

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 [14, 19, 20], fuel cell [21, 25], ion particles in the electrokinetic fluids [3, 12, 15, 18], and ion channels in cell membranes [2, 6, 22]. Traditionally, the PNP system can be derived by explicit averaging of correlated Brownian trajectories [5], while the actual dynamics of charged particles in water and protein channels are much more complicated [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) [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 [23, 24], that has an attribution to Lord Rayleigh's 1873 paper [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 \mathcal{K} and the internal energy \mathcal{U} is equal to the sum of the rates of change of work \mathcal{W} and heat \mathcal{Q} , so $\frac{d(\mathcal{K}+\mathcal{U})}{dt} = \frac{d\mathcal{W}}{dt} + \frac{d\mathcal{Q}}{dt}$. From the standard statistical physics, the internal energy \mathcal{U} takes into account the particles interactions. Such interactions can be local, such as hard core interactions and nonlocal, such as Coulomb electro static interactions. The Second Law of Thermodynamics, in the isothermal case, is given by, $T \frac{d\mathcal{S}}{dt} = \frac{d\mathcal{Q}}{dt} + \Delta$, where T is temperature, \mathcal{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,

$$\frac{d}{dt}(\mathcal{K} + \mathcal{U} - T\mathcal{S}) = \frac{d\mathcal{W}}{dt} - \Delta, \quad (1.1)$$

where $\mathcal{F} := \mathcal{U} - T\mathcal{S}$ is the Helmholtz free energy, and $\mathcal{K} + \mathcal{F}$ is the total energy E^{total} . In case no external forces or fields are applied, i.e., $\frac{d\mathcal{W}}{dt} = 0$, the above expression yields the usual energy dissipation law [8, 9, 26, 27], where the entropy production is the sole contribution to the dissipation,

$$\frac{d}{dt}E^{total} + \Delta = 0 \Leftrightarrow \frac{d}{dt}E^{total} = -\Delta. \quad (1.2)$$

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 $A = \int_0^{t^*} \int_{\Omega} (\mathcal{K} - \mathcal{F}) dx dt$ 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 , $\delta A = \int_0^{t^*} \int_{\Omega_0} [F_{con}] \cdot \delta x dX dt$, where F_{con} is the conservative force and Ω_0 is the Lagrangian reference domain of Ω . In particular, in equilibrium, we have the condition $F_{con} = 0$ 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 $\delta(\frac{1}{2}\Delta) = \int_{\Omega} [F_{dis}] \cdot \delta u dx$, where F_{dis} is dissipative force. Note that the factor $\frac{1}{2}$ corresponds to the underlying assumption that Δ is quadratic in the function \mathbf{u} . In particular, F_{dis} is linear in \mathbf{u} , 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 $f_t + \nabla \cdot (\mathbf{u}f) = 0$. Define $W = \int_{\Omega} \omega(f) dx$ and $\Pi(\omega) = \omega_f f - \omega$, 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 $F_t + \mathbf{u} \cdot \nabla F = \nabla \mathbf{u} F$, where $f_0(X)$ is the initial density, $J = \det F$, $F(X, t) = \frac{\partial x(X, t)}{\partial X}$ is the deformation gradient tensor [9]. Rewrite the integration in the Lagrangian coordinate system and obtain $W = \int_{\Omega_0} \omega(\frac{f_0(X)}{J}) J dX$. Taking the variation with respect to flow map $x \mapsto x + \varepsilon y$, it yields

$$\begin{aligned} \delta W &= \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} W(x + \varepsilon y) = \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \int_{\Omega_0} \omega\left(\frac{f_0(X)}{J(x + \varepsilon y)}\right) J(x + \varepsilon y) dX \\ &= - \int_{\Omega_0} \omega_f \left(\frac{f_0(X)}{J}\right) \frac{f_0(X)}{J^2} \cdot \text{tr}\left(\frac{\partial X}{\partial x} \frac{\partial y}{\partial X}\right) \cdot J^2 dX + \int_{\Omega_0} \omega\left(\frac{f_0(X)}{J}\right) \cdot J \cdot \text{tr}\left(\frac{\partial X}{\partial x} \frac{\partial y}{\partial X}\right) dX \\ &= \int_{\Omega} -(\omega_f f - \omega, \nabla_x \tilde{y}) dx = \int_{\Omega} (\nabla(\omega_f f - \omega), \tilde{y}) dx, \end{aligned} \quad (1.3)$$

where $\tilde{y}(x(X, t), t) = y(X, t)$. 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 $\frac{d}{dt}E^{total} = \frac{d}{dt} \int_{\Omega} \omega(f) dx =$*

$-\int_{\Omega} f|\mathbf{u}|^2 dx$, if $\omega(f) = cf \ln f$ only contains the Gibbs entropy, i.e. no particle interactions, hence ideal gas, then $\Pi = \omega_f f - \omega = cf$. In particular, f satisfies $f_t = c\Delta f$, which is a simple diffusion equation [8].

