

Generalized Langevin equation approach for the rotational relaxation of a molecule trapped in a 3D crystal. I. Theoretical considerations

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The stochastic classical trajectory method is developed for the interpretation of the orientational relaxation of a diatomic molecule trapped in a rare gas matrix. The primary system formed by the molecule and four neighboring atoms is described as a 2D effective dynamical system, while the bath formed by the remaining degrees of freedom has the spatial (3D) dimension. Special emphasis is devoted to the determination of the viscous terms (connected to the molecule rotation and translation and to the four atoms vibrations) which are responsible for the various channels of energy dissipation in the bath. A Monte Carlo numerical procedure is applied in paper II to the dynamics of CO and CH₃F molecules trapped in an argon crystal.

I. INTRODUCTION

Phase and energy relaxations of impurity molecules trapped in solids have become subjects of much experimental¹⁻⁹ and theoretical¹⁰⁻¹⁸ work in the last decade. Electronic to vibrational energy transfers and vibrational energy relaxations have been extensively considered from an experimental point of view, especially for diatomic molecules such as hydrogenated molecules^{6,7} (HCl, NH, OH) or as molecules with relatively large moments of inertia³⁻⁵ (CO, N₂,...). The theoretical approach for the description of the vibrational relaxation mechanism rests, in the lack of migration processes, on the general theory of multiphonon processes^{11,12,15} less or more assisted by local modes^{13,14,16-18} such as the rotational or translational modes connected to the motions of the impurity in the lattice.

Most of these theories are quantum interpretations of the vibrational and rotational relaxations of diatomic, and more recently, of polyatomic molecules. According to the degree of description of the physical system, the proposed models can explain, with various success, the measured relaxation rates, but the most realistic models require very tedious calculations which have prevented a systematic analysis for various molecules.

Beside these quantum methods, classical approaches have been studied either through the molecular dynamics simulation¹⁹ or through the stochastic trajectory formalism.^{20,21} Given the increasing complexity of the dynamical equations, the applications of these approaches have been limited to 1D models. Indeed, even if, in the stochastic trajectory method, the 3D specificity of the crystal is introduced, the system formed by the molecule and the nearest neighbor matrix atoms is assumed to be monodimensional. Moreover, the interactions between the particles forming the system and the bath have generally very simplified forms.

Therefore, a direct comparison with experiments is only qualitative.

A similar approach, based on the elaboration of generalized Langevin equations describing the time evolution of a limited number of motions connected to the molecule and to its closest surrounding, is described in this paper. In contrast with previous papers, the harmonic description of the various motions is not considered as a basic hypothesis; but the adequacy of its use in some of the equations of motion is discussed by introducing the distorted matrix equilibrium configuration, the distortion being due to the inclusion of the diatomic impurity.

Here, the physical system is a diatomic molecule undergoing orientational motions in the close neighborhood of a given symmetry plane in a rare gas matrix. The molecular axis can in fact undergo small magnitude oscillations outside the plane, and the vibrations of the centers of mass of the molecule and of the matrix atoms are typically 3D motions.

The stochastic classical trajectory method is based on the assumption that the molecule interacts directly with a limited number of neighboring crystal atoms. For the fcc crystal symmetry, the number of neighbors is equal to 12. In fact, since the molecule nearly rotates in a given plane, the four nearest-neighbor atoms located in this plane play a singular role regarding the coupled dynamics of the molecule and of the matrix. Therefore, the motions of the primary system will be assumed to be constituted by the in-plane motions of the molecule and of the four nearest-neighbor atoms, and the remaining degrees of freedom will form the bath.

Such a model seems to give a convenient schematization of the motions of relatively heavy diatomic molecules such as CO or N₂ trapped in an argon crystal.²² It can also be applied²³ to prolate symmetric tops such as CH₃F which, in first approximation, can be viewed as a diatomic (CH₃)-F rotor in the rare gas matrices.

In Sec. II, one presents the gross equations of motions

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for the diatomic embedded in the lattice, using a pairwise potential to describe the molecule–matrix and matrix atom–matrix atom interaction. Section III is devoted to the transformation of these equations into generalized Langevin equations for the primary system, and Sec. IV defines the various damping terms and forces occurring in the stochastic trajectory approach.

In a second paper (II), the computational procedure involved in the solutions of the Langevin equations is developed and applied to the diatomic molecule C–O and to the idealized molecule (CH₃)–F.

II. THE MODEL

The diatomic molecule trapped in a rare gas matrix is constrained to move and rotate in a given plane of the lattice, for instance the (100) plane of a cubic close-packed argon crystal. A limited number of degrees of freedom are required to study the coupled dynamics of the rotation θ and of the vibration of the center of mass of the molecule with instantaneous position \mathbf{r}_0 , and the vibrations of the centers of mass of the four nearest-neighbor (NN) matrix atoms with instantaneous locations \mathbf{r}_j ($j = 1, 4$). All these motions proceed in the plane. The other degrees of freedom are connected to the remaining motions not considered before, and they are assumed to pertain to the bath. This is the case for the eight NN atoms of the molecule, which do not belong to the molecule plane and for all the other matrix atoms which undergo 3D motions. The primary system, formed by the molecule and the four in-plane atoms, thus appears as an effective 2D dynamical system embedded in a 3D static and dynamical bath.

Figure 1 displays the instantaneous configurations of the molecule and of the matrix atoms which are decomposed as follows:

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{d}_i + \mathbf{u}_i; \quad i = 0, j, k, \quad (1)$$

where \mathbf{R}_i , \mathbf{d}_i , and \mathbf{u}_i characterize the perfect crystal location, the lattice distortion, and the dynamics with respect to $\mathbf{R}_i + \mathbf{d}_i$ of the i th atom, respectively ($\mathbf{R}_0 \equiv 0$).

