Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Colloid and Interface Science 281 (2005) 236–239
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

An oscillating electric field with thermal noise increases the rotational diffusion and drives rotation in a dipole

José A. Fornés *

Instituto de Física, Universidade Federal de Goiás, C.P. 131, 74001-970 Goiânia, GO, Brazil

Received 6 April 2004; accepted 10 August 2004
Available online 12 October 2004

Abstract

Here we consider a dipole in a viscous medium under the influence of an oscillating electric field and thermal noise. Because of the very low Reynolds numbers involved in molecular processes, we considered overdamped Langevin dynamics. As a consequence the inertia term becomes negligible. We observed a great increase in the rotational diffusion and also net rotation for some values of the parameters.

1. Introduction

In recent years, with the advance of nanotechnology, new techniques have evolved to visualize single molecules, such as scanning tunneling [1] and atomic force microscopies [2]. Grimzewski et al. [3] observed rotation of a single molecule within a supramolecular bearing. After the first examples of unidirectional rotating molecular motors based on simple organic molecules [4,5], several works reported on this subject [6–14]. Also great theoretical efforts have been devoted to understanding and proposing nanoscale rotors and stators as molecular motors capable of transforming a driven random rotation efficiently into a directed translational motion [15–17]. A biological example of a molecular motor consisting of a rotor and stator is the rotatory motor of the bacterial flagellum which is driven by a transmembrane electrochemical gradient of protons [18]; another is ATP synthase, which has been very well studied [19–21]. Most of these motors are called Brownian motors. For an excellent review on this subject see Ref. [22] and references in it.

Although Brownian motors are known to permit thermally activated motion in one direction only, the concept of channelling random thermal energy into controlled motion has not yet been very extended to the molecular level and the basic principles are not very well understood. Experiments suggest that dynamics is inescapable and may play a decisive role in the evolution of nanotechnology [23].

In a recent paper [17], it was shown that colloidal suspension of ferromagnetic nanoparticles, so-called ferrofluids, are ideal systems to test theoretical predictions on fluctuation driven transport experimentally.

Here we consider one of the simplest rotors in nature: a dipole in a viscous medium under the influence of an oscillating electric field and thermal noise. By applying the Langevin equation we observe rotation for some values of the parameters.

2. Langevin equation for the rotor

The energy of a dipole in an electric field (Fig. 1) is given by

$$W_{\text{dipole}} = -\vec{p}\vec{E}(t) = -pE(t)\cos\theta, \tag{1}$$

where $|\vec{p}| = qd$, q being the positive charge of the dipole and d the distance between both charges; the vector $\vec{p}$ goes from the negative to the positive charge. In our case the field varies as $E(t) = E_0 \sin(\omega_{\text{E}} t)$, with $\tau_{\text{E}} = 2\pi\omega_{\text{E}}^{-1}$. Then

$$W_{\text{dipole}} = -pE_0 \sin(\omega_{\text{E}} t)\cos\theta. \tag{2}$$

* Fax: +55-62-214-1165.
E-mail address: fornes@fis.ufg.br.

0021-9797/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2004.08.088

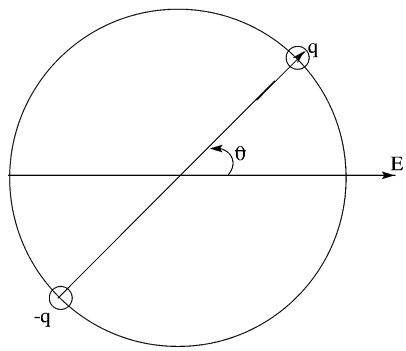

Fig. 1. Schematic of the system.

The corresponding torque on the dipole is

$$\Gamma_{\text{dipole}}(\theta, t) = -\partial_\theta W_{\text{dipole}} = -pE(t)\sin\theta \tag{3}$$

or

$$\Gamma_{\text{dipole}}(\theta, t) = -pE_0 \sin(\omega_{\text{E}} t)\sin\theta. \tag{4}$$

Then the corresponding Langevin equation for the system is

$$I\frac{d^2\theta}{dt^2} = \Gamma_{\text{dipole}}(\theta, t) - f_{\text{rot}}\frac{d\theta}{dt} + \Gamma_{\text{B}}. \tag{5}$$

