Brownian dipole rotator in alternating electric field

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The study addresses the azimuthal jumping motion of an adsorbed polar molecule in a periodic n-well potential under the action of an external alternating electric field. Starting from the perturbation theory of the Pauli equation with respect to the weak field intensity, explicit analytical expressions have been derived for the time dependence of the average dipole moment as well as the frequency dependences of polarizability and the average angular velocity, the three quantities exhibiting conspicuous stochastic resonance. As shown, unidirectional rotation can arise only provided simultaneous modulation of the minima and maxima of the potential by an external alternating field. For a symmetric potential of hindered rotation, the average angular velocity, if calculated by the second-order perturbation theory with respect to the field intensity, has a nonzero value only at $n=2$, i.e., when two azimuthal wells specify a selected axis in the system. Particular consideration is given to the effect caused by the asymmetry of the two-well potential on the dielectric loss spectrum and other Brownian motion parameters. When the asymmetric potential in a system of dipole rotators arises from the average local fields induced by an orientational phase transition, the characteristics concerned show certain peculiarities which enable detection of the phase transition and determination of its parameters.

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I. INTRODUCTION

Being relatively loosely bound to the surface, physisorbed molecules are rather motile and exhibit, in particular, high rotational mobility. Hindered rotational movement is also typical of chemisorbed polyatomic molecules or polyatomic groups tightly bound to a surface through one atom, whereas other atoms can have several equilibrium positions in the potential induced by the nearest substrate atoms [1,2]. Much recent interest has been attracted by so-called molecular rotors artificially formed on surfaces [3,4]. These molecular engines provide an insight into the physical principles of controlled mechanical movement and friction on the nanoscale as well as the effects of random thermal movement which are inherent in nanodevices as opposed to conventional macromachinery.

Rotational movement of molecules and atomic groups on a solid surface manifests itself in a variety of experiments. Vibrational spectroscopy detects characteristic absorption in the frequency regions of both stretching and deformation (angular) vibrations, the former also giving rise to the spectral lines at combined frequencies, i.e., at sums and differences of the frequencies of original lines. In addition, rotational movement causes specific broadening of spectral lines, with its temperature dependence governed by the rotational reorientation frequencies. For instance, rotations of hydroxyl groups on oxide surfaces become possible due to relatively small reorientation barriers ($\Delta U_{\varphi} \approx 55$ meV), which are comparable to the characteristic thermal energy ($k_B T \approx 26$ meV at $T=300$ K). As a result, characteristic IR absorption arises in the frequency region $100-200$ cm^{-1} and a typical temperature dependence (of the Arrhenius type) is observed for the spectral bands of the valent OH vibrations [1].

Dielectric measurements offer another promising method to detect rotational movement of polar surface species. To exemplify, the temperature dependence of the dielectric loss tangent reflects the stochastic resonance [5] which arises when the frequency of the applied electric field approaches that of thermally activated molecular reorientations between the equilibrium angular positions. Experiments of this kind are very sensitive to the local environment of a surface center thus being structurally informative. This motivates the development of models which depict the frequency dependence of polarizability for rotationally mobile polar surface centers. The origin of unidirectional rotation in a linearly polarized alternating electric field is also of great interest: it has much in common with Brownian motors in which directed motion arises from the ratchet effects governed by an asymmetric fluctuating potential [6–9].

The present paper addresses the angular Brownian motion of a particle in a periodic n-well potential under the action of the external alternating electric field (Sec. II). Starting from the perturbation theory of the Pauli equation with respect to the weak field intensity, explicit analytical expressions have been derived for the time dependence of the average dipole moment and the frequency dependences of polarizability and the average angular velocity of a dipole rotator. The general prerequisites for the initiation of unidirectional rotation have been analyzed (Sec. III). As found by the second-order perturbation theory with respect to the field intensity, unidirectional rotation in a symmetric potential is only possible at $n=2$, i.e., when two azimuthal wells specify a selected axis in the system (Sec. IV). Therefore, the case of a two-well potential is considered in detail and we also include the effect of asymmetry induced by local fields, which result both from environmental inhomogeneities and from orientational ordering in the low-temperature region (Sec. V). The results obtained demonstrate that stochastic resonance clearly manifests itself in temperature dependences of experimentally observable characteristics of dipole rotators; this phenomenon gives valuable structural evidence about the local environ-

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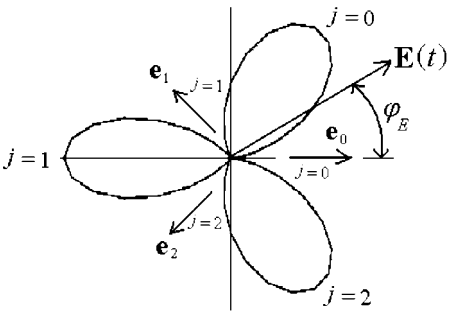

FIG. 1. An azimuthal potential of hindered rotation with n wells and n barriers labeled by the index $j=0,1,\ldots,n-1$ (for definiteness, here $n=3$). The unit vectors $\mathbf{e}_j$ refer to equilibrium rotator orientations. The alternating electric field is oriented at the angle φ_E to the vector $\mathbf{e}_0$.

ment of rotating species and also depicts the features of their orientational ordering (Sec. VI).

II. BASIC EQUATIONS

Consider the azimuthal jumping motion of a Brownian particle in a periodic n-well potential under the action of an external alternating electric field (as shown in Fig. 1 for $n=3$). The complete description should be based on the continuous process and the corresponding Fokker-Planck or Smoluchowski equations. In some cases, when the particle motion dynamics can be subdivided into a fast and a slow component, the reduction of the continuous description to a kinetic one is possible [10]. The azimuthal jumping motion represents the slow component, whereas the time scale for the intrawell motion is assumed to be much shorter, so that quasiequilibrium in each well can be established during the characteristic period of the external governing process. The separation of the two time scales is possible, if the interwell barrier heights ΔU_φ exceed the thermal energy of the moving particle k_BT (where k_B is the Boltzmann constant and T is the absolute temperature) and the potential fluctuation frequencies ω are much less than the inverse time D/L^2 of the particle diffusion over distances of order L (where D is the diffusion coefficient and L is the potential period) [11]. Then the kinetic description in terms of the Pauli master equation is quite adequate.

