Electrokinetic motion of polarizable particles

Synonyms

Dielectrophoresis, induced-charge electrophoresis, electrophoresis of the second kind.

Definition

The electrokinetic motion of polarizable particles results from electro-osmotic flow (induced-charge electrophoresis) of the first of second kind, in addition to electrostatic forces (dielectrophoresis).

Overview

The classical theory of electrophoresis (particle motion due to electro-osmotic flow) assumes that surface charge remains fixed at its equilibrium value, when electric fields (or other perturbations) are applied (1). For thin electrical double layers, the assumption of "fixed charge" implies that particles of uniform composition all have the same electrophoretic mobility b (velocity/field)

$$b = \frac{U}{E} = \frac{\varepsilon\zeta}{\eta} \qquad [1]$$

regardless of their sizes and shapes. This naturally poses problems for electrophoretic separation and has led to the use of capillaries or gels to exploit additional effects.

In equation [1], the "zeta potential" ζ can be viewed as simply expressing the mobility in units of voltage, after factoring out the permittivity ε and viscosity η of the bulk solution. In Smoluchowski's original theory, still widely a century later, the zeta potential is equal to the voltage ψ of the "slip plane" (atomically close to the surface) relative to the nearby bulk solution (just outside the diffuse part of the double layer), and, through the double-layer capacitance, it also measures the surface charge. The assumption of fixed charge thus becomes equivalent to that of constant zeta potential, and the mobility [1] reduces to a coefficient of linear response, $U \propto E$.

Since all materials are polarizable to some degree, the surface charge is generally not fixed. This leads to a broad class of nonlinear electrokinetic phenomena, where bulk electric fields interact with *induced* diffuse charge in solution to produce nonlinear electrophoretic motion, $\vec{U} = \vec{f}(\vec{E})$. In electrolytes, such effects of induced-charge electrophoresis (ICEP) occur in addition to the purely electrostatic effect of dielectrophoresis (DEP) in low-frequency AC fields (< 100 kHz), where there is enough time for diffuse-charge relaxation around the particle within each period. ICEP is a complex phenomenon, which can lead not only to nonlinear mobility (in the field direction) but also to rotation and motion in arbitrary directions, even in uniform fields.

At still lower frequencies (< 1 kHz), the passage of current through a particle, either by Faradaic reactions, surface conduction, or selective ionic conduction, can produce bulk salt concentration gradients and coupled effects of diffusiophoresis. If a superlimiting current is reached (typically in the DC limit), then electrophoresis of the second kind can occur, driven

by extended space charge. Understanding all of these effects and exploiting them in microfluidic devices is an active field of research.

Basic Methodology

The theoretical description of nonlinear electrokinetic phenomena is challenging and not yet fully developed. In most of our examples below, we focus on the motion of an ideally polarizable particle, which maintains uniform potential $\varphi_0(t)$ and constant total charge Q without passing any direct current; we also neglect surface conduction and specific adsorption of ions. Under these conditions, induced-charge electro-osmotic flows are strongest, and a general mathematical framework has been developed (2-5) for the "weakly nonlinear" limit of thin double layers where the bulk salt concentration (and conductivity σ_b) remains nearly constant.

The calculation goes as follows for the motion of an isolated particle of arbitrary shape, subjected to a non-uniform, time-dependent electric field at infinity for $t > 0$. The bulk electrostatic potential satisfies Laplace's equation, $\nabla^2 \varphi = 0$, subject to the far-field boundary condition,

$$\varphi \sim -\vec{E}_b \cdot \vec{r} - \frac{1}{2}\vec{r} \cdot \vec{\vec{G}}_b \cdot \vec{r} - \ldots \quad \text{as } r \to \infty \qquad [2]$$

where $\vec{E}_b$ is the uniform component of the background field, $\vec{\vec{G}}_b$ is the field-gradient tensor, etc. (Note that the constant "background voltage" has been set to zero.) The "RC" boundary condition is applied on the particle, just outside the double layer,

