^{-1}(0). \qquad (15)$$

IV. APPLICATION TO TWO-DIMENSIONAL ORIENTATIONAL MOTION

In this section, the discussion is restricted to the example of a N_2 impurity in a fcc argon crystal. The phenomenological rate equation can be simplified because of the cubic symmetry, which leads to $k_{xy} = k_{zx} =$ etc. If, furthermore, it is used, that $c_x + c_y + c_z = 1$, the phenomenological rate equation, Eq. (9), becomes diagonal:

$$\dot{c}_i(t) = -\tfrac{2}{3}kc_i + \tfrac{1}{3}k(1 - c_i) \quad \text{with} \quad k = 3k_{xy}. \qquad (16)$$

From this differential equation it is easy to see, that

$$\Delta c_i(t) = e^{-kt}\Delta c_i(0) \quad \text{with} \quad c_i^{\text{eq}} = \tfrac{1}{3}. \qquad (17)$$

The phenomenological rate constant k, defined in Eq. (16), has obviously the meaning of an inverse relaxation time.

In the microscopic formulation, k has to be replaced by a time-dependent $k(t)$, whose plateau value at small times corresponds to k. To do this, we use Eq. (15) and the fact that, due to $G_{xx}(t) + G_{xy}(t) + G_{xz}(t) = 0$ and $G_{xy} = G_{xz}$ (cubic symmetry), the off diagonals of $G_{ij}(t)$ are equal to $-G_{ii}(t)/2$. This leads to

$$k(t) = \langle \Delta\theta_i(t)\Delta\dot{\theta}_i(0) \rangle / \langle \Delta\theta_i(0)\Delta\theta_i(0) \rangle \qquad (18)$$

i being either x, y, or z. For the next step, $c_x = \frac{1}{3}$ is used and the definition of θ_x in Eq. (8) is inserted in Eq. (18). This leads to

$$k(t) = \frac{9}{2}[\langle \dot{\xi}(0)\Delta\theta(2-\xi(0))\Delta\theta_x(t)\rangle_{\xi=0} \cdot \langle \delta(\xi(0))\rangle$$

$$+ \langle \dot{\xi}(0)\Delta\theta(\xi(0))\Delta\theta_x(t)\rangle_{\xi=2} \cdot \langle \delta(2-\xi(0))\rangle].$$

$$(19)$$

$\langle \bullet \rangle_{\xi=0}$ denotes a conditional average for $\xi=0$ and $\langle \delta(\xi(0))\rangle$ is the probability density at the x-y transition. Both quantities have to be determined separately, according to the methods existing for one channel reactions. Of course, the analogous statements are valid for $\langle \bullet \rangle_{\xi=2}$ and for $\langle \delta(2-\xi(0))\rangle$.

Although only one transition coefficient $k(t)$ is mentioned in Eq. (19), we are clearly dealing with a multichannel reaction, because the first term of the right-hand side of Eq. (19) refers to the x-y transition and the second refers to the z-x transition. Furthermore the $\tilde{K}(t)$ matrix can be reconstructed by just knowing the function $k(t)$, as in the phenomenological case.

The whole computational treatment can now be carried out as for the case of one channel reactions.

V. COMPUTATION AND RESULTS

The model system refers to a fcc argon crystal. One of its atoms is replaced by a N_2 molecule. The molecule is treated as a rigid unit of two nitrogen atoms, separated by a distance $d_{NN} = 1.09$ Å. Interaction takes place by the standard Lennard-Jones potential $v(r) = 4\epsilon(\sigma/r)^6[(\sigma/r)^6 - 1]$. The potential parameters have been chosen to be $\epsilon_{ArAr} = 0.927 \cdot 10^{-21}$ J, $\epsilon_{ArN} = 0.691 \times 10^{-21}$ J, $\sigma_{ArAr} = 3.405$ Å, and $\sigma_{ArN} = 3.357$ Å. If not mentioned otherwise, the masses are $m_{Ar} = 40$ amu, $m_N = 18$ amu, and the lattice constant is $a_0 = 5.3$ Å.

