Electrokinetic motion of heterogeneous particles

Synonyms

Electrophoresis, induced-charge electrophoresis, transverse electrophoresis.

Definition

The electrokinetic motion of heterogeneous particles, having non-uniform composition and/or irregular shape, involves translation, rotation, and deformation due to the combined effects of electrophoresis, induced-charge electrophoresis, and dielectrophoresis.

Overview

The electrokinetic motion of colloidal particles and molecules in solution in response to applied electric fields can be rather complicated, so many approximations have been made in theoretical treatments. The classical theory of electrophoresis, dating back over a century to Smoluchowski, considers homogeneous particles, which are (i) non-polarizable, (ii) spherical, (iii) uniformly charged, (iv) rigid, (v) much larger than the thickness of the electrical double layer, (vi) in an unbounded fluid, very far from any walls or other particles, and subjected to (vii) uniform and (viii) weak fields, applying not much more than the thermal voltage (kT/e=25mV) across the particle in (ix) dilute electrolytes. Under these assumptions, the particle's velocity is linear in the applied electric field, $U = bE$, where the electrophoretic mobility $b = \varepsilon\zeta/\eta$ is given by the permittivity ε and viscosity η of the fluid and the zeta potential ζ of the surface. In Smoluchowski's theory, the latter is equal to the voltage across the double layer, which is proportional to the surface charge at low voltage.

Much less attention has been paid to the electrokinetic motion of heterogeneous particles, which have non-spherical shape and/or non-uniform physical properties. By far the most theoretical work has addressed the case linear electrophoresis of non-polarizable particles with a fixed, equilibrium distribution of surface charge (1). In that case, relaxing only assumption (ii) leads to the classical prediction that the mobility of a particle of uniform composition (uniform zeta) is independent of the shape and size of the particle. Perhaps it was this insensitivity to geometry that led to the common belief that the electrophoretic mobility measures some kind of "average" surface charge, until the Anderson was the first to clearly point out that this is generally not the case (2). By carefully relaxing only assumption (iii), he predicted that a sphere of non-uniform zeta potential can move in a different direction from the field and that its mobility is not simply related to its total charge. Generalizing work of Fair and Anderson on doublet particles (3), Long and Ajdari showed that relaxing *both* (ii) and (iii) leads to even more complicated behaviour, including particles that rotate continuously or translate perpendicular to a uniform DC field (4). Relaxing assumption (iv), the electrophoresis of flexible heterogeneous particles has also been studied, such as DNA molecules connected to beads (5) and interacting with obstacles (6).

Nonlinear electrokinetic phenomena, such as the electrokinetic motion of polarizable particles, have only been studied for a few decades, and attention is just beginning to be paid to the nonlinear motion of heterogeneous particles due to induced-charge electrophoresis (7-9). Recent theoretical work has relaxed assumptions (i)-(iii), but much remains to be done. Surprising new possibilities include particles that rotate continuously or translate perpendicular to a uniform AC field (9).

Basic Methodology

The underlying physical mechanisms for the electrokinetic motion of particles are described in other articles on electro-osmotic flow, electrophoresis, dielectrophoresis, nonlinear electrokinetic phenomena and electrokinetic motion of polarizable particles, along with various mathematical models. The effects of relaxing the assumptions above in these models, however, are often unexpected and have not yet been fully explored, either theoretically or experimentally. Here, we simply give a few examples of how heterogeneous particles can move in electric fields.

Key Research Findings

Linear Electrophoresis

It is tempting to think of the electrophoretic mobility of a heterogeneous particle as a measure of its "average charge", when in fact it has a nontrivial dependence on the spatial distribution of surface charge (1-5). This is clearly demonstrated by a counter-example of Long and Ajdari, motivated by chain-like polyelectrolytes, such as DNA molecules (5). Consider a dumbbell-shaped particle consisting of two uniformly charged spheres with electrophoretic mobilities b_1 and b_2 and hydrodynamic drag coefficients ξ_1 and ξ_2, held together by an uncharged, rigid rod. As a first approximation, the rod has negligible drag and is long enough that hydrodynamic and electrostatic interactions between the spheres can be neglected. In a uniform electric field, the dumbbell rotates to a stable configuration aligned with the field axis, as shown in Figure 1a and moves a velocity, $U = bE$, where b is the overall mobility. In order for each particle (*i=1,2*) to move at the same velocity, the rod must exert a force $F_i = \xi_i(U - b_i E)$. Force balance on the rod, $F_1 = -F_2$, then yields the mobility

