AN ENERGETIC VARIATIONAL APPROACH FOR ION TRANSPORT

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Abstract. The transport and distribution of charged particles are crucial in the study of many physical and biological problems. In this paper, we employ an Energy Variational Approach to derive the coupled Poisson-Nernst-Planck-Navier-Stokes system. All physics is included in the choices of corresponding energy law and kinematic transport of particles. The variational derivations give the coupled force balance equations in a unique and deterministic fashion. We also discuss the situations with different types of boundary conditions. Finally, we show that the Onsager’s relation holds for the electrokinetics, near the initial time of a step function applied field.

Key words. Energetic Variational Approach, Poisson-Nernst-Planck (PNP) system, (Least) Action Principle, (Maximum) Dissipation Principle, Onsager’s relation.

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1. Introduction and Background

The Poisson-Nernst-Planck (PNP) system is one of the most extensively studied models for the transport of charged particles in many physical and biological problems, such as free moving electrons in semiconductors \cite{14,19,20}, fuel cell \cite{21,25}, ion particles in the electrokinetic fluids \cite{3,12,15,18}, and ion channels in cell membranes \cite{2,6,22}. Traditionally, the PNP system can be derived by explicit averaging of correlated Brownian trajectories \cite{5}, while the actual dynamics of charged particles in water and protein channels are much more complicated \cite{7}. In continuum description, the PNP system can also be viewed as the consequence of both conservation of ion distributions and the Fick’s law. The limitation of this method is that the specific interactions of particles are usually ambiguous or totally neglected. The purpose of this paper is to present an alternative way, an Energetic Variational Approach (EnVarA) \cite{8}, in which a consistent, coupled system of equations can be derived for the description of charged particles transport. Our approach is motivated by the seminal work of Lars Onsager \cite{23,24}, that has an attribution to Lord Rayleigh’s 1873 paper \cite{30}.

The general framework of EnVarA is the combination of the statistical physics and nonlinear thermodynamics. The First Law of Thermodynamics states that the rate of change of the sum of the kinetic energy $K$ and the internal energy $U$ is equal to the sum of the rates of change of work $W$ and heat $Q$, so $\frac{d(K+U)}{dt} = \frac{dW}{dt} + \frac{dQ}{dt}$. From the standard statistical physics, the internal energy $U$ takes into account the particles interactions. Such interactions can be local, such as hard core interactions and nonlocal, such as Coulomb electrostatic interactions. The Second Law of Thermodynamics, in the isothermal case, is given by $T\frac{dS}{dt} = \frac{dQ}{dt} + \Delta$, where $T$ is temperature, $S$ is entropy and $\Delta \geq 0$ is entropy production. As a reformulation of the linear response assumption, this entropy production functional can be represented as the sum of various rates such as the velocities and the strain rates. By subtracting the Second Law from the First

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Law, under the isothermal assumption, we have,
\[ \frac{d}{dt}(\mathcal{K} + \mathcal{U} - TS) = \frac{dW}{dt} - \Delta, \quad (1.1) \]
where \( \mathcal{F} := \mathcal{U} - TS \) is the Helmholtz free energy, and \( \mathcal{K} + \mathcal{F} \) is the total energy \( E^{\text{total}} \).

In case no external forces or fields are applied, i.e., \( \frac{dW}{dt} = 0 \), the above expression yields the usual energy dissipation law \([8, 9, 26, 27]\), where the entropy production is the sole contribution to the dissipation,

\[ \frac{d}{dt}E^{\text{total}} + \Delta = 0 \iff \frac{d}{dt}E^{\text{total}} = -\Delta. \quad (1.2) \]

The (Least) Action Principle (LAP) states that the equation of motion for a Hamiltonian system is the direct result of the variation of the action functional \( A = \int_0^t \int_{\Omega_0} (\mathcal{K} - \mathcal{F}) \, dx \, dt \) with respect to the flow map \( x(t) = x(X,t) \) (with \( x(X,0) = X \) \[1\]). In other words, LAP optimizes the action with respect to all trajectories \( x(t) = x(X,t) \) by taking the variation with respect to \( x \), \( \delta A = \int_0^t \int_{\Omega_0} [F_{\text{con}}] \cdot \delta x \, X \, dt \), where \( F_{\text{con}} \) is the conservative force and \( \Omega_0 \) is the Lagrangian reference domain of \( \Omega \). In particular, in equilibrium, we have the condition \( F_{\text{con}} = 0 \) for a Hamiltonian dynamics.