Now, we briefly describe our implementation of the Bennett–Chandler approach. At the top of the above defined free energy barrier, the equilibration of the system is carried out within a Monte Carlo (MC) program. Every fifth MC step the whole configuration has been written out. Such a configuration is the input configuration of a MD program, in which the initial momenta are chosen according to the relevant equilibrium distribution. Functions of the type $\dot{\xi}(0)\Delta\theta_x(\xi(0))\theta_x(\xi(t))$, see Eq. (18), have then be computed for every input configuration with four different momenta distributions. The total observation time is $t_{\mathrm{obs}} \approx 2 \times 10^{-12}$ s. We obtained small statistical error bars, being approximatively 1% large, by averaging 1000 configurations.

For the time propagation in the MD program, the Verlet algorithm has been used. The elementary time step has been chosen be $\Delta t = 1.08 \times 10^{-14}$ s. The total computational effort for the determination of the full rate constant, containing the plateau value of the transmission coefficient, therefore corresponds to about 200 000-MD steps and 2500-MC steps.

The probability density at the transition state $\langle \delta[\xi(0)]\rangle$ has been obtained by performing a quasiharmonic approximation of the translational degrees of freedom. This results in $\exp[-\beta(F(T,\vartheta,\varphi) - F(T,0,0))] \approx \exp[-\beta(V_0(\vartheta,\varphi)$
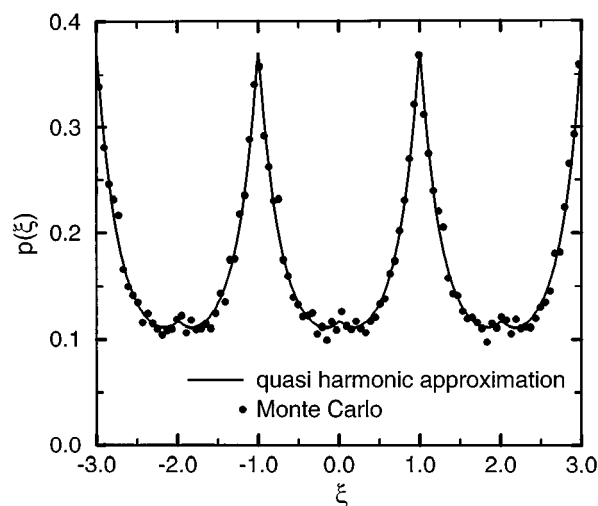

FIG. 2. Probability density $p(\xi)$ of the reaction coordinate at $T = 10$ K, obtained by MC simulation (200 000 averages) and by the quasiharmonic approximation.
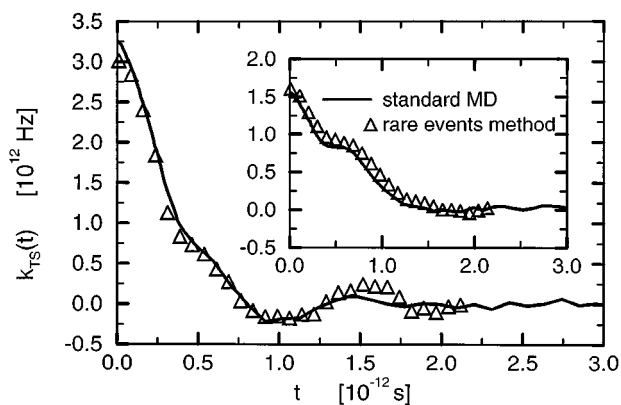
$-V_0(0,0))]$, with $V_0(\vartheta,\varphi)$ the total potential for given ϑ,φ and totally relaxed translational degrees of freedom, see below. Clearly, this relation completely breaks down at the solid–liquid phase transition, but in the solid phase, this approximation works surprisingly well, even at "high" temperatures, where the reorientational motion of the molecule will later turn out to be not activated, see Fig. 2.