Let $\rho_j(t)$ specify a probability for a particle to be in the jth well $(j=0,1,\ldots,n-1)$ at the instant t, with the normalization condition

$$\sum_{j=0}^{n-1} \rho_j(t) = 1. \tag{1}$$

Then the particle flow through the barrier j is expressible in terms of the probabilities $\rho_j(t)$ and the rate constants $w_{j'j}(t)$ referring to the transitions between the wells j and j' closest to the barrier as follows:

$$J_j(t) = w_{j,j+1}(t)\rho_j(t) - w_{j+1,j}(t)\rho_{j+1}(t). \tag{2}$$

On the other hand, the balance equation which defines the functions $\rho_j(t)$ is represented by the known Pauli equation and can be written as

$$\frac{d}{dt}\rho_j(t) = J_{j-1}(t) - J_j(t). \tag{3}$$

Now consider the rate constants for the interwell transitions in the potential

$$U_n(\varphi,t) = U_n(\varphi) - \boldsymbol{\mu}(\varphi)\cdot\mathbf{E}(t). \tag{4}$$

It is assumed that the angular contribution to the potential energy of a polar molecule $U_n(\varphi)$ is represented by an n-well hindered rotation potential and the time dependence arises due to the interaction of the molecular dipole moment $\boldsymbol{\mu}(\varphi)$ with the external alternating electric field $\mathbf{E}(t)$. If the transition is treated as the surmounting of a barrier by a particle in terms of the Arrhenius law, then the transition rate constant is expressed as an inverse exponential function of the ratio of the barrier energy to the thermal energy k_BT; the preexponential factor has the meaning of the characteristic frequency of the particle's attacks on the potential barrier and is specified by the Kramers theory for different motion regimes [12]. Then the quantities $w_{j'j}(t)$ for alternating one-dimensional wells and barriers assume the form

$$w_{j,j+1}(t) = v_j(t)u_j(t), \quad w_{j+1,j}(t) = v_j(t)u_{j+1}(t). \tag{5}$$

Here the function $v_j(t)$ depends only on the position of the jth barrier in the potential $U_n(\varphi,t)$, whereas $u_j(t)$ is specified by the position of the jth well in the same potential and also by other well parameters as, for instance, its curvature.

Taking into account relation (5), we rewrite the definition of flux (2) to obtain

$$J_j(t) = v_j(t)\xi_j(t), \tag{6}$$

with the function

$$\xi_j(t) \equiv u_j(t)\rho_j(t) - u_{j+1}(t)\rho_{j+1}(t), \tag{7}$$

which satisfies the evident condition

$$\sum_{j=0}^{n-1} \xi_j(t) = 0. \tag{8}$$

Assuming a sufficiently small external electric field intensity $\mathbf{E}(t)$, the n-well structure of the potential relief $U_n(\varphi)$ remains unchanged. Moreover, the field can only cause the time dependences of the functions $v_j(t)$ and $u_j(t)$ but does not lead to a notable spatial shift of the extrema of the potential $U_n(\varphi)$. Thus, one can derive a number of important regularities concerning the effect of an external field on the properties of the system. If the field modifies only barrier positions, i.e., only the function $v_j(t)$ is time dependent whereas the well positions $u_j(t)=u_j$ are unchanged, then the quantities $\xi_j(t)$ reduce to zero in the established stationary regime [when the system has already forgotten the initial distribution $\rho_j(0)$]. This corresponds to the thermodynamic equilibrium state in which time-independent probabilities ρ_j satisfy the identity $\rho_j/\rho_{j+1}=u_{j+1}/u_j$ and depend only on statistical weights and the minimum values of the potential $U_n(\varphi)$. In this case, all fluxes also vanish.

Another inference of significance follows from consideration of periodic external fields and the fluxes averaged over the field period τ in the stationary regime,

$$\langle J_j(t)\rangle_\tau = \frac{1}{\tau}\int_0^\tau dt J_j(t). \tag{9}$$

Since the stationary regime implies $\rho_j(t+\tau)=\rho_j(t)$, averaging of Eq. (3) in such a way suggests that average fluxes are independent of the barrier number j ($\langle\langle J_j(t)\rangle_\tau=\langle J\rangle_\tau$). Substitute formula (6) into Eq. (3) as follows:

$$\frac{d}{dt}\rho_j(t) = v_{j-1}(t)\xi_{j-1}(t) - v_j(t)\xi_j(t). \tag{10}$$

With relations (1) and (8), we express the functions $\xi_j(t)$ in terms of $\rho_j(t)$ and substitute the result into Eq. (6). Then we obtain, at $n=2$,

$$J_0(t) = -\frac{v_0(t)}{v_0(t)+v_1(t)}\frac{d}{dt}\rho_0(t), \tag{11}$$

and at $n>2$,

$$J_0(t) = \frac{1}{\sum_{j=0}^{n-1} v_j^{-1}(t)}\left[-\frac{d}{dt}\rho_0(t) + v_{n-1}(t)\sum_{j=2}^{n-1}\left(\sum_{k=j}^{n-1} v_k^{-1}(t)\right)\frac{d}{dt}\rho_j(t)\right]. \tag{12}$$

With the condition that the external field makes only the well functions $u_j(t)$ dependent on time and the barrier functions v_j remain time independent, fluxes (11) and (12) averaged over the field period τ vanish in the stationary regime. As a result, unidirectional motion ($\langle J\rangle_\tau\neq 0$) is possible only provided that both $u_j(t)$ and $v_j(t)$ depend on time. In the crudest approximation, the functions $v_j(t)$ and $u_j(t)$ change linearly with the field intensity. Hence, the response of the probabilities $\rho_j(t)$, which is linear in the field, is determined solely by the well functions $u_j(t)$ and proves sufficient to calculate the average flux using Eqs. (11) and (12). Thus, the expansion of the average flux $\langle J\rangle_\tau$ in the field intensity starts with the terms proportional to the product of the functions $v_j(t)$ and $u_j(t)$, and the flux $\langle J\rangle_\tau$ is thus quadratic in the field. A remarkable feature of representations (11) and (12) is that they allow calculation of the quadratic flux using the first-order perturbation theory for $\rho_j(t)$ and the barrier factors $v_j(t)$.