$$C(\psi)\frac{d\psi}{dt} = n \cdot (\sigma_b \nabla \phi) \qquad [3]$$

where $C(\psi)$ is the differential capacitance of the diffuse part of the double layer, as a function of its voltage drop

$$\psi(\vec{r},t) = \frac{\varphi_0(t) - \varphi(\vec{r},t)}{1+\delta} \qquad [4]$$

where δ is a parameter controlling how much of the total double-layer voltage ends up across the compact layer (the ratio of the diffuse-layer and compact-layer capacitances at the point of zero charge). The particle's potential $\varphi_0(t)$ relative to the background is set by the constraint of constant total charge (2,4),

$$Q = \oint \left(\int_0^{\psi_0} C(\psi')d\psi' \right) dA = \oint \left(\int_0^{\psi(\vec{r},t)} C(\psi')d\psi' \right) dA \qquad [5]$$

This condition simplifies considerably if $C \approx$ constant, e.g. for small voltages $|\psi| << kT/e$ around the point of zero charge: The diffuse-layer voltage (and zeta potential) then redistributes without changing its surface average (3,5)

$$\oint \psi(\vec{r},t)dA \Big/ \oint dA \approx \psi_0 \qquad [6]$$

but it is important to remember that this assumption breaks down for large induced voltages and/or highly charged particles, since generally $dC/d\psi \neq 0$. (See below.)

In the weakly nonlinear regime, the electrochemical and fluid mechanical problems decouple, except that the former provides the slip velocity driving the latter. The bulk fluid velocity satisfies the Stokes equations of viscous flow,

$$\frac{\partial \vec{u}}{\partial t} = -\nabla p + \eta \nabla^2 \vec{u} \quad \text{and} \quad \nabla \cdot \vec{u} = 0 \qquad [7]$$

(keeping the unsteady term for time-dependent applied fields) subject to vanishing velocity at infinity. The boundary condition on the particle surface (just outside the double layer)

$$\vec{u} = \vec{u}_s + \vec{U} + \vec{r} \times \vec{\Omega} \qquad [8]$$

describes electro-osmotic slip in the moving frame translating and rotating with the particle. Assuming constant permittivity and viscosity, the slip velocity is given by Smoluchowski's formula,

$$u_s = \frac{\varepsilon \psi}{\eta} \nabla_{\|} \varphi \qquad [9]$$

where $\psi(\vec{r},t)$ acts as the local zeta potential. Finally, as in classical electrophoresis and dielectrophoresis (effects which are both included here, along with ICEP), the translational and rotational velocities, $\vec{U}$ and $\vec{\Omega}$, are determined by the conditions of vanishing total force and torque, respectively,

$$\oint (\hat{n} \cdot \vec{\sigma}) dA = \oint r \times (\hat{n} \cdot \vec{\sigma}) dA = 0 \qquad [10]$$

since viscous dissipation suppresses acceleration. In [10], the stress tensor includes viscous and electrostatic contributions

$$\sigma_{ij} = -p\delta_{ij} + \eta(\partial_i u_j + \partial_j u_i) + \varepsilon(E_i E_j - \frac{1}{2} E^2 \delta_{ij}) \qquad [11]$$

and the integrals are over any surface containing the particle because the fluid is in mechanical quasi-equilibrium.

This basic methodology can be extended to more complicated situations, as outlined in the article on nonlinear electrokinetic phenomena. For example, if the particle is not ideally polarizable or has a dielectric coating, then Laplace's equation must also be solved for the electrostatic potential inside the particle, with appropriate matching conditions (3). Channel walls can be described by replacing the conditions at infinity with appropriate electrostatic boundary conditions, including possible double-layer relaxation [3] and ICEO slip [9] on fixed metal structures or electrodes; multiple particles can also be described, usually with numerical methods. A greater complication is to allow the particle to selectively conduct ions or pass a Faradaic current and/or to adsorb significant salt from the bulk in its double layers. The resulting gradients in bulk salt concentration require solving the full Poisson-Nernst-Planck equations for the electrochemical relaxation (6) and allowing for bulk electroconvection in the fluid equations (7). Concentration gradients also lead to diffusiophoresis, which adds a term

proportional to $\nabla_{\|} \log c$ to the "first kind" slip formula [9], and, if strong enough to produce bulk space charge, also to electrophoresis of the second kind (8,18).

