



Fluctuation-enhanced electric conductivity in electrolyte solutions

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We analyze the effects of an externally applied electric field on thermal fluctuations for a binary electrolyte fluid. We show that the fluctuating Poisson–Nernst–Planck (PNP) equations for charged multispecies diffusion coupled with the fluctuating fluid momentum equation result in enhanced charge transport via a mechanism distinct from the well-known enhancement of mass transport that accompanies giant fluctuations. Although the mass and charge transport occurs by advection by thermal velocity fluctuations, it can macroscopically be represented as electrodiffusion with renormalized electric conductivity and a nonzero cation–anion diffusion coefficient. Specifically, we predict a nonzero cation–anion Maxwell–Stefan coefficient proportional to the square root of the salt concentration, a prediction that agrees quantitatively with experimental measurements. The renormalized or effective macroscopic equations are different from the starting PNP equations, which contain no cross-diffusion terms, even for rather dilute binary electrolytes. At the same time, for infinitely dilute solutions the renormalized electric conductivity and renormalized diffusion coefficients are consistent and the classical PNP equations with renormalized coefficients are recovered, demonstrating the self-consistency of the fluctuating hydrodynamics equations. Our calculations show that the fluctuating hydrodynamics approach recovers the electrophoretic and relaxation corrections obtained by Debye–Hückel–Onsager theory, while elucidating the physical origins of these corrections and generalizing straightforwardly to more complex multispecies electrolytes. Finally, we show that strong applied electric fields result in anisotropically enhanced “giant” velocity fluctuations and reduced fluctuations of salt concentration.

fluctuating hydrodynamics | electrohydrodynamics | Navier–Stokes equations | multicomponent diffusion | Nernst–Planck equations

The interaction between ionic species and an externally imposed electric field is at the core of many electrokinetic problems and applications (1) such as electrophoresis. Studying these types of problems usually involves solving the Poisson–Nernst–Planck equation, which assumes that the solution is ideal with no cross-diffusion between the different ions. In a recent publication (2), we presented a numerical scheme based on fluctuating hydrodynamics for simulating electrokinetic problems at mesoscopic scales where thermal fluctuations are nonnegligible. In this approach, the generalized Poisson–Nernst–Planck (PNP) equations are combined with the fluctuating Landau–Lifshitz Navier–Stokes equations, yielding a set of stochastic partial differential equations that can be solved either analytically or numerically. In this paper we use theoretical calculations to show that, in dilute electrolyte solutions under an applied electric field, there exists a coupling phenomenon between the fluctuations of local net charges and fluid velocity. This coupling results in an effective enhancement of the electric conductivity, which we refer to as “fluctuation-induced electroconvection.” This enhancement is similar to but distinct from the enhancement of mass diffusion (3–5) associated with giant fluctuations (6, 7). Furthermore, we show that in the presence of an electric current there exists a coupling between the fluctuations of

ion density and charge density that results in a reduction of the electric conductivity. We show that the renormalized conductivity is consistent with Onsager’s reciprocal relations provided that there exists a Maxwell–Stefan (MS) cross-diffusion coefficient between the cation and anion, as, indeed, is measured in experiments. The renormalized electrodiffusion equations are different from the starting fluctuating PNP equations to order square root of the salt concentration, which implies strong cross-coupling corrections even for dilute solutions. Nevertheless, at infinite dilution the enhancement of conductivity is consistent with the enhancement of the salt diffusion coefficient, even though the two originate from seemingly unrelated mechanisms, leading to the simple PNP equations in the limit of vanishing salt concentration. Finally, we show that the coupling produces an anisotropic enhancement of the momentum fluctuations of the fluid that scales as the square of the magnitude of the applied electric field.

Problem Description

We model a homogeneous solution composed of a neutral solvent fluid (e.g., water) and two ionic solute species of opposite charge. We assume that a uniform electric field E_{ext} is externally applied. Both for simplicity and for the sake of focusing on the coupling between charge fluctuations and the applied electric field, we assign the same physical parameters to the anion and the cation (i.e., equal “bare” diffusivity D_0 in the solvent, absolute charge per mass z , and molecular mass m). Generalizations to different ions are straightforward. We denote the mass fraction of the cation and anion by w_+ and w_- , respectively, which are both w_0 in the homogeneous system. The density ρ , the kinematic and dynamic viscosity ν and η ($\eta = \rho\nu$), and the dielectric permittivity ϵ are all assumed constant. We assume that the system remains isothermal at temperature T and neglect both viscous and ohmic heating.

