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Brownian motion of an asymmetrical particle in a potential field

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It is well known that a free ellipsoidal Brownian particle exhibits anisotropic diffusion for short times which changes to isotropic at long times, and, that the long-time diffusion coefficient is an average of the translational diffusion coefficients along the different semiaxes of the particle. We show analytically that in the presence of external forces, the long-time diffusion coefficient is different from that of a free particle. The magnitude of the difference in the two diffusion coefficients is found to increase proportionately with the particle's asymmetry, being zero only for a perfectly spherical Brownian particle. It is also found that, for asymmetrical particles, the application of external forces can amplify the non-Gaussian character of the spatial probability distributions which consequently delays the transition to the classical behavior. We illustrate these phenomena by considering the quasi-two-dimensional Brownian motion of an ellipsoidal rigid particle in linear and harmonic potential fields. These two examples provide insight into the role played by particle asymmetry in electrophoresis and microconfinement due to a laser trap or due to intracellular macromolecular crowding. © *2007 American Institute of Physics*.
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I. INTRODUCTION

Studies of anisotropic particles have a long history because of the fundamental relationship between shape and experimentally measurable properties. There is renewed interest in this problem because of the strong dependence of the mechanical and electrical properties of nanosized objects with their shape. At the same time, shape is frequently connected with biological function, for example, the reactive specificity of an enzyme due to its particular conformation. One of the main experimentally measurable properties of molecules and aggregates are their translational diffusion coefficients and it is in this context that we discuss the consequences of asymmetrical shape in this work.

The theory of Brownian motion (for a recent commentary, see Ref. 1) is well developed for free spherical particles.[2–4] Free ellipsoidal or cylindrical particles, which constitute a first-order approximation to a wide variety of asymmetrical molecules, have also been studied.[5–7] The analysis of the Brownian motion of asymmetrical particles is considerably more complicated compared to the spherical case due to the coupling of rotational and translational motion. In particular, the dependence of the instantaneous translational diffusion coefficient on the current orientation of the particle leads to anisotropic motion for short times. This introduces substantial complications in both the Langevin[5,7] and the Fokker-Planck[6] descriptions of the problem.

These complications are frequently circumvented by assuming that anisotropic diffusion lasts only for very short times and that isotropic diffusion is recovered for all reasonable times, in which case one can simply use the mathematical formalism valid for a spherical Brownian particle. The transition in dynamical behavior with time is due to the fact that rotational diffusion eventually washes out the initial anisotropic translational motion of the particle. The long-time translational diffusion coefficient is equal to the average of the translational diffusion coefficients along the three semiaxes of the ellipsoidal or cylindrical particle. For example, the long-time diffusion coefficients along the axes of prolate or oblate ellipsoids in three dimensions have been given by Perrin.[8,9]

Although the crossover in behavior typically occurs quickly in three dimensions, it has recently been experimentally shown[5] that, for a free ellipsoidal particle of micrometer dimensions constrained to move in a quasi-two-dimensional (2D) environment, the transition from anisotropic to isotropic diffusion occurs over a period of a few seconds. This suggests that the proper description of diffusion-based processes in low-dimensional environments, such as those in membranes, cannot be based on the classical theory of isotropic diffusion.

All the results mentioned thus far are for free asymmetrical particles. However, in most situations of interest, one is dealing with reaction-diffusion processes in which molecules both diffuse and interact with each other via potential fields. Unlike spherical particles, there has been little work on ellipsoidal particles with the exception of the theory of rotational Brownian motion of asymmetric particles in an external potential (for a concise treatment, see Chapter 7.6 in Ref. 10) and of a few molecular dynamics simulations of prolate ellipsoids and rods interacting with mobile or static spherical

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molecules.[11–14] In this article, we seek to understand how the intrinsic asymmetry of molecules or aggregates affects the statistical properties of their translational motion in a potential field. These effects are nonintuitive due to the coupling of translational to rotational diffusion via the modulation of the strength of translational noise (dissipative coupling). We find two main results: (i) anisotropic diffusion may be enhanced and the crossover time to isotropic diffusion lengthened as a result of the application of external forces (ii) for long times, when isotropic diffusion sets in, the translational diffusion coefficient of an ellipsoidal particle is different from that in the absence of external forces. The magnitude of these differences is proportional to particle asymmetry, being zero for a spherical particle. This may have important implications for the Brownian dynamics simulation of asymmetrical rigid particles in external fields.

The paper is organized as follows. In Sec. II, we review the derivation of the Langevin equations for an ellipsoidal rigid walker in the presence of a potential field in two dimensions. We exemplify the theory in two dimensions where analytical results can be obtained without loss of generality. It is here shown how the dissipative coupling of translational to rotational motion leads to physics different from that of the classical case of a spherical Brownian walker. In Sec. III, we use the Langevin equations of the previous section to derive expressions for the temporal dependence of the translational diffusion coefficients of an ellipsoidal Brownian particle in a linear potential, which, unlike the classical case of a spherical particle, is nontrivial. These results have applications to the understanding of the effects of molecular asymmetry on band broadening in electrophoretic experiments and to the extraction of data from experiments involving fluorescence correlation spectroscopy (FCS). In Sec. IV, we extract the long-time translational diffusion coefficients of an ellipsoidal particle in a potential field possessing curvature. This has direct application to understanding the Brownian motion of asymmetrical molecules in narrow nonphysical channels such as those provided by optical traps. We conclude in Sec. V.

II. THE LANGEVIN EQUATIONS FOR AN ELLIPSOIDAL BROWNIAN WALKER

In this section we review the derivation of the equations of motion for the two-dimensional Brownian motion of an ellipsoidal rigid body which is acted upon by external force fields. We restrict our analysis to two dimensions. The particle's anisotropy leads to a nontrivial coupling between its rotational and translational motion which substantially complicates the analysis of its motion in lab-frame coordinates. For this reason we shall initially construct the analytical description in terms of body-centered coordinates where there is no such coupling. This description is then translated into that of the frame of reference of experimental measurement (lab-frame coordinates) by means of a straightforward rotation of coordinates.

At time t the particle's displacement $R(t)$ can be described by that of its center of mass in the lab frame, $[\delta x(t), \delta y(t)]$, which also corresponds to the coordinates

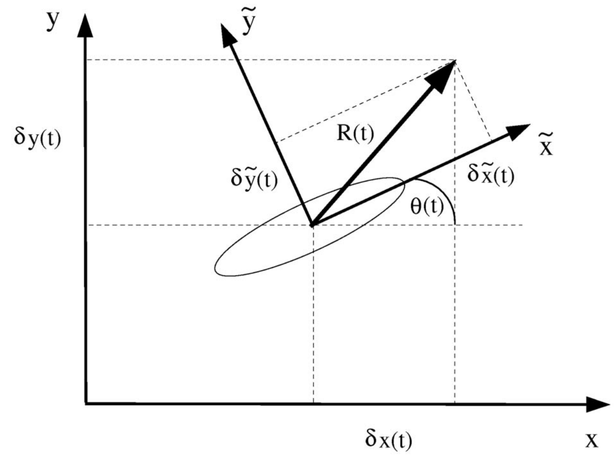

FIG. 1. Schematic diagram illustrating the setup forming the basis of our calculations. The axes $\tilde{x}$ and $\tilde{y}$ are body-fixed coordinates where $\tilde{x}$ denotes the largest semiaxis of the ellipsoid. The axes x and y are the lab-frame coordinates, with respect to which we derive the diffusion coefficients of the ellipsoid in the presence of external forces.

$[\delta\tilde{x}(t), \delta\tilde{y}(t)]$ in the body frame. The angle $\theta(t)$ is that between the $\tilde{x}$ axis of the body frame (which corresponds by definition to the ellipsoid's longest axis) and the x axis of the lab frame. Rotational and translational motion in the body frame are always decoupled and thus it immediately follows from Fig. 1 that the Langevin equations of motion in this frame are

$$\Gamma_1^{-1}\frac{\partial\tilde{x}(t)}{\partial t} = F_x \cos\theta(t) + F_y \sin\theta(t) + \tilde{\eta}_1(t), \tag{1}$$

$$\Gamma_2^{-1}\frac{\partial\tilde{y}(t)}{\partial t} = F_y \cos\theta(t) - F_x \sin\theta(t) + \tilde{\eta}_2(t), \tag{2}$$

$$\Gamma_3^{-1}\frac{\partial\theta(t)}{\partial t} = \tau + \tilde{\eta}_3(t). \tag{3}$$

The constants Γ_1 and Γ_2 are the mobilities, that is, the inverse of the friction coefficients of the ellipsoidal body along its long and short axis, respectively. The body also has associated with it a single rotational mobility Γ_3. The force field has components F_x and F_y along the x and y directions of the lab frame. τ is the torque acting on the body due to its orientation relative to the direction of the potential field. Since in the body frame the translational and rotational movements are decoupled, the noise $\tilde{\eta}_i(t)$ has mean zero and a correlator given by

$$\langle \tilde{\eta}_i(t)\tilde{\eta}_j(t')\rangle = \frac{2k_BT}{\Gamma_i}\delta_{i,j}\delta(t-t'), \tag{4}$$

where k_B is the Boltzmann constant and T is the temperature. Consequently, the diffusion coefficients of the particle in directions parallel and perpendicular to its longest axis are $D_1 = k_bT\Gamma_1$ and $D_2 = k_bT\Gamma_2$, respectively, while the rotational diffusion coefficient is $D_\theta = k_bT\Gamma_3$.