Let the term "Brownian particle" refer to a certain part of a polyatomic polar molecule which reorients by jumpwise rotation about a selected axis. If a dipole moment of such a molecule is defined as $\boldsymbol{\mu}_j=\mu\mathbf{e}_j$, with μ denoting the absolute magnitude of the dipole moment and $\mathbf{e}_j$ denoting the unit orientation vector, then the average dipole moment takes the following form:

$$\langle\boldsymbol{\mu}(t)\rangle = \mu\sum_{j=0}^{n-1}\rho_j(t)\mathbf{e}_j. \tag{13}$$

For the average flux and dipole moment to be found, it is necessary to know the functions $\rho_j(t)$, which are easily calculable using a small parameter, the weak intensity of the external electric field. A general perturbation theory with respect to this small parameter is developed in the next section.

III. PERTURBATION THEORY OF THE PAULI EQUATION

We represent the Pauli equation for the probability of the system $\rho_j(t)$ to be in the state j at the instant t so as to conveniently transform it further [2,13].

$$\frac{d}{dt}\rho_j(t) + \sum_{j'} W_{jj'}(t)\rho_{j'}(t) = 0, \tag{14}$$

$$W_{jj'}(t) = \delta_{jj'}\sum_{j''} w_{jj''}(t) - w_{j'j}(t).$$

Here $w_{j'j}(t)$ is a time-dependent rate constant for the transition from the state j' to the state j, which is expressible as a sum of the stationary unperturbed part $w_{j'j}^{(0)}$ and the time-dependent addition $\tilde{w}_{j'j}(t)$. Likewise, the quantity $W_{jj'}(t)$ can be written as $W_{jj'}(t)=W_{jj'}^{(0)}+\tilde{W}_{jj'}(t)$. If we introduce the Green's function $g_{jj'}(t)$ for the unperturbed Pauli equation, which meets the condition

$$\frac{d}{dt}g_{jj'}(t) + \sum_{j''} W_{jj''}^{(0)}g_{j''j'}(t) = -\delta(t)\delta_{jj'}, \tag{15}$$

then the desired function $\rho_j(t)$ will be a solution of the following integral equation:

$$\rho_j(t) = \rho_j^{(0)} + \sum_{j'j''}\int_{-\infty}^{\infty} dt' g_{jj'}(t-t')\tilde{W}_{j'j''}(t')\rho_{j''}(t'), \tag{16}$$

where $\rho_j^{(0)}$ is an equilibrium occupation probability for the state j obeying the detailed balance principle, $w_{j'j}^{(0)}\rho_{j'}^{(0)} = w_{jj'}^{(0)}\rho_j^{(0)}$. This equality is transformed to $W_{j'j}^{(0)}\rho_j^{(0)}=W_{jj'}^{(0)}\rho_{j'}^{(0)}$ (if the second relation in formulas (14) is taken into account) thus permitting the diagonalization of the matrix $W_{jj'}^{(0)}$ as follows:

$$\sum_{j'} W_{jj'}^{(0)}C_{j'q} = z_q C_{jq}. \tag{17}$$

The eigenvalues z_q of the matrix $W_{jj'}^{(0)}$ are non-negative and the eigenvector matrix C_{jq} is unitary accurate to the weight factors $\rho_j^{(0)}$ as follows:

$$\sum_j (\rho_j^{(0)})^{-1}C_{jq}C_{jq'}^* = \delta_{qq'}, \quad \sum_q C_{jq}^*C_{j'q} = \rho_j^{(0)}\delta_{jj'}. \tag{18}$$

Since $\Sigma_j W_{jj'}^{(0)}=0$, we have $\Sigma_{jj'}W_{jj'}^{(0)}C_{j'q}=z_q\Sigma_j C_{jq}=0$. The linear independence of rows C_j suggests that at least one eigenvalue z_q is equal to zero. Assume that $q=0$ corresponds to $z_0=0$ and that $\Sigma_j C_{jq}=0$ at $q\neq 0$. Using the second equation of Eq. (18) and the normalization condition $\Sigma_j\rho_j^{(0)}=1$, we arrive at the following useful relations:

$$C_{j0} = \rho_j^{(0)}, \quad \sum_j C_{jq} = \delta_{q0}. \tag{19}$$

They enable us to express the matrix $W_{jj'}^{(0)}$ in terms of its eigenvalues and eigenvectors: $W_{jj'}^{(0)}=(\rho_{j'}^{(0)})^{-1}\Sigma_q z_q C_{jq}C_{j'q}^*$, and this result can be used to derive the time dependence of the desired Green's function as follows:

$$g_{jj'}(t) = -\theta(t)(\rho_{j'}^{(0)})^{-1}\sum_q C_{jq}C_{j'q}^* \exp(-z_q t), \qquad (20)$$

where $\theta(t)$ is the theta function equal to 1 at $t>0$ and to 0 at $t<0$. The frequency Fourier transform of the Green's function is defined by the relation $g_{jj'}(\omega)=\int_{-\infty}^{\infty}dt g_{jj'}(t)\exp(i\omega t)$ and becomes

$$g_{jj'}(\omega) = -i(\rho_{j'}^{(0)})^{-1}\sum_q \frac{C_{jq}C_{j'q}^*}{\omega + iz_q}. \qquad (21)$$

