

Symmetry Properties of the Electrophoretic Motion of Patterned Colloidal Particles

Didier Long* and Armand Ajdari

Laboratoire de Physico-Chimie Théorique, CNRS ESA 7083, ESPCI, 10 rue Vauquelin, F-75231 Paris Cedex 05, France

(Received 17 February 1998)

In sedimentation experiments at low Reynolds numbers there are general restrictions for the motion of particles. We show that some of them do not apply for electrophoresis in ionic solutions. In particular, we construct specific examples of objects with patterned shape and surface charge, that (1) undergo a permanent motion of rotation without translation, or (2) move perpendicularly to the applied electric field, whatever the direction of the latter. This demonstrates the broad spectrum of possible electrically induced motions, and could guide the design of microengines and the understanding of biological systems. [S0031-9007(98)06760-X]

PACS numbers: 82.45.+z, 07.10.Cm, 82.65.Fr, 83.50.Pk

Although used in a large number of practical situations, electrophoresis of colloidal particles in solution, i.e., setting them into motion by applying an electric field, is not simple to describe analytically [1–3]. In particular, studies throughout the century have pointed out basic differences with sedimentation or other classical hydrodynamic situations: The electric field pulls not only on the particle but also on the counterion cloud surrounding it, which results in flows very different from the usual Stokes description. As a consequence, surprising behaviors have been predicted: A neutral object can be set into motion [4], the electrophoretic mobility of an object can change sign as the field is increased [5], and an object can be set into motion perpendicularly to the electric field if the latter is applied along a specific direction [6]. In the same spirit we show in this Letter that, due to the counterions, the dynamic response of charged particles to a constant and homogeneous applied electric field does not obey the general symmetry rules of field-induced motion at low Reynolds number hydrodynamics, at work, e.g., in sedimentation experiments or in electrophoresis in the absence of counterions, with an emphasis on the case of chiral particles.

Let us recall the usual hydrodynamic picture: a solid particle submitted to an external force \mathbf{F} and an external torque \mathbf{T} acquires translational and rotational velocities \mathbf{V} and $\mathbf{\Omega}$ [7]. It is possible to choose a particular point of reference in the frame of the solid such that the dynamic law reads

$$\mathbf{V} = \mathbf{M}\mathbf{F} + \mathbf{C}\mathbf{T}, \quad (1)$$

$$\mathbf{\Omega} = \mathbf{C}\mathbf{F} + \mathbf{R}\mathbf{T}, \quad (2)$$

where \mathbf{M} , \mathbf{R} are positive definite symmetric tensors and \mathbf{C} is a symmetric pseudotensor [7–9] which is nonzero only for geometrically chiral objects. These tensors depend only on the shape and size of the particle. In classical situations where motion is induced by an external field \mathbf{E}_0 (for sedimentation $\mathbf{E}_0 = \mathbf{g}$, for electrophoresis in salt-free solutions \mathbf{E}_0 is the applied electric field), one has

$$\mathbf{F} = \mathbf{Q}\mathbf{E}_0; \quad \mathbf{T} = \mathbf{P}\mathbf{E}_0, \quad (3)$$

where \mathbf{Q} is a scalar and thus symmetric tensor and \mathbf{P} is an antisymmetric pseudotensor [10].

We want to contrast this with electrophoresis in ionic solutions (in the presence of salt), focusing for simplicity on the case of particles with thin Debye layers and weak surface potentials. Then the deformation of the Debye layer due to the application of a weak electric field is negligible [2]. Teubner [10] has shown that in this limit the motion of the particle can still be described by Eqs. (1)–(3), the tensors \mathbf{R} , \mathbf{M} , \mathbf{C} being the same as in the case of sedimentation, \mathbf{Q} and \mathbf{P} being, respectively, an effective tensor and an effective pseudotensor that take account of the effect of the backflow due to the presence of the counterions. The latter differ thus from the total electric charge and from the electric dipole of the particle. This leads to new possibilities for the symmetry of the resulting motion: Indeed, we provide in this Letter specific examples where \mathbf{Q} is antisymmetric and others where \mathbf{P} is symmetric.

