

force density. Increasing the electric field increases the instability growth rate and results in an increase in the level of mixing. The results show an increase in conductive aqueous fluid entrainment into the nonconducting organic fluid core (Fig. 5b to e) measured as a percentage of area of entrainment into the fluorescently labeled organic phase. The entrainment area increased from 1.9% to 28.6% as the applied field was increased from 8.0×10^5 to 9.0×10^5 V/m.

Future Directions for Research

Electrokinetic and electrohydrodynamic instability mixing in microsystems is a complex phenomenon which researchers are only beginning to exploit and understand. Future work requires a further development of experimental models and expansion of computational simulations to better understand how the instabilities form and grow. Specific applications of electrokinetic and electrohydrodynamic instabilities are still limited. The application of these instabilities to improve mixing between components should be explored. One example is through the use of multiphase systems where electrohydrodynamic instabilities are utilized to improve component partitioning for liquid extraction devices.

Cross References

- Active Mixer
- Droplet and Bubble Formation in Microchannels
- Electrokinetic Two Phase Flows
- Electroosmotic Flow (DC)
- AC Electro-Osmotic Flow
- Interfacial Instability
- Interfacial Electrokinetic Flow
- Lab-on-Chip Devices for Sample Extraction
- Microfluidic Mixing
- Pressure-Driven Two Phase Flows

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Electrokinetic Flow

Synonyms

Electrokinetic transport; Electrokinetic motion

Definition

Electrokinetic flow covers in principle the transport of liquids (electroosmosis) and samples (electrophoresis) in response to an electric field. Both motions are associated with the electric double layer that is formed spontaneously at the solid–liquid interface in which there is a net charge density. Compared to the traditional pressure-driven flow, electrokinetic flow is more suited to miniaturization due to its nearly plug-like velocity profile and much lower flow resistance. However, Joule heating is a ubiquitous phenomenon in electrokinetic flow that will affect the transport of both liquids and samples via temperature sensitive material properties.

Cross References

- Electrical Double Layers
- Electroosmotic Flow (DC)
- AC Electro-Osmotic Flow
- Electrophoresis
- Streaming Current and Electroviscosity

Electrokinetic Flow and Ion Transport in Nanochannels

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Synonyms

Electroosmotic flow; Ion conductance in nanochannels;
Ion transport in nanopores; Nanopore conductance

Definition

A nano-channel is a conduit between two reservoirs of fluid with a characteristic internal diameter of roughly one to several tens of nanometers. A nanometer is a billionth of a meter (10^{-9} m). The fluid is assumed to be an electrolyte, that is, water with some dissolved salts that dissociate into positive and negative ions. Electrokinetic flow refers to fluid flow generated in such a channel when an externally applied electric field is the primary motive force. Ion transport refers to the average drift of the ions along the channel due to the electric field superimposed on the random molecular motion and collisions with the surrounding water molecules and channel walls.

Overview

Nano vs. Micro-Fluidics

The phrase *one to several tens of nanometers* in the above definition may seem both arbitrary and vague and therefore needs further elucidation. Since the subject of discussion is the flow of water through narrow channels, they must be wide enough to allow the passage of a molecule of water, which is about 0.1 nm. On the other hand, if they are much wider than this size, let us say more than a 100 nm or 0.1 micron we are in the domain of microfluidics, where water can safely be regarded as a continuous material as we do in everyday engineering practice. Thus, the specification of *one to several tens* derives from the scale provided by the water molecule, the subject of discussion is channels that are neither too narrow nor too wide in comparison to the size of a water molecule. These definitions however are based on common usage and are necessarily imprecise; there is no exact boundary as to where nanofluidics ends and microfluidics begins. Nanochannels can be long, that is the length may be many times the characteristic width or short, that is, the length can be of the order of the width. The terms nanopore and nanochannel are usually used interchangeably and we will do so here.

Nanochannels in Nature

Nanochannels and ion transport across nanochannels is a very common feature in living cells [1]. Cells contain various internal and external membranes made out of lipid molecules. These are called lipid bilayers. The nanochannels are made of proteins which form a pore on the lipid bilayer. Various kinds of such channels are known with different biological functions. For example, nerve cells contain channels that are permeable to Sodium, Potassium or Calcium ions. Channels open or close in response to various factors. For example, voltage gated channels open in response to a change in the electrical potential across it.

A ligand gated channel opens if a specific chemical (a ligand) binds to it. Proton pumps in the cell membrane cause the interior of the cell to be maintained at a small negative electric potential relative to the outside. The opening of the ion channels cause an equilibration of the ionic concentrations on either side of the membrane causing a collapse of the potential. Neighboring channels sense this drop in the potential and being voltage gated they respond by opening up and collapsing the potential in their own neighborhood. The effect propagates by the domino effect causing a zone of collapsed potential to propagate outward along the membrane. This is a nerve impulse and it is the mechanism behind all neuronal activity in living things. Another nanochannel in living systems help regulate the water content of cells; these are called aquaporins. They play an important role for example in the functioning of the kidney. The genetic material of a cell is stored in its nucleus. However, the proteins that are coded by the genes are actually manufactured outside the nucleus in the cytoplasm by organelles known as ribosomes. Some of these proteins are actually needed inside the cell nucleus itself or in the mitochondria. How do they cross the mitochondrial or the nuclear membrane? For this, the membranes of these bodies contain nanopores. The proteins are actually unfolded and they translocate across the membrane as a linear polypeptide chain through these nanopores. The details of the mechanism by which this happens is a subject of current research in cell biology.