We can now write down the equations in the lab frame. Since the body frame at time t is simply the lab frame rotated by an angle $\theta(t)$ about the out-of-page z axis, the displacements in the two frames are related by the equations

$$\delta x = \cos\theta\delta\tilde{x} - \sin\theta\delta\tilde{y}, \tag{5}$$

$$\delta y = \sin\theta\delta\tilde{x} + \cos\theta\delta\tilde{y}. \tag{6}$$

Dividing the above equations by δt, taking the limit $\delta t \to 0$, and substituting the linear and angular velocities in the body frame from Eqs. (1)–(3), we get the final equations describing Brownian motion in the lab frame as follows:

$$\frac{\partial x(t)}{\partial t} = F_x\left(\bar{\Gamma} + \frac{1}{2}\Delta\Gamma\cos 2\theta(t)\right) + \frac{1}{2}\Delta\Gamma F_y\sin 2\theta(t) + \eta_1(t), \tag{7}$$

$$\frac{\partial y(t)}{\partial t} = F_y\left(\bar{\Gamma} - \frac{1}{2}\Delta\Gamma\cos 2\theta(t)\right) + \frac{1}{2}\Delta\Gamma F_x\sin 2\theta(t) + \eta_2(t), \tag{8}$$

$$\frac{\partial\theta(t)}{\partial t} = \Gamma_3\tau + \eta_3(t). \tag{9}$$

The quantities $\bar{\Gamma} = \frac{1}{2}(\Gamma_1 + \Gamma_2)$ and $\Delta\Gamma = \Gamma_1 - \Gamma_2$ are the average and difference mobilities of the body, respectively. The noise $\eta_i(t)$ has mean zero and a correlator given by

$$\langle\eta_3(t)\eta_3(t')\rangle^{\eta_3} = 2D_\theta\delta(t-t'), \tag{10}$$

$$\langle\eta_i(t)\eta_j(t')\rangle^{\eta_1,\eta_2}_{\theta(t)} = 2k_BT\Gamma_{ij}(t)\delta(t-t'), \quad i,j=(1,2), \tag{11}$$

where

$$\Gamma_{ij}(t) = \bar{\Gamma}\delta_{ij} + \tfrac{1}{2}\Delta\Gamma\begin{pmatrix}\cos 2\theta(t) & \sin 2\theta(t)\\ \sin 2\theta(t) & -\cos 2\theta(t)\end{pmatrix}.$$

The statistical averages have superscripts to indicate over which noise is the average taken and subscripts to denote quantities which are kept fixed. This convention is used throughout the paper. Note also that movement in the x and y directions are not independent from each other but rather are coupled through the angular position of the particle. This effectively couples the particle's translational diffusion to its rotational diffusion and the strength of this coupling behavior increases proportionally with particle shape asymmetry, being zero for a spherical particle. Inspection of Eqs. (7) and (8) reveals that this phenomenon cannot possibly affect the long-time average velocity of the particle but could affect the long-time mean square displacements (and thus the translational diffusion coefficients) since $\langle\cos 2\theta(t')\cos 2\theta(t'')\rangle$ and $\langle\sin 2\theta(t')\sin 2\theta(t'')\rangle$ have clearly a nonzero value in the long-time limit. The coupling-induced renormalization of the transient and steady-state particle translational diffusion coefficients is the subject of the rest of this article.

III. ELLIPSOIDAL PARTICLE IN A FIELD OF CONSTANT FORCE

In this section we calculate the temporal variation of the diffusion coefficients of an ellipsoidal rigid body which experiences constant forces and which is constrained to move in a plane. An example is an asymmetric, uniformly charged particle in an electric field. In such a case, the electric dipole moment is zero and hence the molecule can rotate freely about its center of mass which implies Gaussian statistics for the angular displacements. This property allows us to fully calculate the statistics obeyed by the translational displacements, in particular, the effect of the application of external force on the particle's diffusive motion. We expect the results obtained here to be generally valid for molecules with small dipole moments. However, the preferential orientation induced by strong moments leads to non-Gaussian behavior for the angular displacements which makes the task of determining exactly the statistics of translational displacements analytically impossible. This is explored numerically in the next section.

We shall calculate the three translational diffusion coefficients, namely, the one in the x direction (D_{11}), the one in the y direction (D_{22}), and the cross-diffusion coefficient ($D_{12}=D_{21}$), which are given by the general formula

$$D_{ij}(t) = \frac{\langle\Delta x_i(t)\Delta x_j(t)\rangle^{\eta_1,\eta_2,\eta_3}_{\theta_0} - \langle\Delta x_i(t)\rangle^{\eta_1,\eta_2,\eta_3}_{\theta_0}\langle\Delta x_j(t)\rangle^{\eta_1,\eta_2,\eta_3}_{\theta_0}}{2t}, \tag{12}$$

where $(x_1,x_2)=(x,y)$. We shall drop superscripts and subscripts throughout the rest of the paper unless the average is taken over one specific noise rather than over all of the three noise sources.

We now describe in detail the calculation of D_{11}. Integrating Eq. (7) with respect to time, one obtains

$$\Delta x_1(t) = F_x\bar{\Gamma}t + \frac{F_x\Delta\Gamma}{2}\int_0^t\cos 2\theta(t')dt' + \frac{F_y\Delta\Gamma}{2}\int_0^t\sin 2\theta(t')dt' + \int_0^t\eta_1(t')dt'. \tag{13}$$

The ensemble average of the sinusoidal functions can be calculated by noting that the angular displacement $\Delta\theta(t)=\theta(t)-\theta_0$ is a Gaussian random variable, in which case the following identity is valid:

$$\langle e^{i[m\Delta\theta(t')\pm n\Delta\theta(t'')]}\rangle^{\eta_3}_{\theta_0} = e^{-D_\theta[m^2t'+n^2t''\pm 2mn\,min(t',t'')]}, \tag{14}$$

which implies $\langle\cos n\theta(t)\rangle^{\eta_3}_{\theta_0}=\cos n\theta_0e^{-n^2D_\theta t}$ and $\langle\sin n\theta(t)\rangle^{\eta_3}_{\theta_0}=\sin n\theta_0e^{-n^2D_\theta t}$. Since the average of the translational noise $\eta_1(t)$ is zero, then it follows from Eq. (13) that the average displacement in the x direction is

$$\langle\Delta x_1(t)\rangle = F_x\bar{\Gamma}t + \frac{\Delta\Gamma}{8D_\theta}(1-e^{-4D_\theta t}) \times(F_x\cos 2\theta_0 + F_y\sin 2\theta_0). \tag{15}$$

The computation of the mean square displacement is more involved. Squaring and averaging Eq. (13), one obtains

$$\langle \Delta x_1^2(t)\rangle = F_x^2\bar{\Gamma}^2 t^2 + F_x^2\bar{\Gamma}\Delta\Gamma t\int_0^t \langle \cos 2\theta(t')\rangle dt' + F_xF_y\bar{\Gamma}\Delta\Gamma t\int^t \langle \sin 2\theta(t')\rangle dt' + \tfrac{1}{4}\Delta\Gamma^2\int_0^t\int_0^t [F_x^2\langle \cos 2\theta(t')\cos 2\theta(t'')\rangle + F_y^2\langle \sin 2\theta(t')\sin 2\theta(t'')\rangle]dt'dt'' + \tfrac{1}{2}\Delta\Gamma^2 F_xF_y\int_0^t\int_0^t \langle \cos 2\theta(t')\sin 2\theta(t'')\rangle dt'dt'' + \int_0^t\int_0^t \langle \eta_1(t')\eta_1(t'')\rangle dt'dt'' + \Delta\Gamma F_x\int_0^t\int_0^t \langle \cos 2\theta(t')\eta_1(t'')\rangle dt'dt'' + \Delta\Gamma F_y\int_0^t\int_0^t \langle \sin 2\theta(t')\eta_1(t'')\rangle dt'dt''. \quad (16)$$

The first two integrals can be straightforwardly evaluated using the above results for the averages of the sine and cosine of the angle. The integrals over statistical averages of products of trigonometric functions are more involved and require careful evaluation.