If $\omega(f) = af^\gamma$, then $\Pi = \omega_f f - \omega = a(\gamma - 1)f^\gamma$. 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,

$$\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (1.4)$$

where ρ 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].

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

where μ_1 and μ_2 are viscosity constants and $\omega(\rho)$ is the Hemholtz free energy density.

By LAP and Lemma 1.1, we obtain the conservative force

$$F_{con} = -(\rho(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}) + \nabla \Pi(\rho)), \quad (1.6)$$

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

$$F_{dis} = -(\nabla \cdot (\mu_1 \nabla \mathbf{u}) + \nabla (\mu_2 \nabla \cdot \mathbf{u})). \quad (1.7)$$

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

$$\rho(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}) + \nabla \Pi(\rho) = \nabla \cdot (\mu_1 \nabla \mathbf{u}) + \nabla (\mu_2 \nabla \cdot \mathbf{u}). \quad (1.8)$$

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 system.

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

$$E^{total} = \int_{\Omega} \underbrace{\frac{\rho}{2} |\mathbf{u}|^2 dx}_{macroscopic} + \underbrace{\left[K_B T \left(n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right]}_{microscopic} dx, \quad (2.1)$$

where ρ 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 ε , and ϕ 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,

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

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,

$$-\varepsilon \Delta \phi = ze(p - n), \quad (2.3)$$

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

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

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

$$\begin{aligned} E^{total} &= \int_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 dx + \int_{\Omega} K_B T \left(n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty} \right) dx \\ &\quad + \frac{ze}{2\varepsilon} \int_{\Omega} (p - n)(x) \int_{\Omega} G(x, y)(n - p)(y) dy dx, \end{aligned} \quad (2.5)$$

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 Δ as a sum of three parts, which are all quadratic in terms of the 'rates', the velocities,

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

where D_n (D_p) is the diffusion constant of negative (positive) ion and η 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,

$$\begin{aligned} F_{n-con} &= \frac{\delta A}{\delta x_n} = \frac{\delta}{\delta x_n} \left[\int_0^{t^*} \left(\int_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 dx - \int_{\Omega} K_B T \left(n \ln \frac{n}{n_\infty} + p \ln \frac{p}{p_\infty} \right) dx \right. \right. \\ &\quad \left. \left. - \frac{ze}{2\varepsilon} \int_{\Omega} (p - n)(x) \int_{\Omega} G(x, y)(n - p)(y) dy dx \right) dt \right] \\ &= -(K_B T \nabla n - zen \nabla \phi) = -n \nabla \mu_n, \end{aligned} \quad (2.7)$$

where $\mu_n := \frac{\delta}{\delta n} E^{total} = K_B T(1 + \ln n) - K_B T \ln n_\infty - ze\phi$ 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 \mathbf{u}_n to get the dissipative force,

$$F_{n-dis} = \frac{\delta}{\delta \mathbf{u}_n} \left(\frac{1}{2} \Delta \right) = \frac{K_B T}{D_n} n(\mathbf{u}_n - \mathbf{u}). \quad (2.8)$$

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

$$n\mathbf{u}_n = n\mathbf{u} - \frac{D_n}{K_B T} n \nabla \mu_n. \quad (2.9)$$

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

$$n_t + \nabla \cdot (n\mathbf{u}) = \nabla \cdot \left(D_n \nabla n - \frac{ze}{K_B T} D_n n \nabla \phi \right). \quad (2.10)$$