Nanochannels in Technology

A number of applications of nanochannels have emerged recently in biotechnology partly inspired by their respective biological counterpart. One such application could lead to novel technologies for sequencing DNA that is orders of magnitude faster than what is currently possible. The idea had its origins in the Coulter counter for counting and sorting cells. The Coulter counter consists of a single micron size pore in an impervious membrane that separates two chambers both filled with an electrolyte. When a voltage is applied, a small current flows due to ion movement through the pore. If one of the chambers contain objects such as cells, occasionally a cell will enter the pore. When this happens, the volume of electrolyte in the pore, and therefore the conductance of the pore is reduced and this can be detected as a drop in the current. Thus, the device can be used to count cells and make estimates of their size. In a 1996 paper it was shown by Kasianowicz et al. [2] that if the microchannel in the membrane is replaced by a nanochannel the device is able to detect the passage of single molecules of DNA and RNA. The nanopore was a recon-

structed version of a natural ion channel from the bacteria *Staphylococcus aureus*. It is formed by a protein called α -hemolysin which self assembles under the right conditions on a lipid bilayer membrane and remains open and stable for extended time periods. Recently, techniques involving a combination of micro lithography followed by treatment using the beam from an electron microscope has been used to create artificial nanopores in the 1 to 10 nm range. These tend to be more stable and are easier to work with than the protein nanopores from living cells. It has been shown that the current signal from the nanopore can be used to determine the lengths of biopolymers and to tell apart homopolymers of identical length. However, the goal of actually reading off the sequence of bases as the polymer threads through the pore (in a manner similar to how the magnetic head in a tape recorder reads the signal encoded in a magnetic tape) still remains elusive. Recently the idea of the *Thousand Dollar Genome*: the goal of reducing the cost of a complete sequence of the three billion base pairs in a human genome to one thousand US dollars or less, has received much attention. This cost level is considered a threshold below which one may expect to see a large scale impact of this technology on the practice of medicine and on the national economy. For the sake of comparison, the Human Genome Project cost 3 billion dollars over a thirteen year period (about \$1 per base). The latest advancement in automation has reduced this to 5 cents per base. It is believed that a revolutionary rather than evolutionary change in sequencing technology is needed to reach the 3 cents per 100,000 bases envisioned by the goal of a thousand dollar genome. The concept of sequencing using nanopores could be just the required revolutionary sequencing technology and is discussed in more detail later in this article (see [6] and [8]).

Nanochannels have been used to make an analogue of semiconductor transistors [3]. Charged surfaces in contact with electrolytes attract a layer of ions of the opposite sign (counter-ions) that neutralize the electric field. If the electrolyte is *ordinary* water (that is, water that has not been de-ionized through special treatment) the electric field near most charged surfaces drops to essentially zero over a distance of several nanometers. Because of this shielding effect, any electric field applied externally across the channel has essentially no effect on the conductance of the channel because the bulk of the electrolyte within the channel simply does not “see” the applied electric field. In nanochannels, the situation changes because now the penetration depth of the external voltage, which is of the same order as the thickness of the layer of counter-ions is comparable to the channel thickness. As a result, the electric conductance of the nanochannel can be con-

trolled by applying a gate voltage across the channel, just as in a MOSFET transistor. If controlling the current with a gate voltage was the sole application of this technology, it would be of little interest, since semiconductor transistors achieve the same effect far more efficiently and it is a mature technology. Of much greater importance is the fact that the permeability to charged macromolecules can also be selectively controlled with a gate voltage. This is because, a negatively charged macromolecule would naturally be excluded from a nanochannel with negatively charged walls until the potential barrier is lowered through the application of a gate voltage. Thus, a pore that is selectively permeable to specific molecules can be created and the selectivity can be tuned. This is analogous to the gated pores in biological systems, though the gating is achieved in perhaps a different manner. Large scale practical uses of the technology is likely, but is still in the future.

Basic Methodology

There are primarily two approaches to modeling flow and transport in nanochannels: continuum models and molecular models.

In the first approach, the fluid and the various charged species in the electrolyte are considered to be continuous and are described by quantities such as $c(\mathbf{x}, t)$ (the concentration of a given species) which are continuous functions of space and time. The continuum model is an approximation to reality because an electrolyte really consists of discrete particles: the individual molecules of the solute, solvent and dissociated ions. The continuum model has a high degree of accuracy as long as the relevant length scales in the problem (such as width of the channel) are much larger than the typical distance between molecules. For liquids, such as water, the molecules are closely packed together. Therefore, the distance between molecules is about the same as the size of the molecules themselves which is on the order of 0.1 nm. For this reason, one can expect the continuum approach to give reasonably accurate results in the case of liquid flow through channels that are tens of nanometers wide. The distance between molecules in gases at atmospheric pressure is about ten times larger so it is easier to detect deviations from classical continuum models in the case of flow of gases in nanochannels. In high vacuum these intermolecular distances are even larger and the continuum approximation can break down even on macroscopic scales. The degree of validity of the continuum approximation is often characterized by the **Knudsen number** defined as $\text{Kn} = \lambda/L$, where λ is the **mean free path** (the average distance a molecule travels before bumping into a neighbor) and L is a characteristic length of the problem of interest. Then, the regime of validity

of continuum models may be characterized by a Knudsen number that is much smaller than one ($\text{Kn} \ll 1$).