Key Research Findings

Field-dependent mobility

A well-known prediction of the classical theory of electrophoresis is that the mobility [1] only depends on the total charge (or average zeta potential), in the limits of thin double layers, small charge, and weak fields (1). This remarkable result holds for any size or shape, even if the particle is polarizable and acquires a non-uniform charge (or zeta) profile in response to the applied field. It is not widely appreciated, however, that this follows from the assumption of constant double-layer capacitance, which reduces [5] to [6].

In the 1970s, SS Dukhin's group was perhaps the first to recognize that the electrophoretic mobility of polarizable particles must generally depend on the electric field (9). In a series of Russian papers, which have yet to gain widespread attention, they predicted perturbations of the mobility as $\Delta b \propto E^2$ and thus nonlinear electrokinetic motion $\Delta U \propto E^3$, which they have come to call the Stotz-Wien effect. For the case of a steady weak field applied to an ideally polarizable sphere of radius *a*, AS Dukhin derived an expansion for the mobility,

$$b \sim \frac{\varepsilon}{\eta}\left[\zeta - \frac{3}{8}\left(\frac{d}{d\psi}\log C\right)_{\psi=\zeta}(Ea)^2 + ...\right] \qquad [12]$$

which holds for any model of the electrical double layer (10). The same result can be derived from the general formalism above by expanding [5] for $\psi \approx \psi_0 = \zeta$ and keeping corrections to [6], and large fields, non-spherical shapes, and AC forcing could also be considered. In principle, any field dependence of the mobility, regardless of its true cause, can be exploited to separate particles using an unbalanced AC field, which cancels the linear response (since $\langle E \rangle = 0$) while amplifying mobility corrections (since $\langle E^3 \rangle \neq 0$) (9,11).

Induced-charge electrophoresis

Mobility perturbations for spherical particles, however, only hint at the rich phenomena that can arise in the electrokinetic motion of polarizable particles. Murtsovkin and co-workers were the first (and to date, the only ones) to experimentally observe nonlinear electrokinetic motion in a uniform AC field in directions *oblique to the field axis* (12). They studied irregular quartz particles moving in water near the wall of a cuvette in surprising directions apparently set only by the particle shape. If a particle rotated enough by Brownian motion when the field was off, it could be seen to reverse direction when the field was turned back on. The velocity scaled with the square of the field amplitude and increased with the particle size. No theory was proposed for this phenomenon, in part since it was only observed near the wall and not in the bulk solution.

Bazant and Squires recently predicted that polarizable particles in the bulk can undergo essentially arbitrary translation and/or rotation by ICEP in a uniform electric field, as long as they possess appropriate *broken symmetries* (2,4), such as non-spherical shapes and/or non-uniform surface properties (e.g. due to coatings of different polarizability or compact-layer capacitance). The former cases begin to explain Murtsovkin's early observations and beg for new experiments to test a variety of specific theoretical predictions, discussed below. The

latter cases, which had not previously been observed, are described in a companion article on electrokinetic motion of heterogeneous particles.

For homogeneous particles, the canonical example is that of an uncharged, ideally polarizable particle of irregular shape in a weak, uniform DC field. In that case, the basic velocity scale for ICEP is

$$U_{ICEP} = \frac{\varepsilon a E^2}{\eta(1+\delta)} \quad \text{(uniform field)} \qquad [13]$$

where a is a characteristic radius (2). Using the low-voltage model [6-11] (with C=constant), Yariv derived general expressions for the translational and rotational velocities, respectively,

$$U_i = U_{ICEP} \sum_{jk} \mathrm{C}_{ijk} E_j E_k \quad \text{and} \quad \Omega_i = \frac{U_{ICEP}}{a} \sum_{jk} \mathrm{D}_{ijk} E_j E_k \qquad [14]$$

where C is a dimensionless tensor and D a pseudo-tensor, each expressible as surface integrals involving the bulk potential, just outside the double layer. Squires and Bazant treated a number of specific examples by solving [6-11] directly using perturbation methods for nearly symmetric objects and discovered some simple principles to predict the motion of a particular shape (4).