Similarly for positive charge, we can get

$$p\mathbf{u}_p = p\mathbf{u} - \frac{D_p}{K_B T} p \nabla \mu_p, \quad (2.11)$$

$$p_t + \nabla \cdot (p\mathbf{u}) = \nabla \cdot \left(D_p \nabla p + \frac{ze}{K_B T} D_p p \nabla \phi \right), \quad (2.12)$$

where $\mu_p := \frac{\delta}{\delta p} E^{total} = K_B T(1 + \ln p) - K_B T \ln p_\infty + ze\phi$ is the chemical potential for positive charge distribution $p(x, t)$. In the absence of the flow field \mathbf{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^ε such that $x^0 = x$, and $\frac{dx^\varepsilon}{d\varepsilon} \Big|_{\varepsilon=0} = y$, and for any ε : $\det \frac{\partial x^\varepsilon}{\partial X} = 1$, which in fact leads to a divergence free condition for $y(X, t) = \tilde{y}(x(X, t), t)$, i.e. $\nabla_x \cdot \tilde{y} = 0$. For LAP, we use the variations x^ε of x as described above and with y satisfying $y(X, 0) = y(X, t^*) = 0$ for any $X \in \Omega_0$. We can calculate the variation of action functional:

$$\begin{aligned} \frac{d}{d\varepsilon} \Big|_{\varepsilon=0} A(x^\varepsilon) &= \frac{d}{d\varepsilon} \Big|_{\varepsilon=0} \int_0^{t^*} \int_{\Omega_0} \frac{1}{2} \rho_0(X) |x_t^\varepsilon|^2 dX dt \\ &= \int_0^{t^*} \int_{\Omega_0} -\rho_0(X) (x_t)_t \cdot y dX dt = \int_0^{t^*} \int_{\Omega} -\rho(x, t) (\mathbf{u}_t + \mathbf{u} \cdot \nabla_x \mathbf{u}) \cdot \tilde{y} dx dt. \end{aligned} \quad (2.13)$$

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

$$-\rho(x, t) (\mathbf{u}_t + \mathbf{u} \cdot \nabla_x \mathbf{u}) = \nabla_x \Pi_1. \quad (2.14)$$

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

$$-\eta \Delta \mathbf{u} + \frac{K_B T}{D_n} n(\mathbf{u} - \mathbf{u}_n) + \frac{K_B T}{D_p} p(\mathbf{u} - \mathbf{u}_p) = \nabla \tilde{\Pi}_2, \quad (2.15)$$

where $\tilde{\Pi}_2$ is the Lagrange multiplier of incompressible constrain.

Substitute (2.9) and (2.11) into above formula and let $\Pi_2 = \tilde{\Pi}_2 - K_B T \nabla n - K_B T \nabla p$,

$$\nabla \Pi_2 = -\eta \Delta \mathbf{u} - (n-p)ze \nabla \phi. \quad (2.16)$$

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

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = \eta \Delta \mathbf{u} - \nabla \Pi + (n-p)ze \nabla \phi, \quad (2.17)$$

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:

$$\begin{cases} n_t + \nabla \cdot (\mathbf{u}n) = \nabla \cdot \left(D_n \nabla n - \frac{ze}{K_B T} D_n n \nabla \phi \right) = -\nabla \cdot \mathbf{J}_n, \\ p_t + \nabla \cdot (\mathbf{u}p) = \nabla \cdot \left(D_p \nabla p + \frac{ze}{K_B T} D_p p \nabla \phi \right) = -\nabla \cdot \mathbf{J}_p, \\ -\varepsilon \Delta \phi = ze(p-n), \\ \rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = \eta \Delta \mathbf{u} - \nabla \Pi + (n-p)ze \nabla \phi, \\ \nabla \cdot \mathbf{u} = 0. \end{cases} \quad (2.18)$$

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,*

$$\begin{aligned} \frac{d}{dt} E^{total} &= \frac{d}{dt} \left[\int_{\Omega} \left(\frac{\rho}{2} |\mathbf{u}|^2 + K_B T \left(n \ln \frac{n}{n_{\infty}} + p \ln \frac{p}{p_{\infty}} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right) dx \right] \\ &= - \int_{\Omega} \left[\frac{D_n}{K_B T} n |\nabla \mu_n|^2 + \frac{D_p}{K_B T} p |\nabla \mu_p|^2 + \eta |\nabla \mathbf{u}|^2 \right] dx \\ &= - \int_{\Omega} \left[\frac{K_B T}{D_n} n |\mathbf{u}_n - \mathbf{u}|^2 + \frac{K_B T}{D_p} p |\mathbf{u}_p - \mathbf{u}|^2 + \eta |\nabla \mathbf{u}|^2 \right] dx \\ &= -\Delta. \end{aligned} \quad (2.19)$$

Reversely, if we choose the action functional as

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

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).