In many cases, such as in most of the nanochannels found in biological systems, the channel diameter is so small that the continuum model would be clearly inappropriate. There are even nanochannels that are too small to permit the passage of even a single molecule of water. In such cases, one is forced to recognize the underlying molecular structure of matter and perform what is called a ► **molecular dynamics** (MD) simulation. It is important to recognize, just like the continuum approximation, the MD approach is also an approximation to reality but at a different level. In the MD approach one ignores the fact that the water molecule for example contains protons, neutrons and electrons which interact with the protons, neutrons and electrons of every other water molecule via quantum mechanical laws. Such a description would be enormously complicated! Instead, each molecule is treated as a discrete indivisible object and the interaction between them is described by empirically supplied pair interaction potentials. For example, the simplest MD model is the hard sphere model where each molecule is modeled by a sphere, and the molecules do not interact except when they touch in which case they rebound elastically like billiard balls. There also exists a range of possibilities that fall between the continuum and molecular models. These are approaches that combine some features of both. For example, in the description of Brownian motion of macromolecules or latex beads in the 10–100 micron size range, one uses classical hydrodynamic results such as the Stokes law for drag on a sphere while at the same time modeling fluctuating forces from molecular collisions that arise at the level of the molecular description. In the theory of ionic solutions, the individual ions are considered to be discrete particles but the surrounding water is treated as if it was a continuous dielectric medium with a constant dielectric permittivity.

Continuum Models

The Basic Equations of Electrokinetics

In the continuum model, electrokinetic flows are described by the incompressible Navier-Stokes equations with a volume density of electrical forces $-\rho_e \nabla \phi$ where ρ_e is the electric charge density and ϕ is the electric potential:

$$\rho_0(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \mu \nabla^2 \mathbf{u} - \rho_e \nabla \phi. \quad (1)$$

This is supplemented by the continuity equation which takes into account the fact that in a liquid the density changes almost not at all even for large changes in pres-

sure :

$$\nabla \cdot \mathbf{u} = 0. \quad (2)$$

In the above, ρ_0 is the (constant) density of the water, p is the pressure, $\mathbf{u}$ is the flow velocity. The relative size of the term on the left of Eq. (1) (due to fluid inertia) and the second term on the right (due to viscosity) is characterized by the ► **Reynolds number**

$$\text{Re} = \frac{UL\rho_0}{\mu} \quad (3)$$

where U and L denote a characteristic velocity and length for the flow. In most applications of nanoscale flows, $\text{Re} \ll 1$ so that the left hand side of Eq. (1) is neglected (the ► **Stokes approximation**). The potential ϕ is related to the charge density through the Poisson equation of electrostatics (in CGS units):

$$\varepsilon \nabla^2 \phi = -4\pi \rho_e, \quad (4)$$

ε being the permittivity of the liquid. If the electrolyte contains N species of ions with charges ez_k and concentration $n_k (k = 1, \dots, N)$, e is the magnitude of the charge on an electron then $\rho_e = \sum_{k=1}^N ez_k n_k$. Each ion species obeys a conservation equation

$$\frac{\partial n_k}{\partial t} + \nabla \cdot \mathbf{j}_k = 0. \quad (5)$$

Here $\mathbf{j}_k$, the flux vector for the species k , can be modeled by the Nernst-Planck equation for ion transport

$$\mathbf{j}_k = -v_k z_k e n_k \nabla \phi - D_k \nabla n_k + n_k \mathbf{u}. \quad (6)$$

In Eq. (6) v_k is the ► **ion mobility**: the velocity acquired by the ion when acted upon by unit force. It is obviously related to the ► **electrophoretic mobility**: the velocity per unit of electric field as $\mu_k^{(ep)} = ez_k v_k$. The diffusivity of the k th species is D_k and $\mathbf{u}$ is the fluid velocity.

Boundary Conditions. The boundary conditions are those of no slip (see [9] for a discussion on the applicability of this condition to small scale systems) for the velocity at rigid boundaries,

$$\mathbf{u} = 0 \quad (7)$$

and no ion flux normal to the wall

$$\mathbf{j}_k \cdot \hat{\mathbf{n}} = 0 \quad (8)$$

where $\hat{\mathbf{n}}$ is the unit normal directed into the fluid. In the absence of external electric fields, the chemistry at the electrolyte substrate interface leads to the establishment

of a potential, $\phi = \zeta$. This so called **▶ zeta-potential** at an interface depends on a number of factors including the nature of the substrate and ionic composition of the electrolyte, the presence of impurities, the temperature and the buffer pH. The ion distribution near a planar wall at $z = 0$ with potential $\phi(z)$ is known from statistical thermodynamics: $n_k = n_k(\infty) \exp(-z_k e \phi / k_B T)$ where k_B is the Boltzmann constant and T is the absolute temperature of the solution. In order that this expression be a steady solution of Eq. (5) we must have the **▶ Einstein relation**

$$D_k / v_k = k_B T. \quad (9)$$

Therefore Eq. (6) can also be written as

$$\mathbf{j}_k = -n_k v_k \nabla \psi_k + n_k \mathbf{u} \quad (10)$$

where $\psi_k = e z_k \phi + k_B T \ln n_k$ is called the chemical potential for the species k .

The Equilibrium Debye Layer

Suppose that the system is in the steady state and that there is no fluid flow or imposed electric fields. Further suppose that the geometry is such that the electrolyte-substrate interface is an iso-surface of ψ_k . Then it readily follows from Eqs. (5) and (10) and the boundary condition of no flux into the wall that $\nabla \psi_k = 0$ everywhere. Therefore, $n_k = n_k^{(\infty)} \exp(-z_k e \phi / k_B T)$ where $n_k^{(\infty)}$ is the ion concentration where the potential $\phi = 0$; usually chosen as a point very far from the wall. Using the solution for n_k in the charge density ρ_e and substituting in Eq. (4), we get the non-linear Poisson-Boltzmann equation for determining the potential

$$\nabla^2 \phi = -\frac{4\pi e}{\varepsilon} \sum_{k=1}^N n_k^{(\infty)} z_k \exp(-z_k e \phi / k_B T). \quad (11)$$

with the boundary condition $\phi = \zeta$ on walls. Equation (11) was the starting point of a detailed investigation of the structure of the **▶ electric Debye layer** (EDL) by Gouy and Chapman. The description in terms of Eq. (11) is therefore known as the Gouy-Chapman model of the EDL.