Significance

Using fluctuating hydrodynamics, we demonstrate that thermal fluctuations contribute to charge transport in binary electrolyte solutions. We show the existence of an enhancement, or renormalization, of the electric conductivity due to the coupling between fluctuations of charge and fluid velocity. This coupling results in nontrivial corrections to the classical Poisson–Nernst–Planck equations, which are of the order of the square root of the salt concentration and therefore significant even for dilute solutions. Our calculations predict a cation–anion cross-diffusion coefficient that is in quantitative agreement with experimental measurements. Our findings have important implications for the fields of both mesoscale hydrodynamics and electrolyte transport.

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The theoretical system we consider is infinite in all directions. The fluid is subjected to fluctuations in species mass flux and stress tensor consistent with the fluctuation–dissipation theorem (7). We use a low Mach approximation (8) and neglect density fluctuations, i.e., $\nabla \cdot \mathbf{v} = 0$, where $\mathbf{v}(\mathbf{x}, t)$ refers to the velocity vector with components (v_x, v_y, v_z) . Assuming the electrolytes are dilute, the equations describing the mass fractions are

$$\partial_t w_{\pm} + \mathbf{v} \cdot \nabla w_{\pm} = D_0 \nabla^2 w_{\pm} \mp \frac{D_0 m z}{k_B T} \nabla \cdot (\mathbf{E} w_{\pm}) + \nabla \cdot \left(\sqrt{2 D_0 m \rho^{-1} w_{\pm} \mathbf{Z}_{\pm}} \right), \quad [1]$$

where k_B is Boltzmann's constant. We used the Nernst–Einstein relation, which states that the electric mobility is given by $D_0 m z / (k_B T)$. Symbols \mathbf{Z}_+ and \mathbf{Z}_- refer to two independent Gaussian white-noise vector fields, and, assuming that the dielectric coefficient is constant, the total electric field is the solution to $\epsilon \nabla \cdot \mathbf{E} = z \rho (w_+ - w_-) \equiv q_f$. The velocity field follows the fluctuating Navier–Stokes equation

$$\partial_t \mathbf{v} + \nabla \cdot (\mathbf{v} \mathbf{v}^T) = \nu \nabla^2 \mathbf{v} + \frac{\nabla p}{\rho} + \frac{q_f \mathbf{E}}{\rho} + \sqrt{\frac{\nu k_B T}{\rho}} \nabla \cdot (\mathcal{W} + \mathcal{W}^T), \quad [2]$$

where p is the pressure and $\mathcal{W}(\mathbf{r}, t)$ is a white-noise tensor field; and superscript T denotes transpose. Physically, the fluctuation-induced electroconvection we are studying arises from mass fraction fluctuations, given by Eq. 1, which result in enhanced velocity fluctuations through the term $q_f \mathbf{E}$ in Eq. 2. The calculations we carry out next closely resemble previous linearized or “one-loop renormalization” calculations of fluctuation-enhanced diffusivity in nonionic binary mixtures (3–5).

Nonequilibrium Fluctuations

We use linearized fluctuating hydrodynamics to compute the spectrum of the steady-state concentration and velocity fluctuations. We first define the fluctuations $\delta w_{\pm} = w_{\pm} - w_0$ and then express the fluctuations in terms of the sum $\delta n = \delta w_+ + \delta w_-$ and difference $\delta c = \delta w_+ - \delta w_-$, which are more suited to describe the problem than the individual mass fractions. Linearizing Eq. 1 yields

$$\begin{aligned} \partial_t \delta n &= D_0 \nabla^2 \delta n - \frac{D_0 m z}{k_B T} \mathbf{E}_{\text{ext}} \cdot \nabla \delta c \\ &\quad + \sqrt{2 D_0 m \rho^{-1} w_0} \nabla \cdot (\mathbf{Z}_+ + \mathbf{Z}_-) \\ \partial_t \delta c &= D_0 \nabla^2 \delta c - \frac{D_0}{\lambda^2} \delta c - \frac{D_0 m z}{k_B T} \mathbf{E}_{\text{ext}} \cdot \nabla \delta n \\ &\quad + \sqrt{2 D_0 m \rho^{-1} w_0} \nabla \cdot (\mathbf{Z}_+ - \mathbf{Z}_-), \end{aligned} \quad [3]$$