The function $V_0(\vartheta,\varphi)$ was obtained in a zero temperature MC program, chosing some representative values of ϑ and φ for the (fixed) orientation of the N_2 molecule. The obtained values are fitted to the equation:

$$V_0(\vartheta,\varphi) = V_0(0,0) + a(1 - x^4 - y^4 - z^4)$$

$$+ b(1 - x^6 - y^6 - z^6) + c(x^2 y^2 z^2), \quad (20)$$

x, y, z being the components of the normalized director. Equation (20) can be interpreted as an expansion of the local cubic potential. The maximal relative error between the given values and the fit function is of the order of 2%. This procedure enables us to integrate functions as mentioned in Eq. (1) with a quasizero discretization error and with a quasizero statistical error.
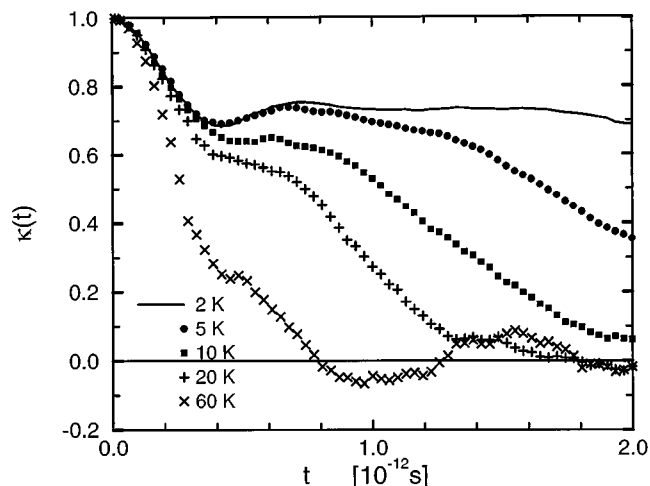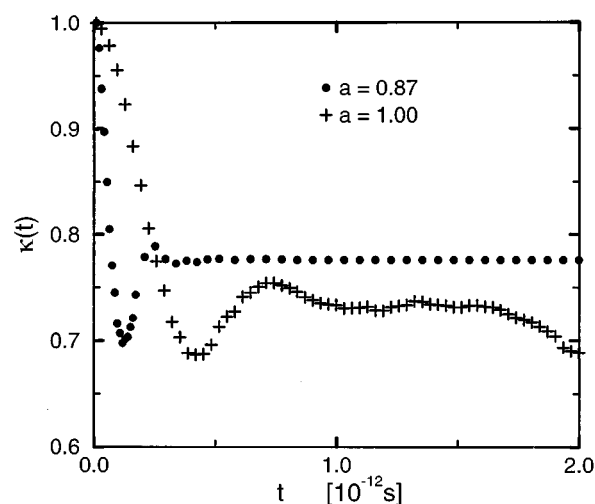
We now present some results, obtained with the procedure defined above. At thermal energies, comparable to or higher than the free energy barrier, standard MD should be still sufficient to compute the rate constant $k(t)$. At these temperatures, one does not deal really with an activated process, but nevertheless the rare event technique can still be applied. Investigations at higher temperatures are therefore useful to check whether or not the rare event technique has been correctly implemented. They are also a test for the approximations, if present. In Fig. 3, we present $k(t)$ for two different temperatures $T = 60$ K and $T = 20$ K. The two standard MD curves are obtained with a computational effort of 200 000-MD steps each. The CPU time needed for these computations at high temperatures compares to the CPU time needed for the "rare event" computations at any temperature.

FIG. 3. The full rate constant $k(t)$, for $T=60$ K and $T=20$ K (inlet).

FIG. 5. Same as Fig. 3 for low lattice constant $a=0.87$ and high lattice constant $a=1.00$. a is measured in units of the experimentally observed lattice constant of pure argon at $T=0$ K.