Consider the integral $\int_0^t\int_0^t\langle \cos 2\theta(t')\cos 2\theta(t'')\rangle dt'dt''$. Using $\Delta\theta(t)=\theta(t)-\theta_0$ and a product identity this can be written in the convenient form

$$\tfrac{1}{2}\int_0^t\int_0^t \langle \cos(4\theta_0 + 2\Delta\theta(t') + 2\Delta\theta(t''))\rangle + \langle \cos(2\Delta\theta(t') - 2\Delta\theta(t''))\rangle dt'dt'', \quad (17)$$

which using the identity Eq. (14) can be written as

$$\tfrac{1}{2}\int_0^t\int_0^t \cos 4\theta_0 e^{-4D_\theta[t'+t''+2\,min(t',t'')]} + e^{-4D_\theta[t'+t''-2\,min(t',t'')]}dt'dt''. \quad (18)$$

Evaluation of this integral leads to the final form

$$\int_0^t\int_0^t \langle \cos 2\theta(t')\cos 2\theta(t'')\rangle dt'dt'' = \cos(4\theta_0)I_a + I_b, \quad (19)$$

where

$$I_a = \frac{1}{2}\int_0^t dt'\int_0^{t'} dt'' e^{-4D_\theta[3t''+t']} + \frac{1}{2}\int_0^t dt''\int_0^{t''} dt' e^{-4D_\theta[3t'+t'']} = \frac{3 + e^{-16D_\theta t} - 4e^{-4D_\theta t}}{192D_\theta^2}, \quad (20)$$

$$I_b = \frac{1}{2}\int_0^t dt'\int_0^{t'} dt'' e^{-4D_\theta[3t''+t']} + \frac{1}{2}\int_0^t dt''\int_0^{t''} dt' e^{-4D_\theta[3t'+t'']} = \frac{4D_\theta t + e^{-4D_\theta t} - 1}{16D_\theta^2}. \quad (21)$$

By a similar procedure one also obtains the following results:

$$\int_0^t\int_0^t \langle \sin 2\theta(t')\sin 2\theta(t'')\rangle dt'dt'' = I_b - \cos(4\theta_0)I_a, \quad (22)$$

$$\int_0^t\int_0^t \langle \sin 2\theta(t')\cos 2\theta(t'')\rangle dt'dt'' = \sin(4\theta_0)I_a. \quad (23)$$

The integral $\int_0^t\int_0^t\langle \eta_1(t')\eta_1(t'')\rangle dt'dt''$ can be reduced to an integral over the average of the cosine of the double angle using the definition of the correlator Eq. (11), leading to $(D_1+D_2)t+\Delta D\int_0^t\langle\cos(2\theta(t'))\rangle_{\theta_0}^{\eta_3}dt'$, which using the identity Eq. (14) reduces to the final form

$$\int_0^t\int_0^t \langle \eta_1(t')\eta_1(t'')\rangle dt'dt'' = 2\bar{D}t + \Delta D\cos 2\theta_0\frac{1 - e^{-4D_\theta t}}{4D_\theta}, \quad (24)$$

where $\bar{D}=\frac{1}{2}(D_1+D_2)$ and $\Delta D=D_1-D_2$.

The last two integrals in Eq. (16), which are over products of sinusoidal functions of the particle's angle $\theta(t)$ and of translational noise η_1, evaluate to zero. This can be deduced by writing the lab-frame noise η_1 in terms of the body-frame noise $\tilde{\eta}_{1,2}$ and sequentially computing the average over translational and angular noise. Given this result and Eqs. (19) and (22)–(24), one can explicitly evaluate the mean square displacement Eq. (16). Substituting the resulting expression together with the expression for the mean displacement Eq. (15) in Eq. (12) gives us the ellipsoid's time-dependent translational diffusion coefficient in the x direction as follows:

$$D_{11}(t) = \bar{D} + \frac{\Delta\Gamma^2(F_x^2 + F_y^2)}{32D_\theta} + \frac{1}{2t}\Bigg[\frac{\cos 4\theta_0}{768D_\theta^2}\Delta\Gamma^2(F_x^2 - F_y^2 + 2F_xF_y\tan 4\theta_0)(3 + e^{-16D_\theta t} - 4e^{-4D_\theta t}) + \frac{\Delta\Gamma^2(F_x^2+F_y^2)}{64D_\theta^2}(e^{-4D_\theta t} - 1) + \Delta D\cos 2\theta_0 \times \frac{1 - e^{-4D_\theta t}}{4D_\theta} - \frac{\Delta\Gamma^2}{64D_\theta^2}(1 - e^{-4D_\theta t})^2(F_x\cos 2\theta_0 + F_y\sin 2\theta_0)^2\Bigg]. \quad (25)$$

By a similar calculation, one obtains the translational diffusion coefficient in the y direction (D_{22}) and the cross-diffusion coefficient (D_{12}). The expression for D_{22} can be obtained from that for D_{11} by interchanging F_x and F_y and replacing $\cos 2\theta_0$ by $-\cos 2\theta_0$. The cross-diffusion coefficient is given by

$$D_{12}(t) = \frac{1}{2t}\left[\frac{F_x F_y \Delta\Gamma^2 \cos(4\theta_0)}{D_\theta^2}\left(\frac{1}{128} - \frac{1}{48}e^{-4D_\theta t} + \frac{1}{64}e^{-8D_\theta t} - \frac{1}{384}e^{-16D_\theta t}\right) + \frac{(F_y^2 - F_x^2)\Delta\Gamma^2 \sin(4\theta_0)}{D_\theta^2}\left(\frac{1}{256} - \frac{1}{96}e^{-4D_\theta t} + \frac{1}{128}e^{-8D_\theta t} - \frac{1}{768}e^{-16D_\theta t}\right) + \Delta D \sin 2\theta_0 \frac{1 - e^{-4D_\theta t}}{4D_\theta}\right]. \quad (26)$$

For the case of zero forces the above expressions reduce to the simple forms, recently derived and experimentally verified by Han *et al.*[5]

$$D_{11}(t) = \bar{D} + \Delta D \cos 2\theta_0 \frac{1 - e^{-4D_\theta t}}{8D_\theta t}, \quad (27)$$

$$D_{22}(t) = \bar{D} - \Delta D \cos 2\theta_0 \frac{1 - e^{-4D_\theta t}}{8D_\theta t}, \quad (28)$$

$$D_{12}(t) = \Delta D \sin 2\theta_0 \frac{1 - e^{-4D_\theta t}}{8D_\theta t}. \quad (29)$$

A. Renormalization of the long-time diffusion coefficients

Similarly to the free particle case, an ellipsoidal particle experiencing external forces performs anisotropic motion for short times which changes to isotropic for longer times. This can be inferred from the fact that generally $D_{11} \neq D_{22}$ and $D_{12} \neq 0$ except in the limit $t \to \infty$. However, there is a major difference between these two cases: the single long-time translational diffusion coefficient of an ellipsoidal particle in a field of constant force $(D_F = \bar{D} + \Delta\Gamma^2(F_x^2 + F_y^2)/32D_\theta)$ is always larger than in the case when there are no external forces acting on it $(D_{NF} = \bar{D})$. This is verified by computer simulation (see Fig. 2). The simulation is carried out by direct numerical integration of the stochastic differential equations in the body frame which yields particle position data from which one can compute the diffusion coefficients in the lab frame. The differences in the two diffusion coefficients increase proportionately with the asymmetry of the particle $(\Delta\Gamma)$ and are zero for a perfectly spherical particle.