Let us discuss first the case of electrophoresis in salt free solutions. Then $\mathbf{Q} = Q\mathbf{I}_d$ and $\mathbf{P}\mathbf{E}_0 = \mathbf{p} \times \mathbf{E}_0$ with Q and \mathbf{p} the total charge and the electric dipole moment of the particle [10]. The torque is always perpendicular to the applied electric field while the force is always colinear to the electric field. Take a particle with zero dipole moment $\mathbf{p} = \mathbf{0}$. Its velocity is $\mathbf{V} = \mathbf{M}\mathbf{Q}\mathbf{E}_0$. As \mathbf{M} is positive definite, the velocity has always a nonzero component along the direction of the electric field, of the same sign as Q . In particular, it is impossible for such a particle to move perpendicularly to the applied field. The angular velocity is $\mathbf{\Omega} = \mathbf{C}\mathbf{Q}\mathbf{E}_0 = \mathbf{C}\mathbf{M}^{-1}\mathbf{V}$. The tensor \mathbf{C} couples translation and rotation: Particles with nonzero \mathbf{C} tensor can undergo a permanent (but not necessarily uniform) motion of rotation, provided they have also a nonzero electrophoretic mobility $\mathbf{M}\mathbf{Q}$, i.e., a nonzero total charge Q . For example, if \mathbf{M} is isotropic and if the electric field is applied along a principal direction of the tensor \mathbf{C} , the particle is set into a permanent and uniform motion of translation and rotation. If \mathbf{C} has two identical eigenvalues and if the electric field is applied at some angle with the third principal axis of \mathbf{C} , the particle undergoes permanent translation and rotation, with a precession around the third axis. The

general case with three different eigenvalues leads to a very complicated motion.

Consider now a particle of zero charge $Q = 0$ and nonzero dipole moment. Then $\mathbf{\Omega} = \mathbf{R}(\mathbf{p} \times \mathbf{E}_0)$. As the tensor \mathbf{R} is positive definite, the angular velocity can never be colinear to the applied field (it has always a nonzero component along the direction of $\mathbf{p} \times \mathbf{E}_0$, unless the electric field is aligned with the dipole and the angular velocity is zero). One can show that $\frac{1}{2} \frac{d}{dt} (\mathbf{p} \times \mathbf{E}_0)^2 = -(\mathbf{p} \cdot \mathbf{E}_0)(\mathbf{p} \times \mathbf{E}_0) \cdot \mathbf{R}(\mathbf{p} \times \mathbf{E}_0)$: As the tensor \mathbf{R} is positive definite, the effect of the rotation is here to align the dipole along the external electric field and thus to reduce its very cause. Once the dipole is aligned with the electric field, motion ceases: \mathbf{R} determines the rate at which the particle reaches "orientational" equilibrium. For a steady rotation to occur, the torque which results from the application of the external field must remain essentially invariant under the resulting rotation, which cannot be the case here.

Thus we recall that, in salt-free electrophoresis conditions, as consequences of general properties of the tensors \mathbf{M} , \mathbf{C} , and \mathbf{R} , (1) the only possibility for a particle to experience a permanent motion of rotation is to be hydrodynamically chiral ($\mathbf{C} \neq \mathbf{0}$) and to have a nonzero electrophoretic mobility (i.e., a nonzero total charge) so as to translate, (2) a particle cannot move perpendicularly to the applied field, whatever the direction of the latter.

Electrophoresis in salty solutions is not limited by these restrictions as we will show. We push this point to its extreme by constructing two clear examples: *Object A* undergoes a uniform motion of rotation around the applied field *without translating*, *object B* translates normally to the applied field, *without rotating for any direction of the latter but one*.

What strategy can be used to reach this goal? In principle, one may want to play with the shape and the charge distribution on the particle. It is well known that in free flow electrophoresis conditions, in the present limit of small Debye length, any uniformly charged and insulating particle undergoes a permanent motion of translation along the electric field, without any rotation, even if it has a chiral (e.g., screwlike) shape [10,11]. In such conditions, using an object of chiral shape is thus not sufficient to obtain a permanent motion of rotation.

