Transient fluctuation-induced forces in driven electrolytes after an electric field quench

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Abstract

Understanding how electrolyte solutions behave out of thermal equilibrium is a long-standing endeavor in many areas of chemistry and biology. Although mean-field theories are widely used to model the dynamics of electrolytes, it is also important to characterize the effects of fluctuations in these systems. We have recently shown that the dynamics of the ions in a strong electrolyte that is driven by an external electric field can generate long-ranged correlations manifestly different from the equilibrium screened correlations; in the nonequilibrium steady state, these correlations give rise to a novel long-range fluctuation-induced force (FIF). Here, we extend the Langevin analysis of the FIF by considering the dynamics of a strong electrolyte after it is quenched from thermal equilibrium by a constant electric field. We show that the asymptotic long-distance limit of both of the charge and density correlation functions is long-ranged and generally diffusive in time. These correlations give rise to long-ranged FIFs acting on uncharged confining plates with long-time regimes that are governed by slow power-law temporal decays toward the steady-state value of the force amplitude; at early times, the temporal variations of the FIF are non-monotonic with possible sign changes in some parameter regimes. These findings show that nonequilibrium fluctuations have nontrivial implications on the dynamics of objects immersed in a driven electrolyte, and they could be useful for exploring new ways of controlling long-distance forces in charged solutions.

1. Introduction

For more than a century, extensive research efforts have focused on understanding various properties of electrolytes and charged solutions [1–3]. Conventional mean-field theories have been remarkably effective in such endeavors and, in addition, the electrostatic correlation effects have been characterized to a great extent [4]. Similar studies of correlation effects and fluctuation phenomena in nonequilibrium electrolytes are, however, relatively scarce [5]. The present manuscript focuses on one such aspect, namely fluctuation-induced forces (FIFs) [6, 7] in electrolyte solutions driven out of equilibrium, by considering the transient behavior of the FIF after a quench by an electric field. The analysis presented in this manuscript aims to establish a simplified framework for analysing dynamical correlation effects of electrolytes whose formulations are otherwise mathematically involved even in the simplest case of binary solutions. The results presented in this manuscript complement reference [8] which is focused on the steady-state properties of the FIF.

Mean-field descriptions of electrolytes are obtained by combining those equations that govern the electrostatic interactions among the charged particles (e.g. the Poisson equation) with the statistical weights that describe the distribution of the charges. In thermal equilibrium, where the statistical weights are given by Boltzmann factors, this combination leads to the so-called nonlinear Poisson–Boltzmann (PB) equation [1], while out of equilibrium one needs to consider more general distributions [9] which are governed by Fokker–Planck equations [5, 10]. Even though the resulting nonlinear models in principle contain the full
mean-field information about the system, it is often difficult to gain insights into the underlying physical mechanisms from them; as such, linear models have been of great importance in conceptual developments toward understanding electrolytes and charged fluids. The celebrated Debye–Hückel (DH) theory [11], for instance, is obtained from linearizing the PB equation, and it shows how correlations in an electrolyte become short-ranged as a result of the screening effects of counterions (i.e. opposite charges). The simple picture provided by the DH theory is, in fact, a good approximation for typical solutions in potentials lower than $\sim 25$ mV which is the case in many biological settings, and it serves as a general starting point to understand and construct models for a wider range of charged systems [1].

Mean-field theories, in general, do not take into account the statistical correlations between the ions in the system. It is well-known that the correlations in electrolytes can give rise to a number of important phenomena, ranging from phase transitions in two-dimensional systems [12], to charge renormalization in colloids [13], and counterion condensation and correlation-induced interactions which are relevant for biological processes [14–18]. In these cases, it can still be useful to combine the phenomenology of the correlation effects, which can lead to the breakdown of the mean-field assumptions, with the linearized DH equations to get mathematically tractable models [4]. Although some related correlation phenomena have also been considered in dynamical settings [19–21], a general understanding of nonequilibrium electrostatic correlations is still far from complete and faces a number of challenging questions [5]. Part of the difficulty lies in characterizing the distribution functions of interacting ions with Brownian motions out of thermal equilibrium [9, 22]. Langevin formulations of the electrolyte dynamics provide a straightforward way of taking into account the stochasticity in the motion of the ions and can be used to obtain the required correlation functions, e.g. to compute the power spectrum of nanopore currents or the conductivity of strong electrolytes [23–25]. Inspired by some of the recent experimental and theoretical investigations of electrolytes and ionic liquids [26–32], we use the Langevin framework to study how fluctuations in a strong electrolyte in the presence of an external electric field may modify the force that is exerted on boundaries that confine the electrolyte. In the long run, this direction would also be relevant for designing more efficient and environmental-friendly batteries and electrochemical capacitors [33–35] as electrolytes and ionic liquids are essential to the underlying conduction processes and energy storage.

FIFs comprise a remarkable aspect of fluctuation effects and arise when external objects disturb a correlated medium, e.g. by imposing specific boundary conditions on its fluctuation modes [6, 7]. If the correlations in the medium are long-ranged, they then give rise to FIFs that can persist between objects at large separations and exhibit a number of universal features [36–39]. Fluctuation forces have many implications and applications in nanosciences [40] and colloidal studies [1, 41], and they are also prevalent in nonequilibrium and driven settings [42–51]. For an electrolyte in thermal equilibrium confined between dielectric slabs, the spatial range of the FIF is limited by the Debye screening length, which is often of the order of a few nanometers [7, 52]. Since nonlocal correlations may generically emerge from conserved dynamics [53–55], it may be expected that nonequilibrium FIFs in driven electrolytes can instead become long-ranged [8]. The underlying cause for this FIF, namely anisotropy in the conserved dynamics, is rather generic; thus similar nonequilibrium forces might also be relevant to modeling electrokinetic and biological systems where there are many instances of ionic currents in confined spaces [10, 56].

In reference [8], we used the Dean–Kawasaki formalism [57–59] along with scaling arguments to investigate the steady-state fluctuations in a simple strong electrolyte that is driven by a constant external electric field. It was shown that the anisotropy caused by the electric field leads to the so-called
scale invariant dynamics [60], and correlation functions in the steady state become long ranged and take power-law forms, despite the screening effects. These correlations then lead to nonequilibrium FIFs on the confining boundaries, which in the flat Casimir geometry, depend on the plate separation $H$ as $H^{-d}$, where $d$ is the spatial dimension. The FIF amplitude in this case has unique non-monotonic changes as the strength of the applied electric field is increased. In the present work, we look into the transient behavior of the FIF after the electric field is switched. To elucidate the fundamental concepts, we keep our focus on the case of a strong binary electrolyte which is initially at thermal equilibrium and is confined between two neutral parallel dielectric walls. The electrolyte is acted upon at time $t = 0$ by a DC electric field parallel to the boundaries (see figure 1). We investigate the temporal variations of the FIF and show that the FIF exhibits a diffusive behavior in time where, after possibly non-monotonic initial changes, its difference with the steady-state value decays as $t^{-d/2}$ in $d$ spatial dimensions at long times (with a possible crossover in the value of the exponent, see section 4). These results cast some light on the emergent behavior in electrolytes out of thermal equilibrium and demonstrate that the dynamical and nonequilibrium effects in electrolytes can be manifestly different from their screened counterparts in equilibrium.

The manuscript is organized as follows: in section 2, we start from the Langevin equations that govern the dynamics of the ions and we derive the stochastic density equations based on the Dean–Kawasaki approach. This is then accompanied by linearization and quasi-stationary approximation schemes. We also discuss the applicability of these approximations to settings where the electric field is a slowly varying function of time and, in addition, to electrolytes with different ionic mobilities. In section 3, we use the linearized density equations to derive the charge and density correlation functions; first, this is done for a bulk solution and then for an electrolyte that is confined between two flat boundaries with given permittivity. In section 4, we compute the stress exerted by the electrolyte on the confining plates. To this end, we use the Maxwell stress formula and make use of the correlation functions to obtain analytical expressions for the normal stress on the boundaries. The steady-state and transient parts of the stress amplitude are investigated using asymptotic expansions and numerical evaluations. Section 5 contains the summary and final concluding remarks. There are also four appendices containing the scaling analysis of the nonlinearities (appendix A), the calculation of the two-point correlation functions of the linearized dynamics at equal times (appendix B) and at different times (appendix C) without using the quasi-stationary approximation, and a simplification of the transient part of the FIF amplitude (appendix D).

2. Formalism

To analyze the dynamics of the electrolyte in the presence of the external electric field, in section 2.1 we start from single particle Langevin equations that describe the motion of the individual ions, and then we recast the set of Langevin equations in terms of the time evolution of their instantaneous density using the Dean–Kawasaki approach [57–59]. The density equations are then linearized in section 2.2 whose applicability on relaxing the assumptions of static electric field and equal ionic mobilities are discussed in sections 2.3 and 2.4.

2.1. Stochastic density equations

The electrolyte we study here is composed of a symmetric collection of charged particles with electric charges $\pm Q$ and equal mobilities $\mu_+ = \mu_- = \mu$. These particles undergo Brownian motion due to microscopic collisions with the implicit solvent’s molecules [we will neglect the hydrodynamic effects of the solvent, assuming that the average inter-particle distances are large compared with the finite (screened) range of hydrodynamic interactions [61, 62]]. In $d$ spatial dimensions, the overdamped trajectory $r_i^\pm(t)$ of a cation or anion, labeled by $a \ (a = 1, 2, \ldots, N)$ is governed by the Langevin equation

$$\dot{r}_i^\pm(t) = \pm \mu Q \left[ -\nabla \phi(r_i^\pm(t)) + E \right] + \sqrt{2D} \eta_i^\pm(t), \quad (1)$$

where $E = E \hat{e}_x$ is the external electric field along the $x$ axis and $\eta_i^\pm$ represent independent Gaussian white noises with correlations $\langle \eta_i^\pm(t) \eta_j^\pm(t') \rangle = \delta_{ij} \delta(t-t')$ and zero means. The fluctuation–dissipation relation connects the noise strength $D$ to the mobility $\mu$ through the Einstein relation $\mu = \beta D$, where $\beta = 1/(k_B T)$ represents the inverse temperature of the system. Moreover, the electrostatic potential field $\phi(r, t)$ is created by the ions in the system, and in Gaussian units it satisfies the Poisson equation

$$- \nabla^2 \phi(r, t) = \frac{S_d Q}{\epsilon_{\text{ion}}} (C^+(r, t) - C^-(r, t)), \quad (2)$$
where $S_d = 2 \pi^{d/2}/\Gamma(d/2)$ is the surface area of $d$-dimensional unit sphere, $\varepsilon_\infty$ is the permittivity of the electrolyte, and the instantaneous (microscopic) density of charge species is defined as

$$C^\pm (r, t) = \sum_{a=1}^{N} \delta^d (r - r_a^\pm (t)). \quad (3)$$

Using the stochastic equations of Dean and Kawasaki [57, 58], one then obtains the exact stochastic dynamics of $C^\pm$ as continuity equations, i.e. $\partial_t C^\pm + \nabla \cdot J^\pm = 0$, where the stochastic currents are given by

$$J^\pm(r, t) = -D \nabla C^\pm \pm C^\pm \mu Q (\nabla \phi + E) - \sqrt{2D\kappa} \zeta^\pm(r, t). \quad (4)$$

Here, $\zeta^\pm(r, t)$ are uncorrelated Gaussian noise fields characterized by zero averages and $\langle \zeta_i^\pm(r, t) \zeta_j^\pm(r', t') \rangle = \delta_{ij} \delta^d(r - r') \delta(t - t')$.