The classical equations of motion connected to the rotation–translation (θ, \mathbf{r}_0) of the molecule and to the translation of the j atoms ($\mathbf{r}_j, j = 1, \dots, 4$) and of the bath atoms ($k = 5, \dots, N$) are then solved from the expression of the Lagrangian \mathcal{L} defined as

$$\mathcal{L} = \sum_{i=0}^N \frac{1}{2} M_i \dot{\mathbf{u}}_i^2 + \frac{1}{2} I \dot{\theta}^2 - v(\mathbf{r}_1, \dots, \mathbf{r}_N) - \sum_{i=1}^N V_i(\theta, \mathbf{r}_0, \mathbf{r}_i). \quad (2)$$

M_i and I are the mass of the i th atom (or molecule for $i = 0$) and the moment of inertia of the diatomic molecule. The

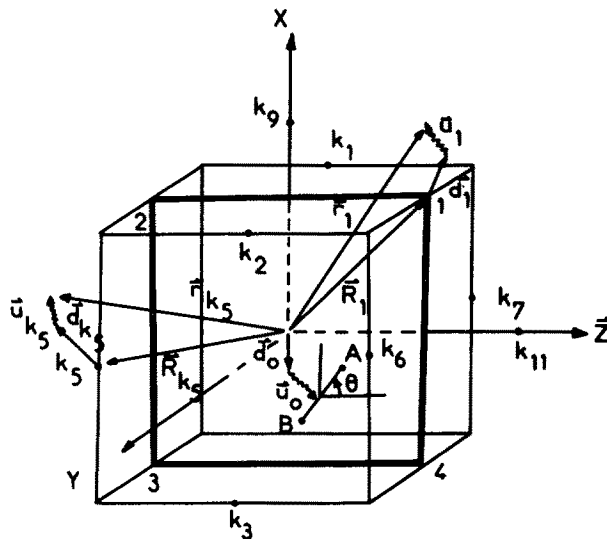


FIG. 1. Geometry of the physical system. The plane formed with atoms $j = 1, 2, 3, 4$ is the rotational plane of the molecule AB. The atoms j and the molecule are the primary system. Atoms k belonging or not to the plane are bath atoms.

potential energy v characterizes the pairwise interactions between matrix atoms, disregarding the guest molecule, and V_i is connected to the molecule–matrix interactions. The energy v is separated into three contributions, depending on the relative location of the atoms with respect to the molecule site, as

$$v(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{j,j'=1}^4 * v_{jj'}(\mathbf{r}_j, \mathbf{r}_{j'}) + \sum_{k,k'=5}^N * v_{kk'} + \sum_{j=1}^4 \sum_{k=5}^N v_{jk}, \quad (3)$$

where the asterisk means that the sums are over $j' > j$ or $k' > k$. In a similar way, the other potential term in Eq. (2) is decomposed into

$$\sum_{i=1}^N V_i = \sum_{j=1}^4 V_j(\theta, \mathbf{r}_0, \mathbf{r}_j) + \sum_{k=5}^N V_k(\theta, \mathbf{r}_0, \mathbf{r}_k). \quad (4)$$

A simplifying assumption is then introduced by considering harmonic vibrations of the k atoms around their distorted equilibrium configurations ($\mathbf{R}_k + \mathbf{d}_k$). A contracted notation is used to define instantaneous positions of the atoms as

$$\begin{aligned} D^{jk} &\equiv (\mathbf{r}_j; \mathbf{R}_k + \mathbf{d}_k), \\ D^{0k} &\equiv (\mathbf{r}_0, \theta; \mathbf{R}_k + \mathbf{d}_k), \\ D^{kk'} &\equiv (\mathbf{R}_k + \mathbf{d}_k, \mathbf{R}_{k'} + \mathbf{d}_{k'}), \end{aligned} \quad (5)$$

and the total interaction energy can be written as a Taylor series expansion in terms of \mathbf{u}_k , after straightforward manipulations, as

$$\begin{aligned} \mathcal{V} = & \left[\frac{1}{2} \sum_{jj'} v_{jj'}(\mathbf{r}_j, \mathbf{r}_{j'}) + \sum_{jk} v_{jk}(D^{jk}) + \frac{1}{2} \sum_{kk'} v_{kk'}(D^{kk'}) + \sum_k V_k(D^{0k}) + \sum_j V_j(\mathbf{r}_0, \theta, \mathbf{r}_j) \right] \\ & + \sum_k \nabla_{\mathbf{u}_k} \left[\sum_j v_{jk}(D^{jk}) + \sum_{k'} v_{kk'}(D^{kk'}) + V_k(D^{0k}) \right] \mathbf{u}_k \\ & + \frac{1}{2} \sum_k \nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_k} \left[\sum_j v_{jk}(D^{jk}) + \sum_{k'} v_{kk'}(D^{kk'}) + V_k(D^{0k}) \right] \mathbf{u}_k \mathbf{u}_k + \frac{1}{2} \sum_{kk'} \nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_{k'}} v_{kk'}(D^{kk'}) \mathbf{u}_k \mathbf{u}_{k'} + \dots \quad (6) \end{aligned}$$