IV. ONE-DIMENSIONAL PERIODIC SYSTEM OF DEGENERATE STATES

A one-dimensional periodic system of degenerate states can be exemplified by the symmetric set of azimuthal equilibrium orientations,

$$\mathbf{e}_j = \left(\cos\frac{2\pi j}{n}, \sin\frac{2\pi j}{n}, 0\right), \quad j = 0,1,\ldots,n-1, \qquad (22)$$

which is realized in an n-well hindered rotation potential

$$U_n(\varphi) = \frac{1}{2}\Delta U_\varphi(1-\cos n\varphi), \qquad (23)$$

with ΔU_φ denoting the rotational potential barrier [1]. In this case, equilibrium probabilities appear as $\rho_j^{(0)}=1/n$, and nonzero unperturbed transition rate constants are all equal to

$$w_{j,j+1}^{(0)} = w_{j+1,j}^{(0)} \equiv w_0, \quad w_0 = \nu_\varphi \exp(-\beta\Delta U_\varphi), \quad \beta \equiv (k_B T)^{-1}. \qquad (24)$$

Thus, according to the second relation (14), we obtain

$$W_{jj}^{(0)} = 2w_0, \quad W_{j,j+1}^{(0)} = W_{j+1,j}^{(0)} = -w_0. \qquad (25)$$

Here the periodicity of the system makes the states $j=n$ and $j=0$ equivalent.

Equation (17) assumes the form

$$2w_0 C_{jq} - w_0(C_{j+1,q} + C_{j-1,q}) = z_q C_{jq}. \qquad (26)$$

With regard to relations (19), its solutions can be written as

$$z_q = 4w_0 \sin^2\frac{\pi q}{n}, \quad C_{jq} = \frac{1}{n}\exp\left(\frac{2\pi i}{n}qj\right). \qquad (27)$$

Substituting these solutions into formulas (20) and (21), one can explicitly represent the time and frequency Fourier transform of the Green's functions for the degenerate periodic system as follows:

$$g_{jj'}(t) = -\frac{\theta(t)}{n}\sum_{q=0}^{n-1}\exp\left[-4w_0 t\sin^2\frac{\pi q}{n} + i\frac{2\pi q}{n}(j-j')\right], \qquad (28)$$

$$g_{jj'}(\omega) = -\frac{1}{n}\sum_{q=0}^{n-1}\frac{\exp[2\pi i q(j-j')/n]}{-i\omega + 4w_0\sin^2\pi q/n}. \qquad (29)$$

The time-dependent addends $\tilde{w}_{j'j}(t)$ to the transition rate constants, which account for the action of the external alternating electric field [see the second term in Eq. (4)] and the relevant matrices $\tilde{W}_{jj'}(t)$ are expressed on the basis that the probabilities $\rho_j(t)$ are dictated only by modulation of potential well minima within the linear-in-field approximation. As the energy of the jth potential well minimum changes by $-\boldsymbol{\mu}_j\cdot\mathbf{E}(t)=-\mu E(t)\cos(2\pi j/n-\varphi_E)$, where φ_E is the angle between the field vector $\mathbf{E}(t)$ and the orientation of the well with $j=0$, we obtain

$$\tilde{W}_{jj}(t) = \tilde{w}_{j,j+1}(t) + \tilde{w}_{j,j-1}(t) = -2w_0\beta\mu E(t)\cos(2\pi j/n - \varphi_E),$$

$$\tilde{W}_{j,j+1}(t) = -\tilde{w}_{j+1,j}(t) = -2w_0\beta\mu E(t)\cos[2\pi(j+1)/n - \varphi_E],$$

$$\tilde{W}_{j+1,j}(t) = -\tilde{w}_{j,j+1}(t) = w_0\beta\mu E(t)\cos(2\pi j/n - \varphi_E). \qquad (30)$$

Substituting relations (28) and (30) into Eq. (16) and solving it within the first-order perturbation theory with respect to the alternating external field $E(t)=E\cos\omega t$ (with the frequency ω), i.e., with the assumption that $\rho_j(t)=\rho_j^{(0)}=1/n$ on its right-hand side, we arrive at the following expression for the stationary regime:

$$\rho_j(t) = \frac{1}{n} + \frac{4w_0\beta\mu E\sin^2(\pi/n)}{n} \times\cos\left(\frac{2\pi}{n}j - \varphi_E\right)\frac{\cos(\omega t - \delta_n)}{\sqrt{16w_0^2\sin^4(\pi/n)+\omega^2}},$$

$$\tan\delta_n = \frac{\omega}{4w_0\sin^2(\pi/n)}. \qquad (31)$$

Calculating the average dipole moment (13) by Eqs. (22) and (31), and summing it over j give the time dependences of $\langle\boldsymbol{\mu}\rangle$ at $n=2$ and $n>2$ as follows:

$$\langle\boldsymbol{\mu}(t)\rangle = 4w_0\beta\mu^2\frac{\cos(\omega t-\delta_2)}{\sqrt{16w_0^2+\omega^2}}\begin{Bmatrix} E\cos\varphi_E \\ 0\end{Bmatrix}, \quad n=2,$$

$$\langle\boldsymbol{\mu}(t)\rangle = 2w_0\beta\mu^2\sin^2(\pi/n) \times\frac{\cos(\omega t-\delta_n)}{\sqrt{16w_0^2\sin^4(\pi/n)+\omega^2}}\begin{Bmatrix} E\cos\varphi_E \\ E\sin\varphi_E\end{Bmatrix}, \quad n>2. \qquad (32)$$

These relations enable us to conveniently calculate the frequency dependence of the polarizability tensor, which is defined as the proportionality factor between the Fourier components of the average dipole moment and the vector of the external electric field: $\langle\mu_\alpha(\omega)\rangle=\chi_{\alpha\beta}(\omega)E_\beta(\omega)$. The indices $\alpha,\beta=x,y$ designate the projections onto the Cartesian coordinate axes, with the x axis oriented along the well with $j=0$, and summation is implied over repeated Greek indices. As a result, the expressions for $\chi_{\alpha\beta}(\omega)$ at $n=2$ and $n>2$ are obtained as follows:

$$\chi_{\alpha\beta}(\omega) = \beta\mu^2\frac{4w_0}{-i\omega+4w_0}\delta_{\alpha\beta}\delta_{\alpha x}, \quad n=2,$$

$$\chi_{\alpha\beta}(\omega) = \beta\mu^2 \frac{2w_0 \sin^2(\pi/n)}{-i\omega + 4w_0 \sin^2(\pi/n)} \delta_{\alpha\beta}, \quad n > 2 \quad (33)$$

($\delta_{\alpha\beta}=1$ at $\alpha=\beta$ and $\delta_{\alpha\beta}=0$ at $\alpha\neq\beta$). It should be noted that the tensor $\chi_{\alpha\beta}(\omega)$ is essentially anisotropic at $n=2$ and isotropic at $n>2$. The phase shift δ_n between the time dependences of the external field and the average dipole moment [see relations (31) and (32)] leads to a nonzero imaginary part of the polarizability tensor and the dielectric loss tangent.