where the Debye length λ is defined by $\lambda^2 = \epsilon k_B T / (2 \rho m w_0 z^2)$. We also linearize Eq. 2 and, as in ref. 7, we apply a double curl operator to eliminate the pressure term. We obtain, in Fourier space,

$$\begin{aligned} -\mathbf{k} \times \mathbf{k} \times \partial_t \hat{\mathbf{v}} &= -\nu k^4 \hat{\mathbf{v}} - z \mathbf{k} \times \mathbf{k} \times [\mathbf{E}_{\text{ext}} \delta c] \\ &\quad - i \sqrt{\nu \rho^{-1} k_B T} \mathbf{k} \times \mathbf{k} \times [\mathbf{k} \cdot (\hat{\mathcal{W}} + \hat{\mathcal{W}}^T)]. \end{aligned} \quad [4]$$

We take $\mathbf{E}_{\text{ext}} = E_{\text{ext}} \mathbf{e}_x$, where \mathbf{e}_x is a unit vector in the x direction, and let θ denote the angle between \mathbf{E}_{ext} and the wavevector \mathbf{k} . In that case, the x -component of Eq. 4 becomes

$$\partial_t \hat{v}_x = -\nu k^2 \hat{v}_x + z E_{\text{ext}} \sin^2(\theta) \delta c + i k \sin(\theta) \sqrt{2 \nu \rho^{-1} k_B T} \hat{\mathcal{V}}, \quad [5]$$

where $\hat{\mathcal{V}}(\mathbf{k}, t)$ is a scalar white-noise process.

Taking the Fourier transform of Eq. 3 and combining it with Eq. 5, we obtain that the vector $\hat{\mathcal{U}}(\mathbf{k}, t) = (\hat{\delta n}(\mathbf{k}, t), \hat{\delta c}(\mathbf{k}, t), \hat{v}_x(\mathbf{k}, t))$ is described by the Ornstein–Uhlenbeck process $\partial_t \hat{\mathcal{U}} = \mathbf{M} \hat{\mathcal{U}} + \mathbf{N} \hat{\mathcal{Z}}$ with

$$\mathbf{M} = \begin{pmatrix} -D_0 k^2 & -i k \cos(\theta) \frac{E_{\text{ext}} D_0 m z}{k_B T} & 0 \\ -i k \cos(\theta) \frac{E_{\text{ext}} D_0 m z}{k_B T} & -D_0 (k^2 + \lambda^{-2}) & 0 \\ 0 & z E_{\text{ext}} \sin^2(\theta) & -\nu k^2 \end{pmatrix}, \quad [6]$$

where $\hat{\mathcal{Z}}(\mathbf{k}, t)$ is a vector of three uncorrelated white-noise processes. The variance matrix is diagonal,

$$\mathbf{N} \mathbf{N}^* = \frac{k^2}{\rho} \begin{pmatrix} 4 m D_0 w_0 & 0 & 0 \\ 0 & 4 m D_0 w_0 & 0 \\ 0 & 0 & 2 \nu k_B T \sin^2(\theta) \end{pmatrix}.$$

The steady-state spectrum of the fluctuations, i.e., the matrix of static structure factors $\mathbf{S}(\mathbf{k}) = \langle \hat{\mathcal{U}} \hat{\mathcal{U}}^* \rangle$, where $\langle \cdot \rangle$ denotes the steady-state average, is given by the solution of the linear system $\mathbf{M} \mathbf{S} + \mathbf{S} \mathbf{M}^* = -\mathbf{N} \mathbf{N}^*$ (9).

The complete expression for $\mathbf{S}(\mathbf{k})$ is quite involved. Here we focus on the linear response to the applied field. For sufficiently weak electric fields, there are only two correlations that are altered by the electric field to linear order in E_{ext} :

$$S_{\delta c, \hat{v}_x} = \frac{2 m w_0}{\rho D_0} \frac{z k^2 \lambda^4 \sin^2(\theta)}{[1 + (\text{Sc} + 1) k^2 \lambda^2][1 + \lambda^2 k^2]} E_{\text{ext}} \quad [7]$$

$$S_{\delta c, \delta n} = i \frac{2 m w_0}{\rho k_B T} \frac{m z k \lambda^2 \cos(\theta)}{(1 + k^2 \lambda^2)(1 + 2 k^2 \lambda^2)} E_{\text{ext}} \quad [8]$$

The autocorrelations $S_{\delta n, \delta n}$, $S_{\delta c, \delta c}$, and $S_{\hat{v}_x, \hat{v}_x}$ are, to leading order, quadratic in E_{ext} .

