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ORIGINAL CONTRIBUTION

Electroosmotic flow on an arbitrarily charged planar surface

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Abstract A general expression for the electroosmotic flow on an arbitrarily (i.e., both uniformly and nonuniformly) charged planar surface under an applied static electric field is derived. We treat the case in which the applied field is weak so that the flow is slow enough to obey the Stokes approximation at low Reynolds numbers and the electric potential is low enough to obey the linearized Poisson-Boltzmann equation. As examples, the flow around a sinusoidally charged planar surface and that around a charged planar surface carrying a square lattice of point charges are considered. The latter is related to the discrete-charge effect upon the electroosmotic flow.

Keywords Electroosmotic flow · Arbitrarily charged surface · Nonuniformly charged surface · Sinusoidally charged surface · Discrete charge effect

Introduction

Electrokinetic measurements are a powerful tool for characterizing the electric properties of charged surfaces [1–19]. It is usually assumed that charges are uniformly distributed on the surface, and accordingly, only a few studies treat nonuniformly charged surfaces [20–29]. In the case of the electroosmotic flow on a uniformly charged surface under an external static electric field applied parallel to the surface, only the component of the liquid velocity parallel to the applied electric field has non-zero values and the other two velocity components are both zero. In the case of a nonuniformly charged surface, the liquid velocity component parallel to the applied electric field alters along the surface due to the charge distribution on the surface. This inevitably causes a change in the other velocity components, resulting in their non-zero values. The purpose of the present paper is to derive a general expression for the electroosmotic flow distribution around an arbitrarily (i.e., both uniformly and nonuniformly) charged planar surface in an electrolyte solution under an applied static electric field. We set the following conditions: (i) the applied static electric field is weak so that we may employ the Stokes approximation for the NavierStokes equation at low Reynolds numbers. (ii) The planar surface is weakly charged so that we may employ the linearized Poisson Boltzmann-equation for the electric potential. As a simple example of a nonuniformly charged surface, we consider a surface carrying a periodic charge distribution, which changes only one direction. We also consider a surface carrying a square lattice of point charges. This example is related to the discrete-charge effect [30–36] upon the electroosmotic flow.

Electric potential distribution

We consider an arbitrarily charged planar surface placed in contact with a liquid containing a general electrolyte composed of N ionic species with valence z_i and bulk concentration (number density) n_i^∞ under an applied static electric field $\boldsymbol{E}$. We treat the case where the surface is infinitely large. We take a Cartesian coordinate system (x, y, z) with its origin on the surface in the x-y plane (Fig. 1). The z-axis is normal to the x-y plane. $\boldsymbol{E}$ is oriented parallel to the surface along the x-axis. We first consider the equilibrium electric potential distribution $\psi(\boldsymbol{r})=\psi(x, y, z)$ at position $\boldsymbol{r}=(x, y, z)$ in the electrical diffuse double layer formed around the surface. We denote the charge density of the surface by $\sigma(\boldsymbol{s})=\sigma(x, y)$, where $\boldsymbol{s}=(x, y)$.

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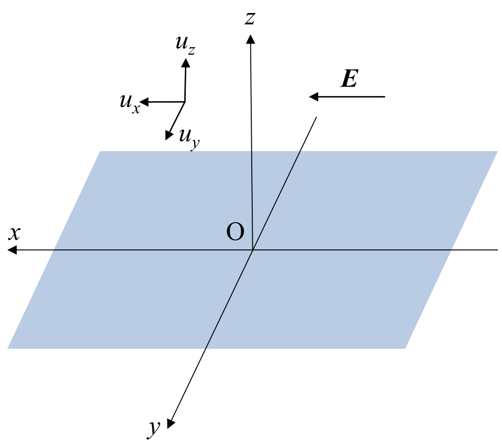

Fig. 1 Electroosmotic flow $\boldsymbol{u}(u_x, u_y, u_z)$ on an arbitrarily charged planar surface in an applied static electric field $\boldsymbol{E}$. Cartesian coordinate system (x, y, z) with its origin on the surface in the x-y plane is used. The z-axis is normal to the x-y plane. $\boldsymbol{E}$ is oriented parallel to the surface along the x-axis

We consider the Poisson-Boltzmann equation for $\psi(\boldsymbol{r})$, viz,

$$\Delta\psi(\boldsymbol{r}) = -\frac{\rho_{\mathrm{el}}(\boldsymbol{r})}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}} \tag{1}$$

with

$$\rho_{\mathrm{el}}(\boldsymbol{r}) = \sum_{i=1}^{N} z_i e n_i(\boldsymbol{r}) = \sum_{i=1}^{N} z_i e n_i^{\infty} \exp\left(-\frac{z_i e\psi(\boldsymbol{r})}{kT}\right) \tag{2}$$

Here, Δ is the Laplacian operator, $\rho_{\mathrm{el}}(\boldsymbol{r})$ is the space charge density resulting from the electrolyte ions, ε_{r} is the relative permittivity of the solution, ε_{o} is the permittivity of a vacuum, $n_i(\boldsymbol{r})=n_i^{\infty}\exp(-z_i e\psi(\boldsymbol{r})/kT)$ is the concentration (number density) of ith ionic species at position $\boldsymbol{r}$, e is the elementary electric charge, k is Boltzmann's constant, and T is the absolute temperature. We treat the case where the potential $\psi(\boldsymbol{r})$ is low enough to allow linearization of Eq. (2) with respect to $\psi(\boldsymbol{r})$. Then Eq. (2) reduces to

$$\rho_{\mathrm{el}}(\boldsymbol{r}) = -\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2\psi(\boldsymbol{r}) \tag{3}$$

where the following electroneutrality condition has been used:

$$\sum_{i=1}^{N} z_i n_i^{\infty} = 0 \tag{4}$$

and

$$\kappa = \left(\frac{1}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}kT}\sum_{i=1}^{N} z_i^2 e^2 n_i^{\infty}\right)^{1/2} \tag{5}$$

is the Debye-Hückel parameter. Equation (1) as combined with Eq. (3) thus yields

$$\Delta\psi(\boldsymbol{r}) = \kappa^2\psi(\boldsymbol{r}), 0 < z < +\infty \tag{6}$$