As we are in the regime of null inertia ($I = 0$), we have

$$f_{\text{rot}}\frac{d\theta}{dt} = \Gamma_{\text{dipole}}(\theta, t) + \Gamma_{\text{B}}, \tag{6}$$

where f_{rot} (J s) is the rotational frictional coefficient and is related to the diffusion rotational constant, D_{rot} (s^{-1}) by the Einstein relation

$$D_{\text{rot}} = \frac{k_{\text{B}}T}{f_{\text{rot}}}, \tag{7}$$

where k_{B} is Boltzmann's constant and Γ_{B} is the Brownian torque, given by

$$\Gamma_{\text{B}} = (2f_{\text{rot}}k_{\text{B}}T)^{1/2}\xi(t), \tag{8}$$

where $\xi(t)$ is the thermal noise, defined by its statistical properties, namely,

$$\langle\xi(t)\rangle = 0, \tag{9}$$

$$\langle\xi(t_2)\xi(t_1)\rangle = \delta(t_2 - t_1); \tag{10}$$

i.e., the correlation time of the noise is zero.

The corresponding discretization of Eq. (6) is performed by multiplying both members by dt, dividing by f_{rot}, and performing the integration in the interval $(t, t + \Delta t)$, namely,

$$\Delta\theta = \frac{1}{f_{\text{rot}}}\int_t^{t+\Delta t}\Gamma_{\text{dipole}}(\theta, t)\,dt + (2D_{\text{rot}})^{1/2}\int_t^{t+\Delta t}\xi(t)\,dt \tag{11}$$

or

$$\Delta\theta = \frac{1}{f_{\text{rot}}}\overline{\Gamma_{\text{dipole}}(\theta, t)}\Delta t + (2D_{\text{rot}})^{1/2}\Delta W(t), \tag{12}$$

where $\overline{\Gamma_{\text{dipole}}(\theta, t)}$ is the mean value of $\Gamma_{\text{dipole}}(\theta, t)$ in the considered interval, and for the last term, we use the definition of the Wiener's process [24]. At the limit $\Delta t \to dt$ the mean value $\overline{\Gamma_{\text{dipole}}(\theta, t)} \simeq \Gamma_{\text{dipole}}(\theta, t)$, and $\Delta W(t) = dW(t)$. We recall that "Wiener's increment" $dW(t)$ is a Gaussian stochastic process, of width $\sigma = (dt)^{1/2}$. Then, at each pass of the integration we have to draw $dW(t)$ and normalize the result properly. Let us call R_{G} an aleatory number, with Gaussian distribution, centered in $R_{\text{G}} = 0$ and width 1. In MATLAB/OCTAVE $R_{\text{G}} = \text{rand}\,n$; consequently we can write $dW(t) = (dt)^{1/2}R_{\text{G}}$. Finally, Eq. (12) is transformed into the corresponding Euler's equation of this process, namely,

$$\theta_{j+1} = \theta_j + \Gamma_{\text{dipole}}(\theta_j)\frac{dt}{f_{\text{rot}}} + (2D_{\text{rot}}\,dt)^{1/2}R_{\text{G}}. \tag{13}$$

The corresponding relaxation time τ_{B} will be

$$\tau_{\text{B}} = \frac{1}{2D_{\text{rot}}}. \tag{14}$$

A first basic quantity of interest is the average angular velocity in the long-time limit, i.e., after transients due to initial conditions have died out, namely,

$$\langle\omega_\infty\rangle = \langle\dot{\theta}\rangle_\infty \equiv \lim_{t\to\infty}\frac{\langle\theta(t)\rangle}{t}. \tag{15}$$

Another quantity of central interest will be the effective diffusion coefficient,

$$D_{\text{eff}} \equiv \lim_{t\to\infty}\frac{\langle\theta^2(t)\rangle - \langle\theta(t)\rangle^2}{2t} = \lim_{t\to\infty}\frac{\sigma^2}{2t}. \tag{16}$$

The means are over the realizations of the stochastic process.

3. Computation

The codes were written in OCTAVE and were run under Linux. The increment in time, dt, was fixed in $10^{-1}\tau_{\text{B}}$. We considered the case $\tau_{\text{E}} > \tau_{\text{B}}$ with $t_{\max} = 10^3\tau_{\text{B}}$. The partition for each iteration was 10^4 points, which were considered 10^3 realizations of the stochastic process. The simulations were performed at room temperature. We divide the integration interval $[0, t_{\max}]$ in n intervals of size dt, creating a "vector" $t = (t_1, t_1, \ldots, t_1, \ldots, t_1) = (0, dt, 2dt, \ldots, t_{\max})$. For procedure efficiency, we draw once all the "Wiener increments," creating a vector dW. In MATLAB/OCTAVE we write

$$dW = \text{sqrt}(dt) \times \text{rand}\,n(1, n).$$

4. Results and discussion

From Fig. 2 we can observe local symmetry breaking of the dipole energy caused by the temporal modulation of the electric field and the drag term. We also observe the sensitivity of the curve shape to variations of the field frequency.