We now use Eqs. (11), (12), and (31) to calculate the average flux [as defined in Eq. (9)] over the external field period $\tau=2\pi/\omega$. According to representation (5), the barrier factors $v_j(t)$ can be expressed as $v_j(t)\approx w_0[1+\beta\mu E(t)\cos(2\pi j/n-\varphi_E+\pi/n)]$ in the first-order perturbation theory with respect to the external field intensity. Thus, we arrive at

$$\langle J\rangle_\tau = \begin{cases} -\frac{1}{4} w_0 \beta^2 \mu^2 E^2 \frac{\omega^2}{\omega^2 + 4w_0^2} \sin 2\varphi_E, & n=2 \\ 0, & n>2. \end{cases} \quad (34)$$

In view of the symmetry of the hindered rotation potential with $n>2$, the average flux vanishes, when treated by the second-order perturbation theory with respect to the external field intensity. At $n=2$, the system has a selected direction along two wells of the hindered rotation potential. If the field is oriented at the angles $\varphi_E\neq 0, \pm\pi/2, \pi$ to this selected axis, the alternating field modulates not only the minimum positions for potential wells but also the maximum positions for potential barriers. All these prerequisites give rise to the ratchet effects and hence to unidirectional rotation at $n=2$, as illustrated in Fig. 2. The figure shows the initial symmetric potentials of hindered rotation defined by Eq. (23) at $n=2$ (dashed lines) and the resulting potentials modified by the external field with the maximum amplitude at two instants separated by the vibration half-period (solid lines). Unidirectional rotation originates from the following two processes. First, the asymmetry of hindered rotation potentials modified by the field makes a particle jump from the shallow well into the deep one, as a result of surmounting the small potential barrier through thermal activation. As the jump is thermoactivated, the unidirectional rotation ceases in the low-temperature limit. Second, a change in the field polarity occurring with time causes vertical transitions of the particle from the deep to the shallow well. The thermally activated transport in the same direction occurs again in the new potential relief and the cycle is repeated over and over.

It is easily seen that the potentials presented in Fig. 2 are mutually shifted by half a period. The Brownian motors with potentials fluctuating in such a manner are noted for their high energy conversion efficiency provided that reverse fluxes are locked by high barriers [14–17]. In our case, when the external field is weak enough, the potential relief is modulated only slightly and unidirectional motion is not energetically efficient. Nonetheless, generation of unidirectional angular motion of a dipole rotator in a two-well hindered rotation potential under the action of a linearly polarized alternating electric field is another vivid example of a Brownian motor with potentials fluctuating by half a period.

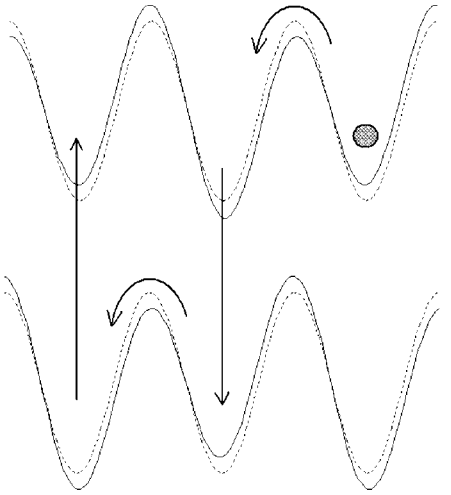

FIG. 2. The mechanism for the occurrence of unidirectional rotation in a periodic symmetric two-well potential (dashed lines), with the wells and barriers modulated with an alternating external field (solid lines at the top and bottom). The asymmetry of the hindered rotation potentials modified by the field leads a Brownian particle to surmount the small potential barrier through thermal activation and to jump from the shallow well into the deep one. The preferred direction of the particle motion remains unchanged on a change of the field polarity which causes vertical transitions of the particle from the deep to the shallow well.

It is noteworthy that though potential energy fluctuations in the system concerned are induced here by the external force, such a Brownian motor still can be regarded as a flashing ratchet. This is due to the rotational nature of the motion, which makes the external-force potential energy a periodic angular function just as a hindered rotation potential. For rocking ratchets (characterized by a nonperiodic fluctuating external force), locking of the reverse flux also largely increases the Brownian motor efficiency and transport parameters [18,19].

In the next section, the temperature dependences of the imaginary part of the polarizability and the average flux will be described in detail for the most interesting case, namely, an asymmetric two-well potential. It should be borne in mind that a system with a selected direction can have such an asymmetry of the angle-dependent potential that clockwise and counterclockwise rotations are still equivalent. If so, the ratchet effects arise not from the potential asymmetry but due to a fluctuating external force periodic in the angular variable.