Next, we treat the dissipation part with the (Maximum) Dissipation Principle (MDP) \([23, 24, 29, 11]\). Take the variation with respect to the velocity (rate) in Eulerian coordinates \( \delta (\frac{1}{2} \Delta) = \int_0^t \int_{\Omega_0} |F_{\text{dis}}| \cdot \delta u \, dx \), where \( F_{\text{dis}} \) is dissipative force. Note that the factor \( \frac{1}{2} \) corresponds to the underlying assumption that \( \Delta \) is quadratic in the function \( u \). In particular, \( F_{\text{dis}} \) is linear in \( \omega \), indicating the fact that we can view MDP as just a reformulation of the linear response assumption of the nonequilibrium thermodynamics \([16]\). Such postulations are the key to Onsager’s approach \([23, 24]\), as realized by Kubo \([16]\) in the more explicit linear response theory.

The final equation of motion, the balance of all forces, includes both conservative and dissipative components.

The following auxiliary Lemma is crucial in the energetic variational derivation of the system of coupled equations.

**Lemma 1.1.** Let \( f \) satisfy the mass conservation law \( \int f + \nabla \cdot (u f) = 0 \). Define \( W = \int_{\Omega_0} \omega(f) \, dx \) and \( \Pi(\omega) = \omega f - \omega \), and then \( \delta W = \int_{\Omega} \nabla \Pi \cdot \delta x \, dx \).

**Proof:** The conservation of mass is equivalent to \( f(x(X,t),t) = \frac{f_0(X)}{J} \), which is a direct consequence of the identity \( F + \mathbf{u} \cdot \nabla F = \nabla \mathbf{u} F \), where \( f_0(X) \) is the initial density, \( J = \text{det} F \), \( F(X,t) = \frac{\partial X(\mathbf{u} , t)}{\partial x} \) is the deformation gradient tensor \([9]\). Rewrite the integration in the Lagrangian coordinate system and obtain \( W = \int_{\Omega_0} \omega(f_0(X)) J \, dX \). Taking the variation with respect to flow map \( x \mapsto x + \varepsilon y \), it yields

\[
\delta W = \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} W(x + \varepsilon y) = \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \int_{\Omega_0} \omega(f_0(X)) J \, dX = -\int_{\Omega_0} \left( \omega(f) J - \omega \right) \delta x \, J \, dx + \int_{\Omega_0} \omega f_0 \mathbf{J} \cdot \nabla x \, J \, dx \]
\[
= \int_{\Omega} \left( \omega f - \omega, \nabla_x y \right) \, dx = \int_{\Omega} \left( \nabla (\omega f - \omega), y \right) \, dx, \quad (1.3)
\]

where \( y(x(X,t),t) = y(X,t) \). Hence the result holds.

**Remark 1.2.** The above Lemma relates the pressure (the equation of states) to the free energy density. For given energy dissipation law \( \frac{d}{dt}E^{\text{total}} = \int_{\Omega} \omega(f) \, dx = \int_{\Omega} \omega f \, dx \).
\[-\int_\Omega f|\mathbf{u}|^2 dx, \text{ if } \omega(f) = cf \ln f \text{ only contains the Gibbs entropy, i.e. no particle interactions, hence ideal gas, then } \Pi = \omega f - \omega = cf. \text{ In particular, } f \text{ satisfies } f_t = c\Delta f, \text{ which is a simple diffusion equation [3].}

If \( \omega(f) = a f^\gamma \), then \( \Pi = \omega f^\gamma - \omega = a(\gamma - 1) f^\gamma \). In particular, \( f \) satisfies \( f_t = \Delta(a(\gamma - 1) f^\gamma) \), which gives the diffusion equation in porous media [31].