This shape-dependent renormalization has implications for band broadening in electrophoresis experiments. We stress, however, that the phenomenon described here is not related to the well known dependence of the diffusion coefficients on the magnitude of the electric field due to Joule heating or due to interactions between the field and the gel medium in which electrophoresis is performed.[15] In practice, the coupling-induced renormalization will only be relevant at large electric field (E-field) strengths, particularly for quasi-spherical particles. A rough estimate of the critical magnitude of the E-field can be obtained as follows. Recently Han *et al.*[5] experimentally showed that for a free prolate ellipsoid with axial radii $r_1 = 2.4$ μm and $r_2 = r_3 = 0.3$ μm confined between two plates a distance 846 nm apart (this effectively confines the movement to two dimensions) the diffusion coefficients along and perpendicular to the long axis of the ellipsoid are $D_1 = 0.179$ $\mu m^2/s$ and $D_2 = 0.044$ $\mu m^2/s$, and the rotational diffusion coefficient is $D_\theta = 0.161$ s^{-1}. If we assume that such a body has a charge equal to that of an electron, then one can show that the actual long-time translational diffusion coefficient D_F is twice as large as that predicted by neglecting effects due to asymmetry (D_{NF}), for an electric field strength of $|E| \simeq 1.5$ kV cm^{-1}. Fields with strengths up to 8 kV cm^{-1} have been used in electrokinetic flow in FCS experiments[16] and strengths up to 50 kV cm^{-1} in electrophoresis experiments.[17] This phenomenon may be particularly relevant to the analysis of the autocorrelation function $G(\tau)$ in FCS experiments where it is customary to assume that the particle diffusion coefficient is independent of the magnitude of the electric field.[16]

The renormalization of the translational diffusion coefficient with force may also have implications for the construction of Brownian motors. Directed motion of spherical particles requires moving the system out of thermal equilibrium.[18] This situation can, for example, be forced by subjecting the particles to spatially periodic temperature conditions[19] or by placing the particles in a periodic spatial potential with broken spatial symmetry (a ratchet) while simultaneously subjecting them to periodic temperature oscillations in time.[18,20] Note that directed motion of spherical particles cannot be obtained by simply placing them in a ratchet potential since this would be the case of thermal equilibrium. However, our results suggest that significantly asymmetric particles placed in a ratchet potential may exhibit directed motion. The renormalization phenomenon implies that the translational diffusion coefficient of the particle (and hence the effective temperature) will spatially oscillate between two or more values as determined by the spatial potential gradient.

B. Transients

As previously remarked, transients in the diffusion coefficients (and the accompanying anisotropical diffusive motion) are usually assumed to be very short lived and thus irrelevant in practice. This may be true in three dimensions. However, in a dimensionally restricted environment, e.g., movement confined to a quasi-2D plane such as a membrane, it has been experimentally determined[5] that for a free ellipsoidal microsized particle with an aspect ratio of 1:8, the time scale of transient decay is of the order of seconds. This suggests that transient behavior may, for example, dominate the reaction kinetics in intracellular environments where reaction time is frequently of the order of microseconds and where the environment is dimensionally restricted since a number of reactions occur only on or inside surfaces such as membranes and also due to the phenomenon of macromolecular crowding.[21–23]

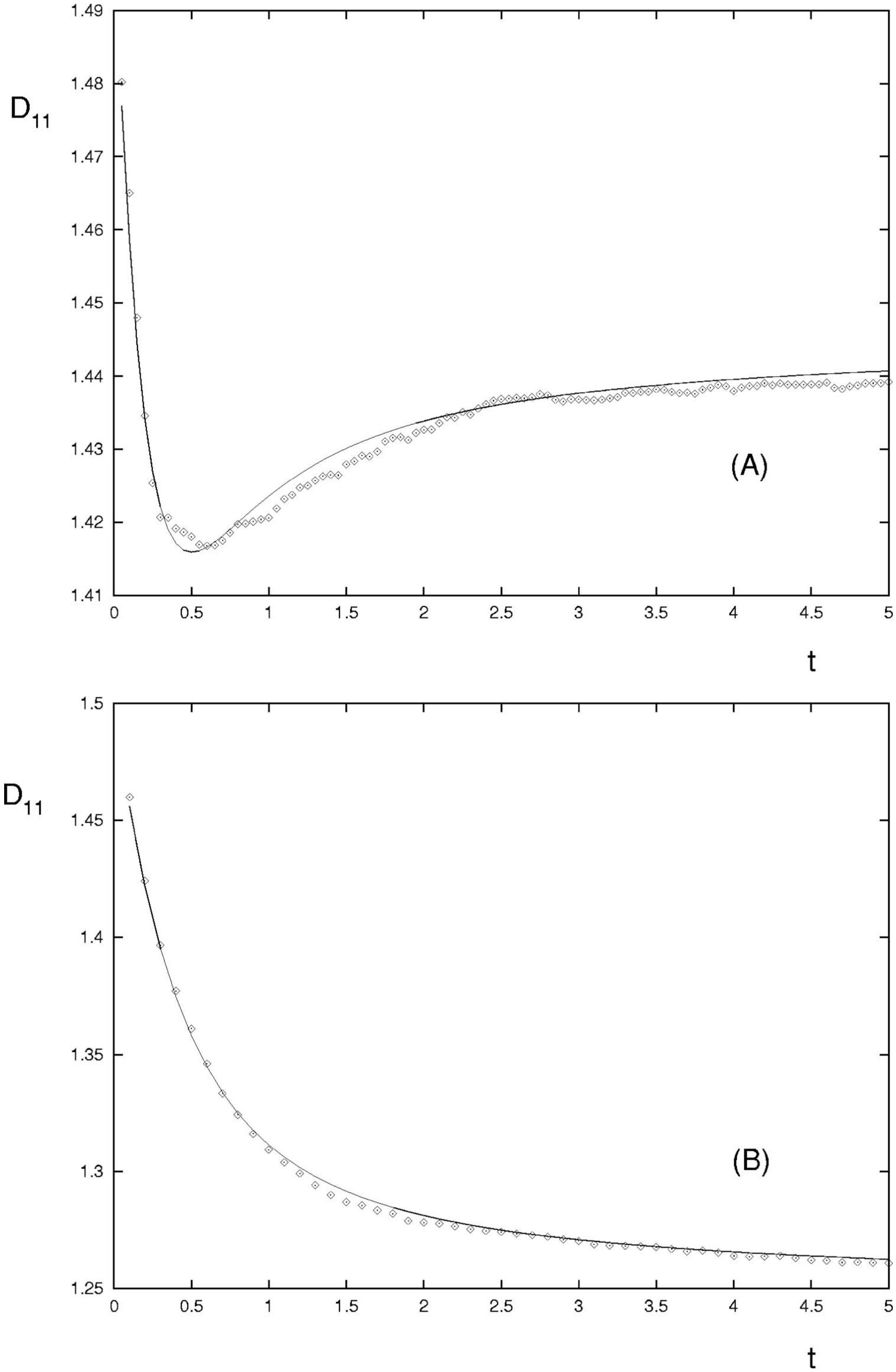

FIG. 2. The translational diffusion coefficient in the x direction D_{11} vs time t for an ellipsoidal particle with parameters $D_1=1.5$, $D_2=1$, $D_\theta=1$, and $\theta_0=0$ in (A) the presence of constant external forces $F_x=5$ and $F_y=0$ and (B) in their absence. The solid lines show the theoretical predictions [Eq. (25)]. The data points are obtained from numerical integration of the governing stochastic differential equations. Note that unless otherwise stated all units in the figures are dimensionless.

One certainly expects that for an asymmetrical molecule experiencing external forces due to other neighboring molecules, the transients are bound to be quantitatively different to those of a free molecule of similar shape. However, our analysis indicates that these differences are also qualitatively dissimilar which has stronger implications. It has been found that, for the free case, the transients invariably decay monotonically with time, as can be directly deduced by inspection of Eqs. (27)–(29). This is not the case when the particle is experiencing external forces. Figure 2(a) illustrates this property for a particular set of parameters. In this case the translational diffusion coefficient decreases for very short times, reaches a minimum, and then starts increasing again to finally reach its long-time value. The translational diffusion coefficient modulates the reaction rate of diffusion-limited reactions suggesting that molecular asymmetry may play an important role in low-dimensional reaction kinetics.

Similar striking differences are observed in the cross-diffusion coefficient (Fig. 3). The practical implications of these differences can be appreciated by considering the physical meaning of the cross-diffusion coefficient. This coefficient is a measure of deviations of the movement of an