$$b = \frac{\xi_1 b_1 + \xi_2 b_2}{\xi_1 + \xi_2} \propto \frac{Q_1}{R_1} + \frac{Q_2}{R_2} \qquad [1]$$

which is the drag-weighted average of the two mobilities. In the last step, we have used Stokes formula, $\xi_i = 6\pi\eta R_i$ (where η is the fluid viscosity), and assumed that the *local* mobility (slip coefficient) is proportional to the surface charge density, $b_i \propto Q_i / 4\pi R_i^2$, where Q_i is the total charge of each sphere. We see that, depending on the geometry, the mobility can have either sign, regardless of the sign the total charge $Q_1 + Q_2$. For example, as shown in Fig. 1a, a small sphere of charge $Q > 0$ connected to a larger sphere of charge $-2Q$ can have a positive mobility, even though its total charge is negative, as long as $R_2 > 2R_1$.

Variations in charge density and shape can lead to even more surprising "transverse" electrophoretic motion, which departs from the field axis. In linear electrophoresis, a spherical particle of non-uniform surface charge (or zeta potential) can move perpendicular to the field, but only for certain orientations; it can also rotate, but only transiently to align its dipole with the field axis (1). If both the surface charge and the shape are perturbed, however, then these restrictions do not apply (4): Figure 1b shows a cylindrical particle of zero total charge, which always moves perpendicular to the electric field, regardless of its orientation. It has four-fold shape perturbation and eight-fold surface charge perturbation, such that each bump on the surface has positive surface charge to the left and negative to the right. By constructing appropriate chiral perturbations of the shape and surface charge, it is also possible to design heterogeneous particles, which rotate continuously around a particular axis without translating, for a particular direction of the electric field.

Flexible objects undergoing electrophoresis also display complicated dynamics. Motivated end-labeled free-solution DNA electrophoresis, Long and Ajdari also considered the electrophoresis of flexible charged chains connected to larger beads (5). As shown in Figure 2, there are three different dynamical regimes for small, intermediate and large velocities, where the chain goes from its equilibrium configurations to a completely elongated state. The same motions would result if the chain were pulled at the end by an effective force. Similar phenomena occur in the electrophoresis of block co-polymers, which consist of two different chains connected at the ends.

Recently, Randall and Doyle have studied the electrophoretic collision of DNA with an obstacle in a microfluidic channel, both experimentally and theoretically (6). In that case, large deformations due to field gradients and hydrodynamic strain near the obstacle quickly stretch and compress the molecule and cause configuration-dependent hooking interactions, as shown in Figure 2b. (See also dielectrophoretic motion of particles and cells.)

Induced-charge Electrophoresis

The preceding examples involve non-polarizable objects with fixed surface charge distributions, which do not respond to the electric field. The resulting electrophoretic motion is linear in the field amplitude and vanishes for AC fields. The electrokinetic motion of polarizable particles, however, has nonlinear field dependence due to the phenomenon of induced-charge electro-osmosis (ICEO), where the field acts on induced diffuse charge in the electrical double layer. At frequencies low enough for capacitive charging of the double layer (typically < 10kHz), the time-averaged motion in an AC field is resembles that in a DC field. In the canonical example of an uncharged metal sphere in a uniform field, the ICEO flow is quadrupolar, drawing in fluid along the field axis and expelling it radially, but there is no net motion.

Motivated by the examples from linear electrophoresis above, Bazant and Squires pointed out that broken symmetry in ICEO flow generally causes particle motion, which they called "induced-charge electrophoresis" (ICEP) (1). Examples of broken symmetries include particles with irregular shapes and/or non-uniform physical characteristics, as well as non-uniform applied fields. In the latter case, ICEP occurs at the same time as dielectrophoresis (DEP), although the combined effects of ICEP and DEP on heterogeneous particles remain to be explored. Besides persisting in AC fields, ICEP also depends much more sensitively on particle shape and surface properties than does linear DC electrophoresis. Cases of non-spherical particles with uniform polarizability are discussed in the article on electrokinetic motion of polarizable particles, so here we focus on ICEP due to heterogenous surface polarizability.