V. ASYMMETRIC TWO-WELL POTENTIAL

Due to the periodicity of the azimuthal potential with $n=2$, a particle can jump both clockwise and counterclockwise between the states $j=0$ and $j=1$. For the clockwise transition, representation (5) of rate constants assumes the following form:

$$\vec{w}_{0,1}(t) = v_1(t)u_0(t), \quad \vec{w}_{1,0}(t) = v_0(t)u_1(t), \tag{35}$$

and the corresponding quantities for counterclockwise motion appear as

$$\overleftarrow{w}_{0,1}(t) = v_0(t)u_0(t), \quad \overleftarrow{w}_{1,0}(t) = v_1(t)u_1(t). \tag{36}$$

The wells in the well function $u_j(t)$ and the barriers in the barrier function $v_j(t)$ are labeled by the index $j=0,1$ (just as for $n=3$ in Fig. 1). Such a system is equivalent to that with two states and two reaction activation barriers, i.e., to the simplest case of a catalytic wheel operating as a Brownian motor under nonequilibrium conditions [20]. If normalized by condition (1) with $n=2$, Eqs. (2) and (3) for the functions $\rho_j(t)$ are reduced to a single first-order differential equation, with its solution expressed explicitly for $j=0$ [5].

$$\rho_0(t) = s(t)[\rho_0(0) + \int_0^t dt'[v_0(t') + v_1(t')]u_1(t')s^{-1}(t')],$$

$$s(t) = \exp[-\int_0^t dt'[v_0(t') + v_1(t')][u_0(t') + u_1(t')]]. \tag{37}$$

To further calculate the polarizability and the average flux in a weak alternating electric field, one can expand solution (37) in terms of the field intensity or employ the perturbation theory of the Pauli equation developed in Sec. III. Introducing four quantities, $v_j^{(0)}$ and $u_j^{(0)}$ at $j=0,1$, as the parameters of the unperturbed two-well potential, we obtain the eigenvalues and eigenvectors of Eq. (17) as follows:

$$z_0 = 0, \quad z_1 = (v_0^{(0)} + v_1^{(0)})(u_0^{(0)} + u_1^{(0)}), \tag{38}$$

$$C_{jq} = \frac{1}{u_0^{(0)} + u_1^{(0)}} \begin{pmatrix} u_1^{(0)} & \sqrt{u_0^{(0)}u_1^{(0)}} \\ u_0^{(0)} & -\sqrt{u_0^{(0)}u_1^{(0)}} \end{pmatrix},$$

which involve the values of the equilibrium probabilities $\rho_0^{(0)}$ and $\rho_1^{(0)}$: $\rho_0^{(0)} = 1 - \rho_1^{(0)} = u_1^{(0)}/(u_0^{(0)} + u_1^{(0)})$. As a result, we arrive at the following expressions for the average flux, the nonzero components of the time-dependent average dipole moment, and the frequency-dependent polarizability:

$$\langle J \rangle_\tau = -\frac{v_0^{(0)}v_1^{(0)}}{v_0^{(0)} + v_1^{(0)}} \frac{u_0^{(0)}u_1^{(0)}}{u_0^{(0)} + u_1^{(0)}} \beta^2\mu^2E^2 \sin 2\varphi_E \frac{\omega^2}{\omega^2 + z_1^2},$$

$$\langle \mu_x(t) \rangle = \frac{u_1^{(0)} - u_0^{(0)}}{u_0^{(0)} + u_1^{(0)}}\mu + (v_0^{(0)} + v_1^{(0)}) \times \frac{4u_0^{(0)}u_1^{(0)}}{u_0^{(0)} + u_1^{(0)}} \beta\mu^2E \cos\varphi_E \frac{\cos(\omega t - \delta_2)}{\sqrt{\omega^2 + z_1^2}},$$

$$\tan\delta_2 = \frac{\omega}{z_1},$$

$$\chi_{xx}(\omega) = \beta\mu^2(v_0^{(0)} + v_1^{(0)}) \frac{4u_0^{(0)}u_1^{(0)}}{u_0^{(0)} + u_1^{(0)}} \frac{1}{-i\omega + z_1}. \tag{39}$$

To analyze the relations derived, we set that two barriers in the two-well potential have the same maxima, i.e., $v_0^{(0)} = v_1^{(0)} = w_0$, where w_0 is given by expression (24), and the asymmetry of the potential relief originates only from different well depths. If the difference of the potential well depths is designated by 2ξ, we have $z_1 = 4w_0 \cosh(\beta\xi)$ and the factor $4u_0^{(0)}u_1^{(0)}/(u_0^{(0)} + u_1^{(0)})$ provides $2\cosh^{-1}(\beta\xi)$. Let us measure the external field frequency in units of $4\nu_\varphi$ (i.e., $\tilde{\omega} = \omega/4\nu_\varphi$) and energies in temperature units ($T_\varphi \equiv \Delta U_\varphi/k_B, T_\xi \equiv \xi/k_B$). It is also expedient to introduce the dimensionless functions of temperature as follows:

$$F(T) = \frac{T_\varphi/T}{\cosh(T_\xi/T)} \frac{\tilde{\omega}\exp(-T_\varphi/T)}{\tilde{\omega}^2 + \exp(-2T_\varphi/T)\cosh^2(T_\xi/T)},$$

$$\Phi(T) = \frac{T_\varphi/T}{\cosh(T_\xi/T)} \frac{\exp(-T_\varphi/T)}{\sqrt{\tilde{\omega}^2 + \exp(-2T_\varphi/T)\cosh^2(T_\xi/T)}},$$

$$R(T) = \frac{(T_\varphi/T)^2}{\cosh(T_\xi/T)} \frac{\tilde{\omega}^2\exp(-T_\varphi/T)}{\tilde{\omega}^2 + \exp(-2T_\varphi/T)\cosh^2(T_\xi/T)}, \tag{40}$$

so as to express the sought-for quantities in the following form:

$$\mathrm{Im}\ \varepsilon = 4\pi C_V\ \mathrm{Im}\ \chi = 4\pi C_V \frac{\mu^2}{\Delta U_\varphi} F(T),$$

$$\langle \mu_x(t) \rangle = \mu\left[\tanh(\beta\xi) + \frac{\mu E\cos\varphi_E}{\Delta U_\varphi}\Phi(T)\cos[\omega t - \delta_2(T)]\right],$$

$$\Omega = 2\pi\langle J \rangle_\tau = -\nu_\varphi \frac{\pi\mu^2E^2\sin 2\varphi_E}{2\Delta U_\varphi^2} R(T). \tag{41}$$