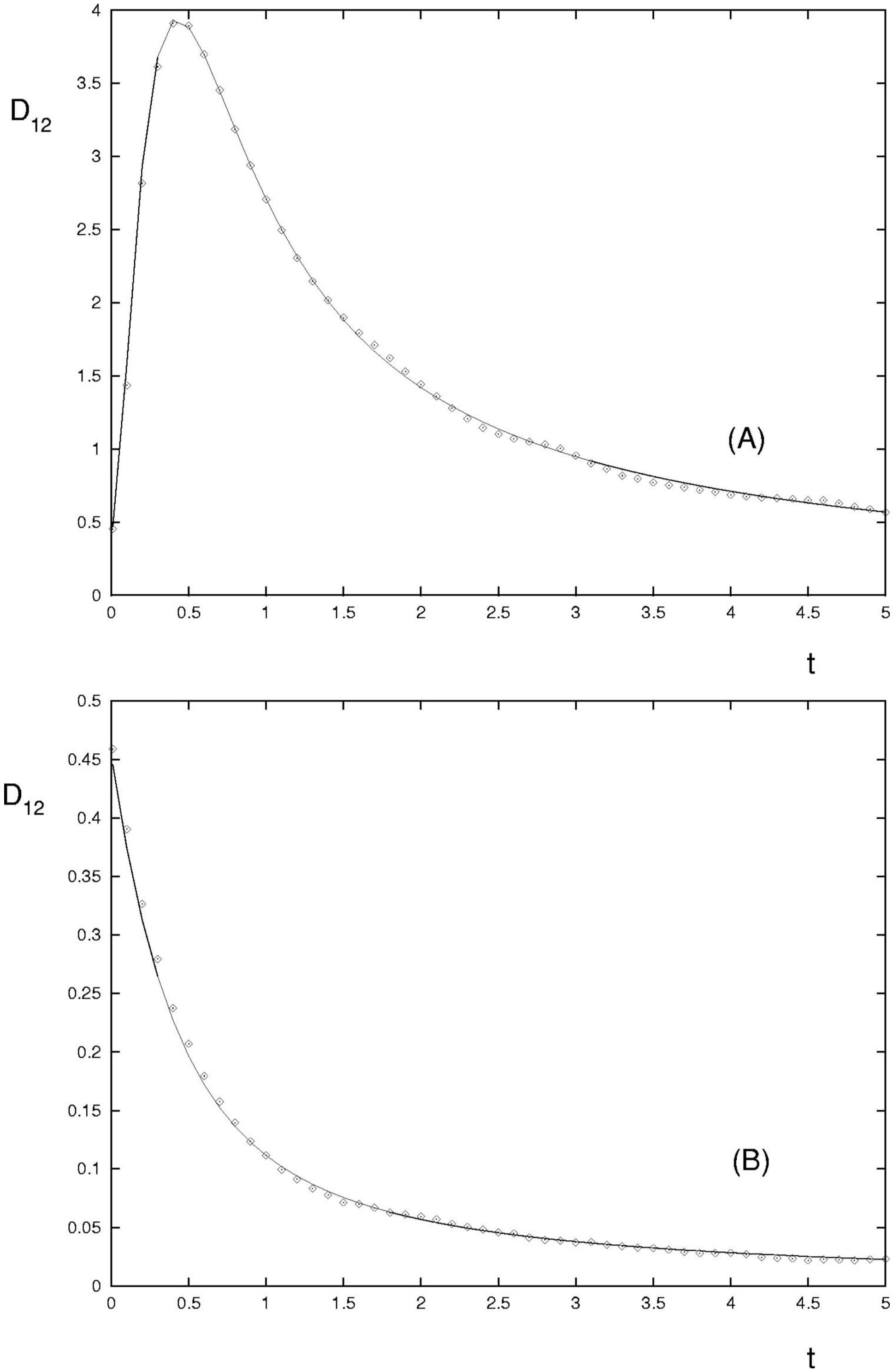

FIG. 3. The cross-diffusion coefficient D_{12} vs time for an ellipsoidal particle with parameters $D_1=2$, $D_2=1$, $D_\theta=1$, and $\theta_0=1$ in (A) the presence of constant external forces $F_x=50$ and $F_y=7$ and (B) in their absence. The solid lines show the theoretical prediction [Eq. (26)] and the data points are those obtained from numerical integration of the stochastic differential equations. Note that the value of D_{12} at long times is negligibly small when the particle is free (B) but it is still approximately equal to its initial value when the particle experiences external forces (A).

ellipsoidal particle from pure random walk behavior (motion driven by white noise) since its magnitude is dependent on the strength of correlations between particle displacements in the lab frame's x and y directions. The nonzero value of this coefficient also implies a term proportional to $\partial_x \partial_y P$ in the diffusion equation for the probability distribution which means that D_{12} is also a measure of the non-Gaussianity of the molecular spatial distribution function.[6] In the limit of long times, $D_{12} \rightarrow 0$, the classical Gaussian distribution is recovered. Hence the results shown in Fig. 3 imply that the temporal deviations of an asymmetrical molecule's spatial probability distribution from that of a spherical molecule (purely Gaussian distribution) are magnified by the presence of external forces. In particular, the time taken for the non-Gaussian character of the distribution to decay can be substantially longer when the molecule is in a potential field compared to when it is free.

The complexity of the expressions for the transient behavior presents a serious obstacle to the rigorous elucidation of the general properties of the temporal particle dynamics. A simple attempt at classifying transient behavior consists in comparing the magnitudes of the short-time and long-time translational diffusion coefficients. The short-time diffusion coefficients can be obtained by truncating to first order in time the Taylor expansion which gives $\bar{D}\pm\frac{1}{2}\Delta D\cos 2\theta_0$, where the positive sign is for the coefficient in the x direction and the negative sign for the coefficient in the y direction; thus the difference between the short-and long-time coefficients, Λ, is given by

$$\Lambda = \Delta\Gamma\left(\pm\frac{1}{2}k_B T\cos 2\theta_0 - \frac{\Delta\Gamma|F|^2}{32D_\theta}\right), \tag{30}$$

where $|F|$ is the force magnitude. Of course this parameter provides no information about the behavior at intermediate times but nevertheless it is an accurate indicator of whether the magnitude of the coefficient overall decreases ($\Lambda>0$) or increases with time ($\Lambda<0$). Since by definition Γ_1 and Γ_2 are the respective mobilities associated with diffusive motion parallel and perpendicular to the ellipsoid's axes, then generally $\Delta\Gamma=\Gamma_1-\Gamma_2$ is a positive quantity[5,24] implying that the sign of Λ is solely dependent on the sign of the bracketed quantity in Eq. (30).

For the free case, the diffusion coefficient in the x direction overall temporally decreases for initial angles in the ranges $0\leqslant\theta_0\leqslant\pi/4$ and $3\pi/4\leqslant\theta_0\leqslant\pi$, while it overall increases for initial angles in the range $\pi/4\leqslant\theta_0\leqslant 3\pi/4$. In the presence of external forces, the behavior is more intricate. For particles with initial angles in the range $\pi/4\leqslant\theta_0\leqslant 3\pi/4$, we have $\Lambda<0$ and thus the x-diffusion coefficient overall increases with time, as for the free particle case. However, in the ranges $0\leqslant\theta_0\leqslant\pi/4$ and $3\pi/4\leqslant\theta_0\leqslant\pi$, the sign of Λ can now be positive or negative, depending on the force magnitude. If $|F|>F_c=4\sqrt{k_B T D_\theta\cos(2\theta_0)/\Delta\Gamma}$ then $\Lambda<0$ otherwise $\Lambda>0$. Similarly a transition in the sign of Λ is observed for transients of the diffusion coefficient in the y direction when the initial angle is in the range $\pi/4\leqslant\theta_0\leqslant 3\pi/4$.

In essence, the force magnitude and the initial angle jointly determine the global features of the transient behavior of the translational diffusion coefficient of an ellipsoidal particle (see Fig. 4 for numerical validation of the theory). These phenomena may be relevant to understanding the anomalous dynamics of small numbers of strongly interacting and approximately oriented molecules in dimensionally restricted environments, e.g., the postulated substrate-product segregation in small parts of membranes due to molecular crowding.[25]