Enhancement of Electric Conductivity

The electroconvective coupling results in a net charge flux. From Eq. 1, we can write the average charge flux as

$$\langle \mathbf{F}_q \rangle = \underbrace{\frac{2 \rho D_0 m z^2}{k_B T} \langle \mathbf{E} \rangle w_0}_{F_{q,0}} + \underbrace{\rho z \langle \mathbf{v} \delta c \rangle}_{F_{q,\text{adv}}} + \underbrace{\frac{\rho D_0 m z^2}{k_B T} \langle \delta \mathbf{E} \delta n \rangle}_{F_{q,\text{relx}}}, \quad [9]$$

where $\delta \mathbf{E} \equiv \mathbf{E} - \langle \mathbf{E} \rangle$. Here $F_{q,0} = C_0 \mathbf{E}_{\text{ext}}$, where $C_0 \equiv 2 m \rho w_0 z^2 D_0 / (k_B T)$ is the electric conductivity resulting from the Nernst–Einstein relation. On the other hand the two other terms modify the charge flux because the correlations $\langle \mathbf{v} \delta c \rangle$ and $\langle \delta \mathbf{E} \delta n \rangle$ are nonzero as we show below. This additional charge flux is proportional to the electric field in the linearized regime and can be related to an enhanced electric conductivity.

We first examine the advective charge flux $F_{q,\text{adv}}$, which is intuitively the most direct consequence of the coupling and results from the correlation between the velocity and the charge density fluctuations. It is also the most important quantitatively. We can physically interpret $\lim_{k \rightarrow \infty} S_{\delta c, \hat{v}_x} = 0$ as charge fluctuations with small wavelength diffusing away before the Lorentz force can advectively accelerate the charged regions. The component of the advective flux parallel to \mathbf{E}_{ext} can be expressed as an integral over Fourier components over all wavevectors,

$$\mathbf{F}_{q,\text{adv}} \cdot \mathbf{e}_x = C_{\text{adv}} E_{\text{ext}} = \frac{\rho z}{8 \pi^3} \int_{k < k_c} S_{\delta c, \hat{v}_x} d\mathbf{k} \quad [10]$$

$$= \frac{\rho z}{4 \pi^2} \int_{k=0}^{k_c} \int_{\theta=0}^{\pi} S_{\delta c, \hat{v}_x} k^2 \sin(\theta) d\theta dk, \quad [11]$$

where, as done in prior work on renormalization of diffusion coefficients (5), we define a cutoff $k_c = \pi / a$, where a is a molecular scale. This is necessary since the integrand is not integrable because it converges toward a nonzero quantity for large

wavenumbers. This “UV divergence” is actually a consequence of a breakdown of the validity of the hydrodynamic equations at a molecular scale. Performing the integral in Eq. 11 using Eq. 7, and using the fact that the Schmidt number in liquids is large, $Sc \gg 1$, we obtain the approximation

$$C_{\text{adv}} \approx \frac{2mw_0z^2}{3\pi D_0 a Sc} \left[1 - \frac{a}{\pi\lambda} \arctan\left(\frac{\pi\lambda}{a}\right) \right] \quad [12]$$

$$\approx \frac{2m\rho w_0z^2}{k_B T} \left[\frac{k_B T}{3\pi a\eta} - \frac{k_B T}{6\pi\lambda\eta} \right] \equiv C_{\text{enh}} + C_{\text{ep}}, \quad [13]$$

where in Eq. 13 we expand to leading order in a/λ since $\lambda \gg a$ for dilute solutions. We note that C_{ep} is known as the electrophoretic term, derived within the Debye–Huckel–Onsager (DHO) theory by rather different means (10, 11). We note that the term in brackets in Eq. 13 can be interpreted as a difference of Stokes–Einstein coefficients for a sphere of radius $a/2$ and a sphere of radius λ . This corresponds to the classical physical picture that the Stokes friction on an ion needs to be adjusted because an ion must drag its ionic atmosphere with it (12) [equivalently, the ion experiences fluid drag relative to an ionic cloud (10)].