Equation (11) is a nonlinear equation. It can be linearized by expanding the exponential terms on the right hand side in Taylor series and discarding all terms that are quadratic or of higher order in ϕ , which gives

$$\nabla^2 \phi - \kappa^2 \phi = 0 \quad (12)$$

where

$$\kappa = \left[\sum_{k=1}^N \frac{4\pi z_k^2 e^2 n_k^{(\infty)}}{\varepsilon k_B T} \right]^{1/2} \quad (13)$$

is a constant determined by the ionic composition of the electrolyte. In arriving at Eq. (12) we used the condition $\sum_{k=1}^N n_k^{(\infty)} z_k = 0$ which expresses the fact that the bulk solution ($\phi = 0$) is free of net charge. It is easily verified that κ has units such that $\lambda_D = \kappa^{-1}$ defines a length scale that is called the Debye-Length, and the linearization of Eq. (11) that lead to Eq. (12) is known as the Debye-Hückel approximation. The solution to Eq. (12) near a charged plate of potential ζ may be written as $\phi = \zeta \exp(-\kappa z) = \zeta \exp(-z/\lambda_D)$ where z is distance normal to the plate. Thus, the potential due to the charged plate is shielded by the free charges in solution and the effect of the charge penetrates a distance of the order of the **▶ Debye-length** λ_D ; which gives a physical meaning to this very important quantity. For *ordinary* water the Debye length is typically 1–10 nm. The linearization proposed by Debye-Hückel is justified provided that $|z_k \phi| \ll k_B T / e$ uniformly in all space and for all k . At room temperature $k_B T / e \approx 30$ mV. However, for silica substrates $|\zeta| \sim 50 - 100$ mV in typical applications. Thus, the **▶ Debye-Hückel approximation** is often not strictly valid. Nevertheless, it is a very useful approximation because it enormously simplifies mathematical investigations related to the Debye layer.

Equation (12) is linear and can be solved analytically under fairly general conditions. It appears in several other contexts such as in the solution of the diffusion equation and in wave propagation problems with evanescent waves. If κ^2 were negative Eq. (12) would be identical to the Helmholtz equation.

Exact solutions to Eq. (11) are known only for symmetric electrolytes (that is, $N = 2$, $z_1 = -z_2 = Z$ where Z is positive) in certain special geometries.

Half Plane. In front of an infinite charged flat plate (defined as $z = 0$) charged to a fixed ζ potential, the solution to Eq. (11) is

$$\tanh \left[\frac{Z e \phi}{4 k_B T} \right] = \tanh \left[\frac{Z e \zeta}{4 k_B T} \right] \exp(-\kappa z) \quad (14)$$

where $z > 0$. This solution can also be used to describe the Debye layers at the walls of a planar channel provided that the channel walls are sufficiently far apart that their Debye layers do not overlap. Clearly, if ϕ and ζ are both sufficiently small that the hyperbolic tangent terms can be approximated by their respective one term Taylor

expansion, $\tanh x = x + \dots$, then the Debye–Hückel theory $\phi(z) = \zeta \exp(-\kappa z)$ is recovered.

Between Parallel Plates. An exact solution of Eq. (11) can be written [4] for a pair of plates separated by a distance $2H$ and each held at a potential ζ . The origin $z = 0$ is chosen on one of the plates so that the second plate is located at $z = 2H$. It is convenient to introduce the intermediate variables $k = \exp(-Ze\zeta/k_B T)$ and Φ defined by $\sin \Phi = k^{-1/2} \exp[-Ze\phi/(2k_B T)]$. Then the solution may be expressed in terms of the elliptic integral $F(\Phi, k)$ defined as

$$F(\Phi, k) = \int_0^\Phi \frac{d\theta}{(1 - k^2 \sin^2 \theta)^{1/2}}. \quad (15)$$

This solution (originally due to Langmuir) is

$$\kappa z = 2k^{1/2} [F(\pi/2, k) - F(\Phi, k)]. \quad (16)$$

For small potentials (in the Debye–Hückel limit) this can be shown to reduce to

$$\phi(z) = \zeta \frac{\cosh[\kappa(H - z)]}{\cosh(\kappa H)} \quad (17)$$

Circular Cylinders. An analytical solution for the region inside infinitely long circular cylinders is available only for Eq. (12). The potential is

$$\phi(r) = \zeta \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad (18)$$

where r is the radial distance and a is the radius of the cylinder.

Electro-Osmotic Flow

In the presence of fluid flow exact analytical solutions of the full electrokinetic equations are rare. An exceptional situation arises when the applied electric field and streamlines of the flow are both in a direction of homogeneity along which there is no variation of any physical quantity. In such cases, the effect of the external influence (such as the applied field) is to produce motion such that all movement of charges are along surfaces of constant charge density and therefore the equilibrium charge density is not altered by the flow. Examples of such a situation are

1. An electric field is applied parallel to a flat plate driving an electro-osmotic flow with streamlines that are also parallel to the plate.
2. An electric field is applied between a pair of parallel plates driving an electro-osmotic flow with streamlines that are also parallel to the plate.
3. An electric field is applied along the cylinder axis resulting in a flow along the axis of the cylinder.