The boundary conditions for Eq. (6) are

$$\left.\frac{\partial\psi(\boldsymbol{r})}{\partial z}\right|_{z=0^+} = -\frac{\sigma(\boldsymbol{s})}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}} \tag{7}$$

$$\psi(r)\to 0, \frac{\partial\psi(\boldsymbol{r})}{\partial z}\to 0 \text{ as } z\to+\infty \tag{8}$$

In order to solve Eq. (6) subject to Eqs. (7) and (8), we write $\psi(\boldsymbol{r})$ and $\sigma(\boldsymbol{s})$ by their Fourier transforms,

$$\psi(\boldsymbol{r}) = \psi(\boldsymbol{s}, z) = \frac{1}{(2\pi)^2}\int \widehat{\psi}(\boldsymbol{k}, z)e^{i\boldsymbol{k}\cdot\boldsymbol{s}}d\boldsymbol{k} \tag{9}$$

$$\sigma(\boldsymbol{s}) = \frac{1}{(2\pi)^2}\int \widehat{\sigma}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{s}}d\boldsymbol{k} \tag{10}$$

where $\widehat{\psi}(\boldsymbol{k}, z)$ and $\widehat{\sigma}(\boldsymbol{k})$ are the Fourier coefficients and $\boldsymbol{k}=(k_x, k_y)$. We thus obtain

$$\widehat{\psi}(\boldsymbol{k}, z) = \int \psi(\mathbf{s}, z)e^{-i\mathbf{k}\cdot\mathbf{s}}d\mathbf{s} \tag{11}$$

$$\widehat{\sigma}(\boldsymbol{k}) = \int \sigma(\mathbf{s})e^{-i\mathbf{k}\cdot\mathbf{s}}d\mathbf{s} \tag{12}$$

Substituting Eqs. (11) and (12) into Eq. (6)–(8), we have

$$\frac{\partial^2\widehat{\psi}(\boldsymbol{k}, z)}{\partial z^2} = (\kappa^2 + k^2)\widehat{\psi}(\boldsymbol{k}, z), 0 < z < +\infty \tag{13}$$

where

$$k = |\boldsymbol{k}| = \sqrt{k_x^2 + k_y^2} \tag{14}$$

and the boundary conditions (Eqs. (7) and (8)) become

$$\left.\frac{\partial\widehat{\psi}(\boldsymbol{k}, z)}{\partial z}\right|_{z=0^+} = -\frac{\widehat{\sigma}(\boldsymbol{k})}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}} \tag{15}$$

$$\widehat{\psi}(\boldsymbol{k}, z)\to 0, \frac{\partial\widehat{\psi}(\boldsymbol{k}, z)}{\partial z}\to 0 \text{ as } z\to+\infty \tag{16}$$

By solving Eq. (13) subject to Eqs. (15) and (16), we obtain

$$\widehat{\psi}(\boldsymbol{k},z)=\frac{\widehat{\sigma}(\boldsymbol{k})}{\varepsilon_r\varepsilon_o\sqrt{k^2+\kappa^2}}e^{-\sqrt{k^2+\kappa^2}z},\ 0<z<+\infty \tag{17}$$

Substitution of Eq. (17) into Eq. (9) yields

$$\psi(\boldsymbol{r})=\frac{1}{(2\pi)^2\varepsilon_r\varepsilon_o}\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}}e^{i\boldsymbol{k}\cdot\boldsymbol{s}}\cdot e^{-\sqrt{k^2+\kappa^2}z}\,d\boldsymbol{k},0\le z<\infty \tag{18}$$

Equation (18) is the general expression for the electric potential $\psi(\boldsymbol{r})$ at position $\boldsymbol{r}$ around an arbitrarily charged planar surface.

Liquid flow velocity distribution

Now, consider the liquid flow velocity $\boldsymbol{u}(u_x, u_y, u_z)$ around an arbitrarily charged planar surface under an applied static electric field $\boldsymbol{E}(E, 0, 0)$ (Fig. 1). We treat the case where the applied electric field is weak so that we may employ the following Stokes approximation for the Navier-Stokes equation for the liquid flow velocity $\boldsymbol{u}(\boldsymbol{r})$ at low Reynolds numbers:

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r})-\nabla p(\boldsymbol{r})-\rho_{el}(\boldsymbol{r})\nabla\Psi(\boldsymbol{r})=\boldsymbol{0} \tag{19}$$

$$\mathrm{div}\boldsymbol{u}(\boldsymbol{r})=0 \tag{20}$$

where η is the viscosity, $p(\boldsymbol{r})$ is the pressure, $\Psi(\boldsymbol{r})$ is the electric potential, and Eq. (20) is the continuity equation for an incompressible fluid. The boundary condition for $\boldsymbol{u}(\boldsymbol{r})$ is given by

$$u(r)=\boldsymbol{0}\ \text{at}\ z=0 \tag{21}$$

The electroosmotic velocity $\boldsymbol{U}$ is given by

$$\boldsymbol{U}=\lim_{z\to\infty}\boldsymbol{u}(r) \tag{22}$$

Since the external electric filed is applied parallel to the charged surface and the surface is infinitely large, the potential $\Psi(\boldsymbol{r})$ may be expressed as the sum of the equilibrium double layer potential $\psi(\boldsymbol{r})$ and the potential $-Ex$ of the applied electric field $\boldsymbol{E}$, viz,

$$\Psi(\boldsymbol{r})=\psi(\boldsymbol{r})-Ex \tag{23}$$

By substituting Eq. (23) into Eq. (19) and replacing $\rho_{el}(\boldsymbol{r})$ with $\psi(\boldsymbol{r})$ on the basis of Eq. (3), we obtain