The flux $\mathbf{F}_{q,\text{relx}}$ is derived here by using the fact that $\epsilon\langle E\delta n \rangle = \rho z \langle \nabla [\nabla^{-2}\delta c] \delta n \rangle$ so that in Fourier space

$$\mathbf{F}_{q,\text{relx}} = \frac{\rho^2 D_0 m z^3}{8\pi^3 \epsilon k_B T} \int_{\mathbf{k}} i \frac{\mathbf{k}}{k^2} S_{\delta c, \delta n} d\mathbf{k} \equiv C_{\text{relx}} \mathbf{E}_{\text{ext}}, \quad [14]$$

which, after using Eq. 8, becomes

$$C_{\text{relx}} = -\frac{D_0 \rho m^3 z^4 w_0 \sqrt{2}}{12\lambda \pi \epsilon k_B^2 T^2 (1 + \sqrt{2})}. \quad [15]$$

Physically, this is due to the anisotropic counterionic cloud surrounding a given ion and known in DHO theory as the relaxation term (10, 11).

Both C_{ep} and C_{relx} scale as $w_0^{1/2}$ and vanish in the limit of infinitely dilute solutions where $\lambda \gg a$. Eqs. 13 and 15 show that the deterministic linear response that is obtained by ensemble averaging the equations is not the bare response expressed by the conductivity C_0 , but is instead enhanced, or renormalized, by the enhanced conductivity C_{enh} due to fluctuation-induced charge transport. Macroscopically, this suggests that the quantity that is experimentally accessible is the renormalized or “dressed” $C = C_0 + C_{\text{enh}} + C_{\text{ep}} + C_{\text{relx}}$ and that particular care should be taken when setting the simulation parameters of a fluctuating hydrodynamics solver, so that this enhancement effect is not double counted (8).

Renormalized Transport Coefficients

The renormalization of the electric conductivity is connected to the renormalization of the diffusion coefficient that results from giant fluctuations (3–5). In ref. 5, a calculation very similar to the one performed above is carried out for the renormalization of the diffusion coefficient in a nonionic mixture, and it is found that diffusion is renormalized* by $D_{\text{enh}} = k_B T / (3\pi a\eta)$. While this result was derived for nonionic solutions, it can easily be generalized since analyzing the giant fluctuations in the linear regime requires imposing electroneutrality of the steady state. Consequently, the macroscopic gradients of the species charge densities must be equal, which in our case reduces to $\nabla w_+ = \nabla w_- = \nabla w_0$. With this condition, the approach developed in ref. 5 shows that the renormalized mass flux for δn is the same as that of nonionic solutions. Qualitatively, the renor-

malization of the diffusion coefficient is not affected by the presence of charges because the thermal velocity fluctuations advect both the ion and the counterion together, thus maintaining electroneutrality. As with nonionic mixtures, the renormalized diffusion coefficient is $D \equiv D_0 + D_{\text{enh}}$. On the other hand, the electric conductivity $C = C_0 + C_{\text{enh}} + C_{\text{ep}} + C_{\text{relx}}$ is renormalized to

$$C \approx \frac{2mw_0z^2\rho}{k_B T} \left(D_0 + \frac{k_B T}{3\pi a\eta} - \frac{k_B T}{6\pi\lambda\eta} - \frac{D_0 z^2 m^2}{12(2 + \sqrt{2})\pi\lambda\epsilon k_B T} \right) \\ \approx \frac{2mw_0z^2\rho}{k_B T} \left(D - \frac{A}{\lambda} \right) = C_{\text{PNP}} - C_0 \frac{A}{D_0\lambda}, \quad [16]$$

where $C_{\text{PNP}} = (2mw_0z^2\rho/k_B T)D$ is the electric conductivity obtained from the PNP equations with the renormalized diffusivity D and where A is a coefficient independent of the concentration of electrolytes.

For infinitely dilute solutions ($\lambda \rightarrow \infty$), the renormalizations of the electric conductivity and the diffusivity are consistent with the PNP equation, i.e., $C = C_{\text{PNP}}$, which amounts to assuming that Fick’s diffusion matrix is diagonal. This is a manifestation of the overall consistency of fluctuating hydrodynamics, even though the two enhancement phenomena stem from distinct noise terms[†]; it is worth noting that in the fully nonlinear diffusion model studied in ref. 13 the only noise term is the stochastic stress and all diffusion arises from advection by thermal velocity fluctuations.