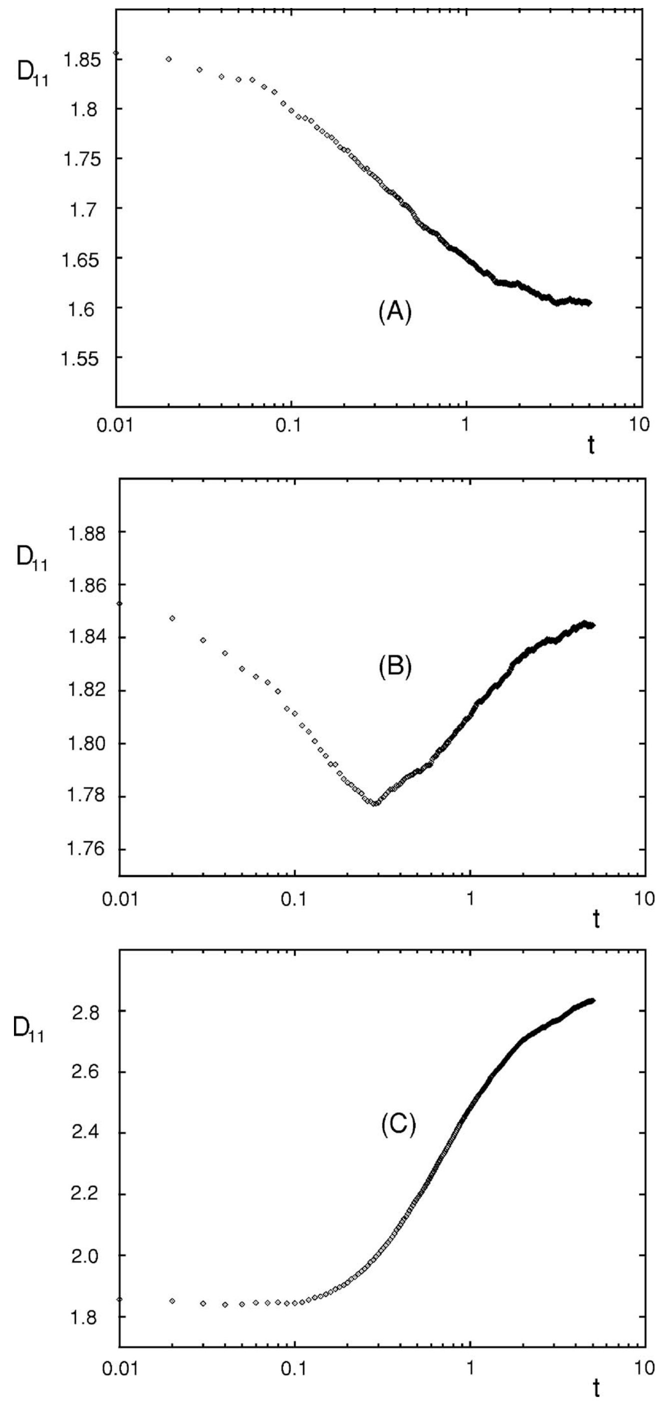

FIG. 4. The translational diffusion coefficient D_{11} in the x direction vs time for an ellipsoidal particle with parameters $D_1=2$, $D_2=1$, $D_\theta=1$, and $\theta_0=\pi/8$ in the presence of constant external forces of magnitude (A) $|F|=0.5F_c$, (B) $|F|=F_c$, and (C) $|F|=2F_c$. The qualitative features of the temporal dependence are completely determined by whether the external force magnitude exceeds the critical value F_c predicted by theory. The data are obtained from numerical integration of the stochastic differential equations.

IV. CONFINEMENT OF AN ELLIPSOIDAL PARTICLE IN A QUASI-1D "CHANNEL"

Next we consider the case of an ellipsoid performing Brownian motion in a semiharmonic well potential $V(x,y)=\frac{1}{2}ky^2$ which effectively confines movement to a quasi- one-dimensional (1D) "channel" or pipe. The spring constant k effectively determines the width of the well. For the moment we shall assume that the particle experiences no aligning torque (the effects of torque are discussed in Sec. IV A). The governing Langevin equations of motion are

$$\frac{\partial x(t)}{\partial t} = -\frac{1}{2}\Delta\Gamma k y\sin 2\theta(t) + \eta_1(t), \tag{31}$$

$$\frac{\partial y(t)}{\partial t} = -ky\left(\bar{\Gamma} - \frac{1}{2}\Delta\Gamma\cos 2\theta(t)\right) + \eta_2(t), \tag{32}$$

$$\frac{\partial\theta(t)}{\partial t}=\eta_3(t). \tag{33}$$

We shall now calculate the mean and mean square displacements in the two directions. Integrating Eq. (32) gives $\Delta y(t)=\int_0^t dt'\,\eta_2(t')e^{-k\bar{\Gamma}(t-t')}e^{(1/2)k\Delta\Gamma\int_{t'}^{t}dt''\cos 2\theta(t'')}$, which upon squaring and computing the statistical average over the translational noise η_2, one obtains

$$\langle\Delta y^2(t)\rangle^{\eta_2}=2k_BTt\int_0^1 du\left[\bar{\Gamma}-\tfrac{1}{2}\Delta\Gamma\cos 2\theta(t-ut)\right]\times e^{-2k\bar{\Gamma}tu}e^{k\Delta\Gamma\int_{t-ut}^{t}dt'\cos 2\theta(t')}. \tag{34}$$

In this expression we have still not computed a statistical average over the angular noise, η_3. The asymptotic dynamics can be extracted by noting that in the limit of long times, $t\gg 1/2k\bar{\Gamma}$, the above integral dominates for small u which practically means that $t-ut$ can be replaced by t. Upon evaluation and the subsequent computation of the average over angular noise, we find that the long-time mean square displacement in the y direction is equal to

$$\langle\Delta y^2(t)\rangle=\frac{k_BT}{k}. \tag{35}$$

Hence the particle, independently of its shape and asymmetry, is effectively trapped to move within a rectangular region of width $L=\sqrt{k_BT/k}$. These predictions are confirmed by simulations of the full equations (see Fig. 5).

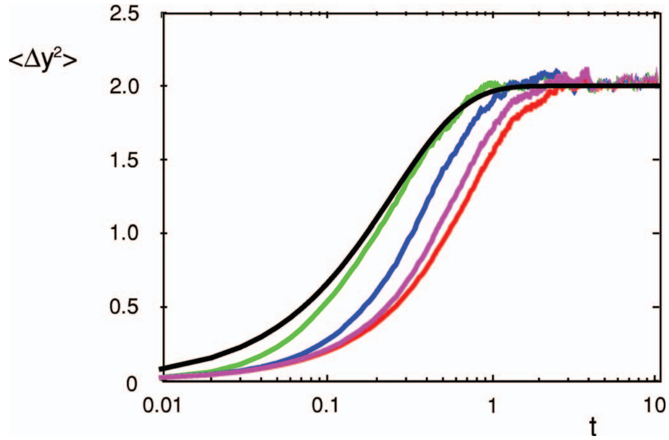

FIG. 5. (Color) The mean square displacement in the y direction vs time for an ellipsoidal particle in a harmonic field $V=\frac{1}{2}ky^2$. The width of the well is determined by the spring constant k. Here $k=1/2$. The energy k_BT is normalized to unity. The parameter values are (from left to right) (a) $\bar{D}=4$, $\Delta D=0$, $D_\theta=1$; (b) $\bar{D}=4$, $\Delta D=6$, $D_\theta=10$; (c) $\bar{D}=4$, $\Delta D=6$, $D_\theta=1$; (d) $\bar{D}=8$, $\Delta D=14$, $D_\theta=0.1$; and (e) $\bar{D}=4$, $\Delta D=6$, $D_\theta=0.1$. Note that independent of particle shape, the long-time mean square displacement is determined solely by the width of the well, as predicted by Eq. (35).

Next we calculate the mean square displacement in the x direction. This is considerably more involved than the previous calculation since the particle's velocity in the x direction is dependent on its y position and the angle θ, both of which are stochastic quantities. Integrating Eq. (31), squaring, and taking the statistical average, we obtain

$$\langle\Delta x^2(t)\rangle=\tfrac{1}{4}\Delta\Gamma^2k^2\int_0^t\int_0^t dt'dt''\langle y(t')y(t'')\sin(2\theta(t'))\sin(2\theta(t''))\rangle-\tfrac{1}{2}\Delta\Gamma k\int_0^t\int_0^t dt'dt''\langle y(t')\sin(2\theta(t'))\eta_1(t'')\rangle$$
$$-\tfrac{1}{2}\Delta\Gamma k\int_0^t\int_0^t dt'dt''\langle y(t'')\sin(2\theta(t''))\eta_1(t')\rangle+\int_0^t\int_0^t dt'dt''\langle\eta_1(t')\eta_1(t'')\rangle. \tag{36}$$

The second and third integrals of this expression must be equal since the dummy integration variables t' and t'' can be interchanged. We have previously computed the last integral and thus our focus now is on computing the first and second integrals.