The equations of motions connected to the molecule, to the j atoms, and to the k atoms are then given by

$$\begin{aligned} I\ddot{\theta} &= F_{\theta}(\mathbf{u}_0, \theta, \mathbf{u}_j) - \sum_k \nabla_{\theta} [\nabla_{\mathbf{u}_k} V_k(D^{0k})] \mathbf{u}_k, \\ M_0 \ddot{\mathbf{u}}_0 &= \mathbf{F}_0(\mathbf{u}_0, \theta, \mathbf{u}_j) - \sum_k \nabla_{\mathbf{u}_0} [\nabla_{\mathbf{u}_k} V_k(D^{0k})] \mathbf{u}_k, \\ M \ddot{\mathbf{u}}_j &= \mathbf{F}_j(\mathbf{u}_0, \theta, \mathbf{u}_j) - \sum_k \nabla_{\mathbf{u}_j} [\nabla_{\mathbf{u}_k} v_{jk}(D^{jk})] \mathbf{u}_k, \\ M \ddot{\mathbf{u}}_k &= \mathbf{F}_k(\mathbf{u}_0, \theta, \mathbf{u}_j) - \sum_{k'} \nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_{k'}} v_{kk'}(D^{kk'}) \mathbf{u}_{k'} \\ &\quad - \left[\nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_k} V_k(D^{0k}) + \sum_{i=1}^N \nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_i} v_{ik}(D^{ik}) \right] \mathbf{u}_k. \end{aligned} \quad (7)$$

The forces F are, respectively, expressed as

$$\begin{aligned} \mathbf{F}_{\theta} &= - \sum_j \nabla_{\theta} [V_j(\mathbf{u}_0, \theta, \mathbf{u}_j)] - \sum_k \nabla_{\theta} [V_k(D^{0k})], \\ \mathbf{F}_0 &= - \sum_j \nabla_{\mathbf{u}_0} [V_j(\mathbf{u}_0, \theta, \mathbf{u}_j)] - \sum_k \nabla_{\mathbf{u}_0} [V_k(D^{0k})], \\ \mathbf{F}_j &= - \nabla_{\mathbf{u}_j} \left[V_j(\mathbf{u}_0, \theta, \mathbf{u}_j) + \sum_{j'} v_{j'}(\mathbf{u}_j, \mathbf{u}_{j'}) + \sum_k v_{jk}(D^{jk}) \right], \\ \mathbf{F}_k &= - \nabla_{\mathbf{u}_k} \left[V_k(D^{0k}) + \sum_{i=1}^N v_{ik}(D^{ik}) \right]. \end{aligned} \quad (8)$$

The brackets in Eqs. (7) and (8) mean that the gradient acts on the functional inside these brackets. This functional is the force experienced by each k atom located at its static equilibrium configuration when the molecule or the j atoms are themselves at given instantaneous positions.

The harmonic approximation is not required for the molecule and the j atom motions. Moreover, in contrast to the models developed in previous papers, the forces F_{θ} , F_0 , and F_j contain *not only* a contribution which depends on the *instantaneous* position of the primary system, but *also* on the *static* positions of all the k atoms. This term acts to renormalize the forces viewed by the dynamical system and due to the bath.

III. GENERALIZED LANGEVIN EQUATIONS OF MOTION

The resolution of the equations of motion requires to make additional assumptions. In Eq. (7), the force constants and the force F_k (but not the other forces F_0 , F_{θ} , F_j) are expanded in terms of \mathbf{u}_0 , θ , \mathbf{u}_j , retaining the linear expansion only. This means that the relaxation terms in Eqs. (7) are considered within the harmonic approximation while the forces on the molecule and on the j atoms are rigorously included. This assumption can still be interpreted by considering that the bath "sees" a harmonic primary system from the point of view of relaxational terms, but a general system regarding the forces. To ensure the convergence of this expansion, \mathbf{u}_0 and \mathbf{u}_j are the instantaneous displacements of the molecule and the j th atom with respect to the *distorted equilibrium configurations* $\mathbf{R}_0 + \mathbf{d}_0$ and $\mathbf{R}_j + \mathbf{d}_j$. Moreover, the orientational coordinate can take any value in the range $[0, \infty[$ with the 2π periodicity. A convergence criterion for θ is not possible, except when one makes a partition of the 2D space viewed by the rotating molecule. The C_4 symmetry of

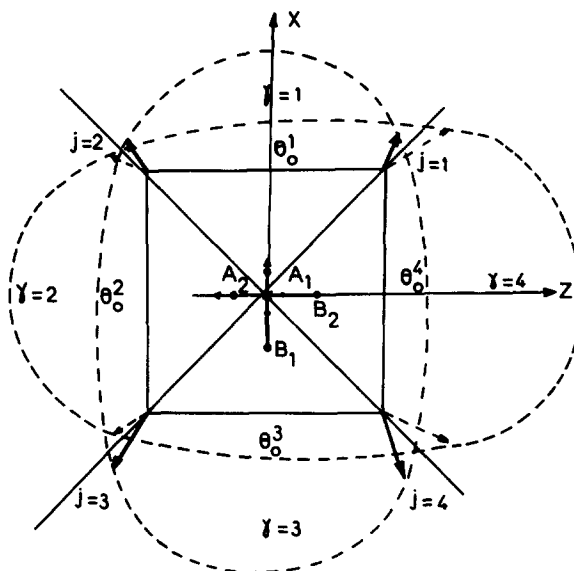


FIG. 2. Rotational motion of the diatomic molecule in the parts $\gamma = 1$ and $\gamma = 2$ and distorted configurations of the j atoms of the primary system (θ is referred to the Z axis).

the lattice in the rotation plane (100) is therefore used to make a partition of the interval $[0, 2\pi]$ into four equal angular parts $[(\pi/4), (3\pi/4)]$, $[(3\pi/4), (5\pi/4)] \dots$ (Fig. 2). For each part, there is an orientational equilibrium configuration for the molecule for $\theta = (\pi/2), \pi, \dots$. If θ_j^γ labels these four configurations ($\gamma = 1, \dots, 4$), the convergence of the previous expansion around θ_j^γ ($\theta' = \theta - \theta_j^\gamma$) is then, at least partially, recovered when the molecular axis is located in the γ th part of the space. Since θ_j^γ corresponds to an orientational equilibrium configuration for the molecule, the force F_k acting on the k th atom vanishes when $(\mathbf{u}_0, \mathbf{u}_j) = 0$ and $\theta = \theta_j^\gamma$.