The component of Eq. (1) in the flow direction then reduces to

$$\mu \nabla^2 \mathbf{u} - \rho_e^{(\text{eq})} \nabla \phi^{(\text{ext})} = \mu \nabla^2 \mathbf{u} + \frac{\varepsilon}{4\pi} \nabla^2 \phi^{(\text{eq})} \nabla \phi^{(\text{ext})} = 0, \quad (19)$$

where $\phi^{(\text{eq})}$ is the potential distribution in the equilibrium EDL and $\nabla \phi^{(\text{ext})}$ is the constant applied field in the homogeneous direction. This may be integrated to give the flow velocity at any location

$$\mathbf{u} = \frac{\varepsilon \nabla \phi^{(\text{ext})}}{4\pi \mu} [\zeta - \phi^{(\text{eq})}]. \quad (20)$$

If the solution to the problem of the equilibrium double layer $\phi^{(\text{eq})}$ is known, then the velocity is determined by the above formula. Thus, the solutions to the respective flow problems for the equilibrium situations considered in the previous subsection are readily written down. Solution to the electrokinetic equations is facilitated if the Debye layer thickness λ_D may be assumed small compared to the characteristic channel width w_0 . This however is not usually the case in nanochannels since w_0 and λ_D are both on the order of nanometers. Exact analytical solutions are therefore rare except in situations with a high degree of symmetry such as noted above.

Molecular Models

At scales approaching a nanometer or less, the continuum equations are entirely inappropriate. In such situations the fluid must be described as a collection of interacting atoms. The equations of motion of these atoms can be evolved in time by computer simulation, a procedure known as Molecular Dynamics. A very brief overview of Molecular Dynamics is provided here, for further details see the entry on that topic in this volume.

Dynamical Equations

The equations of motion of the individual atoms are given by the second law of Newton:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i V. \quad (21)$$

Here m_i is the mass of the i th atom and $\mathbf{r}_i$ is the position vector at time t . The symbol ∇_i indicates the gradient operator with differentiation with respect to the co-ordinates of the i th atom only, that is, in cartesian co-ordinates the right hand side has components $-\partial V/\partial x_i$, $-\partial V/\partial y_i$ and $-\partial V/\partial z_i$. The potential V which depends on the instantaneous location of every atom contains all the information

about how the atoms are held together within individual molecules as well as how two different molecules interact. A full determination of the potential V from first principles will require the solution of the quantum mechanical problem involving interactions of all of the nuclei and electrons. Such a computation is not practical in general but approximations that involve neglecting effects that are not dominant allow approximate interaction potentials to be obtained.

Interaction Potentials

First, the potential V is split into two parts, the *bonded* and *non-bonded* ones

$$V = V_{\text{bonded}} + V_{\text{non-bonded}}. \quad (22)$$

The first, V_{bonded} takes into account all of the forces that keep the atoms bound together into a molecule, the second, $V_{\text{non-bonded}}$ describe the interactions between the atoms within a molecule with those within another molecule.

The Bonded Potential As a simple example one might consider a diatomic molecule. Here one may write

$$V_{\text{bonded}} = \frac{1}{2} k_r (r - r_e)^2 \quad (23)$$

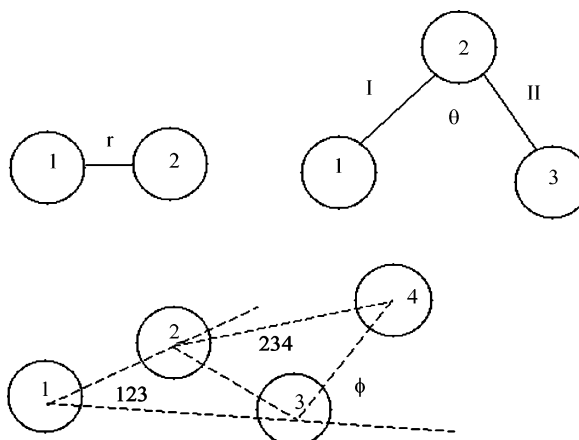
where r_e is the equilibrium bond length, r is the instantaneous distance between the atoms and k_r is a positive constant (like a *spring constant*) that determines the frequency of oscillation of the dumbbell shaped molecule about its equilibrium shape.

If there are three atoms 1, 2 and 3 connected by two bonds I and II then there will be two terms like Eq. (23), one for bond I and one for bond II with possibly different values of k . In addition, there would be a contribution

$$V_{\text{bonded}} = \frac{1}{2} k_\theta (\theta - \theta_e)^2 \quad (24)$$

due to the fact that the bond can flex so that the bond angle undergoes small oscillations about the equilibrium value $\theta = \theta_e$.

If there are four atoms then there is an additional mode of distortion of the molecule. Atoms 1, 2 and 3 always lie on a plane, call this the plane 123. This plane however may not coincide with the plane 234 on which atoms 2, 3 and 4 lie. If it does, then we have a coplanar molecule, otherwise there is a non-zero angle ϕ between the two planes which could change as the molecule moves around and interacts with neighboring ones (see Fig. 1). In general there is a contribution to the potential that determines changes



Electrokinetic Flow and Ion Transport in Nanochannels, Figure 1 Sketch showing the bonded interactions in the case of two, three and four atom molecules in an MD simulation

in ϕ . This piece of the bonded potential is usually written as

$$V_{\text{bonded}} = \frac{1}{2} \sum_{m=1}^{\infty} k_\phi^{(m)} [1 + \cos(m\phi - \phi_m)]. \quad (25)$$