The basic mechanism of ICEP for irregular particles is shown in Figure 1. As shown in (a) and described in the article on nonlinear electrokinetic phenomena, the ICEO flow around a symmetric particle is quadrupolar (2,3), drawing fluid in along the field axis and ejecting it radially. If the particle has broken left/right symmetry as shown in (b), then the radial flow is stronger on one side than the other, leading to ICEP motion perpendicular to the field. Similarly, breaking only fore/aft symmetry produces ICEP motion along the field axis, and combinations of these asymmetries can cause motion in an arbitrary direction.

ICEP can also contribute to the rotation of polarizable particles with elongated shapes (2,4,5,15), as illustrated in Figure 2a. It is well known that DEP causes such particles to align with the axis of a uniform field, due to electrostatic torque on the induced dipole. At low AC frequency (or in the DC limit), if the field persists in one direction long enough for ICEO flow to occur, then ICEP causes a rotational velocity with a basic scale that is independent of the particle size but sensitive to its shape,

$$\Omega_{ICEP} = \frac{U_{ICEP}}{a} = \frac{\varepsilon E^2}{\eta(1+\delta)} \qquad [15]$$

This scale happens to be the same as that of the DEP rotational velocity, so ICEP rotation is easily overlooked and mistakenly interpreted as DEP. It is possible, however, to clearly distinguish the two effects, as recently demonstrated by experiments (14) and simulations (15) involving rod-like, metal particles in uniform AC fields. (See Figure 3.)

More complicated asymmetric particles can undergo essentially arbitrary ICEP motion, even in a uniform field. Even in the context of the simple model above, these effects have not yet been fully analyzed, but some general principles have been identified (4). A striking example is shown in Figure 2b, which illustrates how arrow-like particles of slightly different shapes can move in perpendicular directions in a uniform field, depending on their broken symmetries: On the left, a “short, fat arrow” rotates to align its long axis with the field and then moves

perpendicular to the field, toward its pointed end; on the right, a "long, thin arrow" also rotates to align its long axis, but then moves parallel to the field, toward its blunt end. Such predictions are quite recent, however, and remain to be tested experimentally.

A telltale sign of ICEP is the presence of non-uniform ICEO flow around the particle, which leads to complex hydrodynamic interactions with other particles and walls. For example, the basic quadrupolar flow in Figure 1a causes two symmetric particles to move toward each other along the field axis and then push apart in the normal direction (13,15). A finite cloud of such particles would thus become squashed into a disk-like "spreading pancake" perpendicular to the field axis (3). The same flow field can also cause particles to be repelled from insulating walls (perpendicular to the field) (16) or attracted toward electrodes (normal to the field), but these are only guiding principles. Broken symmetries in particle shape or wall geometry, however, can cause different motion due to combined effects of DEP and ICEP, even opposite to these principles, and the interactions of multiple particles can also be influenced strongly by walls. Such effects have not yet been fully explored in experiments or simulations.

Low-frequency dielectrophoresis

In the 1970s, Shilov and Estrella-Lopis first recognized that electrohydrodynamics (what we now call "ICEO") can contribute to the motion of particles in low-frequency, non-uniform electric fields (17), in addition to the classical effect of DEP, although the effect has not been studied much in theory or experiment. Shilov and Simonova analyzed the problem of an ideally polarizable sphere in a uniform field gradient and made the remarkable prediction that the particle does not move. Due to equal and opposite motions by DEP and ICEP, the sphere levitates in the field while driving a steady ICEO flow, but this is a unique case.