The equation of motion of the k th atom can be written, in a condensed notation, for the γ th orientational well, as

$$\ddot{\mathbf{u}}_k = - \sum_{k'=5}^N R_{kk'} \mathbf{u}_{k'} - \sum_{j=1}^4 H_{kj} \mathbf{u}_j - J_{k0} \mathbf{u}_0 - Q_k \theta', \quad (9)$$

where \mathbf{u} are general 3D vectors; R , H , and J are second-rank tensors with dimensions of the square of a pulsation, and Q is a first-rank tensor. These tensors are expressed, for the k th atom, as

$$\begin{aligned} R_{kk'} &= \frac{1}{M} \nabla_{\mathbf{u}_k} \nabla_{\mathbf{u}_{k'}} \left[v_{kk'}(D_0^{kk'}) (1 - \delta_{kk'}) \right. \\ &\quad \left. + V_k(D_0^{kk'}) \delta_{kk'} + \sum_{i=1}^N v_{ik}(D_0^{ik}) \delta_{kk'} \right], \\ H_{kj} &= \frac{1}{M} \nabla_{\mathbf{u}_j} \nabla_{\mathbf{u}_k} v_{jk}(D_0^{jk}), \\ J_k &= \frac{1}{M} \nabla_{\mathbf{u}_0} \nabla_{\mathbf{u}_k} V_k(D_0^{0k}), \\ Q_k &= \frac{1}{M} \nabla_{\theta} \nabla_{\mathbf{u}_k} V_k(D_0^{0k}), \end{aligned} \quad (10)$$

where, now D_0 means that the potential force constants are calculated for the distorted configuration of the matrix and of the molecule. The equations of motion for all k atoms can then be expressed in a matricial form, with the matrix ele-

ments given by Eqs. (10):

$$\ddot{\mathbf{u}} = -\tilde{\mathbf{R}} \cdot \mathbf{u} - \sum_j \tilde{\mathbf{H}}_j \cdot \mathbf{u}_j - \tilde{\mathbf{J}} \cdot \mathbf{u}_0 - \tilde{\mathbf{Q}} \cdot \theta'. \quad (11)$$

\mathbf{u} is a column matrix with $N - 5$ vector elements defined by Eq. (9); $\tilde{\mathbf{R}}$ is a square matrix of rank $(N - 5)^2$; and $\tilde{\mathbf{H}}$, $\tilde{\mathbf{J}}$, and $\tilde{\mathbf{Q}}$ are column matrices with the dimension $N - 5$ such that the product $A \cdot \mathbf{b}$ (A stands for $\tilde{\mathbf{H}}$, $\tilde{\mathbf{J}}$, and $\tilde{\mathbf{Q}}$ and \mathbf{b} for \mathbf{u}_j , \mathbf{u}_0 , and θ') is given as

$$A \cdot \mathbf{b} \equiv \begin{bmatrix} A_5 & \mathbf{b} \\ A_6 & \mathbf{b} \\ \vdots & \mathbf{b} \\ A_N & \mathbf{b} \end{bmatrix}. \quad (11')$$

The usual Laplace transform of Eq. (11) allows us to integrate the equation of motion for the bath atoms as

$$\begin{aligned} \mathbf{u}(t) = & \mathbf{S}(t) + \beta(t) \left[\sum_j \tilde{\mathbf{H}}_j \cdot \mathbf{u}_j(0) + \tilde{\mathbf{J}} \cdot \mathbf{u}_0(0) + \tilde{\mathbf{Q}} \cdot \theta'(0) \right] \\ & - \beta(0) \left[\sum_j \tilde{\mathbf{H}}_j \cdot \mathbf{u}_j(t) + \tilde{\mathbf{J}} \cdot \mathbf{u}_0(t) + \tilde{\mathbf{Q}} \cdot \theta'(t) \right] \\ & + \int_0^t dt' \beta(t-t') \left[\sum_j \tilde{\mathbf{H}}_j \cdot \dot{\mathbf{u}}_j(t') \right. \\ & \left. + \tilde{\mathbf{J}} \cdot \dot{\mathbf{u}}_0(t') + \tilde{\mathbf{Q}} \cdot \dot{\theta}'(t') \right]. \end{aligned} \quad (12)$$

The random matrix $\mathbf{S}(t)$:

$$\mathbf{S}(t) = \hat{\Theta}(t) \cdot \mathbf{u}(0) + \Theta(t) \cdot \dot{\mathbf{u}}(0) \quad (13)$$

and the kernel in the friction term

$$\beta(t) = \int_t^\infty \Theta(\tau) d\tau; \quad \beta(0) = \hat{\Theta}(z=0) \quad (14)$$

are both expressed in terms of the resolvent function $\Theta(t)$ with Laplace transform given by^{20,21}

$$\hat{\Theta}(z) = [z^2 \mathbf{1}_{(N-5)^2} + \tilde{\mathbf{R}}]^{-1}. \quad (15)$$

The formal inverse Laplace transform of $\hat{\Theta}(z)$ can be written as

$$\Theta(t) = (\sin \tilde{\mathbf{R}}^{1/2} t) \mathbf{R}^{-1/2} \quad (16)$$

and the corresponding $\beta(t)$, after integration, as

$$\beta(t) = (\cos \tilde{\mathbf{R}}^{1/2} t) \tilde{\mathbf{R}}^{-1}. \quad (17)$$

$\mathbf{1}_{(N-5)}$ is the unit matrix with rank $(N - 5)^2$ and z and t are reciprocal variables. The equations connected to the other motions are then, using the same notations,

$$\begin{aligned} \ddot{\mathbf{u}}_0 = & M_0^{-1} [\mathbf{F}_0 - M \tilde{\mathbf{J}}^T \cdot \mathbf{u}(t)], \\ \ddot{\theta} = & I^{-1} [F_\theta - M \tilde{\mathbf{Q}}^T \cdot \mathbf{u}(t)], \\ \ddot{\mathbf{u}}_j = & M^{-1} [\mathbf{F}_j - M \tilde{\mathbf{H}}_j^T \cdot \mathbf{u}(t)], \end{aligned} \quad (18)$$

where the index T means the transposed matrix.