For finite λ , the renormalized diffusion coefficient $D_0 + D_{\text{enh}}$ and the renormalized electric conductivity Eq. 16 do not satisfy the Nernst–Einstein relation so the renormalized PNP equation must be corrected to leading order in a/λ to be consistent with Onsager’s reciprocal relations. Specifically, the renormalized Fick’s diffusion matrix must include off-diagonal coefficients; to satisfy both renormalized coefficients, the mass fluxes \mathbf{F}_+ and \mathbf{F}_- of the two ionic species must be expressed as

$$\begin{pmatrix} \mathbf{F}_+ \\ \mathbf{F}_- \end{pmatrix} = -\rho \underbrace{\begin{pmatrix} D - \frac{A}{2\lambda} & \frac{A}{2\lambda} \\ \frac{A}{2\lambda} & D - \frac{A}{2\lambda} \end{pmatrix}}_D \cdot \begin{pmatrix} \nabla w_+ + \frac{mz}{k_B T} w_+ \nabla \phi \\ \nabla w_- - \frac{mz}{k_B T} w_- \nabla \phi \end{pmatrix}, \quad [17]$$

where ϕ is the electric potential ($\mathbf{E} = -\nabla\phi$).

To give a more physical interpretation of the cross-diffusion coefficient, we link the renormalized Fickian diffusion matrix to a renormalized MS diffusion matrix (14). The MS diffusion coefficients can be physically interpreted as inverse friction coefficients between pairs of distinct species. For a very dilute solution, it has been assumed when writing Eq. 1 that the (bare) MS cross-diffusion coefficient between the two ionic species, $\mathfrak{D}_0^{(+,-)}$, is 0 and that the (bare) cross-diffusion coefficient between the solvent and either ion is identical; i.e., $\mathfrak{D}_0^{(s,+)} = \mathfrak{D}_0^{(s,-)} = D_0$. However, this is inconsistent with the renormalized Fickian diffusion matrix \mathbf{D} with nonzero off-diagonal coefficients. Introducing the renormalized MS diffusion coefficients $\mathfrak{D}^{(+,-)}$ and $\mathfrak{D}^{(s,+)} = \mathfrak{D}^{(s,-)}$ and writing the friction matrix as the inverse of the Fickian diffusion matrix, we obtain, to first order in w_0 , $\mathfrak{D}^{(s,+)} = D$, and the cross-diffusion coefficient

$$\mathfrak{D}^{(+,-)} \approx 12\pi D^2 \left[\frac{k_B T}{\eta} + \frac{D_0 z^2 m^2}{2(2 + \sqrt{2})\epsilon k_B T} \right]^{-1} \frac{M}{m} \lambda w_0, \quad [18]$$

where M denotes the molecular mass of the solvent.

*Quantitatively, assigning the experimental self-diffusion coefficient of the ions to D_{enh} and η provides estimates of the length-scale a on the order of the ionic diameter.

[†]The renormalization of diffusion originates from the velocity fluctuations and their coupling with a concentration gradient, while the renormalization effect studied here results from charge density fluctuations and their coupling with the electric field.

Using the complete formulas for the electrophoretic (C_{ep}) and relaxation (C_{relx}) terms from DHO theory (10), one can easily generalize Eq. 18 to unequal ions. With parameters of water (molecular mass $M = 3 \times 10^{-26}$ kg, $\eta = 1.05 \times 10^{-3}$ kg/ms), we find $\mathfrak{D}^{(+,-)} \approx 0.9 \times 10^{-10} \sqrt{c}$ for salt solutions ($D_{Na} \approx 1.3 \times 10^{-9}$ m²/s and $D_{Cl} \approx 2.0 \times 10^{-9}$ m²/s), where c is in mol/L and where the result is in m²/s, in very good agreement (within 10% difference) with published experimental measurements (12, 15, 16).