We next express the dynamics in terms of the number density $C = C^+ + C^-$ and the charge density $\rho = C^+ - C^-$ which can be written as

$$\partial_t C + \nabla \cdot J = 0, \quad \text{and} \quad \partial_t \rho + \nabla \cdot J_\rho = 0, \quad (5)$$

where the density and charge currents are defined as $J = J^+ + J^-$ and $J_\rho = J^+ - J^-$ and they are explicitly given by

$$J = -D \nabla C + \rho \mu Q (\nabla \phi + E) - \sqrt{2D\kappa} \zeta, \quad J_\rho = -D \nabla \rho + C \mu Q (\nabla \phi + E) - \sqrt{2D\kappa} \zeta. \quad (6)$$

Note that the noise fields $\sqrt{2D\kappa} \zeta_{\rho,\phi}$ are obtained from the addition and subtraction of the Gaussian noise fields $\sqrt{2D\kappa} \zeta_{\rho,\phi}$; consequently, these uncorrelated fields also have zero averages with correlations given by

$$\langle \zeta_{\rho}(r, t) \zeta_{\phi}(r', t') \rangle = \langle \zeta_{\phi}(r, t) \zeta_{\phi}(r', t') \rangle = \delta^d(r - r') \delta(t - t').$$

Substituting these currents into the corresponding continuity equations, we find

$$\partial_t C = D \nabla^2 C + \mu Q \nabla \cdot (\rho \nabla \phi) - \mu Q E \partial_t \rho + \nabla \cdot \left( \sqrt{2D\kappa} \zeta \right), \quad (7)$$

$$\partial_t \rho = D \nabla^2 \rho + \mu Q \nabla \cdot (C \nabla \phi) - \mu Q E \partial_t C + \nabla \cdot \left( \sqrt{2D\kappa} \zeta \right), \quad (8)$$

where now the electric potential satisfies $-\nabla^2 \phi = (S_d Q/\varepsilon_\infty) \rho$. It can be seen that the electric field introduces a source term $\propto \partial_t \rho$ to the dynamics of $C$ and vice versa; this is the origin of the long-range behavior we will obtain later.

### 2.2. Linearized density equations

As equations (7) and (8) contain nonlinear terms and multiplicative stochasticity, they are in general difficult to analyze. It is thus customary to focus on the fluctuations of the density fields about a uniform background baseline $C_0$ (i.e., $C^\pm = C_0^\pm + \delta C^\pm$ with $|\delta C^\pm| \ll C_0$), and to only keep terms in leading order of the fluctuations [23–25, 63, 64]. A scaling analysis of the nonlinearities also shows that they become negligible in the macroscopic limit (see appendix A). We define the density fluctuation field $c(r, t)$ and the charge fluctuation field (in units of $Q$) $\rho(r, t)$ as

$$c(r, t) = \delta C^+ + \delta C^- = C^+ + C^- - 2C_0, \quad \rho(r, t) = \delta C^+ - \delta C^- = C^+ - C^-.$$

Expanding equations (7) and (8) and keeping the linear terms, one arrives at the following linear stochastic equations for the dynamics of $c$ and $\rho$:

$$\partial_t c = D \nabla^2 c - \mu Q E \partial_t \rho + \sqrt{4D\kappa_0} \eta_c,$$  \quad (10)

$$\partial_t \rho = D \nabla^2 \rho - \mu Q E \partial_t c - Dc^2 \rho + \sqrt{4D\kappa_0} \eta_\rho.$$  \quad (11)

In these equations, we have defined the Debye length $\kappa^{-1}$ through

$$\kappa^2 = \frac{2S_d C_0 Q^2}{\varepsilon_\infty k_B T}, \quad (12)$$

and the linearized noise correlations now read $\langle \eta_c(r, t) \eta_c(r', t') \rangle = \langle \eta_\rho(r, t) \eta_\rho(r', t') \rangle = -\nabla^2 \delta^d(r - r') \delta(t - t')$, while $\eta_\rho$ and $\eta_c$ have zero averages and are uncorrelated. Note that in the absence of the electric field ($E = 0$), the linearized dynamics of the density fluctuations, equation (10), describes a normal
diffusion process. On the other hand, with the electric field set to zero, the charge dynamics of equation (11) is a relaxational process as a result of the linear term $\propto D\kappa^{-2}\rho$ on the rhs, and it exhibits exponential screening effects beyond the Debye length $\kappa^{-1}$ and the Debye relaxation time $(D\kappa^{-2})^{-1}$.

The linearized density and charge equations (10) and (11) will be used in section 3 to compute the corresponding correlation functions. These equations allow for the full characterization of the correlation functions in the Fourier space (see appendices B and C). However, since we are interested in the asymptotic long-distance limit, a convenient simplification can already be made by noting that for time and length scales beyond those set by the Debye screening processes, the charge fluctuation has a quasi-stationary solution given by

$$\rho \approx -\kappa^{-2}\beta Q E \partial_x \epsilon,$$

which is obtained by neglecting the temporal and spatial derivatives of the charge density\(^3\). The typical Debye screening length is of the order of $\kappa^{-1} \sim 1-10$ nm [1], beyond which the above approximation is justified for studying the dynamics of the electrolyte. Accordingly, the corresponding FIFs can in principle be realized in settings where the boundary separations are larger than the screening scale of the electrolyte which, for instance, may be the case for wet ion channels such as mechanosensitive channels [65], synthetic nanopores [66], as well as for force measurement setups with large inter-plate separations [30, 32].

Equation (13) shows that the charge density which persists beyond the relaxation time $\sim 1/(D\kappa^{-2})$ is proportional to the gradient of the number density along the direction of the electric field. This is in principle due to the bias introduced to the dynamics of the charged particles by the external field, which competes with the electrostatic forces that tend to relax any excess charge in the bulk of the electrolyte. Upon substituting equation (13) back into the number density dynamics equation (10), we arrive at an anisotropic diffusion equation that reads

$$\partial_t \epsilon = D \left( \epsilon^2 \partial_x^2 + \nabla^2 \right) \epsilon + \sqrt{4D \eta_c} \eta_c,$$

where the dimensionless electric field $\mathcal{E}$ is defined as

$$\mathcal{E} = \frac{\beta Q E}{\kappa} = \left[ \frac{e_{\text{in}} E^2/(2\Sigma \beta)}{k_B T C_0} \right]^{1/2}.$$  

Equation (14) is the central result of this section and one of the main points of this work as it also underlies the long-range FIF that will be calculated later. Note that the Einstein relation $\mu = \beta D$ that holds between mobility and noise strength in the single particle Langevin dynamics (1), is no longer valid at the macroscopic level of equation (14). This introduces a mismatch between the noisy fluctuations and the dissipative forces in the conserved dynamics of the density fluctuations, as a result of which the dynamics of $\epsilon$ represents a realization of generic scale invariance [53, 54, 67]. This also shows the importance of the stochasticity in the electrolyte dynamics, since the deterministic part of the linearized Langevin description has the usual diffusion (Gaussian) propagator; the mean-field values of $\epsilon$ and $\rho$, as obtained from equations (14) and (13) upon discarding the noise, vanish at long times.

Finally, it is worth noting that $\mathcal{E}$ can be regarded as the ratio of the energy density of the electric field ($\epsilon^2 \partial_x^2$) to the thermal energy density ($C V k_B T$) of the electrolyte, which is also the ratio between the typical values of the corresponding stress components. Alternatively, $\mathcal{E}$ could be interpreted as the average distance traversed along the electric field by a charged particle during the charge relaxation process (velocity $\times$ time $\sim (\mu Q E) \times (D\kappa^{-2})^{-1}$), divided by the Debye length ($\kappa^{-1}$) which determines the spatial extent of the counterion cloud around a cation or anion. As such, $\mathcal{E}$ encodes the extent of the deformation of counterion atmospheres from their equilibrium (symmetric) forms as a result of the applied external field [9].

2.3. Slowly varying electric fields

In the preceding analysis, we have assumed the electric field is DC, i.e. it is constant in time. However, maintaining a constant electric field in the bulk of an electrolyte is difficult in experimental setups, as ions will quickly accumulate on the oppositely charged electrode and screen their electric field to a short-ranged residual one acting only on the boundary layers. This naturally raises the question of whether the analysis that led to equation (14) can be extended to cases where the driving field is time-dependent, as such fields are more practical in experiments. To answer this, we note that the main simplifying approximation that allowed us to obtain the anisotropic diffusion process (14) is the quasi-stationary relation between charge and density fluctuations, cf equation (13). In physical terms, this approximation assumes the charge

\(^3\) Note that the noise term is also discarded at this level since it will only have short-range contributions to the correlation [8].
relaxation processes take place over time-scales that are much shorter compared to other dynamical scales. Such an approximation could therefore be applied to time-dependent electric fields as far as the variations in the electric field strength over the charge relaxation time are negligible; in that case, the ionic atmosphere surrounding each ion will have enough time to rearrange itself to the moving position of the central ion before the applied field changes considerably [22]. As the time scale set by the relaxation processes is often of the order of nano-seconds (equivalent to gigahertz frequencies), the condition of slowly changing electric field is, in fact, often met in setups with oscillatory electric fields. In such cases, the anisotropic diffusion of the density fluctuation field $c(t, r)$ is therefore given by

$$\partial_t c = D \left( E^2(t) \partial_t^2 + \nabla^2 \right) c + \sqrt{4 D c_0} \eta_c,$$

with $E(t) = \beta Q \mathcal{E}(t)/\kappa$. This equation shows that with a slowly varying electric field, the diffusion coefficient for density fluctuations along the direction of the electric field becomes a time-dependent factor. It is worth noting that as far as the time-scale for the variations of this diffusion coefficient is slower than the charge relaxation processes, it can, in principle, be faster than other (diffusive) time-scales present in the system.

### 2.4. Unequal mobilities of cations and anions

Another simplifying assumption in deriving equation (14) was the equal mobilities and diffusivities for the cations and anions in the electrolyte solution. However, often the cations and anions in an electrolyte have different ionic radii and as such their mobilities and diffusivities are not the same [1]. It has also been shown that in oscillatory electric fields, such differences in the ionic mobilities lead to a mismatch in the spatial range of the motion of the ions within the solution which, in turn, can give rise to an average electric field in the bulk of the solution [68]. Having this in mind, we now show that once an electric field is established within the bulk, a difference in the mobilities $\mu^\pm$ of the charge species would not change the macroscopic features of the dynamics described by equation (14), as it only gives rise to subleading terms.