To proceed further, a simplification in Eqs. (12) and (18) is introduced by assuming that the friction forces between different motions θ , \mathbf{u}_0 , \mathbf{u}_j , and \mathbf{u}_r are negligible. This means that we disregard the influence, on the dynamics of the system formed by the molecule and the four j atoms, of the modification of the bath motions due to the interactions with the system.

Equations (18), finally, can be written as generalized

Langevin equations:

$$\begin{aligned} \ddot{\mathbf{u}}_0(t) = & M_0^{-1} \mathbf{F}_0 + \Lambda_0(0) \mathbf{u}_0(t) - \Lambda_0(t) \mathbf{u}_0(0) \\ & - \int_0^t \Lambda_0(t-t') \dot{\mathbf{u}}_0(t') dt' + \mathbf{N}_0(t), \\ \ddot{\theta}(t) = & I^{-1} F_\theta + \Lambda_\theta(0) \theta'(t) - \Lambda_\theta(t) \theta'(0) \\ & - \int_0^t \Lambda_\theta(t-t') \dot{\theta}(t') dt' + \mathbf{N}_\theta(t), \\ \ddot{\mathbf{u}}_j(t) = & M^{-1} \mathbf{F}_j + \Lambda_j(0) \mathbf{u}_j(t) - \Lambda_j(t) \mathbf{u}_j(0) \\ & - \int_0^t \Lambda_j(t-t') \dot{\mathbf{u}}_j(t') dt' + \mathbf{N}_j(t), \end{aligned} \quad (19)$$

with the following definition of the 3×3 matrices of the viscous terms and of the corresponding random forces:

$$\begin{aligned} \Lambda_0(t) = & M M_0^{-1} \tilde{\mathbf{J}}^T \cdot \beta(t) \cdot \tilde{\mathbf{J}}; \quad N_0(t) = -M M_0^{-1} \tilde{\mathbf{J}}^T \cdot \mathbf{S}(t), \\ \Lambda_\theta(t) = & M I^{-1} \tilde{\mathbf{Q}}^T \cdot \beta(t) \cdot \tilde{\mathbf{Q}}; \quad N_\theta(t) = -M I^{-1} \tilde{\mathbf{Q}}^T \cdot \mathbf{S}(t), \\ \Lambda_j(t) = & \tilde{\mathbf{H}}_j^T \cdot \beta(t) \cdot \tilde{\mathbf{H}}_j; \quad N_j(t) = -\tilde{\mathbf{H}}_j^T \cdot \mathbf{S}(t). \end{aligned} \quad (20)$$

As mentioned elsewhere,^{20,21} the friction kernels $\Lambda(t)$ are connected, through the second fluctuation-dissipation theorem, to the autocorrelation function of the corresponding random forces $\mathbf{N}(t)$ per unit mass, by

$$\begin{aligned} \langle \mathbf{N}_0(0) \mathbf{N}_0(t) \rangle = & M_0^{-1} k T \Lambda_0(t), \\ \langle \mathbf{N}_\theta(0) \mathbf{N}_\theta(t) \rangle = & I^{-1} k T \Lambda_\theta(t), \\ \langle \mathbf{N}_j(0) \mathbf{N}_j(t) \rangle = & M^{-1} k T \Lambda_j(t) \end{aligned} \quad (21)$$

when the following basic equilibrium thermal conditions are verified:

$$\begin{aligned} \langle \mathbf{u}(0) \dot{\mathbf{u}}^T(0) \rangle = & 0, \\ \langle \mathbf{u}(0) \mathbf{u}^T(0) \rangle = & M^{-1} k T \tilde{\mathbf{R}}^{-1}. \end{aligned} \quad (22)$$

All these equations are obtained for a given γ (Fig. 2). When γ changes, for instance, from $\gamma = 1$ to $\gamma = 2$, we have to change the equations of motion, i.e., the matrix distortion \mathbf{d}_0 , \mathbf{d}_j , \mathbf{d}_k , and θ_0 , the dynamical coordinates \mathbf{u}_0 , \mathbf{u}_j , and the viscous coefficients Λ_0 , Λ_θ , and Λ_j . Within these changes, these equations are formally equivalent for each γ , if we redefine the time origin in each γ position. To overcome this difficulty, a time translation can be done [$\tilde{t} = t + t_\gamma^\%$] which leads to the change of t into \tilde{t} and of the time origin $t = 0$ into $t_\gamma^\%$ [$t_\gamma^\%$ is the new origin, each time the molecule rotates from a $(\gamma - 1)$ portion of space to another γ one]. Of course, there will be as many values of $t_\gamma^\%$ as the molecule will go into the γ th well. So, Eqs. (19) and (20) must be rewritten with index γ for each function and by replacing the zero time origin by $t_\gamma^\%$.

IV. DETERMINATION OF THE VARIOUS TERMS

Three species of terms appear in Eqs. (19), the forces \mathbf{F} , the viscous terms Λ , and the random forces \mathbf{N} .