Consider the averaged quantity $\langle y(t')\sin(2\theta(t'))\eta_1(t'')\rangle$. By integrating Eq. (32) for $y(t')$ and substituting in the above quantity, one obtains

$$\langle y(t')\sin(2\theta(t'))\eta_1(t'')\rangle=\int_0^{t'}dt'''\langle\eta_2(t''')e^{-k\bar{\Gamma}(t'-t''')}e^{(1/2)k\Delta\Gamma\int_{t'''}^{t'}dt''''\cos 2\theta(t'''')}\times\sin(2\theta(t'))\eta_1(t'')\rangle. \tag{37}$$

For long times, the integral dominates by t''' close to t' and thus the second exponential factor on the right hand side of the above equation can be neglected. Computing the statistical average over the translational noise, η_1 and η_2, one obtains

$$\Delta D\int_0^{t'}dt'''\,\delta(t'''-t'')e^{-k\bar{\Gamma}(t'-t''')}\langle\sin(2\theta(t'))\sin(2\theta(t'''))\rangle^{\eta_3}, \tag{38}$$

where the superscript is a reminder that the remaining average to be taken is over the angular noise. If $t''>t'$ then the integral is zero; however, if $t''<t'$ then the delta function collapses the integral and upon computing the statistical average over the angular noise it is found that the second integral in Eq. (36) can now finally be written as

$$\int_0^t \int_0^t dt' dt'' \langle y(t') \sin(2\theta(t')) \eta_1(t'') \rangle$$
$$= \tfrac{1}{2}\Delta D \int_0^t dt' \int_0^{t'} dt'' e^{-k\bar{\Gamma}(t'-t'')} (e^{-4D_\theta(t'-t'')} - \cos(4\theta_0) e^{-4D_\theta(t'+3t'')}). \quad (39)$$

Upon evaluation, we find that for long times the dominant term is directly proportional to time elapsed,

$$\int_0^t \int_0^t dt' dt'' \langle y(t') \sin(2\theta(t')) \eta_1(t'') \rangle \to \frac{\Delta D t}{2(\bar{\Gamma} k + 4D_\theta)}. \quad (40)$$

Now consider the averaged quantity $\langle y(t') y(t'') \sin(2\theta(t')) \sin(2\theta(t'')) \rangle$. Since for long times, the second exponential factor in $y(t) = \int_0^t dt' \eta_2(t') \times e^{-k\bar{\Gamma}(t-t')} e^{(1/2)k\Delta\Gamma \int_{t'}^{t} dt'' \cos 2\theta(t'')}$ can be neglected, we then have

$$\langle y(t') y(t'') \sin(2\theta(t')) \sin(2\theta(t'')) \rangle$$
$$= \langle y(t') y(t'') \rangle^{\eta_2} \langle \sin(2\theta(t')) \sin(2\theta(t'')) \rangle^{\eta_3}$$
$$= \frac{1}{2} \frac{k_B T}{k} e^{-k\bar{\Gamma}|t'-t''|} [e^{-4D_\theta(t'-t'')} - \cos(4\theta_0) e^{-4D_\theta(t'+3t'')}]. \quad (41)$$

Integrating this expression over t' and t'' and keeping only the dominant term for long times, one obtains

$$\int_0^t \int_0^t dt' dt'' \langle y(t') y(t'') \sin(2\theta(t')) \sin(2\theta(t'')) \rangle \to \frac{k_B T t}{k(\bar{\Gamma} k + 4D_\theta)}. \quad (42)$$

Substituting Eqs. (40) and (42) into Eq. (36), we obtain the long-time diffusion coefficient in the x direction as follows:

$$D_{11} = \bar{D} - \frac{\Delta D^2}{8(\bar{D} + 4D_\theta L^2)}. \quad (43)$$

We can see from Eq. (43) that the diffusion of an asymmetrical particle along the length of the channel is determined by its width, L, and that the long-time diffusion coefficient has once again been renormalized according to the magnitude of the particle's asymmetry ΔD. The dynamics of a perfectly spherical particle will be unaffected by the confining potential and hence the strength of the dependence of the translational diffusion coefficient on the channel width is essentially a measure of particle asymmetry. This also means that two differently shaped particles which are indistinguishable in the free case, i.e., $D_{11} = \bar{D}$, become distinguishable when appropriately confined. This is illustrated in Fig. 6 where we plot the variation of the long-time diffusion coefficient of a sphere and three different ellipsoidal bodies with the channel width L. The mobilities of all four particles were chosen so that in the absence of external fields they would be indistinguishable, i.e., $D_{11} = \bar{D}$ as $L \to \infty$. This is accomplished by setting $\Gamma_1 = b + a$ and $\Gamma_2 = b - a$, where b is a constant for all particles, which sets the zero field diffusion coefficient to the fixed value $\bar{D} = k_B T b$. The parameter a, where $a \leq b$, determines the asymmetry of the body: $\Delta D = 2k_B T a$, with $\Delta D = 0$ being a perfect sphere and $\Delta D \simeq 2k_B T b$ being a very needlelike ellipsoid. Since in general, $0 \leq \Delta D \leq 2\bar{D}$, then it follows from Eq. (43) that the values of the translational diffusion coefficient along the channel fall in the range $\frac{1}{2}\bar{D} \leq D_{11} \leq \bar{D}$. Generally, effects due to the channel width become significant below a critical length scale defined by $L_c = \frac{1}{2}(\bar{D}/D_\theta)^{1/2}$.

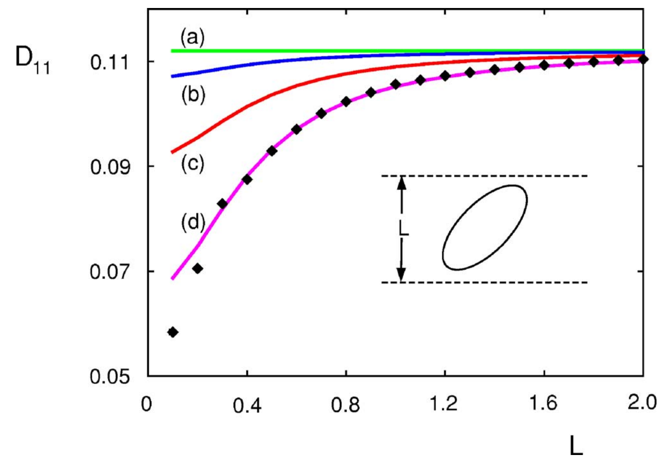

FIG. 6. (Color online) The translational diffusion coefficient in the x direction, D_{11}, vs the channel width, L, in microns for four ellipsoids with the same diffusion coefficient $\bar{D} = 0.112\ \mu\mathrm{m}^2\,\mathrm{s}^{-1}$ in the absence of confinement. The parameter ΔD quantifies the asymmetry of the rigid ellipsoid: (a) $\Delta D = 0$, (b) $0.068\ \mu\mathrm{m}^2\,\mathrm{s}^{-1}$, (c) $0.135\ \mu\mathrm{m}^2\,\mathrm{s}^{-1}$, and (d) $0.203\ \mu\mathrm{m}^2\,\mathrm{s}^{-1}$. Case (c) corresponds to a prolate ellipsoid with axial radii $r_1 = 2.4\ \mu$m, $r_2 = r_3 = 0.3\ \mu$m. The solid curves are those predicted by theory [Eq. (43)]. The diamond shaped data points are those obtained from simulation for the case $\Delta D = 0.203\ \mu\mathrm{m}^2\,\mathrm{s}^{-1}$; this illustrates the good agreement of theory and simulation.

A. Directional alignment

The results previously derived in this section were based on the assumption that the ellipsoidal particle will not align along a particular direction or else will do so only weakly. Alignment of the longest semiaxes of the particle with the length of the channel can occur if there is a net significant fluid flow in this direction. If the particle has a dipole moment then it can also align due to external electric or magnetic fields. The alignment effects can be phenomenologically modeled by considering a torque term of the form $\tau = \alpha \sin(\theta - \phi)$ where α is a constant measuring the strength of alignment and ϕ defines the direction of alignment. The case which can be straightforwardly treated is that of perfect alignment, i.e., $\alpha = \infty$, in which case the governing equations of motion become

$$\frac{\partial x(t)}{\partial t} = -\frac{1}{2}\Delta\Gamma k y \sin 2\phi + \eta_1(t), \quad (44)$$