Squires and Bazant recently showed that broken symmetries in the field gradient and/or the particle shape generally cause a particle to move, due to subtle imbalances between ICEP and DEP (4). Both effects have the same basic scaling,

$$U_{ICEP} = \frac{\varepsilon a^2 |\nabla E|^2}{\eta(1+\delta)} \quad \text{(non-uniform field)} \qquad [16]$$

Moreover, as illustrated in Figure 3, the DEP force and ICEP velocity tend to act in opposite directions, at least for the case of an ideally polarizable particle with thin double layers in a non-uniform electric field (of arbitrary complexity). Similar to the case of rotational motion discussed above, ICEP can be easily overlooked and the observed translational motion attributed solely to DEP, if it is along the field gradient. Experiments clearly separating ICEP and DEP effects are still lacking, and an opportunity exists to exploit these combined effects for manipulating polarizable colloids, once the effects are better understood.

Electrophoresis of the second kind

As described in the article on nonlinear electrokinetic phenomena, electro-osmosis of the second arises when the bulk salt concentration goes to zero at a surface passing a diffusion-limited current. Under conditions of super-limiting current, the density of counterions in the electrical double layer loses its classical quasi-equilibrium profile and a region of dilute space charge extends into the solution to the point where the bulk salt concentration becomes appreciable. In spite of the small counter-ion concentration, the expulsion of co-ions from the space charge layer leads to significant charge density and, in the presence of a tangential electric field, electro-osmosis of the second kind (7).

If a particle is able to sustain a super-limiting current, then such flows can cause it to move by electrophoresis of the second kind, as first noted by S. S. Dukhin in the 1980s. As shown in Figure 5, second-kind electrophoresis has been observed experimentally for large (>10 μm) particles composed of cation-selective porous materials, and the flow structure has been studied in detail (8). Due to the complexity of the phenomenon, however, the theory has mainly been limited to scaling arguments and heuristic boundary-layer approximations (18), but there is hope that the rigorous mathematical study of second-kind flows (7) could soon be extended to second-kind electrophoresis. Effects of walls, multiple particles, and broken symmetries should also eventually be studied.

Future Directions for Research

Compared to the vast literature on linear electrophoresis, the study of nonlinear electrokinetic motion is still its early stages. As indicated above, much remains to be done, both in making theoretical predictions and systematically testing them (or discovering new effects) in experiments. Modern mathematical methods and computational power now allow more sophisticated analysis, going beyond linear and weakly nonlinear approximations, as well as large scale simulations of interacting colloidal particles. Similarly, the advent of microfluidics provides new opportunities to observe and exploit nonlinear electrokinetic phenomena, since polarizable particles can now be fabricated with complicated shapes and material properties and electric fields controlled with submicron precision.

Applications of nonlinear electrokinetic motion are still largely unexplored. Aperiodic electrophoresis and other ICEP phenomena could be used to separate polarizable particles based on shape, size, and/or surface properties, in ways that cannot be accomplished using linear electrophoresis. Sorting, trapping, and assembling particles interacting via ICEP and DEP in microfluidic devices could be used to engineer new materials with anisotropic electrical, mechanical, or optical properties. Polarizable particles can also be attached to biological molecules or cells and manipulated by ICEP and DEP for separation, characterization, or labeling.

Cross-references

AC electro-osmotic flow
Aperiodic Electrophoresis (def)
Dielectrophoresis
Dielectrophoretic Motion of Particles and Cells
Diffusiophoresis
Electrical Double Layers
Electrokinetic Motion of Heterogeneous Particles
Electroosmotic Flow
Electrophoresis of the second kind (def)
Electrophoresis
Induced-charge electrophoresis (def)
Nonlinear electrokinetic phenomena
Space charge (def)
Stotz-Wien effect (def)
Super-limiting current (def)
Unbalanced AC field (def)