The forces \mathbf{F} for the system (\mathbf{u}_0 , θ , and \mathbf{u}_j) are those given by Eqs. (8) without further simplifications.

The viscous terms $\Lambda(t)$ given in Eqs. (20) depend in fact on two quantities. The matrix β describes, through $\tilde{\mathbf{R}}$, the effect of the bath (k atoms) in the relaxation mechanism [cf. Eq. (10)] whereas the matrices $\tilde{\mathbf{J}}$, $\tilde{\mathbf{Q}}$, and $\tilde{\mathbf{H}}_j$ characterize the intensity of the coupling between each motion of the system and the bath. Note that, if the third equation (20)

could be inverted, it would be possible to calculate Λ_0 and Λ_θ in terms of Λ_j . This is obviously not the case since Λ_j is connected to a microscopic description of the relaxation process, whereas $\beta(t)$ characterizes the macroscopic counterpart of the process. An approximation must then be done to correlate β and Λ_j in an unambiguous way. The matrix β is therefore approximately written in a diagonal form as

$$\beta(t) = \lambda(t) \mathbf{1}_{(N-5)^2}, \quad (23)$$

where $\lambda(t)$ is a scalar. Such a slight approximation is equivalent to neglect three (and higher) body interactions in the relaxation mechanism, resulting in a diagonal form for β and to assume that each k atom has the same effect in the relaxation process, resulting in the same diagonal terms λ for β . Therefore, each $\Lambda(t)$ in Eqs. (20) can be expressed as a simple product of a scalar term $\lambda(t)$ characterizing the bath influence only, the same for all the motions \mathbf{u}_0 , θ , and \mathbf{u}_j of the system and of the square of force constants determining the bath-system coupling, which are obviously different for each motion. Equations (20) are written as

$$\begin{aligned} \Lambda_0(t) &= \lambda(t) \mathbf{M} \mathbf{M}_0^{-1} [\tilde{\mathbf{J}}^T \tilde{\mathbf{J}}], \\ \Lambda_\theta(t) &= \lambda(t) \mathbf{M} \mathbf{I}^{-1} [\tilde{\mathbf{Q}}^T \tilde{\mathbf{Q}}], \\ \Lambda_j(t) &= \lambda(t) [\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j]. \end{aligned} \quad (24)$$

Since the λ 's are the same, one can expect the same energy transfer for all motions in a given bath. So, when λ remains small, the transfer process is not efficient for all the system motions and, inversely when λ increases, the transfer process increases. The differential effect in the transfer process for \mathbf{u}_0 , θ , and \mathbf{u}_j is then included in the matrices $\tilde{\mathbf{J}}$, $\tilde{\mathbf{Q}}$, and $\tilde{\mathbf{H}}_j$. Since the $\tilde{\mathbf{Q}}$ matrix is a column $(N-5) \times 1$ matrix, the product $\tilde{\mathbf{Q}}^T \tilde{\mathbf{Q}}$ will give a scalar including the influence of all the k atoms. The $\tilde{\mathbf{J}}$ matrix and, for each atom $j = 1, \dots, 4$, the $\tilde{\mathbf{H}}_j$ matrix are column matrices $(N-5) \times 1$ with each element formed by 3×3 matrices; the products $\tilde{\mathbf{J}}^T \tilde{\mathbf{J}}$ and $\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j$ will give 3×3 matrices summed over all the k atoms. The latter product $\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j$ yields in fact a nearly diagonal matrix due to the overall symmetry of the crystal. Nondiagonal terms would vanish for each j atom if the surrounding crystal around j would be perfect. It is obviously not the case here due to the molecule inclusion which provides a slight space anisotropy around each j atom and thus leads to small but nonzero, nondiagonal terms. For the same reason, the approximate isotropy of the crystal leads to similar values for the diagonal terms, the difference being again due to the presence of the molecule. In contrast the product $\tilde{\mathbf{J}}^T \tilde{\mathbf{J}}$ is strictly diagonal as the molecule "sees" an isotropic crystal around it, but the diagonal elements are more different as the diatomic shape appears anisotropic. From these considerations, the diagonal elements of the $\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j$ product have been approximately expressed as an average value:

$$h = \overline{(\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j)_{\alpha\alpha}} = \sum_{\gamma=1}^4 \frac{1}{48} \sum_{j=1}^4 \text{Tr}(\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j)_{\gamma}. \quad (25)$$

The normalization number 48 corresponds to the sum over the four wells, over the four atoms j , and for the three Cartesian directions. Of course, such an approximate treatment of the matrix product is valid if the embedded molecule does not induce drastic changes in the crystal symmetry. This

condition will be assumed to generally hold for the species considered here. For a nearly isotropic molecule, the nondiagonal terms $(\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j)_{\alpha\alpha'}$ are very small and they can be neglected in a first approximation. Therefore, the equation connected to $\Lambda_j(t)$ [Eq. (24)] can be written as

$$[\Lambda_j(t)]_{\alpha\alpha} \sim \lambda(t) \overline{(\tilde{\mathbf{H}}_j^T \tilde{\mathbf{H}}_j)_{\alpha\alpha}} = \Gamma_j \delta(t), \quad (26)$$

where the Markovian limit has been used to describe the relaxation process of the j atoms on the bath. Γ_j is directly connected to the phonon density of states of the crystal and it can be conveniently described in the Debye scheme as²⁰

$$\Gamma_j \sim \Gamma = (\pi/6) \omega_D, \quad (27)$$

where ω_D is the Debye frequency. Within this scheme, the effective square frequency $\Lambda_j(0)$ will be given by²⁰

$$[\Lambda_j(0)]_{\alpha\alpha} \sim \Omega^2 = \frac{4}{15} \omega_D^2. \quad (28)$$

From Eqs. (26) and (27), one thus calculates $\lambda(t)$ which is then replaced into Eqs. (24) to determine the diagonal and nondiagonal parts of Λ_θ and Λ_0 .