Sketch of Proof: From the energy law to PNP-NS system are above derivations. By adding the first equation multiplied by μ_n , second equation multiplied by μ_p , and fourth equation multiplied by u together, and using the weak form of Poisson equation, we can get the energy law. ■

REMARK 2.2. *Some more complicated models can be derived by including more coupling terms for particle interactions in the total energy E^{total} , such as*

1. In [8, 10], it is shown that, by *EnVarA*, a modified model can be derived naturally for ion particles with finite size effects, through adding interaction term $E^{repulsion} = \sum_{i=1}^N \sum_{j \geq i}^N \frac{1}{2} \int_{\Omega} \Psi_{i,j}(|x-y|) c_i(x) c_j(y) dx dy$ to the total energy, where c_i, c_j mean different species of ions, and $\Psi_{i,j}(|x-y|) = \frac{\varepsilon_{ij}(a_j+a_i)}{|x-y|^{12}}$ is Lennard-Jones (LJ) potential for i th and j th ions located at x and y with the radii a_i, a_j , respectively.
2. If we add $E^{surface} = ze \int_{\Omega} (p-n) \Psi_s$ 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 Ψ_s 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 $\mathbf{J}_n \cdot \nu = \mathbf{J}_p \cdot \nu = 0$ for charge density, with ν being out normal vector, and the nonslip boundary condition $\mathbf{u} = \mathbf{0}$ for velocity. We will focus on the boundary effect of potential ϕ which plays an important role in electrokinetics. For the three different boundary conditions, the PNP-NS system has the following theorem.

THEOREM 3.1. *If n, p satisfy $\mathbf{J}_n \cdot \nu = \mathbf{J}_p \cdot \nu = 0$, and $\mathbf{u} = \mathbf{0}$ on the boundary $\partial\Omega$, then*

1. *if $\phi = \phi_0(x)$, i.e. Dirichlet boundary, then PNPNS satisfies the energy law,*

$$\begin{aligned} \frac{d}{dt} E^{total} &= \frac{d}{dt} \left[\int_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_B T \left(n \ln \frac{n}{n_{\infty}} + p \ln \frac{p}{p_{\infty}} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right] dx \quad (3.1) \\ &= - \left[\int_{\Omega} \frac{D_n}{K_B T} n |\nabla \mu_n|^2 + \frac{D_p}{K_B T} |\nabla \mu_p|^2 + \eta |\nabla \mathbf{u}|^2 dx \right] + \varepsilon \int_{\partial\Omega} \frac{\partial \phi}{\partial \nu} \phi_0 dx; \end{aligned}$$

2. *if $\frac{\partial \phi}{\partial \nu} = \frac{\sigma_0(x)}{\varepsilon}$, i.e. Neumann boundary condition, then PNPNS satisfies the energy law,*

$$\begin{aligned} \frac{d}{dt} E^{total} &= \frac{d}{dt} \left[\int_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_B T \left(n \ln \frac{n}{n_{\infty}} + p \ln \frac{p}{p_{\infty}} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 \right] dx \quad (3.2) \\ &= - \left[\int_{\Omega} \frac{D_n}{K_B T} |\nabla \mu_n|^2 + \frac{D_p}{K_B T} |\nabla \mu_p|^2 + \eta |\nabla \mathbf{u}|^2 dx \right] + \int_{\partial\Omega} \sigma_0 \phi dx; \end{aligned}$$

3. *if $\phi + \zeta \frac{\partial \phi}{\partial n} = \phi_0(x)$, i.e Robin boundary condition, then PNPNS satisfies the energy law,*

$$\begin{aligned} \frac{d}{dt} E^{total} &= \frac{d}{dt} \left[\int_{\Omega} \frac{\rho}{2} |\mathbf{u}|^2 + K_B T \left(n \ln \frac{n}{n_{\infty}} + p \ln \frac{p}{p_{\infty}} \right) + \frac{\varepsilon}{2} |\nabla \phi|^2 + \frac{\varepsilon}{2\zeta} \int_{\partial\Omega} |\phi|^2 dx \right] \\ &= - \left[\int_{\Omega} \frac{D_n}{K_B T} |\nabla \mu_n|^2 + \frac{D_p}{K_B T} |\nabla \mu_p|^2 + \eta |\nabla \mathbf{u}|^2 dx \right]. \quad (3.3) \end{aligned}$$

REMARK 3.2.