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r})-\nabla\left\{p(\boldsymbol{r})-\frac{1}{2}\varepsilon_r\varepsilon_o\kappa^2\psi^2(\boldsymbol{r})\right\}-\varepsilon_r\varepsilon_o\kappa^2\psi(\boldsymbol{r})\boldsymbol{E}=\boldsymbol{0} \tag{24}$$

We take the curl of Eq. (24) to eliminate the gradient term so that we obtain

$$\eta\nabla\times\Delta\boldsymbol{u}(\boldsymbol{r})-\varepsilon_r\varepsilon_o\kappa^2\nabla\times(\psi(\boldsymbol{r})\boldsymbol{E})=\boldsymbol{0} \tag{25}$$

By taking the curl of Eq. (25) again and using Eq. (20), we obtain

$$\Delta^2u_x(\boldsymbol{r})+\frac{\varepsilon_r\varepsilon_o\kappa^2E}{\eta}\left(\frac{\partial^2\psi(\boldsymbol{r})}{\partial x^2}-\Delta\psi(\boldsymbol{r})\right)=0 \tag{26}$$

$$\Delta^2u_y(\boldsymbol{r})+\frac{\varepsilon_r\varepsilon_o\kappa^2E}{\eta}\frac{\partial^2\psi(\boldsymbol{r})}{\partial x\partial y}=0 \tag{27}$$

$$\Delta^2u_z(\boldsymbol{r})+\frac{\varepsilon_r\varepsilon_o\kappa^2E}{\eta}\frac{\partial^2\psi(\boldsymbol{r})}{\partial z\partial x}=0 \tag{28}$$

We note that the linearized Poisson-Boltzmann equation (6) gives

$$\psi(\boldsymbol{r})=\frac{1}{\kappa^2}\Delta\psi(\boldsymbol{r})=\frac{1}{\kappa^4}\Delta^2\psi(\boldsymbol{r}) \tag{29}$$

then we obtain from Eqs. (26)–(29)

$$\Delta^2\left\{u_x(\boldsymbol{r})-\frac{\varepsilon_r\varepsilon_oE}{\eta}\left(\psi(\boldsymbol{r})-\frac{1}{\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial x^2}\right)\right\}=0 \tag{30}$$

$$\Delta^2\left\{u_y(\boldsymbol{r})+\frac{\varepsilon_r\varepsilon_oE}{\eta\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial x\partial y}\right\}=0 \tag{31}$$

$$\Delta^2\left\{u_z(\boldsymbol{r})+\frac{\varepsilon_r\varepsilon_oE}{\eta\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial z\partial x}\right\}=0 \tag{32}$$

The general solution to the biharmonic equation $\Delta^2\Phi=0$ is given by

$$\Phi(\boldsymbol{r})=\frac{1}{(2\pi)^2}\int C_1(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k}+\frac{1}{(2\pi)^2}\int C_2(\boldsymbol{k})ze^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} \tag{33}$$

where $C_1(\boldsymbol{k})$ and $C_2(\boldsymbol{k})$ are functions of $\boldsymbol{k}$ to be determined so as to satisfy the continuity equation (Eq. (20)) and the boundary conditions (Eq. (21)).

After some algebra, we finally obtain

$$u_x(\boldsymbol{r}) = \frac{E}{(2\pi)^2\eta}\left(1-\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}\right)\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}}e^{i\boldsymbol{k}\cdot\boldsymbol{s}}\left(e^{-\sqrt{k^2+\kappa^2}z}-e^{-kz}\right)d\boldsymbol{k} + \frac{E}{(2\pi)^2\eta}\int\frac{\widehat{\sigma}(\mathbf{k})}{\sqrt{k^2+\kappa^2}+k}kze^{i\mathbf{k}\cdot\mathbf{s}-kz}d\mathbf{k} \tag{34}$$

$$u_y(\boldsymbol{r}) = -\frac{E}{(2\pi)^2\eta\kappa^2}\frac{\partial^2}{\partial x\partial y}\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}}e^{i\boldsymbol{k}\cdot\boldsymbol{s}}\left(e^{-\sqrt{k^2+\kappa^2}z}-e^{-kz}\right)d\boldsymbol{k} \tag{35}$$

$$u_z(\boldsymbol{r}) = \frac{E}{(2\pi)^2\eta\kappa^2}\frac{\partial}{\partial x}\int\widehat{\sigma}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{s}}\left(e^{-\sqrt{k^2+\kappa^2}z}-e^{-kz}\right)d\boldsymbol{k} + \frac{E}{(2\pi)^2\eta}\frac{\partial}{\partial x}\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}+k}ze^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} \tag{36}$$