Finally, the autocorrelation functions of the random forces \mathbf{N}_0 , N_θ , and \mathbf{N}_j are connected to the viscous matrices through Eqs. (21).

Within these approximations, the final equations of motions for the primary system are given for each γ well as

$$\begin{aligned} \ddot{\epsilon}(t) &= M_\epsilon^{-1} \mathbf{F}_\epsilon(\mathbf{d}_j + \mathbf{u}_j, \mathbf{d}_0 + \mathbf{u}_0, \theta) \\ &\quad + \Lambda_\epsilon(0) \epsilon(t) - \beta_\epsilon \dot{\epsilon}(t) + \mathbf{N}_\epsilon(t), \end{aligned} \quad (29)$$

where the viscous term

$$\beta_\epsilon \sim (\pi/6) \omega_D \mathbf{M} \mathbf{M}_\epsilon^{-1} h^{-1} [\tilde{\mathbf{A}}_\epsilon^T \tilde{\mathbf{A}}_\epsilon], \quad (30)$$

the effective frequencies

$$\Lambda_\epsilon(0) \sim \frac{4}{15} \omega_D^2 \mathbf{M} \mathbf{M}_\epsilon^{-1} [\tilde{\mathbf{A}}_\epsilon^T \tilde{\mathbf{A}}_\epsilon], \quad (31)$$

and the random forces

$$\langle \mathbf{N}_\epsilon(0) \mathbf{N}_\epsilon(t) \rangle = k T \mathbf{M}_\epsilon^{-1} \beta_\epsilon \delta(t) \quad (32)$$

are all written for $\epsilon = u_0$, $\theta - \theta_0$, and u_j , and M_ϵ respectively equal to M_0 , I , and $\tilde{\mathbf{A}}_\epsilon$ equal to $\tilde{\mathbf{J}}$, $\tilde{\mathbf{Q}}$, and $\tilde{\mathbf{H}}_j$.

Equations (29)–(32) are used in paper II as the basic equations for numerical computations.

V. DISCUSSION

The generalized equations describing the motions of the molecule and the four in-plane NN atoms have a totally symmetric form. They all contain an effective frequency Λ_ϵ , a viscous term β_ϵ , and a random force \mathbf{N}_ϵ . Regarding the theories obtained in previous papers,^{20,21} this is an unusual result since the molecule was not, in general, coupled to the bath directly. In our method we have considered the possibility of direct relaxation of the molecule energy on the bath through $\Lambda_0(t)$ and $\Lambda_\theta(t)$.

The present approach still includes a rotational degree of freedom which can be very anharmonic. Indeed, the rotation can be nearly free over several periods. It has thus been necessary to go beyond the usual harmonic motion approximation of the previous stochastic approaches. The partition of the space into four subspaces characteristic of the angular

symmetry of the physical system has permitted us to treat such anharmonicities and to recover the expressions of the Langevin equations.²⁴ In fact, within the two basic hypotheses on the bath harmonicity and on the harmonic behavior

of the primary system *as viewed by the bath*, the general equations of motions are not strictly Langevin equations. Indeed, instead of Eqs. (19), the motions of the primary system are, in this scheme, given by

$$\begin{aligned} \ddot{\epsilon} = & M \epsilon^{-1} \mathbf{F}_\epsilon - MM \epsilon^{-1} \tilde{\mathbf{A}}_\epsilon^T(\mathbf{u}_0, \theta, \mathbf{u}_j) \beta(0) \tilde{\mathbf{A}}_\epsilon(\mathbf{R}_0 + \mathbf{d}_0, \theta_0, \mathbf{R}_j + \mathbf{d}_j) \epsilon(t) \\ & - MM \epsilon^{-1} \tilde{\mathbf{A}}_\epsilon^T(\mathbf{u}_0, \theta, \mathbf{u}_j) \beta(t) \tilde{\mathbf{A}}_\epsilon(\mathbf{R}_0 + \mathbf{d}_0, \theta_0, \mathbf{R}_j + \mathbf{d}_j) \epsilon(0) \\ & - MM \epsilon^{-1} \int_0^t \tilde{\mathbf{A}}_\epsilon^T(\mathbf{u}_0, \theta, \mathbf{u}_j) \beta(t-t') \tilde{\mathbf{A}}_\epsilon(\mathbf{R}_0 + \mathbf{d}_0, \theta_0, \mathbf{R}_j + \mathbf{d}_j) \dot{\epsilon}(t') dt' - MM \epsilon^{-1} \tilde{\mathbf{A}}_\epsilon^T(\mathbf{u}_0, \theta, \mathbf{u}_j) \mathbf{S}(t), \end{aligned} \quad (33)$$

where the effective frequency, the random force, and the viscous term depend on the instantaneous variables \mathbf{u}_0 , θ , \mathbf{u}_j . Such an equation [Eq. (33)], which approaches its Langevin expression when \mathbf{u}_0 , θ , and \mathbf{u}_j are substituted by their static values \mathbf{d}_0 , θ_0 , and \mathbf{d}_j , although time consuming, could also be solved. Nevertheless, such a procedure may seem superfluous here since the anharmonicities of the motions are already included in the force terms.