1. *When ϕ on the boundary is Robin boundary condition, as time approaches infinity, (3.3) means $\nabla \mu_n = \nabla \mu_p = \nabla \mathbf{u} = \mathbf{0}$. Considering the boundary condition, it yields $\mathbf{J}_n = \mathbf{J}_p = \mathbf{u} = \mathbf{0}$, which means there is no fluid flux in the time limit. Then we can derive a Charge Conservation Poisson Boltzmann (CCPB)*

equation [17, 32]

$$-\varepsilon\Delta\phi = zen_\infty V \left(\frac{\beta \exp(-ze\phi/K_B T)}{\int_\Omega \exp(-ze\phi/K_B T) dx} - \frac{\alpha \exp(ze\phi/K_B T)}{\int_\Omega \exp(ze\phi/K_B T) dx} \right)$$

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 electrodynamic 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 [13, 32].

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 [23, 24]. It dictates that the electric current density \mathbf{J}_e and the fluid current density \mathbf{J}_f be linearly related to the voltage gradient $\nabla\phi$ and the pressure gradient $\nabla\Pi$:

$$\begin{bmatrix} \mathbf{J}_e \\ \mathbf{J}_f \end{bmatrix} = - \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \nabla\phi \\ \nabla\Pi \end{bmatrix}, \quad (4.1)$$

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 [23, 24] is a stability conditions. 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 field E_z and a pressure drop $\frac{\partial\pi}{\partial z}$ are added in z direction, the velocity u_z satisfies

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

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

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

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

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

$$J_p = - \left(D_p \frac{\partial p}{\partial z} + D_p \frac{ze}{K_B T} \left(\frac{\partial\phi}{\partial z} - E_z \right) p \right) = \frac{ze}{K_B T} p D_p E_z. \quad (4.5)$$

The total electric current in z direction is the sum of the current carried (transported) by the flow field \mathbf{u} and the current due to the electric field,

$$\begin{aligned} J_e &= \frac{\int_{-L}^L \int_0^a 2(p-n)zeu_z r dr dz + \int_{-L}^L \int_0^a 2ze(J_p - J_n)r dr dz}{2La^2} \\ &= E_z \left[\frac{\varepsilon}{\mu a^2} \int_0^a rze(p-n)dr + \frac{z^2 e^2}{K_B T} E_z (D_p p_0 + D_n n_0) \right] \\ &\quad + \left(-\frac{\partial \Pi}{\partial z} \right) \frac{1}{2\mu a^2} \int_0^a (p-n)ze(a^2 - r^2)r dr. \end{aligned} \quad (4.6)$$

The fluid flux in z direction is

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

We may write the Onsager relation as

$$\begin{bmatrix} J_e \\ J_f \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} E_z \\ -\frac{\partial \Pi}{\partial z} \end{bmatrix}, \quad (4.7)$$

where we have introduced the function forms of the coefficients,

$$L_{12} = \frac{1}{2\mu a^2} \int_0^a rze(p-n)(a^2 - r^2)dr, \quad L_{21} = \frac{2\varepsilon}{\mu a^2} \int_0^a \phi r dr. \quad (4.8)$$

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

$$\begin{aligned} L_{12} &= -\frac{\varepsilon}{2\mu a^2} \int_0^a (a^2 - r^2) \left(\frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial r^2} \right) r dr \\ &= -\frac{\varepsilon}{2\mu a^2} \left[(-a^2 \phi(0) + 2 \int_0^a \phi r dr) + (a^2 \phi(0) - \int_0^a 6r \phi dr) \right] \\ &= \frac{2\varepsilon}{\mu a^2} \int_0^a r \phi dr = L_{21}, \end{aligned} \quad (4.9)$$

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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Supplement to the “AN ENERGETIC VARIATIONAL APPROACH FOR ION TRANSPORT” by Shixin Xu, Ping Sheng and Chun Liu in CMS

Motivated by the seminal work of Onsager and Rayleigh, the framework of the Energy Variational Approaches had been employed to study many complex fluids systems [Liu2001], [Yue2004], [Eisenberg2010]. Although there is a vast body of literatures on various applications, there lacks a comprehensive reference on the topic. The purpose of the paper “AN ENERGETIC VARIATIONAL APPROACH FOR ION TRANSPORT” is on the specific applications on Poisson-Nernst-Planck system and Poisson-Nernst-Planck-Navier-Stokes system. Due to the 10 pages limitation, we left out some details in that manuscript. This is the motivation of this supplement.