Consider now a spherical particle with a single punctual charge located at \mathbf{r}_0 on its surface and apply an external field \mathbf{E}_0 . Then, by symmetry, the vector \mathbf{F} is a linear combination of \mathbf{E}_0 and $(\mathbf{E}_0 \cdot \mathbf{r}_0)\mathbf{r}_0$ which are the only vectors linear in the applied field \mathbf{E}_0 that can be built in this problem, and the pseudovector \mathbf{T} is proportional to $\mathbf{r}_0 \times \mathbf{E}_0$, which is the only pseudovector linear in the applied field. Then, by linear superposition, for any charge distribution on a sphere, the tensor \mathbf{Q} is symmetric and the pseudotensor \mathbf{P} is antisymmetric (note that this actually holds for any ionic strength). As a consequence, a spherical particle cannot systematically move normally to the applied field ($\mathbf{V} = M \cdot \mathbf{Q} \cdot \mathbf{E}_0$ for

a sphere). Note that—contrarily to the salt-free case—the eigenvalues of \mathbf{Q} can be of different signs, which allows the velocity to be normal to the applied field *for particular directions of the latter* (examples can be found in [3,6]). Also a spherical particle cannot undergo a permanent motion of rotation: Its only motion of rotation in electrophoresis corresponds to the alignment of the dipole associated with \mathbf{P} along the electric field—very similar to the salt-free case. Again, examples have been provided in [3,6] of objects rotating transiently towards equilibrium. Similar symmetry arguments prove that an axisymmetric particle cannot rotate permanently around its symmetry axis. Thus, to design rotating particles, it is not sufficient to pattern a symmetric object with a well-chosen (chiral or not) surface charge distribution. Consequently, we construct examples where *both shape and charge distribution are patterned*.

As we turn to explicit calculations, we recall the usual recipe in the present limit of small Debye length and small surface potentials (see the review of Anderson [3] for details). Applying an electric field \mathbf{E}_0 induces an electroosmotic slip velocity at the surface of the particle: $\mathbf{U} = -\sigma\kappa^{-1}\mathbf{E}/\eta$ [1,3] where η and κ^{-1} are, respectively, the viscosity and the Debye length of the solution, σ is the local surface charge density on the particle, and \mathbf{E} is the local electric field at the surface of the insulating particle, which can differ from \mathbf{E}_0 due to the disturbance caused by the particle itself. The flow around the object (in a reference frame attached to the object) is then obtained by solving the Stokes equation with no body force, with the slip velocity \mathbf{U} as boundary condition on the object's surface [1,3]. The flow at a distance \mathbf{r} from the object tends to the limiting value $\mathbf{v}(\mathbf{r}) \rightarrow -\mathbf{V} - \mathbf{\Omega} \times \mathbf{r}$, which allows one to determine \mathbf{V} and $\mathbf{\Omega}$. This procedure is now applied to various objects.

Consider first an infinitely long charged, insulating cylinder of radius a , decorated with a nonuniform "helical" surface charge density $\sigma(z, \theta) = \sigma_0 \cos(m\theta + qz)$. O_z is the axis of the cylinder, and we use the corresponding cylindrical coordinates (r, θ, z) . An electric field \mathbf{E}_0 is applied along O_z . The electro-osmotic flow around this cylinder is obtained by solving the following Stokes equations: $\eta\Delta\mathbf{U} - \mathbf{grad}p = 0$, $\text{div}\mathbf{U} = 0$, $\mathbf{U}(r = a) = \mathbf{U}_0 \cos(m\theta + qz)$, where p and \mathbf{U} are the pressure and velocity fields, respectively, and $\mathbf{U}_0 = \sigma_0\kappa^{-1}\mathbf{E}_0/\eta$. From the solution [12] in the reference frame of the object, it is clear that no net flow is created at infinity: $\mathbf{V} = \mathbf{0}$ and $\mathbf{\Omega} = \mathbf{0}$, as expected from the symmetry considerations stated above. Therefore, let us couple to the charge modulation a slight modulation of the radius of the cylinder: $a(z, \theta) = a[1 + \alpha \cos(n\theta + kz + \phi)]$ where α is a small number and ϕ a phase shift. The electroosmosis flow can be calculated to first order in α . At this order, the local electric field is $\mathbf{E} = -\nabla\Phi$ with $\Phi = -E_0z - 2a\alpha E_0 \frac{K_n(kr)}{K_{n-1}(ka) + K_{n+1}(ka)} \sin(kz + n\theta + \phi)$, where K_n are modified Bessel functions [13].