Let us consider the mobilities and diffusivities of cations (+) and anions (−) as

$$D^\pm = D \pm \delta D, \quad \mu^\pm = \mu \pm \delta \mu,$$

and assume they are related through the Einstein relation, i.e. $\mu^\pm = \beta D^\pm$ (note that $\delta D$ and $\delta \mu$ may be positive or negative and are not necessarily small). Following the same steps outlined in section 2.1, and using the definition of the number density $\mathcal{C} = C^+ + C^-$ and the charge density $\rho = C^+ - C^-$, we obtain the modified version of the full number density and charge currents as

$$J_\mathcal{C} = -D \nabla \mathcal{C} - \delta D \nabla \rho + [\mu \mathcal{C} + \mathcal{C} \delta \mu] Q(-\nabla \phi + E) - \sqrt{2 \left[ D + \delta D \rho \right]} \zeta_\mathcal{C},$$

$$J_\rho = -D \nabla \rho - \delta D \nabla \mathcal{C} + [\mathcal{C} \delta \mu + \rho \delta \mu] Q(-\nabla \phi + E) - \sqrt{2 \left[ D^2 + D \delta D \rho \right]} \zeta_\rho.$$  

A similar linearization procedure as section 2.2 then yields the dynamics of the fluctuations in the number and charge densities according to

$$\partial_t c = D \nabla^2 c + \delta D \nabla^2 \rho - \delta D c^2 \rho - \mu Q \mathcal{E} \partial_x \rho - \delta \mu Q \mathcal{E} \partial_x c - \sqrt{4 D c_0} \eta_c,$$

$$\partial_t \rho = D \nabla^2 \rho + \delta D \nabla^2 c - D \nabla c^2 \rho - \mu Q \mathcal{E} \partial_x \rho - \delta \mu Q \mathcal{E} \partial_x c - \sqrt{4 D c_0} \eta_\rho.$$  

It could be seen that the quasi-stationary approximation of equation (13) still holds for equation (21) since the extra terms that stem from the difference between the mobilities ($\delta D$ and $\delta \mu$) have a higher number of derivatives, and thus they are scaling-wise irrelevant at macroscopic scales (this can be seen through a scaling analysis similar to appendix A). Therefore to obtain the dynamics of the density fluctuations $c$, we make use of equation (13) and substitute it into the modified density dynamics, equation (20); noting that $\delta \mu/\delta D = \mu/D = \beta$, we then recover the same anisotropic diffusion equation (14) which was derived for the case with equal ionic mobilities and diffusivities (the only modification here is that the diffusion coefficient in equation (14) is now replaced by the average ionic diffusivities, i.e. $D \rightarrow (D^+ + D^-)/2$).

We conclude that as long as an electric field is set in the bulk of the electrolyte, the difference in the diffusivities of the cations and anions may affect the microscopic dynamics of the particles, but it does not change the effective macroscopic equations governing the long-distance distribution of the density and the charge fluctuations.
3. Correlation functions

We now turn to calculating the correlations of the density fluctuation field \(c(r, t)\) and the charge fluctuation field \(\rho(r, t)\) after a quench in the electric field. In section 3.1, we first compute the correlation functions of the density fluctuations in the bulk, using the appropriate Fourier representation of equation (14), and we then make use of equation (13) to obtain the bulk charge correlations. Subsequently, in section 3.2 we compute the correlations in the presence of neutral confining boundaries parallel to the electric field. Our focus will be on the case that a constant (DC) electric field is switched on at \(t = 0\), before which the electrolyte is assumed to have been at thermal equilibrium.

3.1. Bulk correlation functions

Let us first derive the bulk correlations in the absence of any confining boundaries. The translational symmetry makes it convenient to work with the spatial Fourier transform of equation (14) which reads

\[
\partial_t c(k, t) = - D \left( \mathcal{E}^2 k^2 + k^2 \right) c(k, t) + \sqrt{4DC_0} \eta(k, t). \tag{22}
\]

We use the Fourier convention \(f(k) = \int \mathcal{D}r \, e^{-ik \cdot r} f(r)\) with \(r = (y, s) \in \mathbb{R}^d\) where \(s = (s_1, s_2, \ldots, s_{d-1}) \in \mathbb{R}^{d-1}\), and \(k = k_s + k_y \hat{e}_y\) with \(k_s = (k_{s_1}, k_{s_2}, \ldots, k_{s_{d-1}})\). The noise correlation in this Fourier representation reads \(\langle \eta(k, t) \eta(k', t') \rangle = (2\pi)^d \delta^d(k + k') \delta(t - t')\). Using an integration factor, equation (22) can be solved readily as

\[
c(k, t) = c(k, 0) e^{-D(\mathcal{E}^2 k^2 + k^2)t} + \sqrt{4DC_0} \int_0^t dt' \eta(k, t') e^{-D(\mathcal{E}^2 k^2 + k^2)(t-t')} . \tag{23}
\]

Note that for a time-dependent electric field, this expression should be modified to

\[
c(k, t) = c(k, 0) e^{-D(\mathcal{E}^2 k^2 + k^2)\int_0^t dt'} + \sqrt{4DC_0} \int_0^t dt' \eta(k, t') e^{-D(\mathcal{E}^2 k^2 + k^2)(t-t')} . \tag{24}
\]

In other words, the expression for the density fluctuations when the electric field is time-dependent can be obtained from that of the static field case by making the substitution \(\mathcal{E}^2 \rightarrow (\int_{t_1}^{t_2} \mathcal{E}^2(u) du)/\left(t_2 - t_1\right)\). For instance, for a periodic driving field \(\mathcal{E}(t) = E_0 \cos(\Omega t)\), this substitution reads \(\mathcal{E}^2 \rightarrow (\mathcal{E}_0^2/2)\left(1 + \sin(2\Omega t)/(2\Omega t)\right)\), which at long time scales simplifies to \(\mathcal{E}^2 \rightarrow \mathcal{E}_0^2/2\). Keeping in mind that this substitution is also applicable to the results that follow, from here on we will solely focus on the case of static electric fields.

Equipped with equation (23), it is now straightforward to obtain the density correlations as

\[
\langle c(k, t)c(k', t') \rangle_{\text{bulk}} = c(k, 0)c(k', 0) e^{-D(\mathcal{E}^2 k^2 + k'^2)t} e^{-D(\mathcal{E}^2 k^2 + k'^2)t'} + (2\pi)^d \delta^d(k + k') 2C_0 \left[ e^{-D(\mathcal{E}^2 k^2 + k'^2)t'} - e^{-D(\mathcal{E}^2 k^2 + k'^2)(t' - t)} \right] + (2\pi)^d \delta^d(k + k') \frac{2C_0 \mathcal{E}_0^2 k^2}{\mathcal{E}^2 k^2 + k'^2} \left[ e^{-D(\mathcal{E}^2 k^2 + k'^2)t'} - e^{-D(\mathcal{E}^2 k^2 + k'^2)(t' - t)} \right] \tag{25}
\]

where the averaging \(\langle \ldots \rangle_{\text{bulk}}\) is performed over noise realizations, and we have assumed \(t' \geq t\) without loss of generality. The first line of equation (25) represents the decay of the initial conditions; the second line shows the diffusive propagation of density fluctuations between two different times, as well as the establishment of the steady-state correlations; and the third line encodes both the steady-state and the transient correlations of the nonequilibrium fluctuations which vanish for \(\mathcal{E} = 0\). Hereafter, we restrict the calculations to electric field quenches applied to electrolyte solutions which are initially in thermal equilibrium and thus \(\langle c(k, 0)c(k', 0) \rangle_{\text{eq}} = (2\pi)^d \delta^d(k + k') 2C_0\). Denoting the combination of noise averaging and ensemble averaging by \(\langle \ldots \rangle_{\text{bulk}}\), we get

\[
\langle c(k, t)c(k', t') \rangle_{\text{bulk}} = \langle c(k, t)c(k', t') \rangle_{\text{eq}} + (2\pi)^d \delta^d(k + k') c^{(2)}_{\text{bulk}}(k, t; k', t') , \tag{26}
\]

where we have defined the equilibrium contribution of the correlation as

\[
\langle c(k, t)c(k', t') \rangle_{\text{eq}} = (2\pi)^d \delta^d(k + k') 2C_0 e^{-Dk^2(t'-t)} , \tag{27}
\]

while the nonequilibrium field-dependent part is given by

\[
c^{(2)}_{\text{bulk}}(k, t; t') = -\frac{2C_0 \mathcal{E}^2 k^2}{\mathcal{E}^2 k^2 + k'^2} \left[ e^{-D(\mathcal{E}^2 k^2 + k'^2)(t'-t)} - e^{-D(\mathcal{E}^2 k^2 + k'^2)(t' - t)} \right] . \tag{28}
\]
Note that for \( t = t' \), the equilibrium part of the correlation function is \( \propto C_0 \delta^d(k + k') \) which gives localized correlations in the long distance limit (see appendix B for the full expression without taking this limit). Transforming the equal-time correlations \( c^{(2)}_{\text{bulk}}(k, t, t) = c^{(2)}_{\text{bulk}}(k, t) \) to the real space yields

\[
c^{(2)}_{\text{bulk}}(r, t) = \left. -\frac{2C_0 \delta^d(1 - \frac{d}{2} r^2)}{S_d(E^2 + 1)^{3/2} r^d} + \int d^d r' \frac{2C_0 \delta^d(1 - \frac{d}{2} r'^2)}{S_d(E^2 + 1)^{3/2} r'^d} \exp \left( \frac{-(r - r')^2}{8\pi Dt} \right) \right|_{r = r'},
\]

(29)

where \( \tilde{r} \) is obtained from \( r \) by substituting \( x \to \tilde{x} = x/\sqrt{E^2 + 1} \). In equation (29), the first term on the rhs gives the nonequilibrium steady-state correlation function which vanishes without the external electric field, and in \( d \) spatial dimensions it decays as \( \sim r^{-d} \) with distance; moreover, this term is manifestly anisotropic with a dipolar character [67]. The second term on the rhs, on the other hand, represents the transient effects with their long-time decay governed by the power-law tail \( \sim t^{-d/2} \).

Having calculated the density correlations, we can now obtain the charge correlation functions through equation (13) by taking derivatives of equation (28). The long-ranged nonequilibrium contribution (derived from \( c^{(2)}_{\text{bulk}} \)) reads

\[
r^{(2)}_{\text{bulk}}(k, t, t') = \frac{-2C_0 \delta^d(k^2)}{\kappa^2(E^2k^2 + k'^2)} \left[ e^{-D(t^2k^2 + k'^2)/(t' - t)} - e^{-D(t^2k^2 + k'^2)/(t' + t)} \right].
\]

(30)

This is indeed the long-distance limit of the exact expressions provided in the appendices (which also include some short-ranged terms). The real-space form of the non-local charge correlations \( r^{(2)}_{\text{bulk}} \) can subsequently be obtained from equation (29) by taking derivatives with respect to the \( x \) coordinate (i.e. along the electric field) in accordance with equation (13); it is therefore seen that such charge fluctuations are also long-range correlated in the electrolyte solution.

Equations (28) and (30) give both the transient as well as the steady-state correlation functions, within the length and time scales where the approximation (13) holds. In appendices B and C, without making use of this approximation, we derive the density and charge two-point correlations at steady-state, for fluctuation fields considered at equal times as well as at different times.