1 Some basic examples of Energetic Variational Approach

1). Hookean Spring : This is the original example by the Rayleigh [Strutt 1873]

The (Least) Action Principle is the reformulation of the fact that *force* \times *distance* = *work*. Hence variation of the energy with respect to flow map $x(X, t)$ yields the (conservative) force. Let x denote the displacement of the lower end of the spring from its equilibrium position. Then the traditional equation used to describe the spring is

$$mx_{tt} + \gamma x_t + kx = 0, \quad (0.1)$$

where mx_{tt} is the inertia, γx_t is damping, and kx is elastic force.

Multiplying (0.1) by x_t and integrating by parts, it yields

$$\frac{d}{dt} \left(\frac{1}{2} m x_t^2 + \frac{1}{2} k x^2 \right) = -\gamma x_t^2, \quad (0.2)$$

where the total energy is $E^{total} = \frac{1}{2} m x_t^2 + \frac{1}{2} k x^2$, and the dissipation functional is quadratic on velocity $u = x_t$, $\Delta = -\gamma x_t^2$.

Reversely, if we start from energy dissipation law (0.2), the action functional is

$$A = \int_0^{t^*} \left(\frac{1}{2} m x_t^2 - \frac{1}{2} k x^2 \right) dt. \quad (0.3)$$

By LAP and taking variation of A with respect to x , we get immediately

$$F_{con} = -m x_{tt} - kx, \quad (0.4)$$

which is exactly the conservative force for the Hookean spring.

Next we treat the dissipative part. If we denote $x_t = u$, by MDP, it yields, for any smooth test function v ,

$$\left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \frac{1}{2} \Delta(u + \varepsilon v) = \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \left(\frac{1}{2} \gamma (u + \varepsilon v)^2 \right) = \gamma u \cdot v, \quad (0.5)$$

which is also consistent with the optimal transportation [Villani2003]. This yields the dissipative force

$$F_{dis} = \gamma x_t. \quad (0.6)$$

Now we have both the dissipative part (0.6) and the Hamiltonian part (0.4) of the system. The equation for the entire system comes from the force balance $F_{con} = F_{dis}$:

$$-m x_{tt} - kx = \gamma x_t, \quad (0.7)$$

which is equivalent with equation (0.1).

2) Simple Diffusion

Various forms of this derivation can be found in many literatures, for instance, [Xu2013]. Here we take the simple heat equation as example. The diffusion equation

$$f_t = c \Delta f, \quad (0.8)$$

can be viewed as special case in this energetic variational framework. Equation (0.8) can be rewritten as

$$\begin{cases} f_t + \nabla \cdot (\mathbf{u}f) = 0, \\ -c \nabla f = f \mathbf{u}. \end{cases} \quad (0.9)$$

Multiplying the first equation in (0.9) by $c(\ln f + 1)$ and integrating by parts, it yields,

$$\begin{aligned}
\frac{d}{dt} \int_{\Omega} c f \ln f dx &= \int_{\Omega} f_t c (1 + \ln f) dx \\
&= \int_{\Omega} f \mathbf{u} c \nabla (1 + \ln f) dx = \int_{\Omega} f \mathbf{u} c \frac{\nabla f}{f} dx \\
&= - \int_{\Omega} f |\mathbf{u}|^2 dx.
\end{aligned} \tag{0.10}$$

Reversely, we start with the kinematic assumption of density f (conservation law) and energy dissipation law

$$\begin{cases} f_t + \nabla \cdot (\mathbf{u}f) = 0, \\ \frac{d}{dt} E^{total} = \frac{d}{dt} \int_{\Omega} c f \ln f dx = - \int_{\Omega} f |\mathbf{u}|^2 dx. \end{cases} \tag{0.11}$$

By the LAP, we can get

$$F_{con} = \frac{\delta A}{\delta x} = - \frac{\delta E^{total}}{\delta x} = -c \nabla f \tag{0.12}$$

and by MDP, we can get

$$F_{dis} = \frac{\delta}{\delta \mathbf{u}} \frac{\Delta}{2} = f \mathbf{u}. \tag{0.13}$$