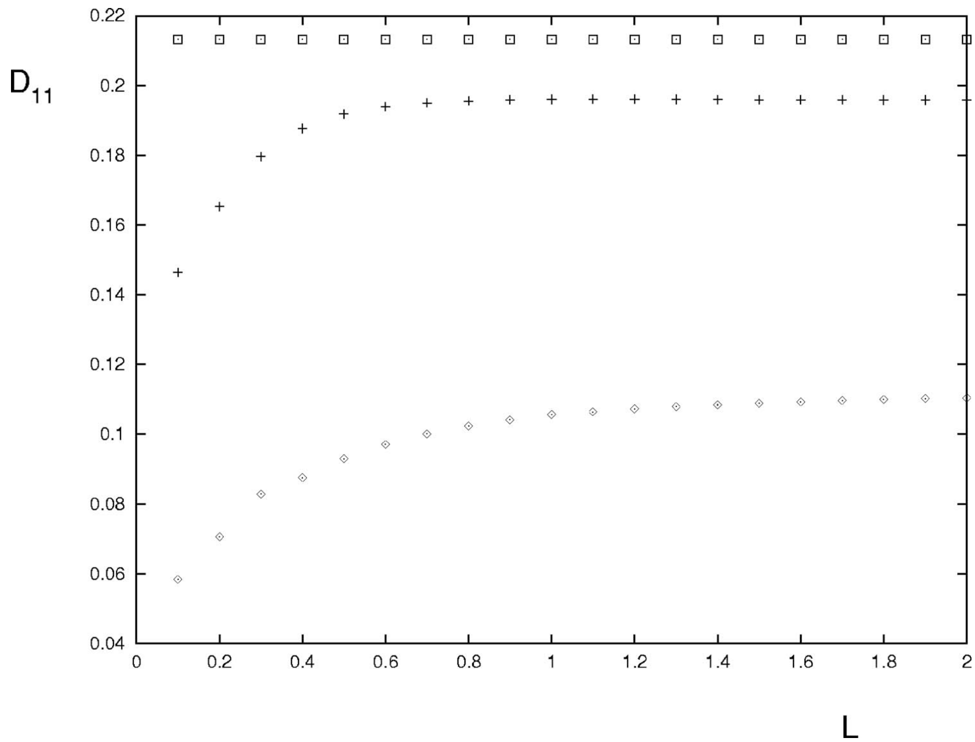

FIG. 7. The translational diffusion coefficient in the x direction, D_{11}, vs the channel width, L, in microns for an ellipsoidal particle for different dipole moments. The parameters here are $\bar{D}=0.112\ \mu m^2\ s^{-1}$, $\Delta D=0.203\ \mu m^2\ s^{-1}$, and $\theta_0=\phi=0$ with (i) zero dipole moment $\alpha=0$ (diamonds), (ii) a significant moment $\alpha=10$ (crosses), and (iii) infinitely strong dipole moment $\alpha=\infty$, that is no rotational motion (squares). The value of the diffusion coefficient for the latter case ($D_{11}=0.213$) agrees well with the theoretical prediction ($D_{11}=0.214$) given by Eq. (46). The percentage change in the diffusion coefficient as the channel width is decreased from $L=2$ to $L=0.1$ is 47% for zero moment, 25% for the significant moment, and 0% for an infinitely strong moment.

$$\frac{\partial y(t)}{\partial t} = -ky\left(\bar{\Gamma} - \frac{1}{2}\Delta\Gamma\cos 2\phi\right) + \eta_2(t), \tag{45}$$

where ϕ is a constant. Analysis similar to that in previous sections shows that the average mean square displacement in the y direction is independent of particle shape and the translational diffusion coefficient in the x direction is given by

$$D_{11} = \bar{D} + \frac{1}{2}\Delta D\cos(2\phi) - \frac{\Delta D^2\sin^2(2\phi)}{4\left[\bar{D} - \frac{1}{2}\Delta D\cos(2\phi)\right]}. \tag{46}$$

This result holds only for $k>0$. Hence if the particle cannot perform rotational Brownian motion because of perfect angular alignment then the diffusion coefficient in the channel becomes independent of the channel width, L. Thus we expect the dependence of D_{11} on L as predicted by Eq. (43) to be apparent only for low to moderate orientational alignment, in which the particle experiences significant stochastic angular displacements about the alignment angle ϕ. These results are verified by simulation, as shown in Fig. 7.

V. CONCLUSION

In this article we have explored the effects of shape asymmetry on the dynamics of particle movement. In particular, we studied the short- and long-time Brownian motion of an ellipsoidal particle in a potential field in the case when movement is restricted to a plane.

It is well known that for short times the behavior is anisotropic but becomes isotropic for longer times. It is thus usually assumed that for practical purposes the short-time behavior can be neglected and the movement of an asymmetric particle can be described by the Langevin equations for a point particle with an isotropic translational diffusion coefficient given by the average of the diffusion coefficients along the major axis of the ellipsoidal particle. We have shown that these assumptions are only valid for a free particle in high dimensions but incorrect for a particle in a potential field in two dimensions. The two main results of our study are as follows.

(i) The translational diffusion coefficients of an asymmetrical free particle and one of similar shape in a potential field are not the same for all times. Crucially, these differences exist even in the limit of long times. The magnitude of these differences is zero for a perfectly spherical particle and increases proportionately with asymmetry. This has an important consequence for the Brownian dynamics simulation of rigid asymmetrical particles in external fields.[26] In such a case it is not correct to model the long-time movement using the classical Langevin equations of a point particle in which the isotropic diffusion coefficient is a constant independent of the magnitude of the applied external forces. Another example in which the renormalization of the long-time translational diffusion coefficients may have important implications is in the extraction of single-molecule data from FCS experiments which involve electrokinetic flow in restrictive geometries.

(ii) For significantly asymmetric particles, transients in the translational diffusion coefficients are long lived (of the order of seconds) in two dimensions. This suggests that the long-time isotropic Langevin equations may not provide a realistic dynamical description of reaction-diffusion processes in dimensionally restricted geometries since the transient time may be significantly longer than the time for a reaction to finish. For a significantly asymmetric particle, we found that the qualitative dependence of the translational diffusion coefficients with time depends strongly on the magnitude of external forces, e.g., for a free particle, the dependence is always monotonic whereas under the application of constant forces the time dependence can suffer undulations. This has important implications for diffusion-limited reactions in two- or quasi-two-dimensions since in such a case the diffusion coefficients modulate the reaction rates and thus indirectly influence the kinetics. We also find that the non-Gaussian character of the particle probability distributions typical of the transient time regimes can be significantly enhanced by external forces such as those stemming from electric fields or confining potentials.

The phenomena elucidated by our study suggest that there exists a strong relationship between molecular asymmetry and the kinetics of diffusion-limited reactions occurring on surfaces, membranes, or in crowded environments such as that found inside cells. Also the fact that the long-time translational diffusion coefficients of asymmetric particles in potential fields encode information about the shape of the particles (unlike the free case) opens the possibility to engineer special experimental setups to measure particle anisotropy, of interest in the fields of nanomaterials and biology. We will explore both these topics in depth in a future article.[27]

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[1] P. Hanggi and F. Marchesoni, Chaos **15**, 026101 (2005).
[2] S. Chandrasekhar, Rev. Mod. Phys. **15**, 2 (1943).
[3] C. W. Gardiner, *Handbook of Stochastic Methods*, 2nd ed. (Springer, Berlin, 1995).
[4] P. Mazur and I. Oppenheim, Physica (Amsterdam) **50**, 241 (1970).
[5] Y. Han, A. M. Alsayed, M. Nobili, J. Zhang, T. C. Lubensky, and A. G. Yodh, Science **314**, 626 (2006).
[6] S. Prager, J. Chem. Phys. **23**, 2404 (1955).
[7] C. Ribrault, A. Triller, and K. Sekimoto, Phys. Rev. E **75**, 021112 (2007).
[8] F. Perrin, J. Phys. Radium **5**, 497 (1934).
[9] F. Perrin, J. Phys. Radium **7**, 1 (1936).
[10] W. T. Coffey, Y. P. Kalmykov, and J. T. Waldron, *The Langevin Equation with Applications to Stochastic Problems in Physics, Chemistry and Electrical Engineering* (World Scientific, Singapore, 2004).
[11] A. J. Moreno and W. Kob, J. Chem. Phys. **121**, 380 (2004).
[12] A. J. Moreno and W. Kob, Europhys. Lett. **67**, 820 (2004).
[13] S. Ravichandran and B. Bagchi, J. Chem. Phys. **111**, 7505 (1999).
[14] R. Vasanthi, S. Ravichandran, and B. Bagchi, J. Chem. Phys. **114**, 7989 (2001).
[15] G. W. Slater, P. Mayer, and P. D. Grossman, Electrophoresis **16**, 75 (1995).
[16] M. Foquet, J. Korlach, W. R. Zipfel, W. W. Webb, and H. G. Craighead, Anal. Chem. **76**, 1618 (2004).
[17] M. L. Plenert and J. B. Shear, Proc. Natl. Acad. Sci. U.S.A. **100**, 3853 (2003).
[18] P. Hanggi, F. Marchesoni, and F. Nori, Ann. Phys. **14**, 51 (2005).
[19] R. Landauer, J. Stat. Phys. **53**, 233 (1988).
[20] P. Reimann, R. Bartussek, R. Haussler, and P. Hanggi, Phys. Lett. A **215**, 26 (1996).
[21] D. J. Bicout and M. J. Field, J. Phys. Chem. **100**, 2489 (1996).
[22] S. Schnell and T. E. Turner, Prog. Biophys. Mol. Biol. **85**, 235 (2004).
[23] S. B. Zimmerman and A. P. Minton, Annu. Rev. Biophys. Biomol. Struct. **22**, 27 (1993).
[24] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Kluwer, Netherlands, 1991).
[25] H. Berry, Biophys. J. **83**, 1891 (2002).
[26] M. X. Fernandes and J. G. de la Torre, Biophys. J. **83**, 3039 (2002).
[27] R. Grima, B. Cipriany, H. G. Craighead, and S. N. Yaliraki (unpublished).