We can also go further and obtain the full correlations (both transient and steady state) by solving the stochastic dynamics of equations (10) and (11), which in the matrix form reads

\[
\dot{S} = -MS + \mathcal{N}, \tag{31}
\]

where we have defined

\[
S(k, t) = \left( \begin{array}{c} c(k, t) \\ \rho(k, t) \end{array} \right), \quad \mathcal{M}(k, \kappa) = \left( \begin{array}{cc} Dk^2 & i\mu QEk_x \\ i\mu QEk_x & D(k^2 + \kappa^2) \end{array} \right), \quad \mathcal{N}(k, t) = \sqrt{4DC_0} \left( \begin{array}{c} \eta_k(k, t) \\ \eta_\rho(k, t) \end{array} \right). \tag{32}
\]

The formal solution to this equation is given by

\[
S(k, t) = e^{-\mathcal{M}t}S(k, 0) + \int_0^t du e^{-\mathcal{M}(t-u)}\mathcal{N}(k, u), \tag{33}
\]

from which the correlations for \( t' \geq t \) are computed as [69]

\[
\langle S(k, t)S^\dagger(k', t') \rangle_{\text{bulk}} = e^{-\mathcal{M}t} \langle S(k, 0)S^\dagger(k', 0) \rangle_{\text{bulk}} e^{-\mathcal{M}t'}
\]

\[
+ (2\pi)^d \delta^d(k + k') 4DC_0k^2 \int_0^t du e^{-\mathcal{M}(t-u)} e^{-\mathcal{M}(t'-u)} \tag{34}
\]

where \( \langle \ldots \rangle_{\text{bulk}} \) and \( \langle \ldots \rangle \) are the same as used in equation (28), \( \mathcal{M} = \mathcal{M}(k, \kappa) \), and \( \mathcal{M}' = \mathcal{M}(k', \kappa') \). The matrix \( e^{-\mathcal{M}t} \) is evaluated from the eigenvalues and eigenvectors of \( \mathcal{M} \), namely

\[
\lambda_{\pm} = D\left(k^2 + \kappa^2/2\right) \pm \Delta c^2 \Delta/2, \quad \text{and} \quad \mathbf{w}_{\pm} = \left( \begin{array}{c} i\kappa \\ 2Ec \end{array} \right) \left( 1 \pm \Delta \right), \tag{35}
\]

where we have defined

\[
\Delta = \Delta(E, k, \kappa) = \sqrt{1 - \frac{4E^2k^2}{\kappa^2}}, \tag{36}
\]

which then allows for computing the full correlation functions (the lengthy expressions will not be computed here). It can be seen from equation (34) that \( \lambda_{\pm} \) control the temporal approach of the correlation functions toward their steady-state form. In particular, the relative values of \( \kappa, E, \) and \( k_c \) determine whether \( \lambda_{\pm} \) have an imaginary part. Two different dynamical behaviors can then be inferred from these eigenvalues:
For $\kappa > 2E k_\nu$, both $\lambda_\pm$ and $\Delta$ lie on the real axis, and the full solution is the superposition of a (fast) decaying term with relaxation time $1/(D n^2)$, and a soft diffusive mode (similar to the dynamic structure factors, cf appendix C).

For $2E k_\nu > \kappa$, on the other hand, $\lambda_\pm$ and $\Delta$ are complex, and the full correlation functions are damped oscillatory with relaxation time $1/(D n^2)$. (This behavior also appears in two-point correlation functions evaluated at different times, while the equal-time correlations at steady state remain the same in both regimes, see appendix C.)

These results imply that equation (14) captures the diffusive dynamics of the electrolyte at length scales beyond $2E/\kappa$, while for smaller length scales the dynamics is relaxational. This therefore introduces an additional scale for the dynamics of the solution which should be taken into account along with the fact that the approximate charge profile given by equation (13) is already restricted to scales beyond $\kappa^{-1}$.

### 3.2. Correlation functions in flat confinement

We now turn to computing the density and charge correlation functions of the driven electrolyte in the presence of flat and neutral boundaries located at $y = 0$ and $y = H$ (figure 1). The boundaries are assumed to be impenetrable (i.e. they are blocking uncharged electrodes), and therefore they impose no-flux Neumann boundary conditions on equation (14), namely $\partial_x c|_{y=0} = \partial_x c|_{y=H} = 0$. One can construct the corresponding solutions that satisfy these boundary conditions by making use of the Neumann eigenmodes $\cos(p_n y)$ with $p_n = \frac{2\pi n}{H}$ through

$$c(r, t) = \sum_{n=0}^{\infty} \frac{2}{H} \cos(p_n y) \int \frac{d^{d-1}k}{(2\pi)^{d-1}} e^{ik}\cdot c_n(k, t),$$

where $s = (s_1 = x, s_2, \ldots, s_{d-1}) \in \mathbb{R}^{d-1}$ is the position along the boundary surfaces, $k = (k_0 = k_y, k_2, \ldots, k_{d-1})$ is the corresponding momentum vector (with $k_0 = |k|$), and $\sum'$ indicates a summation where the $n = 0$ term takes an additional factor of 1/2. Performing a similar transformation on the noise term $\eta_s$, and assuming the electrolyte is initially in thermal equilibrium (cf equation (26)), the correlation functions between the density modes $c_n(k, t)$ are then obtained, which after simplification read

$$\langle c_s(k, t)c'_s(k', t') \rangle = (2\pi)^{d-1}\delta^{d-1}(k + k') \delta_{n, n'}(1 + \delta_{n, 0}) C_0 H \times \left[ 1 - \frac{H^2 k_0^2}{E^2 k_0^2 + p_n^2 + k_t^2} \left( e^{-D(E^2 k_0^2 + p_n^2 + k_t^2)(t' - t)} - e^{-D(E^2 k_0^2 + p_n^2 + k_t^2)(t' + t)} \right) \right].$$

This expression could be used in order to obtain the following partial Fourier transformation of the density correlation functions along the $s$ coordinates:

$$\langle c(y, \mathbf{k}; t)c'(y', \mathbf{k}'; t') \rangle = (2\pi)^{d-1}\delta^{d-1}(\mathbf{k} + \mathbf{k}') \frac{4C_0}{H} \sum_{n=0}^{\infty} \cos(p_n y) \cos(p_n y') \times \left[ 1 - \frac{H^2 k_0^2}{E^2 k_0^2 + p_n^2 + k_t^2} \left( e^{-D(E^2 k_0^2 + p_n^2 + k_t^2)(t' - t)} - e^{-D(E^2 k_0^2 + p_n^2 + k_t^2)(t' + t)} \right) \right].$$

Narrowing down to correlations of density fluctuations at equal times, similar to the case of bulk correlations and noting that $\sum_{n=0}^{\infty} (2/H) \cos(p_n) \cos(p_n) = \delta(y - y')$, we define

$$\langle c(y, \mathbf{k}; t)c(y', \mathbf{k}; t) \rangle = (2\pi)^{d-1}\delta^{d-1}(\mathbf{k} + \mathbf{k}') \left[ 2C_0 \delta(y - y') + c^{(2)}(y, \mathbf{k}; t, t) \right]$$

and get

$$c^{(2)}(y, y'; \mathbf{k}; t) = \frac{4C_0 E^2 k_0^2}{H} \sum_{n=0}^{\infty} \frac{\cos(p_n y) \cos(p_n y')}{E^2 k_0^2 + p_n^2 + k_t^2} \left[ 1 - e^{-2D(E^2 k_0^2 + p_n^2 + k_t^2)t} \right].$$

This correlation consists of a steady-state contribution plus a diffusive part which vanishes at long times; in real space, both of these contributions are long-ranged (cf equation (29)).

Upon taking derivatives of equation (39) according to equation (13), we finally get for the charge correlation functions at equal times

$$\rho^{(2)}(y, y'; \mathbf{k}; t) = \frac{4C_0 E^4 k_0^4}{\kappa^2 H} \sum_{n=0}^{\infty} \frac{\cos(p_n y) \cos(p_n y')}{E^2 k_0^2 + p_n^2 + k_t^2} \left[ 1 - e^{-2D(E^2 k_0^2 + p_n^2 + k_t^2)t} \right],$$

4 A more involved approach is to use the method of images together with the real-space diffusive Green’s functions, and then make use of the Poisson summation formula to represent the solution in terms of the Neumann modes [77].
which we will use in the next section to compute the Maxwell stress.

It is worth mentioning that the correlation functions for the two half-spaces out of the confined space (i.e. for \( y < 0 \) and \( y > H \)) are obtained from equations (39) and (40) by making the substitution \( \frac{1}{\pi} \sum_n g(p_n) \rightarrow \int_{-\infty}^{\infty} \frac{d^2q}{2\pi} g(q) \) where \( p_n = \frac{2\pi n}{H} \) and \( g(p) \) stands for the summand in equations (39) and (40). These bulk correlations will be used to compute the stress exerted from the electrolyte outside the confinement, which are then subtracted from the internal stress to obtain the net total stress on the boundaries.

4. Stress tensor

In this section, we turn to calculating the stress exerted by the driven electrolyte on confining parallel boundaries. Since the system under consideration is out of thermal equilibrium due to the driving electric field, the stress or pressure cannot be calculated from thermodynamic relations. Based on the mechanical definition of stress, one can instead obtain stress formulas that also work in nonequilibrium conditions [70, 71]; such procedure for electric forces yields the well-known (electrostatic) Maxwell stress [72, 73] which also circumvents the ambiguity often faced in deriving the stress tensor from body forces (due to the freedom in inverting the divergence operator). In section 4.1, we derive a simplified formula for the noise-averaged Maxwell stress exerted by a general charge distribution confined between two parallel plates, assuming the charge distribution is invariant under translations along the boundaries. In section 4.2 we implement the charge correlations given by equation (40) into this formulation to obtain the FIF, whose steady-state and transient parts are subsequently analyzed in sections 4.3 and 4.4.

4.1. General expression for Maxwell stress in plane parallel geometry

For an electrostatic potential field \( \phi \), the noise-averaged Maxwell stress tensor in \( d \) spatial dimensions reads

\[
\langle \sigma_{ij} \rangle = \frac{\epsilon_{in}}{2d} \left( 2(\nabla_i \phi \nabla_j \phi) - \delta_{ij} \langle (\nabla \phi)^2 \rangle \right),
\]

where the electric potential satisfies the Poisson equation \(-\nabla^2 \phi = S_{d, \rho} Q_\text{in} / \epsilon_{in} \). With free boundary conditions, the solution to this Poisson equation is given by \( \phi_{\text{free}}(r, t) = \frac{\epsilon_{in}}{md} \int d^d r \frac{d^d \rho}{(r - r')^d} \) [74]. As noted before, at the mean-field level \( \rho \) vanishes at long times, and so do the average values of the electric field and the electrolyte Maxwell stress.

To proceed with equation (41), the correlation function of the electric potential \( \phi(r, t) \) in confinement are needed. We thus first construct the solutions of the Poisson equation taking into account the electrostatic boundary conditions imposed by the walls. Assuming the boundaries located at \( y = 0 \) and \( H \) do not carry free charges, these electrostatic boundary conditions read

\[
\begin{align*}
\epsilon_{in} \partial_y \phi|_{y=0^+} &= \epsilon_{out} \partial_y \phi_{\text{out}}|_{y=0^-}, & \nabla_s \phi|_{y=0^+} &= \nabla_s \phi|_{y=0^-}, \\
\epsilon_{in} \partial_y \phi|_{y=H^-} &= \epsilon_{out} \partial_y \phi_{\text{out}}|_{y=H^+}, & \nabla_s \phi|_{y=H^-} &= \nabla_s \phi|_{y=H^+},
\end{align*}
\]

where \( \nabla_s = \sum_{i=1}^{d-1} \partial_i \hat{e}_i \). The potential \( \phi \) that satisfies these boundary conditions can be obtained using the method of electrostatic image charges [72]. We group the (infinite number of) image charges into two sets: image charges in group \( \mathbb{I}_L \) are obtained from first reflecting the source charge distribution with respect to the bottom boundary (i.e. \( y = 0 \)), and then subsequently reflecting with respect to the top boundary, and so on. For this group, the location of the image charges are

\[
\mathbb{I}_L = \left\{ y_n = (-1)^n \left( \frac{n}{2} H + y_{\text{source}} \right) ; \quad s_n = s_{\text{source}} \mid n \in \mathbb{N} \right\}.
\]