The force balance yields

$$-c \nabla f = f \mathbf{u}. \tag{0.14}$$

Combining above formula and the conservation law, we can get

$$f_t = c \Delta f. \tag{0.15}$$

2. The derivation of compressible Navier-Stokes equation

This is motivated by the classical derivations of Euler equation by (Least) Action Principle [Arnold1989] and also the (Maximum) Dissipation Principle of Onsager [Onsager1931a, Onsager1931b] which is another version of the linear response theory [Kubo1976]. The density ρ satisfies the kinematic assumption (conservation of mass),

$$\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0. \tag{0.16}$$

From the energy variation point of view, the following energy dissipation law includes all the physics of Newtonian fluids

$$\frac{d}{dt} E^{total} = \frac{d}{dt} \int_{\Omega} \left(\frac{1}{2} \rho |\mathbf{u}|^2 + \omega(\rho) \right) dx = - \int_{\Omega} [\mu_1 |\nabla \mathbf{u}|^2 + \mu_2 |\nabla \cdot \mathbf{u}|] dx, \quad (0.17)$$

where μ_1 and μ_2 are viscosity constants, the Hemholtz free energy density $\omega(\rho)$ includes both the entropic contributions and the internal energy describing the particle interactions. The action functional in Lagrangian coordinates, after Legendre transformation, is

$$\begin{aligned} A(x) &= \int_0^{t^*} \int_{\Omega} \left(\frac{1}{2} \rho |\mathbf{u}|^2 - \omega(\rho) \right) dx dt \\ &= \int_0^{t^*} \int_{\Omega_0} \left(\frac{1}{2} \frac{\rho_0}{J} |x_t(X, t)|^2 - \omega\left(\frac{\rho_0}{J}\right) \right) J dX dt \\ &= \int_0^{t^*} \int_{\Omega_0} \left(\frac{1}{2} \rho_0 |x_t(X, t)|^2 dX dt - \omega\left(\frac{\rho_0}{J}\right) J \right) dX dt, \quad (0.18) \end{aligned}$$

where $J = \det F$, $F(X, t) = \frac{\partial x(X, t)}{\partial X}$ is the deformation gradient. Taking the variation with respect to x yields, for any $y(X, t) = \tilde{y}(x(X, t), t)$ smooth with compact support

$$\begin{aligned} \frac{d}{d\varepsilon} \Big|_{\varepsilon=0} A(x(X, t) + \varepsilon y(X, t)) &= \frac{d}{d\varepsilon} \Big|_{\varepsilon=0} A(x + \varepsilon y) \\ &= \frac{d}{d\varepsilon} \Big|_{\varepsilon=0} \int_0^{t^*} \int_{\Omega_0} \frac{1}{2} \rho_0(X) |x_t + \varepsilon y_t|^2 - \omega \left(\frac{\rho_0(X)}{\det\left(\frac{\partial(x + \varepsilon y)}{\partial X}\right)} \right) \left(\det\left(\frac{\partial(x + \varepsilon y)}{\partial X}\right) \right) dX dt \\ &= \int_0^{t^*} \int_{\Omega_0} \rho_0(X) x_t y_t dX dt + \int_0^{t^*} \int_{\Omega_0} \omega_{\rho} \left(\frac{\rho_0(X)}{J} \right) \frac{\rho_0(X)}{J^2} \cdot \text{tr} \left(\frac{\partial X}{\partial x} \frac{\partial y}{\partial X} \right) \cdot J^2 \\ &\quad - \omega \left(\frac{\rho_0(X)}{J} \right) \cdot J \cdot \text{tr} \left(\frac{\partial X}{\partial x} \frac{\partial y}{\partial X} \right) dX dt. \quad (0.19) \end{aligned}$$

Here we use the fact $\delta(\det F) = \det F \cdot \text{tr}(F^{-T} \frac{\partial \delta x}{\partial X})$.