The right hand side is nothing but one way of writing a Fourier series expansion of the potential in ϕ . Since the potential has to be periodic with period 2π it can always be written in this way for some values of the constants $k_\phi^{(m)}$ and ϕ_m . For $m = 1$, the ϕ dependence is given by $[1 + \cos(\phi - \phi_1)]$. This is identical to the potential that describes the motion of a simple pendulum where ϕ is the angular displacement and $\phi = \phi_1$ the position of stable equilibrium. It is useful to recall that the pendulum has two kinds of motion, oscillations about the position of stable equilibrium and rotation about its point of support. Similarly, Eq. (25) allows both small oscillations about equilibrium as well as full 360° rotations. For example, the ethane molecule C_2H_6 rotates very easily around the C–C bond. For longer molecules V_{bonded} is constructed by first identifying all bonds between atom pairs and adding up the contributions of the form of Eq. (23). Then all the bond angles are identified and each contributes a term like Eq. (24). Finally, all of the angles between planes of atoms are identified and each such angle will result in a contribution of type Eq. (25). This procedure describes the simplest kind of bonded interactions possible. The forms of Eqs. (23), (24) and (25) are not the only possible description of these interactions, different cross terms (such as *stretch-bend*) may be included for greater accuracy.

The Non-Bonded Potential It is convenient to decompose the non-bonded potential into 1-body, 2-body, 3-body, ... interactions:

$$V_{\text{non-bonded}} = \sum_i U_i + \sum_{i < j} U_{ij} + \dots \quad (26)$$

Here U_i is the potential of atom i due to some external field (such as an applied electric field or due to confinement in a finite domain such as within the walls of a nanotube). The i - j pair interactions describe the force between atoms i and j in the absence of all other atoms. This however is only an approximation to the true force, because the presence of a third atom in the vicinity would generally cause some distortion in the electron cloud around atoms 1 and 2 and therefore change the interaction force. Such three and higher body interactions are however relatively small and are usually neglected. That is, the series Eq. (26) is usually truncated at the second term. We now discuss the most common types of pair interactions.

If a pair of atoms i - j on two different molecules carry a net charge of Q_i and Q_j then there is a Coulomb contribution to the non-bonded potential that arises out of this pair interaction

$$V_{\text{non-bonded}} = \frac{Q_i Q_j}{r_{ij}} \quad (27)$$

(in CGS units) where r_{ij} is the distance between the pair. There is an analogous contribution for each distinct pair of atoms and the total potential is given by the sum of all such terms. For example, in an ionic solution the ions will interact via such Coulomb interactions. In addition, every pair of atoms (charged or not) that sit on different molecules interact via an intermolecular potential for which most often the Lennard-Jones form is used:

$$V_{\text{non-bonded}} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]. \quad (28)$$

The parameters ϵ and σ depends on the kinds of atoms in the i - j pair. The important thing about the **Lennard-Jones potential** is that it is repulsive at short range (characterized by a length scale σ) and attractive at long range with the attractive interaction inversely proportional to the sixth power of the distance. The short range repulsion is caused by the mutual repulsion of the electron clouds of the atoms that keep the atoms apart. The attractive interaction at long range is known as the **Van-der Waals** attractions. For an explanation of its origin the reader is referred to the contribution on that subject in this volume. In addition

particular classes of applications require the addition of special kinds of interaction potentials (e.g. hydrogen bonds, hydrophobic effects etc.) and these are described in more specialized books and papers.

Numerical Integration

Computer simulation of the molecular motion calls for the numerical integration of Eq. (21) for each atom starting from some random initial conditions. Various algorithms for doing this are known with their advantages and drawbacks. The simplest most robust and almost universally used technique is the Velocity-Verlet algorithm also known as the *Leap Frog Method*. To apply this algorithm, we first write Eq. (21) as a pair of first order equations:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} \quad (29)$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{f}_i = -\nabla_i V. \quad (30)$$

Here $\mathbf{p}_i$ is the momentum of atom i and $\mathbf{f}_i$ is the force on it. The velocity Verlet algorithm with step size δt is:

$$\mathbf{p}_i(t + \frac{1}{2}\delta t) = \mathbf{p}_i(t) + \frac{\delta t}{2}\mathbf{f}_i(t) \quad (31)$$

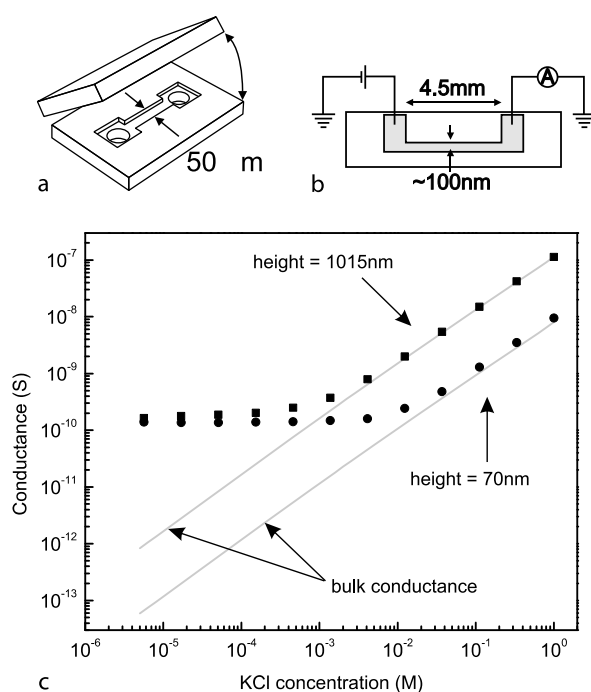
$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{p}_i(t + \frac{1}{2}\delta t) \frac{\delta t}{m_i} \quad (32)$$

$$\mathbf{p}_i(t + \delta t) = \mathbf{p}_i(t + \frac{\delta t}{2}) + \frac{\delta t}{2}\mathbf{f}_i(t + \delta t). \quad (33)$$

Key Research Findings

The research literature on nanopores or nano-channels of biological origin is vast and spans more than half a century. These channels are a fraction of a nanometer to a few nanometer wide and are made of proteins embedded in lipid bi-layer membranes. The main scientific questions here relate to the physical mechanism of selectivity and gating, that is, questions such as what makes a sodium channel permeable to only sodium ions but not to potassium or calcium ions which are very similar. Further, by what physical mechanism do these channels open and close in response to voltage changes, ligand binding and other events? Electrokinetic flows is usually not the focus in this area of study and hence this is an area that we do not touch upon. The reader whose primary interest is in nanopores in the biological context could use [1] as an introduction to that subject.