Next, we use the compressible Navier-Stokes (NS) equations as an example to illustrate the framework of EnVarA. We start with the kinematic mass conservation,

\[
\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0, \tag{1.4}
\]

where \( \rho \) is mass density of fluid and \( \mathbf{u} \) is velocity of fluid. This is equivalent to the relation \( \rho(x(X,t),t) = \frac{\rho_0(X)}{J} \), where \( J = \det F \), \( F(X,t) = \frac{\partial x(X,t)}{\partial X} \) is the deformation gradient tensor and \( \rho_0(X) \) is the initial density [9]. The following energy dissipation law includes all the physics for these Barotropic fluids [28].

\[
\frac{d}{dt} \int_\Omega \left( \frac{1}{2} \rho |\mathbf{u}|^2 + \omega(\rho) \right) dx = - \int_\Omega \left[ \mu_1 |\nabla \mathbf{u}|^2 + \mu_2 |\nabla \cdot \mathbf{u}| \right] dx, \tag{1.5}
\]

where \( \mu_1 \) and \( \mu_2 \) are viscosity constants and \( \omega(\rho) \) is the Helmholtz free energy density.

By LAP and Lemma 1.1 we obtain the conservative force

\[
F_{con} = - (\rho(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}) + \nabla \Pi(\rho)), \tag{1.6}
\]

with \( \Pi(\rho) = \omega_\rho - \omega \) being the pressure. By MDP, the dissipative force is

\[
F_{dis} = - (\nabla \cdot (\mu_1 \nabla \mathbf{u}) + \nabla (\mu_2 \nabla \cdot \mathbf{u})). \tag{1.7}
\]

Finally, the total force balance gives the Navier-Stokes equation,

\[
\rho(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}) + \nabla \Pi(\rho) = \nabla \cdot (\mu_1 \nabla \mathbf{u}) + \nabla (\mu_2 \nabla \cdot \mathbf{u}). \tag{1.8}
\]

The conservative force corresponds to the compressible Euler equation, while the dissipative force corresponds to the Stokes equation. Navier-Stokes equation can be viewed as a hybrid model combining these two independent systems.

In this paper, we use the EnVarA to derive the electrokinetic systems by considering the particles interactions in the dissipation part and the corresponding energy law. The outline of paper is as follows: in §2, we present the derivation of the electrokinetic system, Poisson-Nernst-Planck-Navier-Stokes(PNP-NS) system, by using the EnVarA; in §3 we focus on the energy law of the PNP-NS system with different types of boundary conditions; the Onsager relation is proved in §4; conclusion part is given in §5.

2. Derivation of Electrokinetic System Using EnVarA

Ion transport in solutions by nature is a multiscale-multiphysics system. With the macroscopic hydrodynamics description, the microscopic dynamics takes account of diffusion and convection as well as electrostatics. The cross scale coupling can be modeled in the general EnVarA framework. The total energy include all the equilibrium physics included in system

\[
E^{total} = \int_\Omega \left[ \frac{\rho}{2} |\mathbf{u}|^2 + \left( K_B T \left( n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right) \right] dx, \tag{2.1}
\]
where \( \rho \) is the mass density of fluid, \( \mathbf{u} \) is the macroscopic velocity of fluid, \( K_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( n_\infty(p_\infty) \) is the characteristic negative(positive) charge distribution, \( n(p) \) is negative (positive) charge distribution, the dielectrics of solution is chosen to be the constant \( \varepsilon \), and \( \phi \) is electric potential. The first term is the macroscopic kinetic energy of the solution fluids. The second and third terms are the thermo-fluctuations (Gibbs entropy) of the ion species. The last term is the electro energy.