Further Reading

1. Anderson JL (1989) Colloid transport by interfacial forces. Annual Reviews of Fluid Mechanics 21: 61-99.
2. Bazant MZ & Squires TM (2004) Induced-charge electrokinetic phenomena: theory and microfluidic applications. Physical Review Letters 92: art. no. 066010.
3. Squires TM and Bazant MZ (2004) Induced-charge electro-osmosis. Journal of Fluid Mechanics 509: 217-252.
4. Squires TM & Bazant MZ (2006) Breaking symmetries in induced-charge electro-osmosis. Journal of Fluid Mechanics 560: 65-101.
5. Yariv E (2005) Induced-charge electrophoresis of nonspherical particles. Physics of Fluids 17: art. no. 051702.
6. Chu KT & Bazant MZ (2006) Nonlinear electrochemical relaxation around conductors. Physical Review E 74: art. no. 011501.
7. Zaltzman, B. & Rubinstein, I. (2007) Electro-osmotic slip and electroconvective instability. Journal of Fluid Mechanics 579: 173 – 226.
8. Mishchuk NA & Takhistov PV (1995) Electroosmosis of the second kind. Colloids and Surfaces A: Physicochemical and Engineering Aspects 95: 119-131.
9. Dukhin AS & Dukhin SS (2005) Aperiodic capillary electrophoresis method using an alternating current electric field for separation of macromolecules. Electrophoresis 26: 2149-2153.
10. Dukhin AS (1993) Biospecific mechanism of double layer formation and peculiarities of cell electrophoresis. Colloids and Surfaces A: Physicochemical and Engineering Aspects 73: 29-48.
11. Chimenti RJL (1992) Electrophoretic separation. US Patent 5,106,468.
12. Murtsovkin VA & Mantrov GI (1990) Study of the motion of anisometric particles in a uniform variable electric field. Colloid Journal of the USSR 52: 933-936.
13. Gamayunov NL, Mursovkin VA & Dukhin AS (1986) Pair interactions of particles in electric field. 1. Features of hydrodynamic interaction of polarized particles. Colloid Journal of the USSR 48: 197-203.
14. Rose K & Santiago JG (2007) Rotational electrophoresis of striped metallic microrods. Physical Review E 75: 011503.
15. Saintillan D, Darve E & Shaqfeh ESG (2006) Hydrodynamic interactions in the induced-charge electrophoresis of colloidal rod suspensions. Journal of Fluid Mechanics 563: 223-259.
16. Zhao H & Bau HH (2007) On the effect of induced-charge electro-osmosis on a cylindrical particle next to a surface. Langmuir 23: 4053-4063.
17. Simonova TS, Shilov VN & Shramko OA (2001) Low-frequency dielectrophoresis and the polarization interaction of uncharged spherical particles with an induced debye atmosphere of arbitrary thickness. Colloid Journal 63: 108-115.
18. Y. Ben, E. A. Demekhin, and H.-C. Chang (2004) Nonlinear electrokinetics and "superfast" electrophoresis, Journal of Colloid and Interface Science 276: 483-497.

Figure Legends

Figure 1

(a) Induced-charge electro-osmotic (ICEO) flow around a symmetric, uncharged, ideally polarizable particle (from Ref. 3); (b) An example of ICEO flow and the resulting induced-charge electrophoretic (ICEP) velocity for an asymmetric shape (from Ref. 4).

Figure 2

(a) Mechanism for ICEP torque on a rod-like, polarizable particle in a uniform electric field, which enhances dielectrophoretic (DEP) torque. (b) Possible ICEP velocities for asymmetric shapes, once their long axes have aligned with the field.

Figure 3

Experiments on cylindrical silver particles (.318μm diameter, 6μm length) sedimenting in de-ionized water by gravity alone (a) and in a 100 Hz, 100 V/cm AC field aligned with gravity (b). The experimental distribution of angles in different fields (c) agrees well with theoretical curves (solid) which take into account both ICEP rotation and electrostatic torque. (from Ref. 14)

Figure 4

An ideally polarizable cylinder subjected to a non-uniform DC electric field in an electrolyte with thin double layers: (a) Field lines and the DEP force, typically directed down the field gradient. (b) Streamlines of ICEO flow and the ICEP velocity, which always directed opposite to the DEP force. (from Ref. 4).