The canonical example is that of a Janus particle with one metallic and one insulating hemisphere (9), using the standard low-voltage model for electrokinetic motion of polarizable particles. In response to an applied electric field, the Janus particle rotates to align the interface between the two hemispheres with the field axis, due to both ICEP (electrohydrodynamics) and DEP (electrostatics). At the same time, for any orientation, the particle translates in the direction of its insulating end, propelled by ICEO flow on the metallic end, with a velocity

$$U = \frac{9\varepsilon R E^2}{64\eta(1+\delta)} \qquad [2]$$

where ε is the permittivity, R is the particle radius, and δ is a dimensionless measure of the compact-layer capacitance. In particular, once the particle aligns in the field, it continues to move perpendicular to the electric field, with an azimuthal angle set by its initial orientation.

All the generic features of the dynamics still hold if the particle's insulating end is smaller or larger than the metallic end, since it is determined by the broken symmetry. Motion transverse to a uniform AC field cannot have any contribution from DEP, but it is easily understood by considering the ICEO flow in Figure 3a. After alignment in the field, part of the usual quadrupolar ICEO flow is suppressed on the insulating end. The remaining ICEO flow over the metallic end sucks in fluid along the field axis and pushes it outward from the metallic pole, as shown in Figure 3b, which propels the particle toward the insulating pole.

This example suggests how to design particles that spin continuously in a uniform field, as noted by Squires and Bazant (9). Since a Janus particle always translates towards its less polarizable end, a set of three Janus particles connected by rigid rods can be set into continuous motion like a pinwheel, if connected as shown in Figure 3c. This "ICEP pinwheel" responds to any DC or AC electric field (of sufficiently low frequency) by tilting to align the particle plane perpendicular to the field and then spinning around the field axis until the field is turned off. Perhaps such particles could be used to sense electric fields or to apply torques to attached molecules or cells.

Transverse ICEP motion of metallo-dielectric Janus particles in a uniform AC field has recently been observed by Gangwal et al. (10). Consistent with theoretical predictions in Figure 3, the particles align and translate perpendicular to the field in the direction of the less polarizable (light) end, as shown in Figure 4. Larger particles move faster than smaller ones, as expected from Eq. [2], and the velocity scales like the field squared in dilute NaCl solutions. The ICEP velocity decays at higher concentrations, extrapolating to zero around 10 mM. The same concentration dependence is also observed in AC electro-osmotic flow and other nonlinear electrokinetic phenomena, which, although poorly understood, further reinforces that the motion is indeed due to ICEP.

Current research is focusing on how heterogeneous particles undergoing electrokinetic motion due to ICEP and DEP interact with walls and other particles. An interesting feature of the experiments in Figure 3 is that the Janus particles are attracted to nearby glass walls, and the transverse motion is also observed close to the walls, where the theory of Ref. 9 does not strictly apply. The attraction can be understood as a consequence of ICEP torque, which redirects the Janus particle toward a nearby wall and causes it to tilt while translating transverse to the field.

Future Directions for Research

As illustrated by the examples above, the electrokinetic motion of heterogeneous particles is quite complicated and relatively unexplored. From a theoretical point of view, there are many opportunities to discover new phenomena by further relaxing the nine assumptions listed at the beginning of this article. From an experimental point of view, much remains to be done to characterize the motion of heterogenous particles in electric fields, especially by ICEP and DEP at low frequency.

A major motivation to develop this subject is the possibility of new applications, opened by advances in microfluidics and nanotechnology. In principle, heterogenous particles of specific irregular shapes and non-uniform electrical and/or chemical properties can be designed and fabricated for specific applications. The complex electrokinetic motion of these particles could potentially be used for separation or sample concentration in chemical or biological assays, self-assembly in the fabrication of anisotropic materials, directional transport of attached "cargo", electric-field sensing and applying forces and torques to molecules or cells.