In the macroscopic scale, we consider the fluid to be incompressible, i.e. \( \nabla \cdot \mathbf{u} = 0 \). At the same time, we observe the following kinematic conservation of charge distributions,

\[
n_t + \nabla \cdot (n \mathbf{u}_n) = 0, \quad p_t + \nabla \cdot (p \mathbf{u}_p) = 0, \tag{2.2}
\]

where \( \mathbf{u}_n \) and \( \mathbf{u}_p \) are the effective velocities of negative and positive charges, respectively. The Gauss’s law yields the Poisson equation,

\[
-\varepsilon \Delta \phi = ze(p-n), \tag{2.3}
\]

where \( z \) is valence of ion and \( e \) is the charge for one electron. Equivalently, the potential \( \phi \) can be given by the Green’s kernel \( G(x,y) \) in the form of

\[
\phi(x) = ze \frac{1}{\varepsilon} \int_\Omega G(x,y)(n-p)(y)dy. \tag{2.4}
\]

By substituting (2.4) into (2.1), the energy can be written in the following form

\[
E_{total} = \int_\Omega \frac{\rho}{2} |\mathbf{u}|^2 dx + \int_\Omega K_B T(n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty}) dx \tag{2.5}
\]

\[
+ \frac{ze}{2\varepsilon} \int_\Omega (p-n)(x) \int_\Omega G(x,y)(n-p)(y)dydx,
\]

where the last term, the electrostatic energy, represents the nonlocal Coulomb interactions.

In order to take into account the more detailed interactions of particles, we furthermore consider the dissipation functional \( \Delta \) as a sum of three parts, which are all quadratic in terms of the ‘rates’, the velocities,

\[
\Delta = \int_\Omega \left[ \frac{K_B T}{D_n} n|\mathbf{u}_n - \mathbf{u}|^2 + \frac{K_B T}{D_p} p|\mathbf{u}_p - \mathbf{u}|^2 + \eta |\nabla \mathbf{u}|^2 \right] dx, \tag{2.6}
\]

where \( D_n (D_p) \) is the diffusion constant of negative (positive) ion and \( \eta \) is the viscosity of fluid. The first and second terms represent the frictions between particles and the solvents. The last term is the fraction caused by the viscosity of the solutions.

Now we begin to use the EnVarA to derive the electrokinetic system. In this case, there are three flow maps corresponding to three velocities fields, \( \mathbf{u}, \mathbf{u}_n, \mathbf{u}_p \): macroscopic flow map \( x(X,t) \), negative charge map \( x_n(X,t) \) and positive charge map \( x_p(X,t) \), respectively. For map \( x_n \), Lemma 1.1, Remark 1.2 and the variation yield,

\[
F_{n-con} = \frac{\delta A}{\delta x_n} = \frac{\delta}{\delta x_n} \left[ \int_0^t \left( \int_\Omega \rho |\mathbf{u}|^2 dx - \int_\Omega K_B T(n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty}) dx 
\right.
\right.
\]

\[
- \frac{ze}{2\varepsilon} \int_\Omega (p-n)(x) \int_\Omega G(x,y)(n-p)(y)dydx \bigg] dt
\]

\[
= -(K_B T \nabla n - zen \nabla \phi) = -n \nabla \mu_n, \tag{2.7}
\]
where \( \mu_n := \frac{\delta}{\delta n} E^{\text{total}} = K_B T (1 + \ln n) - K_B T \ln n_\infty - z e \phi \) is the chemical potential for negative charge distribution \( n(x,t) \).

Using MDP, we calculate the variation of \( \frac{1}{2} \Delta \) with respect to the velocity \( u_n \) to get the dissipative force,

\[
F_{n \text{-dis}} = \frac{\delta}{\delta u_n} \left( \frac{1}{2} \Delta \right) = \frac{K_B T}{D_n} n (u_n - u).
\]

The total force balance for negative charge yields (including (2.7) and (2.8)):

\[
n u_n = n u - \frac{D_n}{K_B T} n \nabla \mu_n.
\]

Substituting (2.9) into (2.2), the mass conservation of negative charge is:

\[
n_t + \nabla \cdot (n u) = \nabla \cdot \left( D_n \nabla n - \frac{z e}{K_B T} D_n n \nabla \phi \right).
\]

Similarly for positive charge, we can get

\[
p u_p = p u - \frac{D_p}{K_B T} p \nabla \mu_p,
\]

\[
p_t + \nabla \cdot (p u) = \nabla \cdot \left( D_p \nabla p + \frac{z e}{K_B T} D_p p \nabla \phi \right),
\]

where \( \mu_p := \frac{\delta}{\delta p} E^{\text{total}} = K_B T (1 + \ln p) - K_B T \ln p_\infty + z e \phi \) is the chemical potential for positive charge distribution \( p(x,t) \). In the absence of the flow field \( u \), equations (2.10) (2.12) with the Poisson equation (2.3) give the PNP system.