Alternative equivalent expressions for $u_x(\boldsymbol{r})$, $u_y(\boldsymbol{r})$, and $u_z(\boldsymbol{r})$ in terms of $\psi(\boldsymbol{r})$ are given below

$$u_x(\boldsymbol{r}) = \frac{\varepsilon_r\varepsilon_o E}{\eta}\left\{\psi(\boldsymbol{r})-\frac{1}{\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial x^2}\right\}-\frac{E}{(2\pi)^2\eta}\left(1-\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}\right)\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}}e^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} + \frac{E}{(2\pi)^2\eta}\int\frac{\widehat{\sigma}(\mathbf{k})}{\sqrt{k^2+\kappa^2}+k}kze^{i\mathbf{k}\cdot\mathbf{s}-kz}d\mathbf{k} \tag{37}$$

$$u_y(\boldsymbol{r}) = -\frac{\varepsilon_r\varepsilon_o E}{\eta\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial x\partial y} + \frac{E}{(2\pi)^2\eta\kappa^2}\frac{\partial^2}{\partial x\partial y}\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}}e^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} \tag{38}$$

$$u_z(\boldsymbol{r}) = -\frac{\varepsilon_r\varepsilon_o E}{\eta\kappa^2}\frac{\partial^2\psi(\boldsymbol{r})}{\partial z\partial x} - \frac{E}{(2\pi)^2\eta\kappa^2}\frac{\partial}{\partial x}\int\widehat{\sigma}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} + \frac{E}{(2\pi)^2\eta}\frac{\partial}{\partial x}\int\frac{\widehat{\sigma}(\boldsymbol{k})}{\sqrt{k^2+\kappa^2}+k}ze^{i\boldsymbol{k}\cdot\boldsymbol{s}-kz}d\boldsymbol{k} \tag{39}$$

Results and discussion

Equations (34)–(36) (or Eqs. (37)–(39)) for the liquid flow velocity distribution around an arbitrarily charge planar surface are the principal results of this paper.

Consider several cases of charge distribution $\sigma(\boldsymbol{s})$.

(i) Uniform smeared charge density

For the case of continuous distribution of smeared charges with a uniform density σ_o, that is,

$$\sigma(\boldsymbol{s}) = \sigma_o = \text{constant} \tag{40}$$

From Eqs. (12) and (40), we have

$$\widehat{\sigma}(\boldsymbol{k}) = \sigma_o\int e^{-i\boldsymbol{k}\cdot\boldsymbol{s}}d\boldsymbol{s} = (2\pi)^2\sigma_o\delta(\boldsymbol{k}) \tag{41}$$

where $\delta(\boldsymbol{k})$ is Dirac's delta function and we have used the following relation:

$$\delta(\boldsymbol{k}) = \frac{1}{(2\pi)^2}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{s}}d\boldsymbol{s} \tag{42}$$

Substituting Eq. (41) into Eqs. (18) and (34)–(36), we have the following results obtained via a smeared charge model:

$$\psi(\boldsymbol{r}) = \psi(z) = \frac{\sigma_o}{\varepsilon_r\varepsilon_o\kappa}e^{-\kappa z} \tag{43}$$

$$u_x(\boldsymbol{r}) = u_x(z) = -\frac{\sigma_o E}{\eta\kappa}(1-e^{-\kappa z}) \tag{44}$$

$$u_y(\boldsymbol{r}) = 0,\ \ u_z(\boldsymbol{r}) = 0 \tag{45}$$

and from Eq, (22), we obtain the electroosmotic velocity

$$\boldsymbol{U} = \lim_{z\to\infty}\boldsymbol{u}(\boldsymbol{r}) = \left(-\frac{\sigma_o E}{\eta\kappa}, 0, 0\right) \tag{46}$$

(ii) Sinusoidal charge distribution

Consider a planar surface carrying a sinusoidal charge distribution, viz,

$$\sigma(\boldsymbol{s}) = \sigma_o\{1+\cos(\boldsymbol{Q}\cdot\boldsymbol{s})\} \tag{47}$$

where $\boldsymbol{Q}$ is a constant vector. From Eqs. (12) and (47), we have

$$\widehat{\sigma}(\boldsymbol{k}) = (2\pi)^2\sigma_o\left[\delta(\boldsymbol{k})+\frac{1}{2}\{\delta(\boldsymbol{k}-\boldsymbol{Q})+\delta(\boldsymbol{k}+\boldsymbol{Q})\}\right] \tag{48}$$

By substituting Eq. (48) into Eq. (18), we obtain

$$\psi(\boldsymbol{r}) = \frac{\sigma_o}{\varepsilon_r\varepsilon_o\kappa}e^{-\kappa z} + \frac{\sigma_o}{\varepsilon_r\varepsilon_o\sqrt{Q^2+\kappa^2}}\cos(\boldsymbol{Q}\cdot\boldsymbol{s})e^{-\sqrt{Q^2+\kappa^2}z} \tag{49}$$

where $Q = |\boldsymbol{Q}|$.

Consider the special case of a sinusoidal charge distribution in the x-direction so that $\boldsymbol{Q}\cdot\boldsymbol{s} = Qx$. The potential distribution $\psi(\boldsymbol{r})$, which is found to be a function of x and z, becomes

$$\psi(x,z) = \frac{\sigma_o}{\varepsilon_r\varepsilon_o\kappa}e^{-\kappa z} + \frac{\sigma_o}{\varepsilon_r\varepsilon_o\sqrt{k^2+\kappa^2}}\cos(Qx)e^{-\sqrt{Q^2+\kappa^2}z} \tag{50}$$

The liquid velocity distribution $\boldsymbol{u}(\boldsymbol{r})\equiv(u_x(\boldsymbol{r}), u_y(\boldsymbol{r}), u_z(\boldsymbol{r}))$ can be derived from Eqs. (34)–(36) and we found that $u_y(\boldsymbol{r})=0$ and that u_x and u_y are functions of x and z, given by

$$u_x(\boldsymbol{r}) = u_x(x,z) = -\frac{\sigma_o E}{\eta\kappa}(1-e^{-\kappa z}) + \frac{\sigma_o E}{\eta\kappa^2}\cos(Qx)\left\{\sqrt{Q^2+\kappa^2}\left(e^{-\sqrt{Q^2+\kappa^2}z}-e^{-Qz}\right) + \frac{\kappa^2 Qze^{-Qz}}{Q+\sqrt{Q^2+\kappa^2}}\right\} \tag{51}$$

$$u_y(\boldsymbol{r}) = 0 \tag{52}$$

$$u_z(\boldsymbol{r}) = u_z(x,z) = -\frac{\sigma_o E}{\eta\kappa^2}Q\sin(Qx)\left(e^{-\sqrt{Q^2+\kappa^2}z}-e^{-Qz} + \frac{\kappa^2 ze^{-Qz}}{Q+\sqrt{Q^2+\kappa^2}}\right) \tag{53}$$