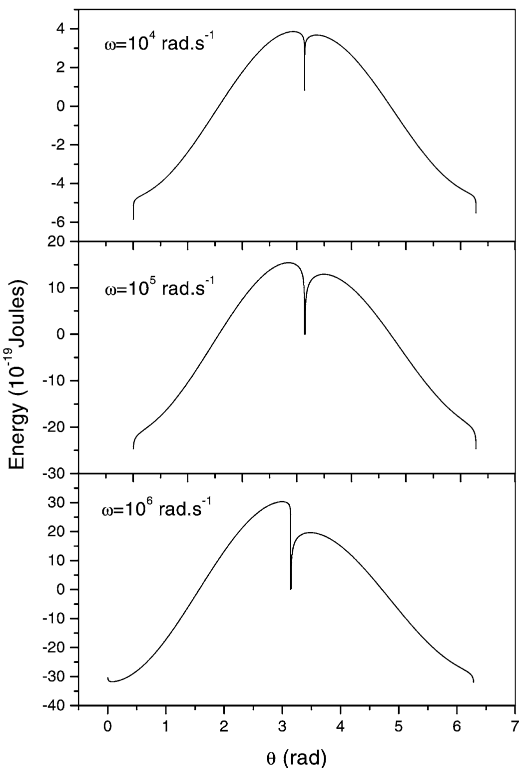

Fig. 2. Plot of the dipole energy, Eq. (2), using the solution of Eq. (6) with $\Gamma_B = 0$.

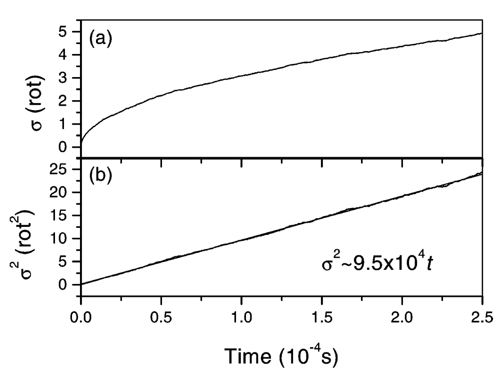

Fig. 3. $E = 0.0$, (a) statistical angular dispersion $\sigma(t)$, (b) $\sigma(t)^2$, $D_{eff} = D_{rot} = 2.0 \times 10^6\ rad^2\,s^{-1}$.

The input of energy from the field, the symmetry breaking, and the thermal noise are the necessary requirements to produce a directed rotation (movement) [25].

In Fig. 3, we observe the behavior of the system for $E = 0$. By the shapes of $\sigma(t)$ and $\sigma^2(t)$ we can observe a pure diffusive process as expected.

In Fig. 4a, we can observe an angular velocity in the long-time limit, $\omega_\infty \simeq 5.6 \times 10^4\ rot\,s^{-1}$ which is approximately 14 times the frequency of the electric field ($\omega_E \simeq 4.0 \times 10^3\ rot\,s^{-1}$).

Fig. 4b shows the rotor path expressed in number of rotations, showing a slow increase in the number of rotations with a small range of stabilization at the center.