It is assumed here that the imaginary part Im ε of the dielectric permittivity of a highly dispersed powder, with its particles containing rotators on the surface, is proportional to the imaginary part Im χ of the polarizability of an individual rotator and to the bulk concentration C_V of rotators. The experimentally measured dielectric loss tangent is equal to the ratio Im $\varepsilon(\omega)$/Re $\varepsilon(\omega)$ and is actually dictated by the value of Im ε, because $C_V\chi \ll 1$ and Re $\varepsilon(\omega) \sim 1$. Since realistic values of external electric field intensities are estimated as $\mu E/\Delta U_\varphi \ll 1$, the oscillation amplitude for the average dipole moment appears small relative to the dipole moment μ of an individual rotator. For the same reason, a rotator in the potential well has the average angular velocity Ω, which is also small as compared to its characteristic angular vibration frequency ν_φ and falls in the radio frequency range. Characteristic parameter values for a hydroxyl group on the oxide surface (a typical surface rotator) are as follows: $\Delta U_\varphi \sim 50$ meV ($T_\varphi \sim 600$ K), $\nu_\varphi = 100-200$ cm^{-1}, $\mu \sim 1D$, $C_V \sim 10^{20}$ cm^{-3} [1]. Then $\mu^2/\Delta U_\varphi \sim 10^{-23}$ cm^3 and Im $\varepsilon \sim 10^{-2}$ at such temperatures that $F(T) \sim 1$, i.e., surface rotators significantly contribute to the dielectric loss tangent. To rationalize temperature dependences (40), we put T_φ

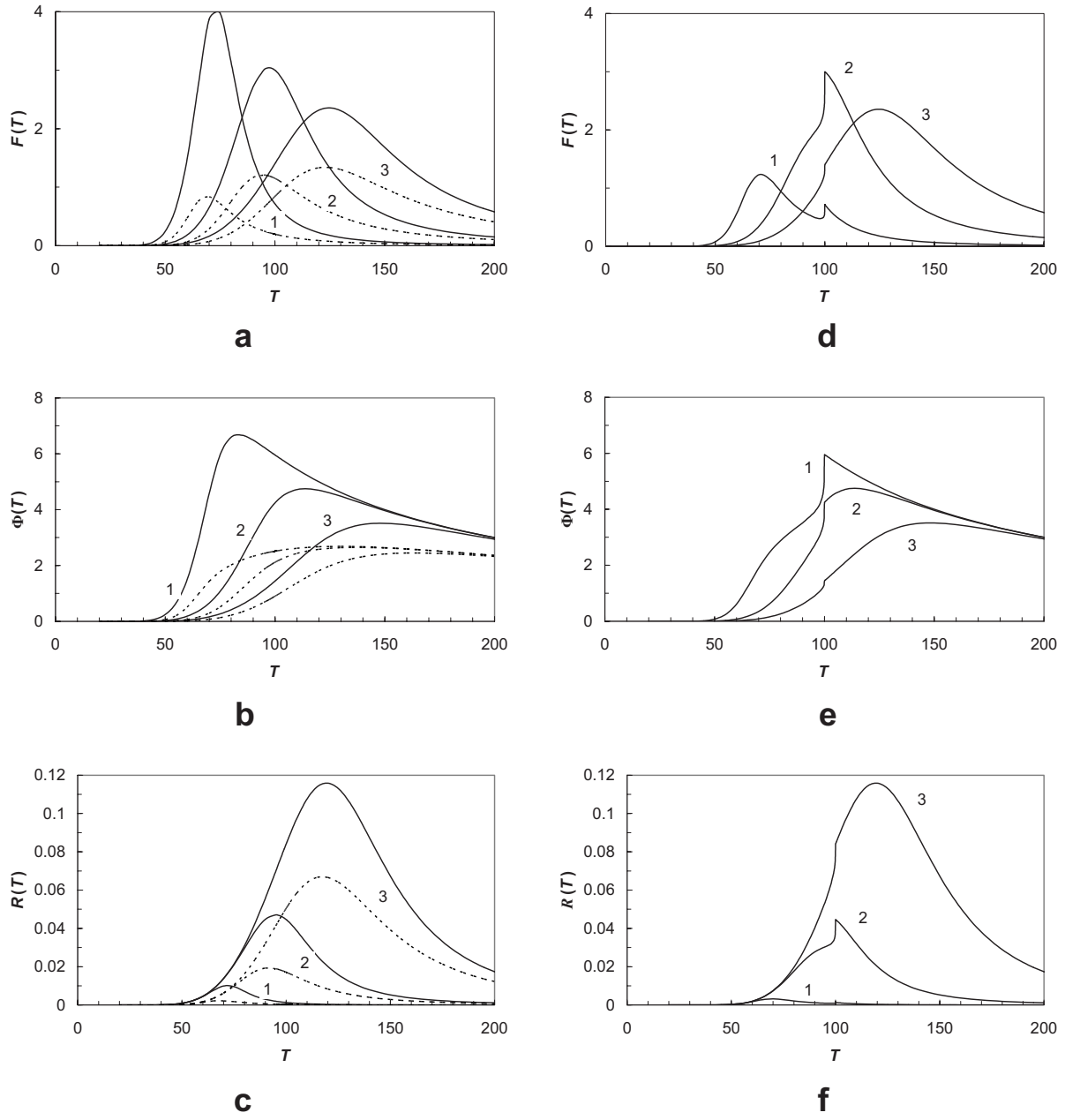

FIG. 3. The temperature dependences of the imaginary part of polarizability [(a),(d)], the oscillation amplitude for the average dipole moment [(b),(e)], and the average angular velocity [(c),(f)] expressed by relations (41) in terms of dimensionless reduced functions (40) with $T_\varphi \equiv \Delta U_\varphi / k_B = 600$ K. The temperature is measured in K. Curves 1, 2, and 3 correspond to the reduced frequencies of the alternating electric field, $\tilde{\omega} = \omega / 4\nu_\varphi = 0.0003, 0.0025, 0.01$. Solid and dashed lines in panels (a), (b), and (c) respectively represent the symmetric potential ($T_\xi = 0$) and that with the time-independent asymmetry ($T_\xi = 100$ K). The effect of the orientational phase transition on the above-mentioned system characteristics in the low-temperature region is shown in panels (d), (e), and (f) at $T_\xi(T) = T_0(1 - T/T_c)^{1/8}$, $T < T_c$ and $T_\xi(T) = 0$, $T > T_c$ with $T_0 = T_c = 100$ K.