As for the macroscopic flow map \( x(X,t) \), considering the incompressible condition, we use 1-parameter family of volume preserving diffeomorphisms to perform the variation, i.e. function \( x^\varepsilon \) such that \( x^0 = x \), and \( \frac{dx^\varepsilon}{dx} \bigg|_{\varepsilon=0} = y \), and for any \( \varepsilon \) : \( \det \frac{\partial x^\varepsilon}{\partial X} = 1 \), which in fact leads to a divergence free condition for \( y(X,0) = y(X,t^*) = 0 \) for any \( X \in \Omega_0 \). We can calculate the variation of action functional:

\[
\left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} A(x^\varepsilon) = \int_0^{t^*} \int_{\Omega_0} \frac{1}{2} \rho_0(X) |x^\varepsilon_t|^2 dX dt
= \int_0^{t^*} \int_{\Omega_0} \rho_0(X)(x_t)_t \cdot y dX dt = \int_0^{t^*} \int_{\Omega} -\rho(x,t)(u_t + u \cdot \nabla u) \cdot y dxdt.
\]

Hence by the Weyl’s decomposition or Helmholtz’s decomposition, for some \( \Pi_1 \in W^{1,2}(\Omega) \), we have,

\[
-\rho(x,t)(u_t + u \cdot \nabla u) = \nabla_x \Pi_1.
\]

By MDP and incompressible constrain, we obtain the following equation of motion for the dissipative part,

\[
-\eta \Delta u + \frac{K_B T}{D_n} n (u - u_n) + \frac{K_B T}{D_p} p (u - u_p) = \nabla \tilde{\Pi}_2,
\]
where $\Pi_2$ is the Lagrange multiplier of incompressible constrain.

Substitute (2.9) and (2.11) into above formula and let $\Pi_2 = \Pi_1 - K_B T \nabla n - K_B T \nabla p$,

$$\nabla \Pi_2 = -\eta \Delta u - (n - p) z e \nabla \phi.$$  \hspace{1cm} (2.16)

Then using the force balance, (2.14) and (2.16) yield

$$\rho \frac{\partial u}{\partial t} + (u \cdot \nabla) u = \eta \Delta u - \nabla \Pi + (n - p) z e \nabla \phi,$$  \hspace{1cm} (2.17)

with $\Pi = \Pi_1 - \Pi_2$. The last term is the Lorentz force induced by the charges in the fluids. It is the reaction to the convected term in (2.10) and (2.12), which is consistent with the Newton’s third Law. Combining (2.3), (2.10), (2.12), (2.17) and incompressibility, we get the coupled Poisson-Nernst-Planck-Navier-Stokes (PNP-NS) system:

Finally in this section, we verify the following theorem satisfied by the derived coupled PNP-NS system (2.18).

**Theorem 2.1.** With the isothermal assumption and vanishing boundary conditions, the system (2.18) satisfies the following energy dissipation law,

$$\frac{d}{dt} E_{\text{total}} = \int_\Omega \left[ \frac{1}{2} \rho |u|^2 + K_B T (n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty}) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right] dx$$

$$- \int_\Omega \left[ D_n \nabla n |\nabla \mu_n|^2 + \frac{D_p}{K_B T} |\nabla \mu_p|^2 + \eta |\nabla u|^2 \right] dx$$

$$- \int_\Omega \left[ K_B T D_n |u_n - u|^2 + \frac{K_B T}{D_p} |u_p - u|^2 + \eta |\nabla u|^2 \right] dx$$

$$= -\Delta.$$  \hspace{1cm} (2.19)

Reversely, if we choose the action functional as

$$A = \int_0^1 \int_\Omega \left( \frac{1}{2} \rho |u|^2 dx - \int K_B T (n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty}) dx - \frac{\varepsilon}{2} |\nabla \phi|^2 dx, \right.$$

and the dissipation functional as (2.6), then by (Least) Action Principle and (Maximum) Dissipation Principle, under the kinematic assumption of distribution (conservation law) (2.2) and Poisson equation, we can obtain the Poisson-Nernst-Planck-Navier-Stokes system (2.18).