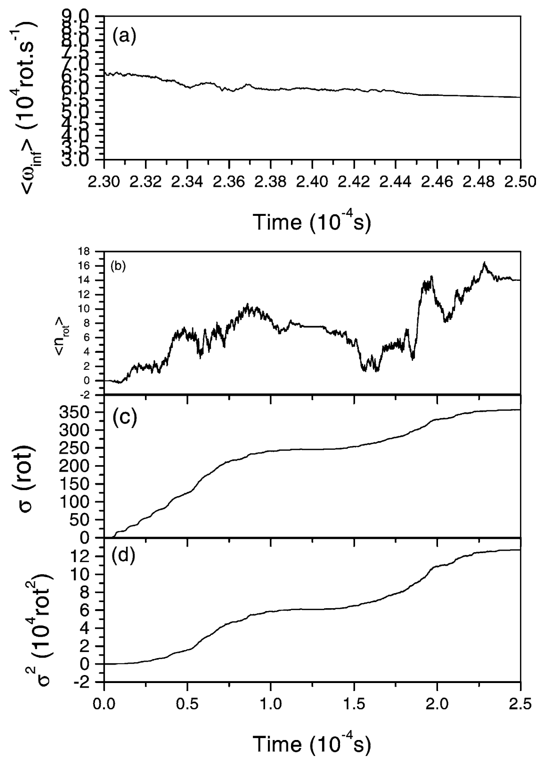

Fig. 4. $\omega_E = 2.51 \times 10^4\ rad\,s^{-1}$, $\tau_E = 2.5 \times 10^{-4}$ s, $\tau_B = 2.5 \times 10^{-7}$ s, $E_0 = 4 \times 10^9\ V\,m^{-1}$, $p = 5e_0$ nm = 240 debye, $D_{rot} = 2 \times 10^6\ rad^2\,s^{-1}$, $D_{eff} = 1.0 \times 10^{10}\ rad^2\,s^{-1}$, $\Gamma_E^{max} = 3.2 \times 10^3$ pN nm, $\Gamma_B^{max} = 4.14 \times 10^{-3}$ pN nm. (a) Average angular velocity in the long-time limit (Eq. (15)). (b) Average number of rotations. (c) $\sigma(t)$. (d) $\sigma(t)^2$.

In Figs. 4c and 4d are represented $\sigma(t)$ and $\sigma^2(t)$, respectively. We can observe in both two consecutive sigmoid-type curves with small modulations. This effect is different from the anomalous rotational diffusion [26] in which $\sigma(t) \approx t^\alpha$.

In Fig. 5a, we can observe an angular velocity in the long-time limit, $\omega_\infty \simeq 3.6 \times 10^4\ rot\,s^{-1}$, which is approximately 0.6 time the frequency of the electric field ($\omega_E \simeq 6.4 \times 10^4\ rot\,s^{-1}$).

Fig. 5b shows an inversion of the rotation compared with Fig. 4b. We observe a negative increase in the rotations till 7.8×10^{-5} s, followed by a rather stable plateau around −12.5 rotations.

Figs. 5c and 5d show $\sigma(t)$ and $\sigma^2(t)$, respectively. We can observe a typical diffusive process with slow modulations caused by the electric field.

The conclusions of the results are the following:

(1) The oscillating field in the presence of thermal noise drives net rotation in a dipole. The efficiency of the rotations depends on various parameters: ω_E, E_0, τ_B, p, D_{rot}.
(2) The net rotation is quite sensitive to the field frequency. Observe the inversion of the rotation when the frequency goes from 2.5×10^4 to $4.0 \times 10^5\ rad\,s^{-1}$.
(3) The main effect of the field is a great increase in the rotational diffusion: compare D_{eff} of Figs. 4 and 5 with

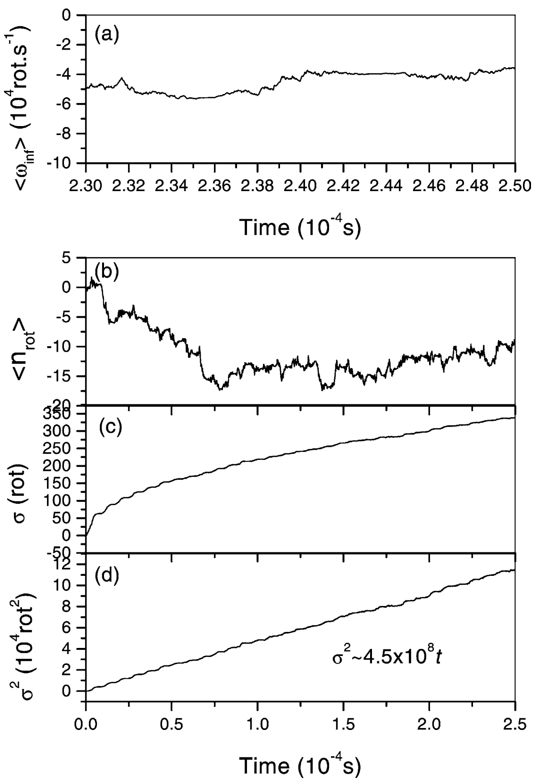

Fig. 5. $\omega_E = 4.0 \times 10^5\ \mathrm{rad\,s^{-1}}$, $\tau_E = 1.57 \times 10^{-5}$ s, $D_{\mathrm{eff}} = 9.04 \times 10^9\ \mathrm{rad^2\,s^{-1}}$. The rest of the parameters: same as in Fig. 4. (a), (b), (c), (d) same as in Fig. 4.