On the other hand, image charges in group \( \mathbb{I}_R \) are obtained by first reflecting the source charge distribution with respect to the top boundary (i.e. \( y = H \)), and then reflecting with respect to the bottom boundary, and so on; in this case, the image locations are given by

\[
\mathbb{I}_R = \left\{ y_n = (-1)^{n+1} \left( \frac{n}{2} H - y_{\text{source}} \right) ; \quad s_n = s_{\text{source}} \mid n \in \mathbb{N} \right\}.
\]

(Note that \( \lfloor \ldots \rfloor \) and \( \lceil \ldots \rceil \) are the floor and the ceiling functions, respectively.) For both groups, the \( n \)th image has electric charge \( Q_n = \lambda^n Q_{\text{src}} \) where we have defined the dielectric contrast \( \lambda \) between the electrolyte solution and the boundary material as (\( \epsilon_{in} \) and \( \epsilon_{out} \) are the permittivities of the solvent and the boundaries, respectively)

\[
\lambda = \frac{\epsilon_{in} - \epsilon_{out}}{\epsilon_{in} + \epsilon_{out}}.
\]
which determines the electric charge ratio between successive images. The electric potential \( \phi \) that satisfies the boundary conditions (42) is then calculated as

\[
\phi(y; k_i; t) = \frac{Q}{\epsilon_{in}(d-2)} \int_0^H dy' \rho(y'; k_i; t) e^{-k_i|y-y'|} + \sum_{l \neq i} \frac{Q_l}{\epsilon_{in}(d-2)} \int_0^H dy' \rho(y'; k_l; t) e^{-k_l|y-y'|},
\]

where the first term is the electric potential created directly by the source charge distribution, and we have made use of the translation invariance of the system along directions parallel to the surfaces (i.e. the \( s \) coordinates) by taking the Fourier transform of \( \phi_{\text{free}} \) with momentum \( k_i \in \mathbb{R}^{d-1} \) along them. The noise-averaged normal component of the Maxwell stress corresponding to this electric potential is then calculated as

\[
\langle \sigma_{ij}(r, t) \rangle = \frac{Q^2S_d}{8\epsilon_{in}} \int_0^H dy' \int_0^H dy'' \int (2\pi)^{d-1} \rho^{(2)}(y', y''; k_i; t) \times \left[ \sum_{s':s''=\pm} \lambda^{d+s''} e^{-k_i|y-y'|} e^{-k_i|y''|} \{ \text{sgn}(y-y'') \text{sgn}(y-y''') - 1 \} \right].
\]

(47)

To calculate the (excess) stress at the location of the boundaries, we next perform the summation over the image charges, noting that

\[
\sum_{n=1}^\infty (\pm \lambda)^n e^{-b\|z\|} = \frac{\lambda(\pm 1 - \lambda^2)}{e^b - \lambda^2}, \quad \text{and} \quad \sum_{n=1}^\infty (\pm \lambda)^n e^{-b\|z\|} = \frac{\lambda(\pm 1 - \lambda^2)}{e^b - \lambda^2}.
\]

(48)

One can readily show that the stress at the location of the two plates is equal, and after some algebraic manipulation it can be written as

\[
\langle \sigma_{ij}(t) \rangle = -\frac{\lambda Q^2 S_d}{2\epsilon_{in}} \int_0^H dy' \int_0^H dy'' \int (2\pi)^{d-1} \rho^{(2)}(y', y''; k_i; t) \times \left[ e^{-k_iy'} e^{2k_iH} + e^{-k_iy''} e^{-2k_iH - \lambda^2} + e^{-k_iy''} e^{2k_iH} + e^{-k_iy''} e^{-2k_iH - \lambda^2} \right].
\]

(49)

Note that this expression holds for a generic charge distribution which is statistically invariant with respect to translations along the \( s \) coordinates (i.e. parallel to the surfaces) and has the charge correlation function \( \rho^{(2)}(y', y''; k_i; t) \).

**4.2. Stress exerted by the confined driven electrolyte**

We now substitute the specific charge correlation function given by equation (40) into the stress formula in equation (49) and perform the required integrations over \( y' \) and \( y'' \) to obtain the stress for the specific settings at hand (figure 1). Note that the resulting expressions contain formally divergent terms which will be removed upon subtracting the bulk stress (this is necessary to obtain the net force acting on the boundaries). The net force per unit area of the top boundary is then obtained as

\[
\frac{F(t)}{S} = -\frac{k_b T}{H^2} e^4 \mathcal{A}(\mathcal{E}, \lambda; t),
\]

(50)

with the dimensionless amplitudes \( \mathcal{A} \) defined as

\[
\mathcal{A}(\mathcal{E}, \lambda; t) = \int d^{d-1} \nu_s \left\{ \sum_{n=0}^\infty \lambda \mathcal{R}_n(\lambda, \nu_s) g(\mathcal{E}, n, \nu_s) \left[ 1 - e^{-2\pi^2 \tau (s^2 + \mathcal{E}^4 \nu_s^2 + \nu_s^2)} \right] 
- \lambda \int_0^\infty dt g(\mathcal{E}, n, \nu_s) \left[ 1 - e^{-2\pi^2 \tau (s^2 + \mathcal{E}^4 \nu_s^2 + \nu_s^2)} \right] \right\}.
\]

(51)

Here, \( \tau = D t / H^2 \) and we have also defined

\[
\mathcal{R}_n(\lambda, \nu_s) = \begin{cases} \left( \frac{e^{\nu_s} - 1}{e^{\nu_s} - \lambda} \right)^2 \equiv \mathcal{Y}_-^n(\lambda, \nu_s) & n \text{ even}, \\ \left( \frac{e^{\nu_s} + 1}{e^{\nu_s} + \lambda} \right)^2 \equiv \mathcal{Y}_+^n(\lambda, \nu_s) & n \text{ odd}, \end{cases}
\]

(52)

where \( \lambda \mathcal{R}_n \) represents the electrostatic response from the image charges. Moreover, we used the definition
where \( \mathbf{\nu}_t = (\nu_{t1}, \nu_{t2}, \ldots, \nu_{td}) \in \mathbb{R}^{d-1} \) is a dimensionless vector and \( \nu_t = |\mathbf{\nu}_t| \) (note that \( \mathbf{\nu}_y = \mathbf{k}/(\hbar/\pi) \), i.e. it is the dimensionless form of the parallel wavevector in the previous section).

To analyze the time-dependent stress amplitude given by equation (51), it is convenient to separate its steady-state and transient parts as

\[
A(\mathcal{E}, \lambda; t) = A_s(\mathcal{E}, \lambda) + A_t(\mathcal{E}, \lambda; t)
\]

(54)

where \( A_s \) denotes the long-time steady-state amplitude and is given by the general expression

\[
A_s(\mathcal{E}, \lambda) = \lambda \int d^{d-1} \mathbf{\nu}_s \left\{ \sum_{n=0}^{\infty} R_n(\lambda, \mathbf{\nu}_s) g(\mathcal{E}, n, \mathbf{\nu}_s) - \int_0^{\infty} \text{d} n g(\mathcal{E}, n, \mathbf{\nu}_s) \right\},
\]

(55)

and \( A_t \) is the transient part of the amplitude which reads

\[
A_t(\mathcal{E}, \lambda; t) = -\lambda \int d^{d-1} \mathbf{\nu}_s \left\{ \sum_{n=0}^{\infty} R_n(\lambda, \mathbf{\nu}_s) g(\mathcal{E}, n, \mathbf{\nu}_s) e^{-\nu^2 t (\nu^2 + \nu_s^2 + \nu_t^2)} \right\}.
\]

(56)

The transient part \( A_t \) determines the initial behavior of the force amplitude after the quench, but it vanishes at long times. As will be shown in the following section, for \( \tau \gg 1 \), the temporal decay of \( A_t \) takes a power-law form (with possible crossover regimes) which corresponds to the long-time tails of diffusion processes.

### 4.3. Steady-state stress amplitude

The steady-state properties of the stress and the amplitude were investigated in reference [8]. Here, we present a brief account of those results. Performing the summations involved in equation (55) and after some simplifications we arrive at the following expression for \( A_s \) in \( d \) spatial dimensions

\[
A_s(\mathcal{E}, \lambda) = \frac{\lambda \zeta(3)}{2^{d-1}} \int d^{d-1} \mathbf{\nu}_s \frac{\pi \nu_s}{4 \mathcal{E}^4} \left\{ \left(1 - \frac{\mathcal{E}^2 \cos^2 \theta}{2}\right) \right\} \left[ 2 - \mathcal{Y}_+(\lambda, \nu_s) \coth \left( \frac{\nu_s}{2} \right) \right.
\]

\[
- \mathcal{Y}_-(\lambda, \nu_s) \tan \left( \frac{\nu_s}{2} \right) \left[ 2 - \mathcal{Y}_+(\lambda, \nu_s) \coth \left( \frac{\nu_s}{2} \right) + \mathcal{Y}_-(\lambda, \nu_s) \tanh \left( \frac{\nu_s}{2} \right) \right] \right\}.
\]

(57)

where \( \nu_s \cos \theta = \nu_s \) and \( \mathcal{Y}_\pm(\lambda, \nu_s) \) are defined in equation (52). For \( d = 3 \), some of the integrations in equation (57) can be carried out, yielding

\[
A_s(\mathcal{E}, \lambda) = \frac{\lambda \zeta(3)}{16 \pi} \frac{\mathcal{E}^2 + 2}{\mathcal{E}^4 (\mathcal{E}^2 + 1)^{3/2}} \left[ \left( \frac{\lambda - 1}{4} \right) \text{Li}_2(\lambda^2) + \frac{1}{2} \left( \lambda + \frac{1}{4} \right) \text{Li}_3(\lambda^2) \right]
\]

\[
+ \frac{3 \text{Li}_3(\lambda^2)}{32 \pi^2 \mathcal{E}^2} + \frac{\lambda \pi}{16} \int_0^{\frac{\pi}{2}} \text{d} \theta \int_0^{\mathcal{E}^2} \nu_s^2 \text{d} \nu_s
\]

\[
\times \left[ \mathcal{Y}_-(\lambda, \nu_s) - 1 \right] \coth \left( \frac{\nu_s}{2} \right) \left( \mathcal{E}^4 (\mathcal{E}^2 + 1) \right) + \left[ \mathcal{Y}_+(\lambda, \nu_s) - 1 \right] \tanh \left( \frac{\nu_s}{2} \right) \left( \mathcal{E}^4 (\mathcal{E}^2 + 1) \right),
\]

(58)

where \( \text{Li}_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n} \) is the polylogarithm function. This expression can be evaluated by numerical methods, and we also report simple asymptotic expressions for its limiting cases in table 1 (for more details on the derivation of the asymptotic formulas and also similar analysis for the \( d = 2 \) case, see the supplemental material of reference [8]).
Table 1. Asymptotic expressions for the dimensionless steady-state stress amplitude \( A_s(E, \lambda) \) in \( d = 3 \), obtained from expanding equation (58) (corrections are \( O(E^2) \) for \( E \ll 1 \), and \( O(E^{-4}) \) for \( E \gg 1 \)).

| \( \varepsilon \ll 1 \) | \( \varepsilon \gg 1 \) |
|---|---|
| \( \lambda \ll 1 \) | \( \lambda = 1 \) | \( \lambda = -1 \) |
| \( \frac{\nu(3)}{84 \lambda} \left( \frac{\lambda + \nu s}{\lambda - \nu s} \right) \) | \( \frac{\nu(3)}{84 \lambda} \) | \( \frac{\nu(3)}{84 \lambda} \) |
| \( 9(4 \zeta(5) + 1) \frac{\pi}{512} \lambda^2 \) | \( \frac{9(4 \zeta(5) - 1)}{1024} \frac{\pi}{\lambda \lambda} (6 \lambda - 1) \frac{64}{\pi} \lambda^{-2} \) | \( \frac{9 \zeta(3)}{64 \pi} \) |
| \( \frac{9 \zeta(3)}{256 \pi} \) | \( \frac{9 \zeta(3)}{16 \pi} \) | \( \frac{9 \zeta(3)}{16 \pi} \) |

Figure 2. The full FIF amplitude \( A = A_s + A_\tau \) as a function of the reduced time \( \tau = \frac{D \tau}{H^2} \) for positive values of the dielectric contrast \( \lambda \) and different values of the electric field strength \( E \). In each case, the inset shows the transient part of the force amplitude, \( A_\tau \) (or its absolute value if \( A_\tau \) is negative), as a function of \( \tau \) in logarithmic scales. For \( \lambda = 1 \), the transient amplitude \( A_\tau \) decays to zero as \( \tau^{-1} \); for other values of \( \lambda \), the decay is governed by \( \tau^{-3/2} \). The long-time limit of the full amplitude \( A \) corresponds to the FIF at the steady state and can change sign for \( -0.17 \leq \lambda \leq 0.31 \). Note that for \( \lambda = 0.12 \), the sign change is not observable here for \( E = 3 \) since it requires very large values of the electric field strength.