Moreover, without anticipating on the numerical results of paper II, it may be noted, going back to the occurrence of the quantities β_0 and β_θ in Eqs. (27) and (30), that they exhibit some general features. Indeed, since β_0 and β_θ depend on the same characteristics of the bath as β_j , an increase of Γ [Eqs. (27) and (30)] will produce a concomitant increase of β_0 and β_θ . Of course, the efficiency of energy dissipation will depend on the relative magnitude of the transfer matrices $\tilde{\mathbf{J}}$, $\tilde{\mathbf{Q}}$, and $\tilde{\mathbf{H}}_j$, but the relative increase of β_0 and β_θ will be the same as for β_j . This means that, on the one hand, the molecule will relax efficiently its energy on the surrounding (j or k atoms) in a direct way. But, on the other hand, an increase of β_j will also imply an increase of the viscous forces connected to the motions of the j atoms. Therefore, the j atoms will not be able to accept energy from the molecule, due to the high viscosity β_j . So we will expect, as shown in Fig. 3, two antagonistic effects, one effect which will tend to increase the energy transfer from the molecule to the atoms, and another effect which will increase the damping of the j atoms and decrease the energy transfer efficiency to these atoms. The accurate determination of the more effi-

cient relaxation channel depends therefore on the quantities Γ , $\tilde{\mathbf{J}}$, $\tilde{\mathbf{Q}}$, and $\tilde{\mathbf{H}}_j$, but also on the quantity which characterizes the coupling between the molecule and the j atoms (Fig. 3). Such a quantity is not analytic here and appears only through the forces \mathbf{F}_0 , \mathbf{F}_θ , and \mathbf{F}_j . If this latter coupling nearly vanished, we would expect a direct relaxation process to the bath (k atoms). In cubic close packed lattice, there is no reason that the couplings between the molecule and the j atoms, on the one hand, and between the molecule and the eight NN k atoms located outside the rotational plane, on the other hand, will be very different. Therefore, in the lack of numerical data, it is difficult to conclude what is the more efficient relaxation channel. We can nevertheless conclude that the direct transfer of energy to the bath is favored, whereas the transfer to the NN j atoms is impeded when λ increases.

The numerical results applied to the systems formed by CO or CH₃F molecules trapped in ccp rare gas crystals will show if the general tendency discussed here is rather the direct transfer to the bath or the transfer through the primary atoms.

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APPENDIX: NOTATIONS AND SYMBOLS

Molecule:

M_0 : mass;

I : moment of inertia;

\mathbf{r}_0 : instantaneous position;

θ : instantaneous orientation;

$\mathbf{R}_0 = 0$: molecular site at equilibrium for the perfect crystal;

θ_0 : molecular equilibrium orientation;

\mathbf{d}_0 : displacement of the molecule center of mass (distorted configuration for the crystal);

\mathbf{u}_0 : dynamical variable ($\mathbf{r}_0 = \mathbf{d}_0 + \mathbf{u}_0$).

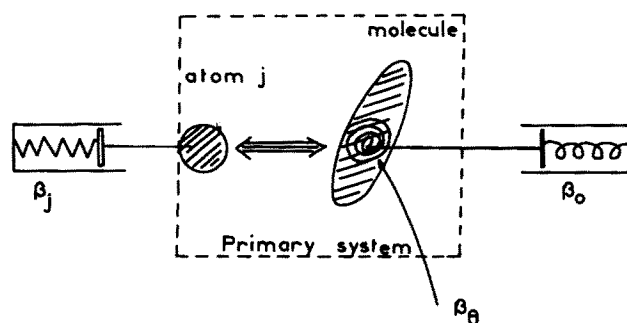


FIG. 3. Analogic system for a part of the primary system. The arrow characterizes the coupling between the j th atom and the molecule. The bath influence is schematized by two linear pistons and one spiral.

Atoms j of the primary system:

- $M_j \equiv M$: mass;
 \mathbf{r}_j : instantaneous position;
 \mathbf{R}_j : atomic site for the perfect crystal equilibrium;
 \mathbf{d}_j : displacement due to the molecule inclusion;
 \mathbf{u}_j : dynamical variable ($\mathbf{r}_j = \mathbf{R}_j + \mathbf{d}_j + \mathbf{u}_j$).

Atoms k of the bath:

- $M_k \equiv M$: mass;
 \mathbf{r}_k : instantaneous position;
 \mathbf{R}_k : atomic site for the perfect crystal;
 \mathbf{d}_k : displacement due to the molecule inclusion;
 \mathbf{u}_k : dynamical variable ($\mathbf{r}_k = \mathbf{R}_k + \mathbf{d}_k + \mathbf{u}_k$).

Interactions:

- v : interaction between two matrix atoms (j or k atoms);
 V : interaction between the molecule and a matrix atom.

Equilibrium:

- D : instantaneous configuration ($\mathbf{r}_0, \theta, \mathbf{r}_j$) for the primary system and distorted equilibrium configuration ($\mathbf{R}_k + \mathbf{d}_k$) for the bath;
 D_0 : distorted equilibrium configurations for the primary system ($\mathbf{d}_0, \theta_0, \mathbf{R}_j + \mathbf{d}_j$) and for the bath ($\mathbf{R}_k + \mathbf{d}_k$).

Generalized forces:

- $F_\epsilon = -[\nabla_\epsilon V]_{D_0}$; $\epsilon = \mathbf{u}_0, \mathbf{u}_j, \theta, \mathbf{u}_k$; and calculated for the D configuration.

Generalized force constants:

- $[R_{kk'}]_{D_0}$: force constant between the bath atoms k and k' calculated for the D_0 configuration;
 $[H_j]_{D_0}$: bilinear coupling constant between the atoms j and k calculated for the D_0 configuration;
 $[J]_{D_0}$: bilinear coupling constant between the molecule translation and the k th atom;
 $[Q]_{D_0}$: bilinear coupling constant between the molecule rotation and the k th atom.

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