In Fig. 4, we present the transmission coefficient $\kappa(t)$, which is defined as

$$\kappa(t)=k(t)/\lim_{t\to 0^+}k(t). \qquad (21)$$

The plateau value of $\kappa(t)$ gives the deviations between the full rate constant and transition state theory value. In Fig. 4 we compare $\kappa(t)$ for $T=60$, 20, 10, 5, 4, 2 K, all obtained by the method presented and a statistical effort as mentioned above. A clear separation between molecular time scales and the reorientation time scale only is observable for temperatures, $k_BT<0.2F(T,\xi^{TS})\approx 3k_BK$. Furthermore, we want to examine how the density influences the plateau value of $\kappa(t)$. To do this, the temperature is fixed at $T=2$ K and the lattice constant a is varied. We choose $a=1.0$ and $0.85a_0$, with $a_0=5.30$ Å, the experimentally observed lattice constant of pure argon at $T=0$ K. In Fig. 5 we report the result. The plateau value of $\kappa(t)$ only changes in the order of 5%, although the total potential energy of the dense crystal already is slightly positive. However, a drastic decrease of the microscopic time scale can be observed indicating an increased mechanical modulus. Also the plateau of $\kappa(t)$ can be

seen more clearly in the case of the low lattice constant. This means that the time scale separation is better.

We have also studied, at $T=2$ K, the effect of the chosen isotope on the transmission coefficient. In order to obtain clear effects we choose very high and very low masses of the investigated isotopes, namely ten times bigger and ten times smaller than the mass of natural nitrogen. Even if such extreme cases of the N atom do not exist in nature, they can exist in a computer simulation. As demonstrated in Fig. 6, the high mass case results in a plateau value close to one, while in the low mass case it is close to $\frac{1}{3}$, which represents the lower bound due to the three times degenerated stable orientational state. One can conclude for the case of activated reorientational motion that the plateau value of $\kappa(t)$ increases with increasing mass of the rotator impurity. This results in the following inequality for the isotope dependent full rate:

FIG. 4. The transmission coefficient, $\kappa(t)$ [see Eq. (21)], for $T=2$, 5, 10, 20, 60 K.
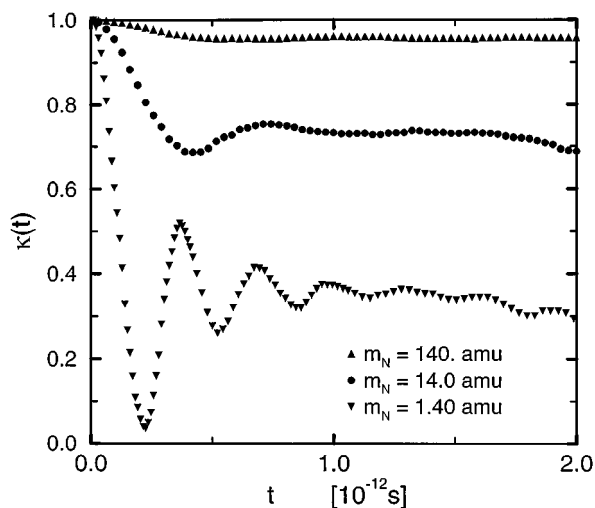
FIG. 6. Same as Fig. 3 for various "isotopes" of the N_2 molecule.

$$\frac{k_1}{k_2} < \sqrt{\frac{m_2}{m_1}} \quad \text{with} \quad m_2 > m_1, \tag{22}$$

m_1, m_2 the masses of the isotopes, respectively. Therefore, a deviation from the usual classical law $k_1/k_2 = \sqrt{m_2/m_1}$ cannot always be attributed only to quantum isotope effects, but it may also have its origin in purely classical memory effects.

VI. SUMMARY AND OUTLOOK

The reaction coordinate formalism has been developed and applied for the first time to a multichannel reaction. The application, a computer simulation study, has been concentrated on the thermally activated reorientational diffusion of a N_2 impurity in a fcc argon crystal. The plateau in the transmission coefficient is only clearly observable at thermal energies smaller than 0.2 times the free energy barrier. While at given temperature, the plateau value does not depend strongly on the density, it is sensitive to the mass of the isotopes, chosen to form the molecule.

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