Enhancement of Velocity Fluctuations

The fluctuation-induced electroconvection derived in this paper is associated with a corollary phenomenon, namely, the enhancement of velocity fluctuations in the direction of the electric field, as shown by the expression of $S_{\hat{v}_x, \hat{v}_x}$, written below in the case where \mathbf{k} and \mathbf{E}_{ext} are orthogonal ($\theta = \pi/2$):

$$S_{\hat{v}_x, \hat{v}_x}^\perp = \frac{k_B T}{\rho} + \frac{2mw_0}{\rho\nu D_0} \frac{z^2 E_{ext}^2 \lambda^4}{[1 + (Sc + 1)k^2 \lambda^2][1 + \lambda^2 k^2]}. \quad [19]$$

In Fig. 1 we show a comparison between the theoretical structure factor of velocity fluctuations (when the wavevector and the electric field are orthogonal) and the same quantity obtained with the code developed in ref. 2. The main finding here is that, provided the field is strong enough, the amplitude of the low wavenumber fluctuations is noticeably enhanced. As in the phenomenon of giant fluctuations (6, 7), this results in large-scale patterns, with the key difference that these patterns are found in the x -component (i.e., colinear to the applied electric field) of the velocity instead of the mass fractions.

For small wavenumbers (large length scales), the structure factor for wavevectors orthogonal to \mathbf{E}_{ext} ($\theta = \pi/2$) converges toward

$$S_{\hat{v}_x, \hat{v}_x}^\perp(k \rightarrow 0) = \frac{k_B T}{\rho} \left[1 + \frac{\epsilon E_{ext}^2 \lambda^2}{\rho\nu D_0} \right]. \quad [20]$$

The effect of the electric field on the velocity fluctuations is significant when $E_{ext} \geq \lambda^{-1} \sqrt{\epsilon^{-1} \rho \nu D_0}$. Using the Maxwell approximation $\nu \approx v_{th} \lambda_{th}$ where v_{th} and λ_{th} refer, respectively, to the molecular speed and length (e.g., sound speed and mean free path), we can write it as

$$\frac{\epsilon E_{ext}^2 / 2}{\rho v_{th}^2 / 2} \gtrsim \frac{1}{Sc} \frac{\lambda_{th}^2}{\lambda^2}, \quad [21]$$

where the left-hand side is the ratio of the electric and the thermal energy densities. This condition may seem constraining, but in dilute liquid solutions the right-hand side is much smaller than 1. In fact, for the parameters chosen for Fig. 1, the condition on the electric field is $E_{ext} \gtrsim 6$ kV/cm, which is the higher end of the electric fields applied in electrophoresis experiments (17).

We note that, on the other hand, the fluctuations of δn are reduced anisotropically by the electric field,

$$S_{\delta n, \delta n}(k \rightarrow 0) = 2mw_0 \rho^{-1} \left[1 + \left(\frac{mzE_{ext} \cos(\theta)\lambda}{k_B T} \right)^2 \right]^{-1}, \quad [22]$$

$$= 2mw_0 \rho^{-1} \left[1 + \frac{m\epsilon E_{ext}^2 \cos^2(\theta)}{\rho n_0 k_B T} \right]^{-1}, \quad [23]$$

where n_0 is the total ion mass fraction. Note that the second term in the brackets is the ratio of the typical magnitude of the Maxwell stress tensor and the osmotic pressure of the ions. The reduction of the ion number density fluctuations is significant when $mz\lambda E_{ext} \gtrsim k_B T$ or, equivalently, when the energy lost (or gained) by an ion crossing a distance λ in the direction of the field is larger than the thermal energy $k_B T$.