Cross-references

AC Electro-osmotic Flow
Dielectrophoresis
Dielectrophoretic Motion of Particles and Cells
Electrical Double Layers
Electrokinetic Motion of Polarizable Particles
Electroosmotic Flow
Electrophoresis
Induced-charge electrophoresis (def)
Janus particle (def)
Nonlinear electrokinetic phenomena

Further Reading

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Figure Captions

FIGURE 1. Examples of unusual linear electrophoretic motion of heterogeneous particles. (a) A dumbbell consisting of two oppositely charged spheres of connected by a rigid rod rotates to align as shown and moves in the direction of the electric field (positive mobility), even though the total charge is negative, if the positive sphere is smaller. (b) A particle of zero total charge with four-fold and eight-fold perturbations in shape and surface charge, respectively, moves perpendicular to the electric field, regardless of its orientation [from (4)].

FIGURE 2. (a) Linear electrophoresis of a flexible, charged chain connected to a neutral bead in regimes of small, moderate, and large velocity as a model of end-labeled free-solution DNA electrophoresis [from (5)]. (b) Centerline trajectories of DNA electrophoresis around a cylindrical obstacle in a microchannel, showing compression and extension of the molecule [from (6)].

FIGURE 3. Induced-charge electrophoresis of Janus particles, illustrated for the case of metal partially coated with insulating thin films [from (9)]. (a) Stable orientation in a uniform field, showing induced charge and slip velocities on the metallic side, resulting in motion toward the insulating end, perpendicular to the field. (b) Streamlines of ICEO flow. (c) An ICEP pinwheel, consisting of three Janus particles connected by rigid rods, which tilts to align and then spins continuous around the field axis.

FIGURE 4. Experimental observation of ICEP of metallo-dielectric Janus particles in a uniform 10kHz AC field [from (10)]. (a) Sequence of micrographs demonstrating motion transverse to the field in the direction of the dielectric (light) end propelled by the metallic (dark) end, where the velocity increases with the particle size as in Eq. [2]. (b) Velocity versus field amplitude squared at different bulk concentrations of NaCl.