The expression for the electroosmotic velocity $\boldsymbol{U}$ for $Q\neq0$ is the same as Eq. (46) for the smeared charge model. Note, however, that the electroosmotic velocity $\boldsymbol{U}$ for $Q=0$ is given by the result for the smeared-charge model for a surface carrying a uniform charge density $2\sigma_o$. Equations (51)–(53) agree with Ajdari's results [22, 23].

It follows from Eqs. (51)–(53) that in the limit $Q/\kappa\to\infty$, $u_x(\boldsymbol{r})$ tends to the result of the smeared charge model for a surface carrying a uniform surface charge of density σ_o (Eqs. (43)–(46)) and that in the opposite limit $Q/\kappa\to0$, $u_x(\boldsymbol{r})$ tends to the result of the smeared charge model for a surface carrying a uniform surface charge of density $2\sigma_o$, viz,

$$u_x(\boldsymbol{r}) = u_x(x,z) = -\frac{2\sigma_o E}{\eta\kappa}(1-e^{-\kappa z}) \tag{54}$$

$$u_y(\boldsymbol{r}) = 0, u_z(\boldsymbol{r}) = 0 \tag{55}$$

and

$$\boldsymbol{U} = \lim_{z\to\infty}\boldsymbol{u}(\boldsymbol{r}) = \left(-\frac{2\sigma_o E}{\eta\kappa}, 0, 0\right) \tag{56}$$

Figures 2 and 3 show some results of the calculation of the liquid velocity distribution. Figure 2 shows the x component $u_x(0,z)$ of the liquid velocity directed parallel to $\boldsymbol{E}$ in the x-axis as a function of scaled distance κz from the charged surface calculated at $x=0$ for several values of Q/κ, where $u_x^*(0,z)=u_x(0,z)/(-\sigma_o E/\eta\kappa)$. We see that $u_x(0,z)$ actually tends to Eqs. (44) and (54) in the limit of large Q/κ (dotted line) and

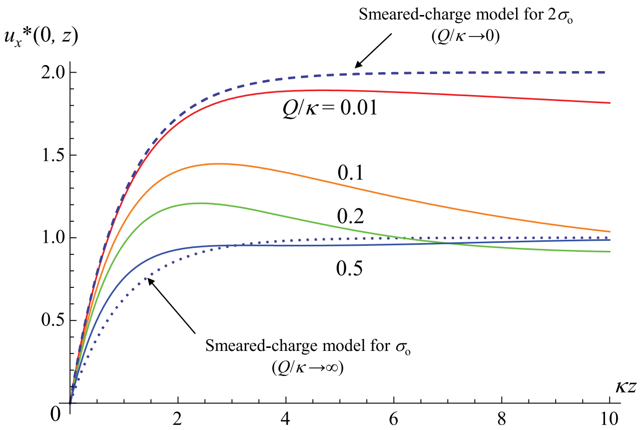

Fig. 2 The x component $u_x(0,z)$ of the liquid velocity on a surface with a sinusoidal charge distribution $\sigma(x)=\sigma_o\{1+\cos(Qx)\}$ as a function of κz calculated at $x=0$ for several values of Q/κ, where $u_x^*(0,z)=u_x(0,z)/(-\sigma_o E/\eta\kappa)$. The *dotted* and *dashed lines*, which are obtained via the smeared charge model, respectively, correspond to uniformly charged surfaces carrying surface charge densities of σ_o ($Q/\kappa\to\infty$) and $2\sigma_o$ ($Q/\kappa\to0$)