The first order correction to the flow is obtained by solving the Stokes problem, with slip velocity $\delta\mathbf{U}$ on the unperturbed boundary $a(z) = a$, where $\delta\mathbf{U}$ is the difference between the true boundary condition $\mathbf{U} = -\sigma\kappa^{-1}\eta^{-1}\mathbf{E}$ and the value the *zeroth* order solution takes on the actual boundary of the cylinder. $\delta\mathbf{U}$ contains terms proportional to $\cos[(m+n)\theta + (q+k)z + \phi] + \cos[(m-n)\theta + (q-k)z - \phi]$ and

$q\{\sin[(m+n)\theta + (q+k)z + \phi] + \sin[(m-n)\theta + (q-k)z - \phi]\} + k\{\sin[(m+n)\theta + (q+k)z + \phi] - \sin[(m-n)\theta + (q-k)z - \phi]\}$, respectively. Only the first term can generate a net flow at infinity, and then only for $m = n$ and $q = k$ or $m = -n$ and $q = -k$. This term is then proportional to $\cos\phi$. The boundary conditions for this part of the first order correction are then $u_\theta^{(1)}(r = a) = \alpha C_\theta U_0$, $u_z^{(1)}(r = a) = \alpha C_z U_0$, $u_r^{(1)}(r = a) = 0$, with [12]

$$C_\theta = -\cos\phi \left[\frac{\gamma(ka)}{2} k^2 a^2 \left(\frac{K_n^2(ka)}{K_{n+1}(ka)} - \frac{K_n^2(ka)}{K_{n-1}(ka)} + \frac{2nK_n(ka)}{ka} \right) - \frac{nK_n(ka)}{K_{n-1}(ka) + K_{n+1}(ka)} \right], \quad (4)$$

$$C_z = \cos\phi \left[\frac{ka}{4} \frac{K_{n-1}(ka) + K_{n+1}(ka)}{K_n(ka)} - \gamma(ka) k^2 a^2 \left(\frac{K_{n-1}(ka)K_{n+1}(ka)}{K_n(ka)} - K_n(ka) \right) + \frac{kaK_n(ka)}{K_{n-1}(ka) + K_{n+1}(ka)} \right], \quad (5)$$

and $\gamma(ka)$ is defined by

$$\gamma(ka)^{-1}(K_{n-1}K_{n+1}) = ka[K_{n+1}^2K_{n-1} + K_{n-1}^2K_{n+1} - K_n^2K_{n+1} - K_n^2K_{n-1}] - 4K_{n-1}K_nK_{n+1}. \quad (6)$$

The corresponding flow and pressure fields in the solution are then given by $u_\theta^{(1)}(r, z) = \alpha C_\theta U_0 r/a$, $u_z^{(1)}(r, z) = \alpha C_z U_0$, $u_r^{(1)}(r, z) = 0$, $p^{(1)}(r, z) = 0$. Thus in the reference of the lab, the object translates at $\mathbf{V} = -\alpha C_z U_0 \mathbf{e}_z$ and rotates with $\mathbf{\Omega} = -\alpha(C_\theta/a)U_0 \mathbf{e}_z$. C_θ is an increasing function of ka , with the two limiting behaviors: $C_\theta(ka) \approx ka \cos\phi$ for $ka \ll 1$, and $C_\theta(ka) \approx n \cos\phi$ for $ka \gg 1$ [12]. If one considers an electric field of 10^3Vm^{-1} , an electrophoretic mobility $\sigma\kappa^{-1}/\eta$ of $10^{-8} \text{ms}^{-1}/(\text{Vm}^{-1})$, which is typical of the high salt concentration regime [2], and $\alpha C_\theta \approx 0.1$, one obtains $\Omega \cdot a \approx 10^{-6} \text{ms}^{-1}$, i.e., an angular velocity of 10 rad/s for a cylinder of radius 0.1 μm .

Thus, we have solved the electrohydrodynamic equations (in the limits described above), for cylinders with any shape and charge modulations, respectively, of the form $\sigma = \sigma_0 \cos(qz + m\theta)$ and $a(z, \theta) = a_0[1 + \alpha \cos(kz + n\theta + \phi)]$, at first order in α . The angular velocity, as well as the electrophoretic mobility, are found to be nonzero only when these charge and shape modulations are correlated, i.e., $k = q$ and $n = m$ or $n = -m$ and $k = -q$. As the electrohydrodynamic equations are linear, we can calculate, in the limit of small shape modulations $\alpha(z, \theta)$ (i.e., at linear order in α), the angular velocity and the electrophoretic mobility of cylinders for any shape and charge modulation by a simple superposition.