**Remark 2.2.** Some more complicated models can be derived by including more coupling terms for particle interactions in the total energy $E_{\text{total}}$, such as
1. In [30], it is shown that, by EnVarA, a modified model can be derived naturally for ion particles with finite size effects, through adding interaction term \( E^\text{repulsion} = \sum_{i=1}^{N} \sum_{j \geq i}^{N} \oint_{\Omega} \Psi_{i,j}(|x-y|)c_{i}(x)c_{j}(y)dx \) to the total energy, where \( c_{i}, c_{j} \) mean different species of ions, and \( \Psi_{i,j}(|x-y|) = \frac{a_{i}a_{j}}{|x-y|^{12}} \) is Lennard-Jones (LJ) potential for ith and jth ions located at \( x \) and \( y \) with the radii \( a_{i}, a_{j} \), respectively.

2. If we add \( E^\text{surface} = ze \oint_{\Omega} (\sigma - n)\Psi \) to the total energy, we can derive the surface potential trap model [32] to describe the electrokinetics induced by the interface of solid and solution, where \( \Psi \) is a surface potential only depending on the property of material.

3. Boundary Conditions In electrokinetics, most physically interesting properties arise from different boundary conditions [4, 17, 33]. These boundary conditions represent the interactions between particles in the bulk solutions and the particles in or near the boundary [32]. The interactions can also be included into the energy functionals. As in the previous sections, we assume the non-flux boundary condition \( \mathbf{J}_{n} \cdot \mathbf{v} = \mathbf{J}_{p} \cdot \mathbf{v} = 0 \) for charge density, with \( \mathbf{v} \) being out normal vector, and the non-slip boundary condition \( \mathbf{u} = 0 \) for velocity. We will focus on the boundary effect of potential \( \phi \) which plays an important role in electrodynamics. For the three different boundary conditions, the PNP-NS system has the following theorem.

**Theorem 3.1.** If \( n, p \) satisfy \( \mathbf{J}_{n} \cdot \mathbf{v} = \mathbf{J}_{p} \cdot \mathbf{v} = 0 \), and \( \mathbf{u} = 0 \) on the boundary \( \partial \Omega \), then

1. if \( \phi = \phi_{0}(x) \), i.e. Dirichlet boundary, then PNPNS satisfies the energy law,

\[
\frac{d}{dt} E^\text{total} = \frac{d}{dt} \left[ \oint_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_{B}T(n_{\infty} \ln \frac{n}{n_{\infty}} + p\ln \frac{p}{p_{\infty}}) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right] dx \tag{3.1}
\]

\[
= - \left[ \oint_{\Omega} \frac{D_{n}}{K_{B}T} n |\nabla \mu_{n}|^2 + \frac{D_{p}}{K_{B}T} |\nabla \mu_{p}|^2 + \eta |\nabla \mathbf{u}|^2 \right] dx + \oint_{\partial \Omega} \frac{\partial \phi}{\partial n} \phi_{0} dx;
\]

2. if \( \frac{\partial \phi}{\partial n} = \sigma_{0}(x) \), i.e. Neumann boundary condition, then PNPNS satisfies the energy law,

\[
\frac{d}{dt} E^\text{total} = \frac{d}{dt} \left[ \oint_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_{B}T(n_{\infty} \ln \frac{n}{n_{\infty}} + p\ln \frac{p}{p_{\infty}}) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right] dx \tag{3.2}
\]

\[
= - \left[ \oint_{\Omega} \frac{D_{n}}{K_{B}T} |\nabla \mu_{n}|^2 + \frac{D_{p}}{K_{B}T} |\nabla \mu_{p}|^2 + \eta |\nabla \mathbf{u}|^2 \right] dx + \oint_{\partial \Omega} \sigma_{0} \phi dx;
\]