Fig. 3 ($D_{\mathrm{eff}}(E = 0) = 2.0 \times 10^6$ and $D_{\mathrm{eff}}(E \neq 0) = 10^{10}$).

(4) The oscillating field modulates the rotational diffusion.

We know through the literature that a great insight into the properties of macromolecules can be obtained by studying the relaxation of an oriented system to a state of random orientation when the field is suddenly turned off. Here we are concerned with the nonequilibrium process of the rotational diffusion. The rotational diffusion coefficient, similarly to the translational diffusion coefficient, will depend on the size and shape of the macromolecule. We believe that this small contribution will help in better understand new processes emerging in this area, for instance, the great increase in the rotational diffusion by an oscillating field in a dipolar macromolecule in a viscous medium. To test this effect we suggest measuring by fluorescence spectroscopy the rotational diffusion coefficient of a dipolar dye inserted in a biological membrane under the influence of the electric field produced by oscillating electric charges on the membrane surface. We also suggest performing a deep study relating the shape of the dipole profile energy (ω_E) and rotation of the dipole.

Acknowledgment

This work was partially supported by the Conselho Nacional de Desenvolvimento Cinetífico e Tecnológico (CNPq-Brazil).

References

[1] G. Binning, C.F. Quate, C. Gerber, Phys. Rev. Lett. 56 (1986) 930.
[2] G. Binning, H. Rohrer, Rev. Mod. Phys. 59 (1987) 615.
[3] J.K. Gimzewski, C. Joachim, R.R. Schlittler, V. Langlais, H. Tang, I. Johannsen, Science 281 (1998) 531.
[4] T.R. Kelly, H. De Silva, R.A. Silva, Nature 401 (1999) 150.
[5] N. Koumura, R.W.J. Zijistra, R.A. Van Delden, N. Harada, B.L. Feringa, Nature 401 (1999) 152.
[6] B.L. Feringa, N. Koumura, R.A. Van Delden, M.K.J. Ter Wiel, Appl. Phys. A 75 (2002) 301.
[7] P. Palffy-Muhoray, T. Kosa, E. Weinan, Appl. Phys. A 75 (2002) 293.
[8] R.A. Van Delden, N. Koumura, A.A. Schoevaars, A. Meetsma, B.L. Feringa, Org. Biomol. Chem. 1 (2003) 33.
[9] P. Galajda, P. Ormos, Appl. Phys. Lett. 78 (2001) 249.
[10] P. Galajda, P. Ormos, Appl. Phys. Lett. 80 (2002) 4653.
[11] J.P. Sestelo, T.R. Kelly, Appl. Phys. A 75 (2002) 337.
[12] J. Vacek, J. Michl, Proc. Natl. Acad. Sci. USA 98 (2001) 5481.
[13] D. Horinek, J. Michl, J. Am. Chem. Soc. 125 (2003) 11900.
[14] D.A. Leigh, J.K.Y. Wong, F. Dehez, F. Zerbetto, Nature 424 (2003) 174.
[15] A.V. Zolotaryuk, P.L. Christiansen, B. Nordén, A.V. Savin, Y. Zolotaryuk, Phys. Rev. E 61 (2000) 3256.
[16] M. Porto, Phys. Rev. E 63 (2001) 030102(R).
[17] A. Engel, H.W. Müller, P. Reiman, A. Jung, Phys. Rev. Lett. 91 (2003) 060602.
[18] B. Kleutsch, P. Läuger, Biophys. J. 18 (1990) 175.
[19] T. Elston, H. Wang, G. Oster, Nature 391 (1998) 510.
[20] G. Oster, H. Wang, M. Grabe, Phil. Trans. R. Soc. Lond. B 355 (2000) 523.
[21] C. Bustamante, D. Keller, G. Oster, Acc. Chem. Res. 34 (2001) 412.
[22] P. Reimann, Phys. Reports 361 (2002) 57–265.
[23] J.K. Gimzewski, C. Joachim, Science 283 (1999) 1683.
[24] C.W. Gardiner, Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences, Springer-Verlag, Berlin, 1985.
[25] P. Reimann, P. Hängii, Appl. Phys. A 75 (2002) 169–178.
[26] R. Metzler, J. Klafter, Phys. Reports 339 (2000) 1–77.