Figure 5

Experiments on electrophoresis of the second kind for cationite KU-2-8 particles in 10^{-4} M NaCl. (a) Velocity versus time for particles diameters 0.42mm (1), 0.33mm (2), and 0.21mm (3) with sketches of the observed flow fields. (b) Scaling of velocity with applied field for diameters 0.31mm (1), 0.28mm (2), and 0.26mm (3). (from Ref. 8)

Figure 1

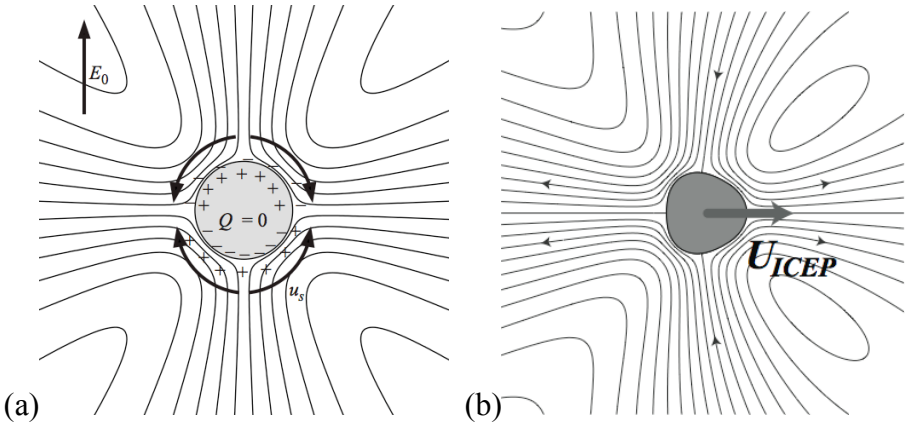


Figure 2

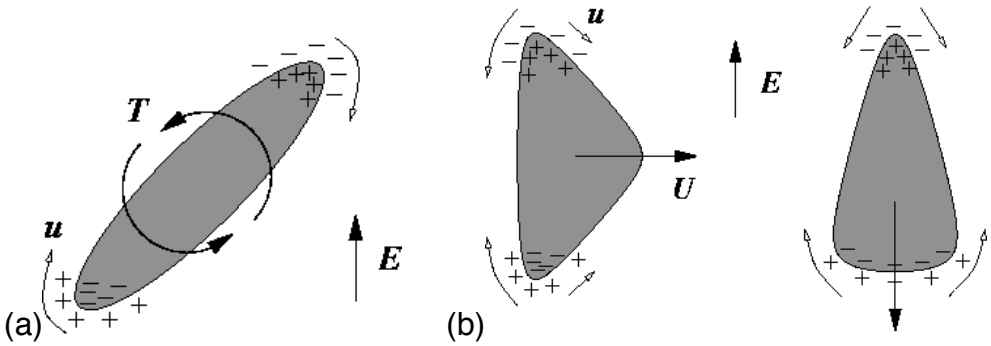


Figure 3

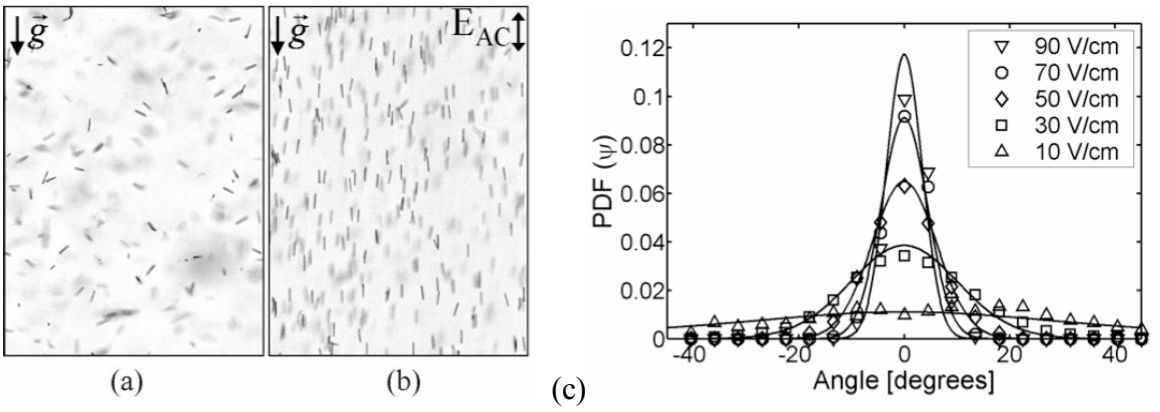


Figure 4

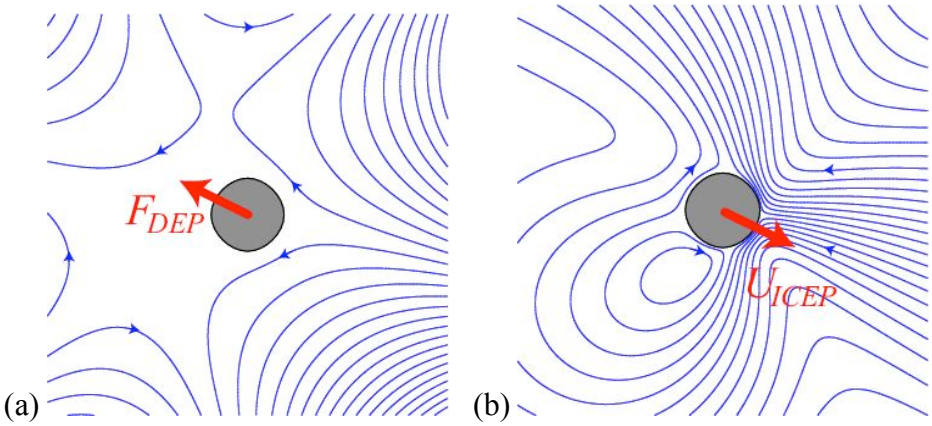
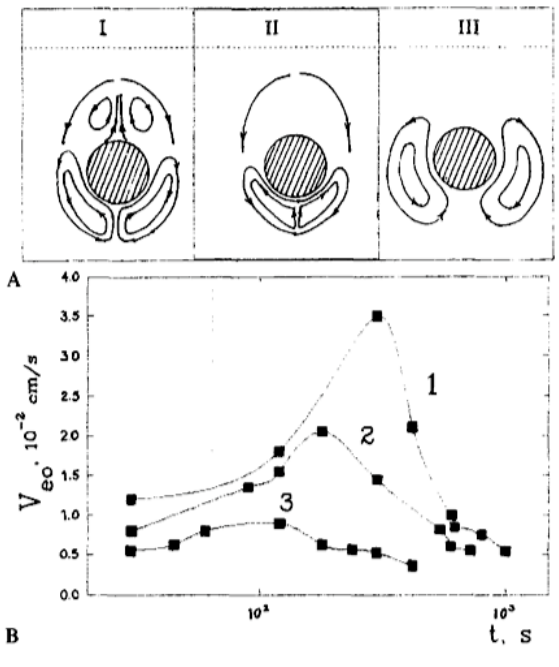
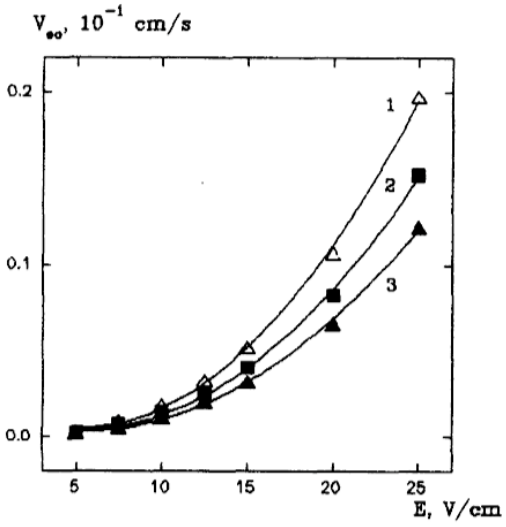


Figure 5



(a)



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