4.4. Transient stress amplitude

We now focus on the transient part of the stress amplitude as per equation (56). First, we note that the initial rate of change of \( A_\tau \) is given by

\[
\left. \frac{\partial A_\tau}{\partial \tau} \right|_{\tau=0} = 2\pi^2 \lambda \int d^{d-1} \nu \left\{ \sum_{n=0}^{\infty} R_n(\lambda, \nu) \frac{2^{1-d} \nu_s^2 \cos^4 \theta}{(n^2 + \nu_s^2)^2} - \int_0^{\infty} dn \frac{2^{1-d} \nu_s^2 \cos^4 \theta}{(n^2 + \nu_s^2)^2} \right\} \tag{59}
\]

\[
= \frac{\pi^3}{2^{d+1}} \int d^{d-1} \nu \nu_s^2 \cos^4 \theta \left\{ \frac{\pi \nu_s}{2} \left[ Y_-(\lambda, \nu_s) \text{csch}^2 \left( \frac{\pi \nu_s}{2} \right) - Y_+(\lambda, \nu_s) \text{sech}^2 \left( \frac{\pi \nu_s}{2} \right) \right] - \left[ 2 - Y_-(\lambda, \nu_s) \coth \left( \frac{\pi \nu_s}{2} \right) - Y_+(\lambda, \nu_s) \tanh \left( \frac{\pi \nu_s}{2} \right) \right] \right\} \tag{60}
\]
Figure 3. The full FIF amplitude $A = A_s + A_\tau$ as a function of the reduced time $\tau = Dt$ for negative values of the dielectric contrast $\lambda$ and different values of the electric field strength $\varepsilon$. In each case, the inset shows the transient part of the force amplitude, $A_\tau$, as a function of $\tau$ in logarithmic scales. In these cases, $A_\tau$ is negative, and its magnitude decays to zero as $\tau^{-3/2}$.

where we have used $\nu_s \cos \theta = \nu_x$. This initial rate does not depend on the electric field strength, and it is thus a function of the dielectric contrast $\lambda$ only (note that higher-order derivatives at $\tau = 0$ do depend on $\varepsilon$). For $d = 3$, we carry out the integrals in equation (60) and obtain the exact expression

$$\frac{\partial A_\tau}{\partial \tau} \bigg|_{\tau=0} = \frac{9}{64\pi} \left[ \left( \lambda - \frac{1}{\lambda} \right) \text{Li}_4(\lambda^2) + \left( 5 + \frac{1}{2} \left( \lambda + \frac{1}{\lambda} \right) \right) \text{Li}_5(\lambda^2) \right],$$

which can be approximated for small dielectric contrasts to second order in $\lambda$ as

$$\frac{\partial A_\tau}{\partial \tau} \bigg|_{\tau=0} = \frac{9\lambda(-1 + 10\lambda)}{128\pi} + O(\lambda^3).$$

Since the total stress at $t = 0$ vanishes, this approximate form shows that for $0 \lesssim \lambda \lesssim 0.1$ the stress amplitude initially decreases and becomes negative (i.e. the force between the plates is initially repulsive). Having calculated the initial rate of $A_\tau$ and using the asymptotic expansions of $A_s$ given in table 1 which determine the long-term behavior of the stress, one can see there are a number of different dynamical behaviors that the FIF exhibits

- For $\lambda \lesssim -0.31$ and $\lambda \geq 0.17$, both the initial slope $\partial A_\tau|_{\tau=0}$ and the steady-state amplitude $A_s$ are positive.
- For $-0.31 \lesssim \lambda < 0$, the initial slope of $A_\tau$ is positive, and $A_s$ is negative for weak electric fields while it becomes positive for strong fields.
- For $0 < \lambda \lesssim 0.1$, the initial slope is negative, and $A_s$ is positive for weak fields and negative for strong fields.
- For $0.1 \lesssim \lambda \lesssim 0.17$, the initial slope is positive, and $A_s$ is positive for small electric fields while it is negative for strong fields.
To investigate how $A_r$ decays at long times, we define $\tilde{\nu}_s = \sqrt{\tau} \nu_s$ with which equation (56) is given by

$$A_r = \frac{-\lambda}{(\sqrt[4]{\tau})^{d-1}} \int d^{d-1} \nu_s \left\{ \sum_{n=0}^{\infty} \left( \frac{\nu_s^{\lambda} \sqrt{\tau}}{\nu_s^{\lambda} \sqrt{\tau} + 1} \right)^2 \frac{\tilde{\nu}_s^n \tilde{\nu}_s^d e^{-2s^2(\nu_s^4 + \tau^2\tilde{\nu}_s^2 + \tilde{\nu}_s^2)}}{(n^2 \tau + E^2 \tilde{\nu}_s^2 + \nu_s^2)(n^2 \tau + \nu_s^2)^2} \right\} \left( \tilde{\nu}_s^4 \tilde{\nu}_s^d e^{-2s^2(\nu_s^4 + \tau^2\tilde{\nu}_s^2 + \tilde{\nu}_s^2)} \right).$$

(In the second line we have defined $\tilde{n} = \sqrt{\tau} n$ for the integration variable.) Since the exponential factors suppress the integrands at large values of $\tilde{\nu}_s$, the final outcome of the integration is effectively determined by the behavior of the integrand for $\tilde{\nu}_s \sim O(1)$. In addition, for $\tau \to \infty$, to leading order the summation is given by the $n = 0$ term. We thus only keep this contribution and also expand the exponential factor $e^{\pi \tilde{\nu}_s^{\lambda} \sqrt{\tau}}$ to obtain

$$\lim_{\tau \to \infty} A_r = \frac{-\lambda}{(\sqrt[4]{\tau})^{d-1}} \int d^{d-1} \tilde{\nu}_s \left( \frac{\pi \tilde{\nu}_s^{\lambda} \sqrt{\tau}}{1 + \pi \tilde{\nu}_s^{\lambda} \sqrt{\tau} - \lambda} \right)^2 \frac{\cos^4 \theta}{1 + E^2 \cos^2 \theta} e^{-2s^2(\tilde{\nu}_s^2 + (1 + E^2 \cos^2 \theta))} - \frac{1}{\sqrt{\tau}} \int_0^{\infty} d\tilde{n} \frac{\tilde{\nu}_s^n \cos^4 \theta e^{-2s^2(\tilde{n}^2 + (1 + E^2 \cos^2 \theta))}}{(\tilde{n}^2 + \tilde{\nu}_s^2)(\tilde{n}^2 + \nu_s^2)^2} + O(\tau^{-1}).$$

From the second line, it becomes evident that the transient force amplitude due to the bulk electrolyte outside the boundaries decays as $\sim \tau^{-d/2}$; this is, in fact, the usual power-law tail of the diffusion process in $d$ spatial dimensions. On the other hand, the temporal decay of the transient stress coming from the electrolyte confined between the plates exhibits two different regimes: for $\tau \lesssim \pi^2/(1 - \lambda)$ the decay is governed by the power-law form $\sim \tau^{-(d-1)/2}$, while for $\tau \gtrsim \pi^2/(1 - \lambda)$ it follows the form $\sim \tau^{-(d-1)/2}$. Since these expressions are obtained for $\tau \gg 1$, the first of these two regimes is only accessible when $1 - \lambda \ll 1$. (However, note that $A_r$ may also exhibit a sign change at times comparable to the crossover time which in principle can make it difficult to observe the crossover between the two regimes.)

The above analysis shows that at the longest time scales, the decay of the FIF amplitude is governed by the diffusive tails of the bulk electrolyte outside the boundaries (and not those of the confined electrolyte between the plates). It is worth mentioning that in equation (64), the sign of this asymptotic long-time behavior is determined by $\lambda$. A comparison with the (sign of the) steady-state amplitude $A_s$ shows that for negative values of dielectric contrast and with weak applied electric fields $E \ll 1$, the total amplitude $A$ overshoots $A_s$ at a finite time before approaching it at long times. This phenomenon also happens for $\lambda \gtrsim 0.17$ with strong applied fields.

As it was mentioned before, the factors $\lambda R$ in equation (51) are due to the electrostatic image charges, an infinite number of which are required for the confined space between the walls whereas only one image charge is seen by the bulk ions outside the walls. At early times, the factor $[1 - e^{-2s^2(\nu_s^4 + \tau^2\tilde{\nu}_s^2 + \tilde{\nu}_s^2)}]$ in both of the confinement and bulk terms in equation (51) is negligible for large wavelengths and it can only pick contributions from wavelengths smaller than a characteristic value $L_D$ where $L_D \lesssim \sqrt{Dt}$ defines the diffusion front of the fluctuations. When $L_D$ is negligible with respect to $H$, the fluctuation spectrum in the confined space between the walls is effectively similar to those in the bulk electrolyte outside the walls and, in addition, the contribution of the infinite number of the image charges is reduced to that arising from the first (i.e. closest) image only. Therefore, during these initial times, the variations in the FIF amplitude have diffusive origins while the fluctuation spectrum develops toward the steady-state, similar to other cases of transient FIFs [43, 45, 47]. Once $L_D$ becomes comparable with $H$, fluctuations are almost developed to their confined spectrum and, moreover, the contributions due to further image charges also become relevant. Therefore at long time scales, the stress at each boundary is determined by interactions between image charges on the two sides of that boundary which, depending on the dielectric contrast $\lambda$, can be overall attractive or repulsive.