$= 600$ K and consider two cases, a symmetric potential with $T_\xi = 0$ and an asymmetric one with $T_\xi = 100$ K as the characteristic temperature of asymmetry initiation. Well-defined stochastic resonance observed in the former case manifests itself by maxima arising at such temperatures that the average frequency z_1 of interwell transitions is much the same as the frequency ω of the alternating external electric field [see the solid lines in Figs. 3(a)–3(c)]. At low temperatures, the response to the external field is weak due to the small probability for a particle to surmount potential barriers through thermal activation. In the high-temperature region, this response decays with increasing temperature; so, the quantities concerned exhibit nonmonotonic temperature dependences with the maximum at $z_1 \sim \omega$.

Stochastic resonance appears most conspicuously for the dielectric loss tangent and the average rotation velocity. The oscillation amplitude for the average dipole moment is characterized by broader bands and slowly decays at high temperatures. The temperature dependence of the phase shift between the external (input) and the response (output) signals

behaves monotonically decreasing from $\pi/2$ to zero as the temperature rises. Stochastic resonance occurs at about $\delta_2 = \pi/4$. Figure 3 presents a family of functions (14) for three values of the frequency ω (curves 1–3), the middle one corresponding to stochastic resonance at $T=100$ K. The smaller the frequency ω, the higher the curve maxima for the dielectric loss tangent and the oscillation amplitude for the average dipole moment. At the same time, the temperature-dependent average angular velocity shows lower maxima for small frequencies since this parameter is quadratic in ω.

The asymmetry of the potential leads functions (40) to decrease in the low-temperature region [see the dashed lines in Figs. 3(a)–3(c)]. As a result of the asymmetry-induced suppression, the oscillation amplitude for the average dipole moment undergoes no stochastic resonance at all. The temperature-independent asymmetry of the potential relief can arise from perturbation of the hindered rotation potential by its local environment, e.g., by structural surface defects or by adsorption of some other molecules (if their desorption temperature is over the range of stochastic resonance). Thus, the quantities concerned prove sensitive to environmental effects and can, therefore, provide significant information about them.

Another interesting case of the temperature-dependent asymmetry of the potential refers to two-dimensional rotator systems which undergo orientational phase transitions due to dipole-dipole interactions between rotators. These interactions give rise to the collective effects which govern the dynamics of such systems. At the same time, one can consider, as a zero-order approximation, the static limit in which interparticle interactions cause only the average local field ξ acting on each individual rotator and thus deepening one of the potential wells. The field intensity ξ is proportional to the constant component of the average dipole moment, which is itself expressible in terms of ξ [see the first term in formula (41) for $\langle \mu_x(t) \rangle$]. This self-consistent model underlies the known average-field approximation, which qualitatively accounts for the thermodynamic characteristics of the phase transition. Quantitative description is offered by numerical methods, while analytical treatment is possible only in very rare cases of exactly soluble models. For instance, the two-dimensional Ising model provides the following temperature dependence of the order parameter and, hence, of the average field: $T_\xi(T)=T_0(1-T/T_c)^{1/8}$ at $T<T_c$ and $T_\xi(T)=0$ at $T>T_c$ [21] (this function with $T_0=T_c=100$ K is used in Figs. 3(d)–3(f) to illustrate the effect of the orientational phase transition on the low-temperature characteristics of a surface rotator system). As the potential becomes asymmetric only at $T<100$ K, solid curves shown in Fig. 3 in panels (a)–(c) and (d)–(f) respectively coincide in the temperature range $T>100$ K. Solid curves in panels (d)–(f) differ from the dashed lines in panels (a)–(c) in that the quantity T_ξ is itself temperature dependent. Curves 1, 2, and 3 plotted for varied $\tilde{\omega}$ contain a singular point at the phase transition temperature $T_c=100$ K, where the first derivative is infinite. On going from the symmetric case to that with temperature-dependent T_ξ, curves 1 change most of all, since stochastic resonance for them falls in the region of ordered average dipole moments, $T<100$ K. As an example, curve 1 in Fig. 3(d) has two peaks, the left one corresponding to stochastic resonance and the right one to the orientational phase transition. Hence, phase transition characteristics can be judged by the temperature dependences of the quantities under study.

VI. CONCLUSIONS

A Brownian particle, if placed into a periodic n-well potential with barrier energies larger than k_BT, executes thermally activated random jumps between the minima of neighboring potential wells. Motion of this kind is typical of adsorbed polar molecules in the hindered rotation potential, with the relief shaped by the local molecular environment. An external alternating electric field applied to the system gives rise to a dielectric response, which is detectable experimentally and provides significant information about the hindered rotators as well as their local environment.

Starting from the perturbation theory of the Pauli equation with respect to the weak field intensity, we have derived explicit analytical expressions for the time dependence of the average dipole moment, as well as the frequency dependences of polarizability and the average angular velocity, the three quantities exhibiting conspicuous stochastic resonance. As shown, unidirectional rotation is possible only if the external alternating field simultaneously modulates minima and maxima of the potential. For a symmetric potential of hindered rotation, the average angular velocity (treated by the second-order perturbation theory with respect to the field intensity) does not vanish only at $n=2$, i.e., when two azimuthal wells specify a selected axis in the system.

Special attention is paid to a two-well asymmetric potential, with the asymmetry induced by local fields which arise from environmental inhomogeneities or from orientational ordering in the low-temperature region. As a result of the ordering, the dielectric loss spectrum exhibits specific features, namely, some additional peaks in the low-temperature region and a singular point with an infinite first derivative at the phase transition temperature.

Unidirectional angular motion of a dipole rotator in a two-well hindered rotation potential occurring under the action of a linearly polarized alternating electric field is caused by the same mechanism as translational motion in Brownian motors with potentials fluctuating by half a period. Motors of this kind are therefore illustrated well by the dipole rotator model developed here.

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