3. if \( \phi + \zeta \frac{\partial \phi}{\partial n} = \phi_{0}(x) \), i.e Robin boundary condition, then PNPNS satisfies the energy law,

\[
\frac{d}{dt} E^\text{total} = \frac{d}{dt} \left[ \oint_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_{B}T(n_{\infty} \ln \frac{n}{n_{\infty}} + p\ln \frac{p}{p_{\infty}}) + \frac{\varepsilon}{2} |\nabla \phi|^2 + \frac{\varepsilon}{2} \oint_{\partial \Omega} |\phi|^2 dx \right]
\]

\[
= - \left[ \oint_{\Omega} \frac{D_{n}}{K_{B}T} |\nabla \mu_{n}|^2 + \frac{D_{p}}{K_{B}T} |\nabla \mu_{p}|^2 + \eta |\nabla \mathbf{u}|^2 \right] \cdot \tag{3.3}
\]

**Remark 3.2.**

1. When \( \phi \) on the boundary is Robin boundary condition, as time approaches infinity, \([33]\) means \( \nabla \mu_{n} = \nabla \mu_{p} = \nabla \mathbf{u} = 0 \). Considering the boundary condition, it yields \( \mathbf{J}_{n} = \mathbf{J}_{p} = \mathbf{u} = 0 \), which means there is no fluid flux in the time limit. Then we can derive a Charge Conservation Poisson Boltmann (CCPB)
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\[ -\varepsilon \Delta \phi = z e n_\infty \Omega \left( \frac{\beta \exp(-z e \phi / K_B T)}{\int_{\Omega} \exp(-z e \phi / K_B T) dx} - \frac{\alpha \exp(z e \phi / K_B T)}{\int_{\Omega} \exp(z e \phi / K_B T) dx} \right) \]

as the time limit of PNPNS system, where \( \alpha = \frac{n_0}{n_\infty} \) and \( \beta = \frac{p_0}{n_\infty} \) with \( n_0 \) (\( p_0 \)) being the initial negative (positive) ion distribution.

2. In the ion transport process, most of time an extra field is added to the domain to generate the electrodynamics phenomena. When there is an external field added to the PNPNS system, there will be an extra term \( \int_{\Omega} (p - n) \Psi \, dx \) added to the total energy in Theorem 3.1, where \( -\nabla \Psi \) is the extra electric field.

4. Onsager’s Relation in Cylindrical Situation

The coupling between the flow field and the electric field gives rise to all the important properties and applications of the electrokinetic fluids. For instance, when the fluid-solid interface is charged, the application of an electrical voltage difference can induce a fluid flow. This effect is known as electroosmosis (EO). Conversely, the application of a pressure gradient can generate, besides fluid flow, a voltage difference that is denoted as the streaming potential (SP). The EO and SP coefficients are not independent. They are related by the well-known Onsager’s reciprocal relation.

\[
\begin{bmatrix} J_e \\ J_f \end{bmatrix} = - \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \nabla \phi \\ \nabla \Pi \end{bmatrix}, \quad (4.1)
\]

where \( L_{11} \) is the electrical conductivity and \( L_{21} \) is the hydrodynamic permeability. In literature [33], the proportional matrix is treated as symmetric and attributed to Onsager’s relation. Onsager’s reciprocal relation, the microscopic reversibility is a stability condition. It is manifested by specific coupling effects in different physical settings. In (4.1), it is a reformulation of the fact that Lorentz force and the transport of charge are action and reaction.

Onsager’s reciprocal relation has many forms in different settings. Here we take the axisymmetric cylinder coordinate for low Reynolds number situations with constant initial values, i.e. \( p(\cdot, 0) = p_0, \, n(\cdot, 0) = n_0 \) as an example. Then the PNP-NS system is simplified to be the Poisson-Nernst-Planck-Stokes (PNP-S) system. If an extra filed \( E_z \) and a pressure drop \( \partial \Pi / \partial z \) are added in \( z \) direction, the velocity \( u_z \) satisfies

\[
\frac{\partial \Pi}{\partial z} - \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z}{\partial r} \right) \right] = (p - n) z e (\frac{\partial \phi}{\partial z} + E_z), \quad (4.2)
\]

with \( u_z(r = a) = \phi(r = a) = 0 \). At the initial several steps, \( \frac{\partial \phi}{\partial z}, \, \frac{\partial p}{\partial z}, \, \frac{\partial n}{\partial z} \) and \( \frac{\partial u_z}{\partial z} \) are small and negligible. Then we can get

\[
u_z = \frac{E_z \phi}{\mu} + \frac{a^2 - r^2}{4\mu} \left( -\frac{\partial \Pi}{\partial z} \right), \quad (4.3)
\]