In the realm of artificial nano-channels in the biotechnology context, a key issue concerns the electrical conductance of such channels. Artificial nano-channels are

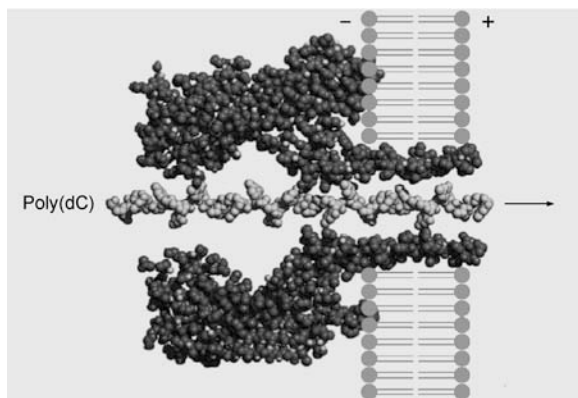


Electrokinetic Flow and Ion Transport in Nanochannels, Figure 2 The measured conductance of a nanochannel as a function of electrolyte concentration showing the transition from the expected behavior (lines) to a conductance determined by the surface charge. Panels (a) and (b) show the set up of the experiment [11]

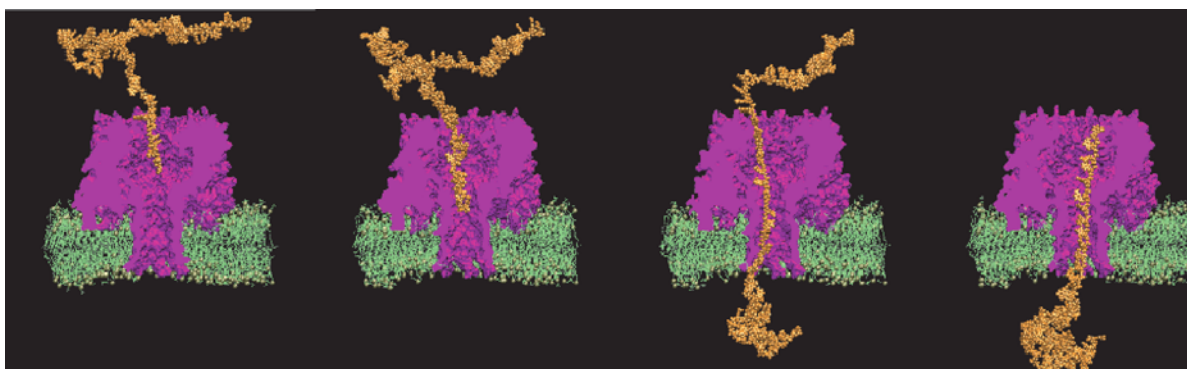
tens of nanometers wide, so a length of the channel equal to its diameter contains of the order of a million water molecules. The interface between the channel wall and the water that it contains typically has an electrostatic charge which is characterized by its zeta-potential typically in the range of tens of millivolts. In an ionic solution the wall charge results in the formation of a Debye Layer of counter-ions next to it. Nano-channels differ from micro-channels with respect to the thickness of this Debye layer relative to the channel diameter: whereas in microchannels this fraction is extremely small, in a nanochannel it is typically of order unity. As a result, the conductance of nano-channels differ from the bulk conductance (conductance per unit volume of the electrolyte in the absence of confining walls multiplied by the volume of the channel). The channel conductance is found to depend on the electrolyte concentration as well as on the surface charge density of the channel. The dependence is shown in Fig. 2 and may be summarized as follows: at sufficiently high concentrations of the electrolyte the measured conductance approaches the bulk conductance which is proportional to the electrolyte concentration. As the concentration is lowered, the conductance deviates from the proportionality

relation and approaches a value independent of the concentration. This constant value is higher the higher the surface charge density is in the nano-channel. Further, the transition from constant to proportionate behavior with respect to the electrolyte concentration shifts upwards with higher surface charge. This is because at high electrolyte concentrations, the Debye Layer is very thin so that most of the current is carried by the ions in the core of the channel. Thus, the conductance approaches the bulk conductance. At low concentrations, there are very few co-ions and the nano-channel attracts a sufficient number of counter-ions so that the channel as a whole is charge neutral. The conductance is determined by the number of such counter-ions present and this is determined by the surface charge not on the ion density in the bulk electrolyte. Thus, the conductance becomes independent of the electrolyte concentration and increases with the surface charge. A quantitative calculation based on the above physical picture gives reasonably good agreement with the measured data as seen in Fig. 2. In view of the fact that the conductance is controlled by the surface charge, it has been suggested that it may be possible to control the conductance of a channel by controlling the surface charge by an externally applied voltage. In fact, not just the electrical conductance but the flux of macro-ions can be controlled this way creating a *nano-transistor* that can be tuned to be selectively permeable to specific biomolecules much like the “gated” nanopores in biological systems.