In figures 2 and 3, the temporal variations of the full FIF amplitude $A$ and its transient part $A_r$ as obtained from the numerical evaluation of equations (55) and (56) (and the corresponding expressions in $d = 3$) are shown. One can observe that initial variations, long-time decays, and the sign (and magnitude) of the amplitude at steady states agree with the analysis we have presented in this section.
5. Concluding remarks

In this work, we studied the correlation functions and the fluctuation effects in a strong electrolyte in the transient regime after an electric field quench that drives the solution out of the thermal equilibrium state. We showed the density and charge fluctuations are generally long-range correlated both in this transient period as well as in the long-time nonequilibrium steady state, as a result of the generic scale invariance of the stochastic dynamics. Such fluctuations give rise to novel long-ranged forces on the confining boundaries. We analyzed these forces as a function of the time elapsed from the electric field quench which, together with the steady-state results previously presented in reference [8], provides a complete account of the forces at different time scales. Similar to the steady-state case, the FIF scales with the plate separation as $H^{-d}$ in $d$ spatial dimensions, and in general it has a diffusive character in its approach toward the steady-state form (see equations (50) and (51)). This diffusive approach in time gives rise to power-law temporal decays of the transient part of the force at long times. Figures 2 and 3 show the variety of temporal variations of the total force amplitude $A$ at early times and at long times, depending on the dielectric contrast $\lambda$ and the dimensionless electric field $\mathcal{E}$, as depicted by $A$ vs $\tau$ plots in figures 2 and 3 for $d = 3$. It was shown in reference [8] that the strength and the direction (i.e. attraction or repulsion) of the steady-state force can be controlled by the strength of the applied electric field. Here we demonstrated that the strength and direction of the FIF in the transient regime, on the other hand, may vary non-monotonically with time. The initial slope of the force amplitude does not depend on the strength of the applied field and is solely determined by $\lambda$ through equation (60) (which reduces to equation (61) for $d = 3$); in early times, the temporal variations of the force amplitude is non-monotonic in some cases and it can even result in changes in the sign of the force. The long-time trend of the force amplitude, on the other hand, is power-law and monotonic, and it depends on both $\lambda$ and $\mathcal{E}$ indicated by equation (57) (equation (58) in $d = 3$ dimensions).

Although to derive the correlation functions, which form the basis of the force calculation, we focused on the case of a static external electric field, in section 2.3 we argued these results are also applicable when the electric field varies slowly over time. Since the time-scale of the charge relaxation is often of the order of a few nanoseconds, this condition applies to many experiments where oscillatory electric fields are used. The long-time description employed here can then be used by making minimal modifications as described below equation (24). It has been shown that an oscillatory driving field accompanied by different mobility coefficients for cations and anions can give rise to steady electric fields within the electrolyte [68]; however, once an electric field driving the ions in opposite directions is set up in the electrolyte, the analysis in section 2.4 shows that the asymptotic long-distance limit of the fluctuation correlations is still governed by equations similar to the case of equal ionic mobilities, while the mobility differences give subleading correction terms.

The rich features of the nonequilibrium FIF investigated in this work point toward unexplored methods of force manipulation in practical applications, for example to control neutral colloidal particles that are immersed in an electrolyte solution. It is a well-known fact that in equilibrium, the presence of an electrolyte solution between dielectric materials gives rise to screening of the zero-frequency (thermal) part of the dispersion forces [1, 7, 52, 75]. Within the linearized description used here, the charge fluctuation correlations, which give rise to FIFs, are given by the superposition of equilibrium and nonequilibrium correlations (see equation (26)). If the boundary materials are in thermal equilibrium, the equilibrium part of the electrolyte correlations is what will give rise to the aforementioned force screening effects, while the nonequilibrium correlations examined in this manuscript lead to unscreened long-ranged forces. FIFs between flat boundaries that consist of charge species driven by an external field (without electrolyte in between the walls) have recently been investigated using the Langevin and Dean–Kawasaki framework [50, 51]. It would be an interesting direction to investigate the interplay of the nonequilibrium FIFs in the presence of driven ions both within as well as in between the confining walls.

The transient forces studied here may be relevant to some experimental setups, for instance to interpret and analyze force measurement data in colloidal systems. In such cases, it is important to have a knowledge of all different sources of force, including various types of dispersion and fluctuation forces, which are effective at the observation scale, in order to gain a correct understanding of the mechanisms at work. For more accurate quantitative predictions, other effects such as hydrodynamic interactions should also be included in a theoretical model. For example, hydrodynamic effects become relevant for concentrated systems where inter-particles distances become comparable to their hydrodynamic radii; however, as noted in section 2, these interactions are negligible for typical electrolyte solutions considered in this work. It is nevertheless noteworthy that the variations of the force amplitude in figures 2 and 3 resemble some of the experimentally observed temporal patterns of force variation in surface measurements (although in a different setting) [30, 32]; these observations hint at nonequilibrium fluctuation effects which are generally...
discarded in mean-field models and can indeed be relevant to understanding the force generation mechanisms in charged solutions out of equilibrium. In the future, we plan to investigate the experimentally relevant case of oscillatory electric fields, both parallel as well as perpendicular to the boundaries, to determine how the FIF amplitude studied here would be modified. In addition, one can also investigate the perpendicular setup with static fields to reveal the role of the nonequilibrium fluctuation forces during the double layer formation processes.

Finally, note that although we investigated a simple system here (constant electric field, flat boundaries, symmetric binary electrolyte) in order to be able to focus on the main features of the dynamics and correlations, similar analysis may also be applied to other settings such as driven and tactic active particles, since the underlying notion of generic scale invariance in anisotropic conserved dynamics generally emerge in driven systems with screening effects.

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Data availability statement

No new data were created or analysed in this study.

Appendix A. Scaling analysis of the nonlinear terms

In this section, we look into the scaling analysis of the full stochastic equations of motion, and show that the nonlinearities are irrelevant in the macroscopic limit for $d > 2$.

The full (not linearized) Dean–Kawasaki stochastic equations of motion for density and charge are given by equations (5) and (6). First, we determine the Gaussian scaling exponents through the linearized dynamics, equations (10) and (11). We consider the scaling of these equations according to $r \to b r, t \to b^{}\frac{1}{2} t, \rho \to b^{\nu} \rho, c \to b^{\nu} c$, which yield

$$\partial_t c = (b^{-2+\chi_c}) \nabla^2 c - (b^{-1+\frac{1}{2}+\chi_c}) \mu Q E \partial_c \rho + \left(b^{-1+\frac{1}{2}+\frac{d}{2}+\frac{1}{2}} \sqrt{4D_{\text{c}}\eta_c}\right)$$

$$\partial_t \rho = (b^{-2+\chi_c}) \nabla^2 \rho - (b^{-1+\frac{1}{2}+\chi_c}) \mu Q E \partial_c \rho - (b^{\frac{1}{2}}) D_{\text{c}} \rho + \left(b^{-1+\frac{1}{2}+\frac{d}{2}+\frac{1}{2}} \sqrt{4D_{\text{c}}\eta_c}\right).$$

From the first equation, the mean-field exponents are obtained as

$$z = 2, \quad \chi_c = 1 + \chi_c = -\frac{d}{2}. \quad \text{(A3)}$$

Note that the equation of motion for $\rho$ is clearly not scale-invariant since on the rhs of equation (A2), the second term ($\propto \mu Q E \partial_c \rho$) and the third term ($\propto D_{\text{c}} \rho$) scale as $b^\nu$, and therefore they grow under rescaling. This reflects the relaxational nature of the charge dynamics that underlies the bulk electroneutrality, and which we have also made use of to obtain the quasi-stationary solution for $\rho$ (equation (13)). Using these mean-field exponents, we can then examine the scaling behavior of the nonlinear terms in the dynamics of density fluctuations $c$. Note that the nonlinear term in equation (5) is $\mu Q \nabla \cdot (\rho \nabla \phi)$ which scales as $b^{-\chi + 2\chi_p} = b^{-d/2}$. Since the corresponding scaling exponent is always negative, this nonlinearity is irrelevant in the renormalization group (RG) sense in the vicinity of the Gaussian fixed point.

One may also consider other nonlinear terms that could potentially be incorporated into the dynamics of $c$, e.g. those generated through a coarse-graining procedure. Treating the external field as a parameter, the most general nonlinearity is given by $E \cdot \partial_{\text{lin}}\nabla \cdot p^m c^n (\nabla \phi)^p$ where $\zeta = 0$ or $1$ (such that it only affects the vectorial structure of the expression), and only gradients of the electric potential $\phi$ are considered since a constant shift in the potential shall not make any observable differences in the dynamics. For a meaningful interaction term, we need to impose a few constraints on the values of $l, m, n,$ and $p$ (for a similar analysis in the context of chemotaxis see reference [76]): first, since the total number of the particles is conserved, the dynamics is a continuity equation and therefore there should at least be one gradient operator in the nonlinear term, thus $l \geq 1$; second, nonlinear interaction terms at least contain two of the $\rho, c$ and $\phi$, hence $m + n + p \geq 2$; third, the interaction term should be a scalar which implies that for $\zeta = 0$ case, $l + p$ must be an even number, whereas for the $\zeta = 1$ case, $l + p$ must be an odd number; and, finally, since only local interactions in terms of the fields are considered, we have $m, n, p \geq 0$. The scaling dimension of such a term added to the Langevin equation (10) turns out to be $[\partial_{\text{lin}}] = 2 - l - m - \frac{d}{2}(m + n + p - 1)$ whose sign
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should be analyzed in light of the above constraints. For \( d > 2 \), one can easily see that all such interaction terms have a negative scaling exponent and are therefore irrelevant. For \( d = 2 \), there is one marginal (i.e. with vanishing scaling exponent) interaction term \( \nabla \cdot (\mathbf{c} \nabla \phi) \).

The scaling analysis outlined above shows that the nonlinear effects can be discarded from the long-distance description in the vicinity of the Gaussian fixed point for \( d > 2 \). It remains for future studies to use RG analysis to examine the marginal term in the two-dimensional case, as well as the existence of other non-Gaussian fixed points in the phase space for which the scaling exponents differ from those of the linearized theory.

Appendix B. Equal-time correlation functions

In this appendix, we provide a detailed computation of the density and charge two-point correlation functions at equal times, directly from the linearized stochastic dynamics of equations (10) and (11).

Using the Fourier convention \( f(r, t) = \int \frac{d^d k}{(2\pi)^d} e^{-i r \cdot k} f(k, \omega) \), the linearized equations (10) and (11) can be expressed as follows

\[
\mathcal{E}(k, \omega) = \frac{-i \mu Q E k_c \rho(k, \omega) + \sqrt{4 D C_0} \eta_q(k, \omega)}{-i \omega + D k^2}, \quad \rho(k, \omega) = \frac{-i \mu Q E k_c \mathcal{E}(k, \omega) + \sqrt{4 D C_0} \eta_q(k, \omega)}{-i \omega + D (k^2 + \kappa^2)}.
\]

These coupled equations can directly be solved for \( \mathcal{E}(k, \omega) \) and \( \rho(k, \omega) \) in terms of the noise fields \( \eta_q \) and \( \eta_r \), from which the correlation functions read

\[
\langle \mathcal{E}(k, \omega) \mathcal{E}(k', \omega') \rangle_{\text{bulk}} = (2\pi)^d \delta^{(d)}(k + k') \delta(\omega + \omega') \times 
\frac{(4 DC_0 k^2) \left( \omega^2 + (D (k^2 + \kappa^2))^2 + \mu^2 Q^2 E^2 k^2 \right)}{(-i \omega + D k^2)(-i \omega + D (k^2 + \kappa^2)) + \mu^2 Q^2 E^2 k^2},
\]

\[
\langle \rho(k, \omega) \rho(k', \omega') \rangle_{\text{bulk}} = (2\pi)^d \delta^{(d)}(k + k') \delta(\omega + \omega') \times 
\frac{(4 DC_0 k^2) \left( \omega^2 + (D k^2)^2 + \mu^2 Q^2 E^2 k^2 \right)}{(-i \omega + D k^2)(-i \omega + D (k^2 + \kappa^2)) + \mu^2 Q^2 E^2 k^2}.
\]