Integrating by parts, above formula yields

$$\begin{aligned}
& \int_0^{t^*} \int_{\Omega_0} -\rho_0(X) x_{tt} y_t \\
& + \left(\omega_\rho \left(\frac{\rho_0(X)}{J} \cdot \right) \frac{\rho_0(X)}{J} - \omega \left(\frac{\rho_0(X)}{J} \cdot \right) \right) \cdot \text{tr} \left(\frac{\partial X}{\partial x} \frac{\partial y}{\partial X} \right) J dX dt \\
= & \int_0^{t^*} \int_{\Omega} \left(-\rho(x) \frac{d}{dt} \mathbf{u}(x, t) \right) \cdot \tilde{\mathbf{y}} \\
& + (\omega_\rho(\rho(x, t)) \rho(x, t) - \omega(\rho(x, t))) \cdot (\nabla_x \cdot \tilde{\mathbf{y}}) dx dt \\
= & \int_0^{t^*} \int_{\Omega} \left(-\rho(x, t) \frac{d}{dt} \mathbf{u}(x, t) + \nabla_x (\omega_\rho(\rho(x, t)) \cdot \rho(x, t) - \omega(\rho(x, t))) \right) \cdot \tilde{\mathbf{y}} dx dt \\
= & \int_0^{t^*} \int_{\Omega} \left(-\rho(x, t) (\mathbf{u}_t + \mathbf{u} \cdot \nabla_x \mathbf{u}) + \nabla_x \Pi(x, t) \right) \cdot \tilde{\mathbf{y}} dx dt, \tag{0.20}
\end{aligned}$$

where $\Pi(x, t) = \omega_\rho(\rho(x, t)) \cdot \rho(x, t) - \omega(\rho(x, t))$ (same result as Lemma 1.1). Then we obtain the conservative force

$$F_{con} = -(\rho(x, t)(\mathbf{u}_t + \mathbf{u} \cdot \nabla_x \mathbf{u}) + \nabla_x \Pi(x, t)). \tag{0.21}$$

As to the dissipation part, the dissipation functional is

$\Delta = \int_{\Omega} [\mu_1 |\nabla \mathbf{u}|^2 + \mu_2 |\nabla \cdot \mathbf{u}|] dx$. Maximum Dissipation Principle, as a reformulation of the linear response theory, takes the variation of Δ with respect to the rate function \mathbf{u} .

$$\begin{aligned}
& \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \frac{1}{2} \Delta(\mathbf{u} + \varepsilon \mathbf{v}) \\
= & \left. \frac{d}{d\varepsilon} \right|_{\varepsilon=0} \int_{\Omega} \frac{1}{2} \mu_1(x, t) |\nabla_x \mathbf{u} + \varepsilon \nabla_x \mathbf{v}|^2 + \frac{1}{2} \mu_2(x, t) |\nabla_x \cdot \mathbf{u} + \varepsilon \nabla_x \cdot \mathbf{v}|^2 dx \\
= & \int_{\Omega} \mu_1(x, t) \nabla_x \mathbf{u} : \nabla_x \mathbf{v} + \mu_2(x, t) (\nabla_x \cdot \mathbf{u}) (\nabla_x \cdot \mathbf{v}) dx \\
= & \int_{\Omega} \left(-\nabla_x (\mu_1(x, t) \nabla_x \mathbf{u}) - \nabla_x (\mu_2(x, t) \nabla_x \cdot \mathbf{u}) \right) \cdot \mathbf{v} dx, \tag{0.22}
\end{aligned}$$

where \mathbf{v} is any test function with compact support. Hence the dissipative force is

$$F_{dis} = -\nabla_x (\mu_1 \nabla_x \mathbf{u}) + \nabla_x (\mu_2 \nabla_x \cdot \mathbf{u}). \tag{0.23}$$

Finally, by force balance $F_{con} = F_{dis}$, we can get the usual Navier-Stokes equation (momentum equation)

$$\rho(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}) + \nabla \Pi(\rho) = \nabla \cdot (\mu_1 \nabla \mathbf{u}) + \nabla (\mu_2 \nabla \cdot \mathbf{u}). \tag{0.24}$$

3. Interactions between particles

In a dissipation system, the particle interactions attribute to both the free energy functional and dissipation functional. The coarse graining derivation of the Helmholtz free energy $\mathcal{U} - T\mathcal{S}$, or equivalently, the equation of states, takes into account the free energy part. As in the standard statistical physics, the particles interactions contribute to the internal energy \mathcal{U} . Such interactions can be local, such as hard core interactions or nonlocal, such as Coulomb electro static interactions. At the same time, however independently, the non-equilibrium thermodynamics, following the linear response theory of Onsager [Onsager1931a,Onsager1931b] and Kubo [Kubo1976], the dissipative functional (the entropy production) is the sum of the quadratic powers of various rate variables. In PNP, the free energy includes the Gibbs entropy and the particle Coulomb interaction. The dissipation are quadratic of velocities.

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