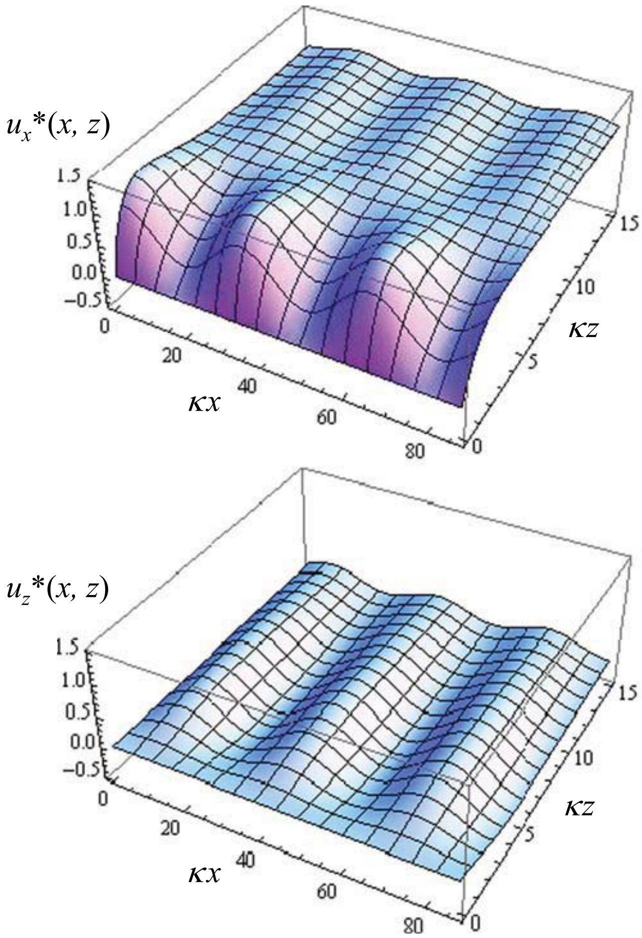

Fig. 3 Profiles of the x component $u_x(x,z)$ and z component $u_z(x,z)$ of the liquid velocity on a surface with a sinusoidal charge distribution $\sigma(x)=\sigma_o\{1+\cos(Qx)\}$ for $Q/\kappa=0.2$, where $u_x^*(x,z)=u_x(x,z)/(-\sigma_o E/\eta\kappa)$ and $u_z^*(x,z)=u_z(x,z)/(-\sigma_o E/\eta\kappa)$

small Q/κ (dashed line), respectively. We also see that for finite values of Q/κ, $u_x(0, z)$ exhibit a maximum in magnitude at $\kappa z \approx 2 \sim 3$, which corresponds to $z \approx 1/Q$. Figure 3 shows $u_x(x, z)$ and $u_z(x, z)$ as functions of x and z for $Q/\kappa = 0.2$. Figures 2 and 3 show that $u_x(\boldsymbol{r})$ does not increase monotonously as z increases. In the region near the surface $z \approx 1/Q$, $u_x(\boldsymbol{r})$ shows a maximum in magnitude (i.e., an overshoot in distance). Far from the surface $z \gg 1/Q$, however, $u_x(\boldsymbol{r})$ increases monotonously, tending to the electroosmotic velocity $\boldsymbol{U}$ (Eq. (22)). In the region near the surface, $u_x(\boldsymbol{r})$ alters periodically along the surface due to the periodic surface charge distribution $\sigma(\boldsymbol{s})$. As a result of the continuity equation for $\boldsymbol{u}(\boldsymbol{r})$ (i.e., $\mathrm{div}\boldsymbol{u}(\boldsymbol{r})=0$, Eq. (20)), the change in $u_x(\boldsymbol{r})$ inevitably causes a change in the other component of $\boldsymbol{u}(\boldsymbol{r})$ (that is, $u_z(\boldsymbol{r})$ in the present case) along the surface, resulting non-zero values of $u_z(\boldsymbol{r})$. That is, $u_z(\boldsymbol{r})$ is larger for the region where $u_x(\boldsymbol{r})$ is smaller and vice versa. The value of $u_z(x, z)$ becomes a minimum, where $u_x(x, z)$ reaches a maximum. Indeed, it follows from Eqs. (51) and (53) that the phase difference between $u_x(\boldsymbol{r})$ and $u_z(\boldsymbol{r})$ is $\pi/2$. Far from the particle surface, $u_z(\boldsymbol{r})$ vanishes.

(iii) A squared lattice of fixed point charges q with a spacing a

Now, we consider the discrete charge effect [30–36] on the electroosmotic flow. We deal with a planar surface carrying a squared lattice of point charges q with spacing a (Fig. 4). The point charges are thus located at lattice points $\boldsymbol{s}=(x, y)=(ma, na)$, where m and n take both positive and negative integers. The surface charge density $\sigma(\boldsymbol{s})$ is then expressed as

$$\sigma(\boldsymbol{s}) = q \sum_{-\infty<m,n<\infty} \delta(x-ma)\delta(y-na) \tag{57}$$

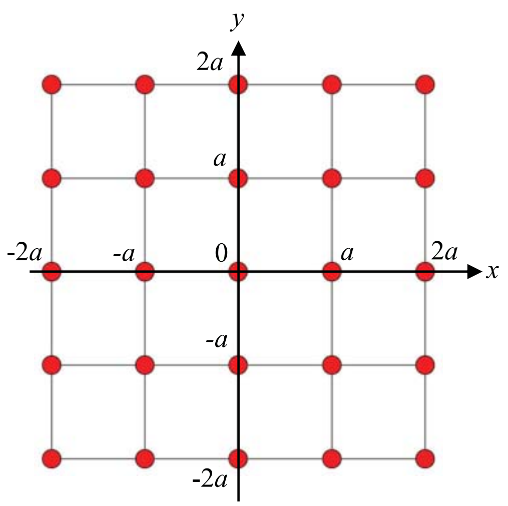

Fig. 4 Square lattice of fixed point charges q with a spacing of a

From Eqs. (12) and (57), we have

$$\begin{aligned}\widehat{\sigma}(\boldsymbol{k}) &= q\int \sum_{-\infty<m,n<\infty} \delta(x-ma)\delta(y-na)e^{i\boldsymbol{k}\cdot\boldsymbol{s}}d\boldsymbol{s} \\ &= q \sum_{-\infty<l,m<\infty} \exp\left(-i\left(k_x ma + k_y na\right)\right)\end{aligned} \tag{58}$$