And the fluxes for the negative and positive charges in \( z \) direction are

\[
J_n = -\left( D_n \frac{\partial n}{\partial z} - D_n \frac{z e}{K_B T} \left( \frac{\partial \phi}{\partial z} - E_z \right) n \right) = -\frac{z e}{K_B T} n D_n E_z \quad (4.4)
\]

\[
J_p = -\left( D_p \frac{\partial p}{\partial z} + D_p \frac{z e}{K_B T} \left( \frac{\partial \phi}{\partial z} - E_z \right) p \right) = \frac{z e}{K_B T} p D_p E_z. \quad (4.5)
\]
The total electric current in z direction is the sum of the current carried (transported) by the flow field \( u \) and the current due to the electric field,

\[
J_e = \int_{-L}^{L} \int_0^a 2(p-n)zeu_z r dr dz + \int_{-L}^{L} \int_0^a 2ze(J_p - J_n) r dr dz
\]

\[
= Ez \left[ \frac{\varepsilon}{\mu a^2} \int_0^a rze(p-n) dr + \frac{z^2 e^2}{K_BT} Ez(D_p n_0 + D_n n_0) \right]
\]

\[
+ \left( -\frac{\partial \Pi}{\partial z} \right) \frac{1}{2\mu a^2} \int_0^a (p-n)ze(a^2 - r^2) r dr.
\]  

(4.6)

The fluid flux in z direction is

\[
J_f = \frac{\int_{-L}^{L} \int_0^a 2u_z r dr}{2La^2} = \frac{2\varepsilon E_z}{\mu a^2} \int_0^a \varphi r dr + \left( -\frac{\partial \Pi}{\partial z} \right) \frac{1}{2\mu a^2} \int_0^a (a^2 - r^2) r dr.
\]

(4.7)

We may write the Onsager relation as

\[
\begin{bmatrix}
J_e \\
J_f
\end{bmatrix} = \begin{bmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{bmatrix} \begin{bmatrix}
E_z \\
-\frac{\partial \Pi}{\partial z}
\end{bmatrix},
\]

where we have introduced the function forms of the coefficients,

\[
L_{12} = \frac{1}{2\mu a^2} \int_0^a rze(p-n)(a^2 - r^2) dr, \quad L_{21} = \frac{2\varepsilon}{\mu a^2} \int_0^a \varphi r dr.
\]

(4.8)

But by the Poisson equation, \( L_{12} \) can be rewritten as

\[
L_{12} = -\frac{\varepsilon}{2\mu a^2} \int_0^a (a^2 - r^2) \left( \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial r^2} \right) r dr
\]

\[
= -\frac{\varepsilon}{2\mu a^2} \left[ (-a^2 \phi(0) + 2 \int_0^a \phi r dr) + \int_0^a \phi(0) - \int_0^a 6r \phi dr \right]
\]

\[
= \frac{2\varepsilon}{\mu a^2} \int_0^a r \phi dr = L_{21},
\]

(4.9)

which gives the symmetric property of the matrix.

5. Conclusion In this paper, we derive the electrokinetic system for ion transport in solutions by using an Energy Variational Approach. Taking into consideration of particles interactions in both the free energy functional and the dissipation functional, we obtain the Poisson-Nernst-Planck-Navier-Stokes system. We can extend our theory to include more detailed description of the solutions, such as the finite size effects of the charged particles and various boundary effects. Since the boundary condition of potential play an important role in electrokinetic, we also present the boundary effects to the energy law. The energy laws with an external electric field under different boundary conditions of potential are also obtained. A short demonstration of Onsager’s relation is presented for the Poisson-Nernst-Planck-Stokes system under cylinder axisymmetric coordinate.

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