To compute the equal-time correlation functions, we need to perform the frequency integrations. For the density correlations, these can be expressed in the following form

\[
\langle \mathcal{E}(k, t) \mathcal{E}(k', t) \rangle_{\text{bulk}} = (2\pi)^d \delta^{(d)}(k + k') \left( \frac{4 DC_0 k^2}{2 \pi} \int \frac{d \omega}{(\omega - \omega_u^+)(\omega - \omega_u^-)(\omega - \omega_l^+)(\omega - \omega_l^-)} \right),
\]

where \( \alpha = D (k^2 + \kappa^2)^2 + \mathcal{E}^2 D^2 \kappa^2 k^2 \) (recall that \( \mathcal{E} = \mu Q E /(D \kappa) \)), and \( \omega_u^+ \) and \( \omega_l^+ \) are defined as

\[
\omega_u^+ = i \lambda_+ = i D (k^2 + \kappa^2/2) \pm i D \kappa^2 \Delta / 2,
\]

\[
\omega_l^+ = -i \lambda_+ = -i D (k^2 + \kappa^2/2) \mp i D \kappa^2 \Delta / 2,
\]

which represent the frequency poles in the upper half and lower half of the complex frequency plane, respectively (equation (36) defines \( \Delta \)). The frequency integration can be carried out, with the final result reading:

\[
\langle \mathcal{E}(k) \mathcal{E}(k') \rangle_{\text{bulk}} \equiv \langle \mathcal{E}(k, t) \mathcal{E}(k', t) \rangle_{\text{bulk}} = (2\pi)^d \delta^{(d)}(k + k') \left( \frac{4 DC_0 k^2}{2 \pi} \int \frac{d \omega}{(\omega - \omega_u^+)(\omega - \omega_u^-)(\omega - \omega_l^+)(\omega - \omega_l^-)} \right).
\]

Here, the first term in the bracket is independent of the applied electric field and represents the local correlations in equilibrium, while the second part vanishes for \( \mathcal{E} = 0 \) and is the nonequilibrium part of the density correlations. In the limit of \( k/\kappa \ll 1 \), the above bulk density correlation is approximated by

\[
\langle \mathcal{E}(k) \mathcal{E}(k') \rangle_{\text{bulk}} \approx (2\pi)^d \delta^{(d)}(k + k') \left( \frac{4 DC_0 k^2}{2 \pi} \int \frac{d \omega}{(\omega - \omega_u^+)(\omega - \omega_u^-)(\omega - \omega_l^+)(\omega - \omega_l^-)} \right).
\]
which recovers the equal-time limit of equation (28).

For the charge correlations, a similar calculation yields

\[
\langle \rho(k)\rho(k') \rangle_{\text{bulk}} \equiv \langle \rho(k, t)\rho(k', t) \rangle_{\text{bulk}} = (2\pi)^d\delta(k + k') 2C_0 \left[ \frac{(k^2 + \xi^2 k_x^2)}{k^2 + \kappa^2} - \frac{\xi^2 k_x^2 (k^2 + \kappa^2)}{(k^2 + \kappa^2)^3} \right] \tag{B8}
\]

Similar to the density correlation functions, the first term in the brackets represents the short-ranged equilibrium correlations (note that in real space this gives the sum of a delta function and a screened-Coulomb (Yukawa-type) term which decays exponentially with Debye screening length \(\kappa^{-1}\)); the second term, on the other hand, is the nonequilibrium part due to the external field, and it vanishes for a non-driven electrolyte (i.e. when \(\mathcal{E} = 0\)). For \(k/\kappa \ll 1\), expanding the charge correlation function yields

\[
\langle \rho(k)\rho(k') \rangle_{\text{bulk}} \approx (2\pi)^d\delta^4(k + k') 2C_0 \left[ \frac{k^2}{k^2 + \xi^2 k_x^2} - \frac{\xi^2 k_x^2}{\kappa^2} \right]. \tag{B9}
\]

Note that this expression agrees with the long-distance limit of equation (30) at late times.

**Appendix C. Steady-state bulk correlation functions at different times**

In this appendix, we extend the computation of the equal-time correlations to obtain the steady-state dynamics factors, which from equation (B2) can be evaluated via

\[
\lim_{t_0 \to \infty} \langle c(k, t_0 + t)c(k', t_0) \rangle = (2\pi)^d\delta^4(k + k') \left[ 4D\kappa^2 2C_0 \right] \int \frac{d\omega}{(2\pi)^4} \frac{e^{-i\kappa \cdot \mathbf{r}}}{(\Omega + \alpha)} \left( \frac{\xi^2 k_x^2}{k^2 + \kappa^2} \right),
\]

where \(\omega^\pm\) and \(\omega^\mp\) are defined in equation (B5).

In order to analyze this expression, we first consider the case of \(\kappa > 2\Delta k_x\), for which \(A = D(\kappa^2 + \xi^2 k_x^2)/2\) and \(B = D\kappa^2 \Delta^2/2\). Carrying out the frequency integration, we obtain for this case

\[
\lim_{t_0 \to \infty} \langle c(k, t_0 + t)c(k', t_0) \rangle = (2\pi)^d\delta^4(k + k') \frac{2C_0 k^2 e^{-i D\kappa^2 \Delta^2/2}}{k^2 + \kappa^2 + \xi^2 k_x^2}
\]

\[
\times \left[ \left( \frac{2\Delta^2 k_x^2}{2\kappa^2 + \kappa^2} \right) \cosh \left( tD\kappa^2 \Delta^2/2 \right) + \frac{k^2 + \kappa^2}{\Delta} \sinh \left( tD\kappa^2 \Delta^2/2 \right) \right]
\]

\[
\approx (2\pi)^d\delta^4(k + k') 2C_0 \left[ \frac{k^2 e^{-i D\kappa^2 \Delta^2/2}}{k^2 + \xi^2 k_x^2} + O \left( \frac{k^2}{\kappa^2} \right) \right]. \tag{C2}
\]

Where in the last line we have performed an expansion for \(k/\kappa \ll 1\) and also we have set terms \(\propto e^{-i D\kappa^2 \Delta^2}\) to zero to obtain the large-scale and long-time behavior.

For \(2\Delta k_x > \kappa\), on the other hand, we instead have \(B = D\kappa^2 \Delta^2/2\) where we have defined \(\Delta = \sqrt{4\kappa^2 k_x^2/\kappa^2 - 1}\). In this case, the density correlation function reads

\[
\lim_{t_0 \to \infty} \langle c(k, t_0 + t)c(k', t_0) \rangle = (2\pi)^d\delta^4(k + k') \frac{2C_0 k^2 e^{-i D\kappa^2 \Delta^2/2}}{k^2 + \kappa^2 + \xi^2 k_x^2}
\]

\[
\times \left[ \left( \frac{2\Delta^2 k_x^2}{2\kappa^2 + \kappa^2} \right) \cos \left( tD\kappa^2 \Delta^2/2 \right) + \frac{k^2 + \kappa^2}{\Delta} \sin \left( tD\kappa^2 \Delta^2/2 \right) \right], \tag{C3}
\]

which shows that for large momenta the density correlations decay exponentially in time due to the presence of the exponential factor \(e^{-i D\kappa^2 \Delta^2/2}\). Finally, note that for \(t \to 0\), both equation (C2) and (C3) reproduce the equal-time correlations of equation (B6).

A similar line of calculation can be carried out for the out-of-time charge correlation functions. When \(\kappa > 2\Delta k_x\), one obtains
\[
\lim_{t_0 \to \infty} \rho(\mathbf{k}, t_0 + t)\rho(\mathbf{k}', t_0) = (2\pi)^d \delta^d(\mathbf{k} + \mathbf{k}') \frac{C_0 k^2 e^{-tD(k^2 + \nu^2/2)}}{k^2(k^2 + \nu^2) + \nu^2 2k^2} \\
\times \left[ \exp \left\{ tD\kappa^2 \Delta/2 \right\} \left( k^2 + 2\nu^2 2k^2 \Delta - k^2/\Delta \right) \right. \\
+ \left. \exp \left\{ -tD\kappa^2 \Delta/2 \right\} \left( k^2 + 2\nu^2 2k^2 \Delta + k^2/\Delta \right) \right].
\]

(C4)

The macroscopic behavior of this correlation function is obtained by taking the hydrodynamic limit (i.e. $k/\kappa \ll 1$); in this case, Taylor expansion gives

\[
\lim_{t_0 \to \infty} \langle \rho(\mathbf{k}, t_0 + t)\rho(\mathbf{k}', t_0) \rangle \approx (2\pi)^d \delta^d(\mathbf{k} + \mathbf{k}') \frac{2C_0 k^2 e^{-tD(k^2 + \nu^2/2)}}{k^2(k^2 + \nu^2) + \nu^2 2k^2} \\
\times \left[ \left( k^2 + 2\nu^2 2k^2 \Delta \right) \cos \left( tD\kappa^2 \Delta/2 \right) + \frac{k^2}{\Delta} \sin \left( tD\kappa^2 \Delta/2 \right) \right].
\]

(C5)

which, for $t = 0$, agrees with the same limit of equation (B8).

For $2\nu^2 \kappa > \kappa$, the charge correlations are given by the following damped oscillatory expression:

\[
\lim_{t_0 \to \infty} \langle \rho(\mathbf{k}, t_0 + t)\rho(\mathbf{k}', t_0) \rangle = (2\pi)^d \delta^d(\mathbf{k} + \mathbf{k}') \frac{2C_0 k^2 e^{-tD(k^2 + \nu^2/2)}}{k^2(k^2 + \nu^2) + \nu^2 2k^2} \\
\times \left[ \left( k^2 + 2\nu^2 2k^2 \Delta \right) \cos \left( tD\kappa^2 \Delta/2 \right) + \frac{k^2}{\Delta} \sin \left( tD\kappa^2 \Delta/2 \right) \right].
\]

(C6)

Appendix D. Simplifying $A_r$

In this section we give the explicit result for the second term on the rhs of equation (56) which can be used to facilitate numerical computations:

\[
\int_0^{\infty} d\nu \tilde{g}(\tilde{E}, \nu, \nu') e^{-2\pi^2 \tau (\nu^2 + \nu'^2 + \nu'^2)} = \frac{\pi \nu}{2 \pi^3 \nu^2 \tau \sqrt{1 + \nu^2 \cos^2 \theta}} \operatorname{erfc} \left( \nu \sqrt{2 \tau} \right) \\
- \frac{\pi \nu}{2 \pi^3 \nu^2 \tau \sqrt{1 + \nu^2 \cos^2 \theta}} \operatorname{erfc} \left( \nu \sqrt{2 \pi^2 \tau} \right) \\
+ \nu^2 \cos^2 \theta \frac{2 \pi^3 \tau}{2 \pi^4} \sqrt{1 + \nu^2 \cos \theta} e^{-2\pi^2 \tau \nu^2 (1 + \nu^2 \cos \theta)} \\
- \frac{\nu \nu'^2 \cos^2 \theta}{2 \pi^3} \frac{4 \pi^2 \nu^2 \tau - 1}{2 \pi^4} e^{-2\pi^2 \tau \nu^2 \nu'^2 \cos \theta} \operatorname{erfc} \left( \nu \sqrt{2 \pi^2 \tau} \right).
\]

(D1)

where $\nu_x = \nu \cos \theta$, and $\operatorname{erfc}(z) = 1 - \frac{1}{\sqrt{2\pi}} \int_0^z e^{-t^2} dt$ is the complementary error function.

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