By substituting Eq. (58) into Eqs. (18) and (34)–(36), we have the following expressions for $\psi(\boldsymbol{r})$ and $\boldsymbol{u}(\boldsymbol{r}) \equiv (u_x(\boldsymbol{r}), u_y(\boldsymbol{r}), u_z(\boldsymbol{r}))$:

$$\psi(\boldsymbol{r}) = \frac{q}{2\pi\varepsilon_r\varepsilon_o} \sum_{-\infty<l,m<\infty} \frac{\exp\left[-\kappa\sqrt{(x-ma)^2+(y-na)^2+z^2}\right]}{\sqrt{(x-ma)^2+(y-na)^2+z^2}}, 0<z<+\infty \tag{59}$$

and

$$\begin{aligned}u_x(\boldsymbol{r}) = {} & \frac{qE}{2\pi\eta} \sum_{-\infty<m,n<\infty} \left(1-\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}\right)\left\{\frac{\exp\left(-\kappa\sqrt{(x-ma)^2+(y-na)^2+z^2}\right)}{\sqrt{(x-ma)^2+(y-na)^2+z^2}}\right\} \\ & -\frac{qE}{2\pi\eta} \sum_{-\infty<m,n<\infty} \left(1-\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}\right)\left\{\int_0^\infty \frac{e^{-kz}}{\sqrt{k^2+\kappa^2}} J_0\left(k\sqrt{(x-ma)^2+(y-na)^2}\right)kdk\right\} \\ & +\frac{qE}{2\pi\eta} \sum_{-\infty<m,n<\infty} \int_0^\infty \frac{ze^{-kz}}{\sqrt{k^2+\kappa^2}+k} J_0\left(k\sqrt{(x-ma)^2+(y-na)^2}\right)k^2dk\end{aligned} \tag{60}$$

$$\begin{aligned}u_y(\boldsymbol{r}) = {} & -\frac{qE}{2\pi\eta\kappa^2} \sum_{-\infty<m,n<\infty} \frac{\partial^2}{\partial x\partial y}\left\{\frac{\exp\left(-\kappa\sqrt{(x-ma)^2+(y-na)^2+z^2}\right)}{\sqrt{(x-ma)^2+(y-na)^2+z^2}}\right\} \\ & +\frac{qE}{2\pi\eta\kappa^2} \sum_{-\infty<m,n<\infty} \frac{\partial^2}{\partial x\partial y}\left\{\int_0^\infty \frac{e^{-kz}}{\sqrt{k^2+\kappa^2}} J_0\left(k\sqrt{(x-ma)^2+(y-na)^2}\right)kdk\right\}\end{aligned} \tag{61}$$

$$\begin{aligned}u_z(\boldsymbol{r}) = {} & -\frac{qE}{2\pi\eta\kappa^2} \sum_{-\infty<m,n<\infty} \frac{\partial^2}{\partial z\partial x}\left\{\frac{\exp\left(-\kappa\sqrt{(x-ma)^2+(y-na)^2+z^2}\right)}{\sqrt{(x-ma)^2+(y-na)^2+z^2}}\right\} \\ & -\frac{qE}{2\pi\eta\kappa^2} \sum_{-\infty<m,n<\infty} \frac{\partial}{\partial x}\left\{\int_0^\infty e^{-kz} J_0\left(k\sqrt{(x-ma)^2+(y-na)^2}\right)kdk\right\} \\ & +\frac{qE}{2\pi\eta} \sum_{-\infty<m,n<\infty} \frac{\partial}{\partial x}\left\{\int_0^\infty \frac{ze^{-kz}}{\sqrt{k^2+\kappa^2}+k} J_0\left(k\sqrt{(x-ma)^2+(y-na)^2}\right)kdk\right\}\end{aligned} \tag{62}$$

where $J_0(z)$ is the zeroth-order Bessel function of the first kind.

It can be shown that the electroosmotic velocity $\boldsymbol{U}$ is given by

$$\boldsymbol{U} = \lim_{z\to\infty} \boldsymbol{u}(\boldsymbol{r}) = \left(-\frac{qE}{\eta\kappa a^2}, 0, 0\right) \tag{63}$$

which is the same as that obtained by the smeared charge model, as shown below. In the limit of $\kappa a \to 0$, Eqs. (60)–(62) tend to the results of the smeared charge model for a planar surface carrying a uniform charge of density q/a^2, viz,

$$u_x(\boldsymbol{r}) = u_x(x,y,z) = -\frac{qE}{\eta\kappa a^2}(1-e^{-\kappa z}) \tag{64}$$

$$u_y(\boldsymbol{r}) = 0, u_z(\boldsymbol{r}) = 0 \tag{65}$$

and the electroosmotic velocity is given by Eq. (63).Figure 5 shows the x component $u_x(0,0,z)$ of the liquid velocity on a surface carrying a squared lattice of point charges q with a spacing a as a function of κz calculated at $x=y=0$ for several values of κa, where $u_x^*(0,0,z)=u_x(0,0,z)/(-qE/\eta\kappa a^2)$. It can be seen that as $\kappa a\to 0$, $u_x(0,0,z)$ actually tends to the results of the smeared charge model (the dotted line). For large κa, however, the deviation of the results of the discrete charge effect from those of the smeared charge model becomes appreciable as in the case of other interfacial electric phenomena [30–36]. From Fig. 5, we see that, as in the case of a sinusoidally charged surface, $u_x(\boldsymbol{r})$ does not increase monotonously as z increases. In the region near the surface $z \sim a$, $u_x(\boldsymbol{r})$ shows a maximum in magnitude (i.e., an overshoot in distance). This is because $u_x(\boldsymbol{r})$ becomes larger at points closer to the fixed point charges q. As a result of the continuity equation for $\boldsymbol{u}(\boldsymbol{r})$ (i.e., div$\boldsymbol{u}(\boldsymbol{r})$=0, Eq. (20)), the change in $u_x(\boldsymbol{r})$ inevitably causes a change in the other components of $\boldsymbol{u}(\boldsymbol{r})$, that is, $u_y(\boldsymbol{r})$ and $u_z(\boldsymbol{r})$. Far from the surface $z \gg a$, however, $u_x(\boldsymbol{r})$ increases monotonously, tending to the electroosmotic velocity $\boldsymbol{U}$ (Eq. (63)) and both of $u_y(\boldsymbol{r})$ and $u_z(\boldsymbol{r})$ vanish.