Let us apply this superposition principle. Take the modified cylinder with surface modulation $\delta a_1(z) = a\alpha \cos(n\theta + kz + \phi)$ and charge modulation $\sigma_0 \cos(n\theta + kz)$. Superimpose to its shape modulation one with opposite chirality $\delta a_2(z) = a\alpha \cos(n\theta - kz)$. The electrophoretic properties are not modified as this additional shape modulation is not correlated to the charge modulation on the cylinder, i.e., $\sigma_0 \cos(n\theta + kz)$. The resulting object has now a nonchiral shape. Eventually

add to the existing modulated charge density a uniform charge density $\sigma' = -\alpha C_z \sigma_0$. This cancels the translation along Oz without modifying the rotation around this axis. We thus have an object with a nonchiral shape set in rotation without any translation.

As a last cylindrical example take an insulating cylinder having a nonuniform charge density $\sigma(z, \theta) = \sigma_0 \cos(n\theta)$ (with $n > 2$) and apply an electric field normal to the axis of symmetry, in the $\theta = 0$ direction (Fig. 2). By symmetry this object does not move. Let us now couple the charge modulation to a modulation of the radius $a(\theta) = a[1 + \alpha \cos(n\theta + \phi)]$, where ϕ is a phase shift. Consider the case $\phi = -\pi/2$ as on Fig. 2. An argument of symmetry prevents the motion in the direction of the electric field, while the symmetry allows in principle for a motion normal to the field. Solving the Laplace and Stokes equations to first order in α for any ϕ [12], we find that the free electrophoretic velocity of the cylinder is given by $v_x = -\alpha U_0 \frac{(3n-3)}{2} \cos\phi$ and $v_y = -\frac{1}{2}\alpha U_0 \sin\phi$. For $\phi = -\pi/2$, one has indeed $v_x = 0$ and $v_y = \frac{1}{2}\alpha U_0$: The velocity of the particle $\mathbf{V} = \mathbf{V}(\mathbf{E}_0)$ is nonzero and normal to the applied

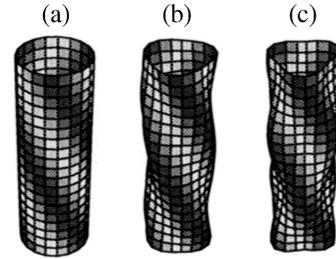


FIG. 1. Cylinders: (a) With a helical charge modulation (darker areas are, e.g., positively charged); (b) same as previous with matching shape modulation; (c) same as previous with additional and chirally symmetric shape modulation. Only (b) is hydrodynamically chiral.

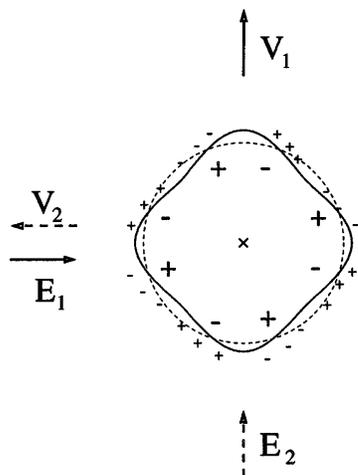


FIG. 2. Cylinder with shape modulation $a(\theta) = a[1 + \alpha \cos(n\theta)]$ and charge modulation $\sigma(z, \theta) = \sigma_0 \cos(n\theta + \pi/2)$ (here $n = 4$ and $\sigma_0 < 0$). Whatever the direction of an applied external electric field (normal to the cylinder axis), the cylinder moves in the direction normal to the field.