Figures

FIGURE 1

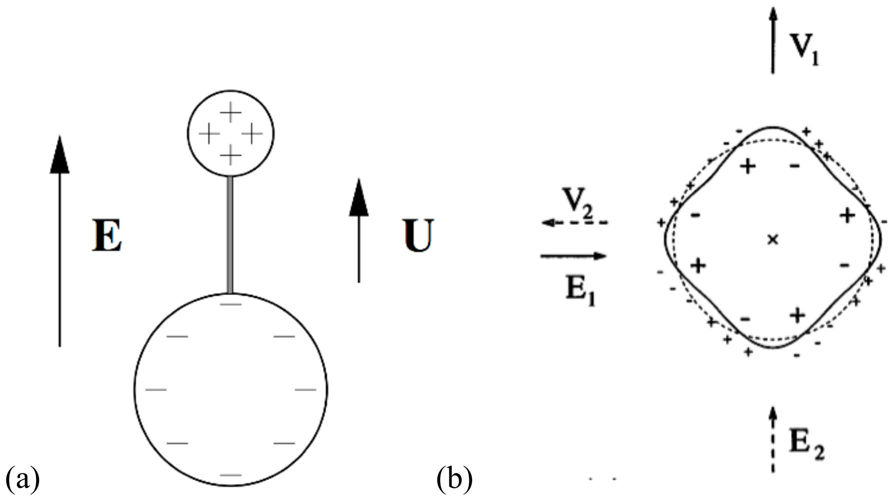


FIGURE 2

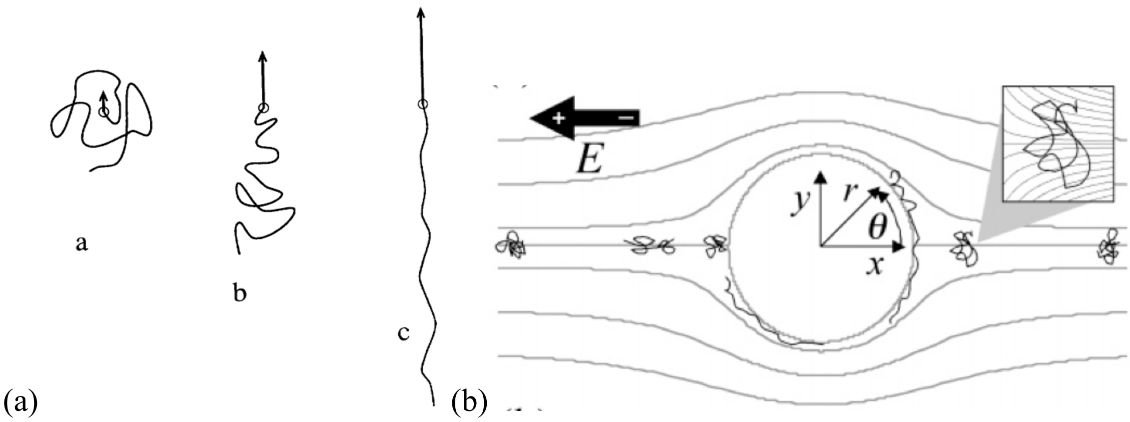


FIGURE 3

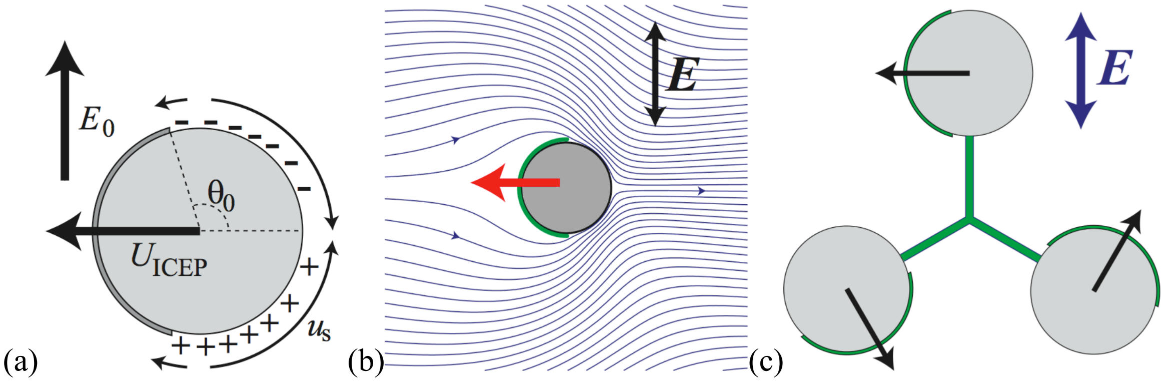
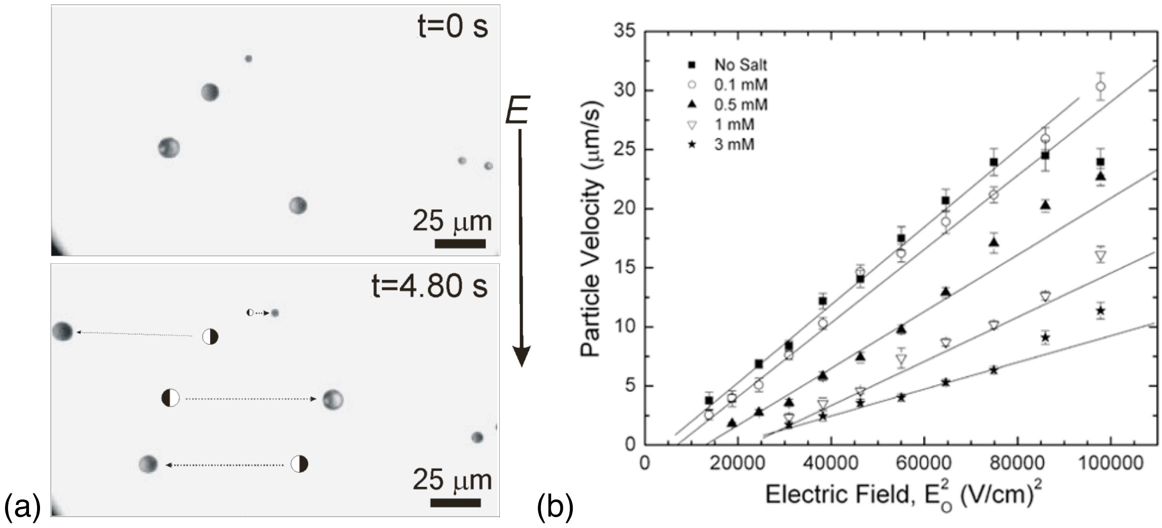


FIGURE 4



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