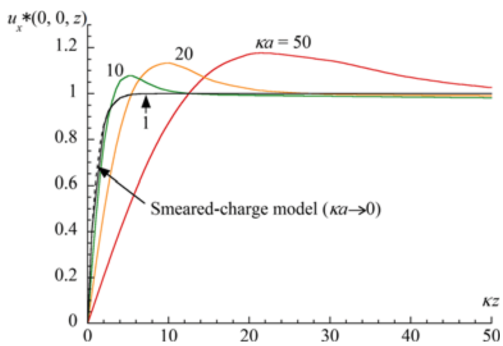

Fig. 5 The x component $u_x(0,0,z)$ of the liquid velocity on a surface carrying a squared lattice of point charges q with a spacing a as a function of κz calculated at $x=y=0$ for several values of κa, where $u_x^*(0,0,z)=u_x(0,0,z)/(-qE/\eta\kappa a^2)$. The *dotted line* corresponds to the smeared charge model c$\kappa a\to 0$

Conclusion

We have derived a general expression Eqs. (34)–(36) (or Eqs. (37)–(39)) for the velocity distribution $\boldsymbol{u}(\boldsymbol{r})$ on an arbitrarily charged planar surface in contact with an electrolyte solution under an applied electric field $\boldsymbol{E}$ for the case where the electric potential is low enough to allow linearization of the Poisson-Boltzmann equation. As examples, the results for a sinusoidal charge distribution (Eqs. (50)–(53)) and a squared lattice of point charges q with a spacing a (Eqs. (59)–(62)) are given.

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Detailed derivation of Eqs. (30)-(32)

Point: A set of the components of $\boldsymbol{u}(\boldsymbol{r})$ and $\psi(\boldsymbol{r})$ satisfies the biharmonic equation $\triangle^2 F = 0$.

Start with the Navier-Stokes equation for the liquid flow $\boldsymbol{u}(\boldsymbol{r})$:

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) - \rho_{\mathrm{el}}(\boldsymbol{r})\nabla\Psi(\boldsymbol{r}) = \boldsymbol{0} \tag{19}$$

where the electric potential $\Psi(\boldsymbol{r})$ is given by the sum of the equilibrium double layer potential $\psi(\boldsymbol{r})$ and the potential $-Ex$ of the applied external field $\boldsymbol{E}$ $(E, 0, 0)$,

$$\Psi(\boldsymbol{r}) = \psi(\boldsymbol{r}) - Ex \tag{23}$$

Assume that $\psi(\boldsymbol{r})$ obeys the linearized Poisson-Boltzmann equation:

$$\Delta\psi(\boldsymbol{r}) = \kappa^2\psi(\boldsymbol{r}) \tag{6}$$

which gives

$$\psi(\boldsymbol{r}) = \frac{1}{\kappa^2}\Delta\psi(\boldsymbol{r}) = \frac{1}{\kappa^4}\Delta^2\psi(\boldsymbol{r}) \tag{29}$$

The charge density $\rho_{\mathrm{el}}(\boldsymbol{r})$, which is related to $\psi(\boldsymbol{r})$ by Eq. (1), is given by, for the low potential case,

$$\rho_{\mathrm{el}}(\boldsymbol{r}) = -\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\Delta\psi(\boldsymbol{r}) = -\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2\psi(\boldsymbol{r}) \tag{3}$$

By substituting Eqs. (3) and (23) into Eq. (19), we obtain

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) + \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2\psi(\boldsymbol{r})\nabla\{\psi(\boldsymbol{r}) - Ex\} = \boldsymbol{0} \tag{19a}$$

which becomes

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r}) - \nabla\left\{p(\boldsymbol{r}) - \frac{1}{2}\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2\psi^2(\boldsymbol{r})\right\} - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\psi(\boldsymbol{r})\nabla x = \boldsymbol{0} \tag{24}$$

We take the rotation of Eq. (24) to eliminate the gradient term so that we obtain

$$\eta\nabla\times\Delta\boldsymbol{u}(\boldsymbol{r}) - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\nabla\times\{\psi(\boldsymbol{r})\nabla x\} = \boldsymbol{0} \tag{25}$$

Since $\nabla\times\nabla x = 0$, Eq. (25) becomes

$$\eta\nabla\times\Delta\boldsymbol{u}(\boldsymbol{r}) - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\nabla\psi(\boldsymbol{r})\times\nabla x = \boldsymbol{0} \tag{25a}$$

Taking the rotation again,

$$\eta\nabla\times\nabla\times\Delta\boldsymbol{u}(\boldsymbol{r}) - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\nabla\times\{\nabla\psi(\boldsymbol{r})\times\nabla x\} = \boldsymbol{0} \tag{25b}$$

Since $\triangle\boldsymbol{u} = -\nabla\times\nabla\times\boldsymbol{u}$ when Eq. (20) holds, Eq. (25b) becomes

$$-\eta\Delta^2\boldsymbol{u}(\boldsymbol{r}) - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\left\{\frac{\partial\nabla\psi(\boldsymbol{r})}{\partial x} - \Delta\psi(\boldsymbol{r})\nabla x\right\} = \boldsymbol{0} \tag{25c}$$

By substituting Eq. (29), Eq. (25c) becomes

$$-\eta\Delta^2\boldsymbol{u}(\boldsymbol{r}) - \varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}}\kappa^2 E\left\{\frac{\Delta^2}{\kappa^4}\nabla\frac{\partial\psi(\boldsymbol{r})}{\partial x} - \frac{\Delta^2\psi(\boldsymbol{r})}{\kappa^2}\nabla x\right\} = \boldsymbol{0} \tag{25d}$$

which is identical with Eqs. (30)-(32) (note that $\nabla x = (1, 0, 0)$).