field. The problem we consider is invariant under the rotation $\rho_{2\pi/n}$ of angle $2\pi/n$ (with $n > 2$) around O_z , i.e., one has $\mathbf{V}(\rho_{2\pi/n}(\mathbf{E}_0)) = \rho_{2\pi/n}(\mathbf{V}(\mathbf{E}_0))$. As $n > 2$, the vectors $\rho_{2\pi/n}(\mathbf{E}_0)$ form a complete set of vectors in the plane normal to O_z . By linear superposition and as the mobility is a second rank tensor, we deduce that the problem is invariant by rotation in the plane, i.e., one has $\mathbf{V} = \mathbf{V}(\rho_\theta(\mathbf{E}_0)) = \rho_\theta(\mathbf{V}(\mathbf{E}_0))$ for any rotation ρ_θ around O_z . This latter property can be proven in more details very similarly as, say, one shows that the heat diffusion tensor of crystals with cubic lattice symmetry is a scalar [15]. As the mobility of an object along O_z is zero, the tensor which relates the applied field to the velocity is antisymmetric: This particle moves normally to any applied external field (but for the specific case of a z -oriented field which induces no motion whatsoever). More precisely, the velocity can be written $\mathbf{V} = M\mathbf{Q}\mathbf{E}_0 = M\mathbf{q} \times \mathbf{E}_0$, where \mathbf{Q} is antisymmetric and $M = M_{xx} = M_{yy}$ is the Stokes mobility in the plane of the modified cylinder (which is a scalar as the modified cylinder is invariant by rotations of $2\pi/n$ with $n > 2$). \mathbf{q} is the pseudovector associated to the antisymmetric tensor \mathbf{Q} , and is oriented in the z direction.

The strategy of coupling charge and shape modulations can, of course, be applied to other particles, such as spherical ones. Though the geometry is different from that studied in this paper, one can, for example, expect that a sphere, modified along a given direction in the same way as our first cylindrical example, can indeed rotate around this privileged direction, as such property for the cylinder is the result of local effects.

In conclusion, electrophoresis in salty solutions displays a wide variety of features which are absent in sedimentation. To take advantage of this richness an appropriate coupling between shape and charge modulations

is necessary. Patterning surfaces along these lines is in principle within the reach of current microtechnology, and could lead to various micropumps or micromotors [14]. Also it may be useful to bear in mind the principles outlined here when analyzing the dynamics and motion of biological systems where (a) due to ionic pump activity, electric currents are generated and (b) patterns are present due to the self-organization of various molecular entities. Indeed, electro-osmotic flows have already been invoked as possible sources of cellular motion, growth, or organization [16–18]. They could also be relevant for understanding the mechanisms at work in some biological rotors, such as those studied in [19].

Our interest in these problems originated from discussions with Jacques Prost, to whom we are deeply indebted. We acknowledge useful conversations with Howard A. Stone.

*Author to whom correspondence should be addressed.

Present address: University of Minnesota, 421 Washington Avenue S.E., Minneapolis, MN 55455.

Email address: long@cems.umn.edu

- [1] V. G. Levich, *Physicochemical Hydrodynamics* (Prentice Hall, Englewood Cliffs, New Jersey, 1962).
- [2] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).
- [3] J. L. Anderson, *Annu. Rev. Fluid Mech.* **21**, 61–99 (1989).
- [4] J. L. Anderson, *J. Colloid Interface Sci.* **105**, 45–54 (1985); M. C. Fair and J. L. Anderson, *ibid.* **127**, 388–400 (1989).
- [5] D. Long and A. Ajdari, *Electrophoresis* **17**, 1161–1166 (1996).
- [6] Y. Solomentsev and J. L. Anderson, *J. Fluid Mech.* **279**, 197–215 (1994).
- [7] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Martinus Nijhoff Publishers, The Hague, 1983).
- [8] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, New York, 1989).
- [9] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1993).
- [10] M. Teubner, *J. Chem. Phys.* **76**, 5564–5573 (1982).
- [11] F. A. Morrison, *J. Colloid Interface Sci.* **34**, 210–214 (1970).
- [12] D. Long (to be published).
- [13] M. Abramovitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover Publications, Inc., New York, 1965).
- [14] A. Ajdari, *Phys. Rev. Lett.* **75**, 755–758 (1995); A. Ajdari, *Phys. Rev. E* **53**, 4496–5005 (1996).
- [15] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, New York, 1986).
- [16] P. E. Lammert, R. Bruinsma, and J. Prost, *J. Theor. Biol.* **178**, 387–391 (1996).
- [17] L. Limozin, B. Denet, and P. Pelcé, *Phys. Rev. Lett.* **78**, 4881–4884 (1997).
- [18] M. Leonetti and E. Dubois-Violette, *Europhys. Lett.* **37**, 231–235 (1997).
- [19] R. M. Berry, *Biophys. J.* **64**, 961–973 (1993).