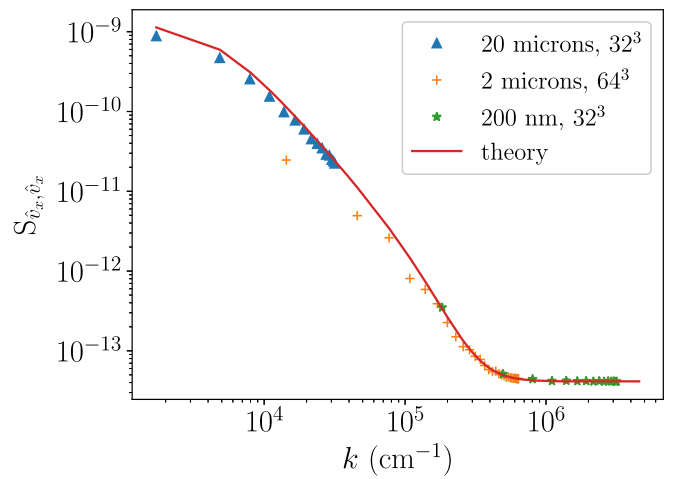


Fig. 1. Structure factor of velocity fluctuations parallel to the applied field vs. wavenumber. The computational system used to verify the theoretical calculations is a cubic domain of dimension L , with periodic boundary conditions in all directions, with $T = 300$ K, $\epsilon = 6.91 \times 10^{-19}$ s²·C²·cm⁻³·g⁻¹, $\nu = 1.05 \times 10^{-2}$ cm²·s⁻¹, $D_0 = 10^{-5}$ cm²·s⁻¹, $z = 10^3$ C·g⁻¹, $w_0 = 10^{-5}$, $m = 3 \times 10^{-23}$ g, $\rho = 1.0$ g·cm⁻³, and $E = 10^6$ V·cm⁻¹ = 10^{13} g·cm·s⁻²·C⁻¹. Since a single computation cannot cover the wide range of wavenumbers shown here, the computational results combine three different systems, of sizes 20 μ m, 2 μ m, and 200 nm. *Inset* shows the number of computational cells. The theoretical calculation is corrected to account for the discrete Laplacian effect (2).

Using parameters for sodium at concentration $w_0 = 10^{-5}$ gives $E_{ext} \gtrsim 20$ kV/cm.

Concluding Remarks

In summary, using a fluctuating hydrodynamics formulation, we show that there exists a coupling between the fluctuations in charge density and fluid velocity that is proportional to the applied electric field. This coupling leads to an effective enhancement, or renormalization, of the measured electric conductivity of an ionic mixture. This enhancement is comparable to the enhancement of the diffusion coefficients that results from giant fluctuations, in that the enhancement coefficients match in the limit of infinite dilution. For finite dilution, the renormalization of mass diffusivity and electric conductivity are different. This shows that, although we started from a diagonal Fickian diffusivity matrix, renormalizing the fluctuating PNP equations yields an off-diagonal Fickian diffusion term, itself linked with a nonzero renormalized cross-diffusion MS coefficient between the two counterions, in good agreement with experimental coefficients reported in the literature. In fact, in our prior work (2) we demonstrated that results from Debye–Hückel theory, including the nonanalytic Debye–Hückel correction to the internal energy, can be obtained from a fluctuating hydrodynamics theory of dilute electrolyte solutions. The present work further demonstrates that fluctuating hydrodynamics provide a generalizable and systematic approach to derive corrective transport coefficients such as the electrophoretic and the relaxation term. Finally, for large electric fields, the applied field can significantly amplify the velocity fluctuations and suppress fluctuations of salt concentration. We expect this phenomenon to be observable experimentally and by molecular dynamics simulations.

The theory developed here can readily be extended in a number of important directions. First, the assumption of dynamically identical ions can be removed so that a more direct comparison with experimental measurements for different salts can be performed, including polyvalent salts. It is also important to consider

solutions with one ion and two counterions, such as for example solutions of NaCl and KCl in water. Although beyond the scope of the present paper, such extensions reveal that the surprising experimental observation of negative MS diffusion coefficients (18, 19) between coions (20) can be explained by fluctuating hydrodynamics and renormalization. Here we considered only strong electrolytes but the generalization to weak electrolytes is possible by using fluctuating hydrodynamics for reactive fluids (21). Finally, we started here with fluctuating hydrodynamics equations based on the PNP equations, i.e., we assumed an ideal solution with no cross-diffusion, so our starting equations had only one mobility coefficient per ion, instead of one MS coefficient per pair of ions. The renormalized equations, on the other hand, have cross-diffusion and also a nonideal Debye–Hückel contribution to the free energy density. This suggests that a more proper theory should start from the more complete equa-

tions, allowing for a nonzero bare MS cross-coefficient $\mathcal{D}_0^{(+,-)}$. As explained in ref. 22 for nonelectrolytes, bare diffusion coefficients can be given a microscopic interpretation in terms of Green–Kubo expressions and can therefore, in principle, be measured in molecular dynamics simulations, and the renormalization due to thermal fluctuations can be computed numerically using a numerical fluctuating hydrodynamics solver (2). Carrying out such an ambitious program for electrolyte solutions is a worthy challenge for the future.

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