Just as a voltage can drive charged macro-ions through nanopores, long chains of such ions or **polyelectrolytes** (charged polymers) can also be driven through nanopores (see Fig. 3 and Fig. 4). Research in this area is driven by the possibility of developing a new technology for super



Electrokinetic Flow and Ion Transport in Nanochannels, Figure 3 Molecular model showing a single strand of poly(dC) DNA passing through an α -hemolysin protein pore in a lipid bi-layer membrane. The surrounding water molecules have not been shown [12]



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Electrokinetic Flow and Ion Transport in Nanochannels, Figure 4 A sequence of four frames (movie available on the online version of this volume) from a MD simulation movie showing a single stranded DNA molecule being pulled through an alpha Hemolysin nanopore by the application of an electric field [13]

fast DNA sequencing. The central fact is that the passage of a polyelectrolyte through a nanopore produces a measurable change in the pore conductance. It has been shown that using this effect DNA in solution can be detected and counted at the single molecule level. Further, based on the duration of the blockage the length of the DNA can be characterized with a margin of error of the order of a few tens of bases. Using a combination of translocation time and intensity of the current blockage, homopolymers of DNA and RNA made of pyrimidine bases can be distinguished from pyrimidines. Furthermore, block co-polymers such as AAAAAA.....CCCCC..... containing more than about 30 or so repeating units can be distinguished from other similar structures. A fundamental theoretical question in this area related to electrokinetic flows is: what determines the translocation time of a single polyelectrolyte across a nanopore? It has been shown that the shape of the distribution function for translocation times can be explained by means of a probabilistic *drift diffusion process*. A calculation of the average speed of translocation of polyelectrolytes of moderate size based on the continuum electrokinetic equations yields values consistent with the measured ones for solid state nanopores (diameter ~ 10 nm). The majority of theoretical papers in this area have focussed on the issue of how the mean translocation time scales with the length of the polymer and there appears to be different scaling regimes for short vs. long polymers (see [5] and references within).

Another key question relates to electroosmotic flow of water in nanochannels where the focus is on the question on whether or not any deviations from the predictions of the classical continuum electrokinetic equations is observable. Computer simulations by MD has shown that the flow profile shows considerable deviation from

the classical regime in certain parameter ranges that can be attributed to a variety of effects (hydrogen bonding of water to negatively charged surfaces, the effect of charge oscillations due to correlations etc.) A fundamental question which is broader than the subject of electrokinetic flows concerns the applicability of the no-slip boundary condition to micro/nanoscale flows. It appears that the so called *Navier slip boundary conditions* $b \partial_z U + U = 0$ better describes the flow at small scales where U is the velocity along the impermeable surface and z is the direction perpendicular to it. The value of b depends on the wetting properties of the surface among other things and is closer to *no-slip* ($b = 0$) for hydrophilic surfaces. Further discussion on this issue may be found in the contribution *Boundary Slip of Liquids* in this volume.

Future Directions for Research

The subject of flow and transport in nanochannels is a very young one and there are many avenues for theoretical as well as experimental investigations and the potential for many novel devices that might be developed as a result of these investigations. The idea of a *Nano Transistor* that can be tuned to be selectively permeable to certain macromolecules while blocking others is an area that may see some rapid development on the practical side. The same can be said about the idea of sequencing biopolymers using nanopore translocation. There are deep theoretical questions surrounding the issue of how fluid and ions flow through nanochannels and in what ways such transport differs from expectations based on classical hydrodynamics and the Poisson-Boltzmann equation [10]. The effect of correlations, finite size of molecules, hydrogen bonding and other short range interactions, wettability are all

expected to play a role and it is in extending our understanding of fluid flow and ion transport to account for these effects that the future challenge lies.

Cross References

- ▶ Boundary Slip of Liquids
- ▶ Electric Double Layer Interaction
- ▶ Electric Double Layers
- ▶ Electroosmotic Flow (DC)
- ▶ AC Electro-Osmotic Flow
- ▶ Gas Flow in Nanochannels
- ▶ Interfacial Electrokinetic Flow
- ▶ Ion Channel
- ▶ Micro- and Nanoscale Gas Dynamics
- ▶ Molecular Dynamics Simulation Method
- ▶ Nanochannel Fabrication
- ▶ Nanofluidic Systems for Single Molecule Detection
- ▶ Nanofluidics in Carbon Nanotubes
- ▶ Van der Waals Attraction Forces

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Electrokinetic Flow in Porous Media

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Synonyms

Electroosmotic flow in porous media; Electroosmosis in porous media

Definition

A porous medium is referred to as a solid frame or matrix permeated by an interconnected network of pores (voids) filled with a fluid (liquid or gas). In the field of micro- and nanofluidics, the term electroosmotic flow (usually interchangeable with electroosmosis or electrokinetic flow) is defined as the migration of bulk ionic liquid due to the interaction between an applied electric field tangentially along a charged surface and the excess net charge density in the electric double layer of such a charged surface. Therefore, electrokinetic flow in porous media is referred to as the motion of bulk ionic liquid flowing through a porous medium as a result of the interplay of an applied electric field and the excess charge density in the electric double layer of the charged porous structure.

Overview

Fluid flow through porous media is a subject of much interest and has a wide spectrum of applications in applied science and engineering. The discovery of electrokinetic flow in porous media can be traced back to the early 1800s when Reuss observed water migration through porous clay diaphragms under an applied electric field. Applications of electrokinetic flow in porous media can be found in many technological processes, such as dewatering of waste sludge and removing poisonous heavy metal ions from contaminated soils for environmental remediation [1]. The charging mechanisms of the porous solid–liquid interface are complex, possibly including the asymmetric dipoles of water molecules residing at the solid–liquid interface, adsorption of ions, disassociation of ionic groups, charge separation, etc. The presence of surface charges will influence the distribution of nearby ions in the solution. Counter-ions (i.e., ions of opposite charge)