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NON-ISOTHERMAL ELECTROKINETICS: ENERGETIC VARIATIONAL APPROACH[*]

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Abstract. Fluid dynamics accompanies with the entropy production, thus increases the local temperature, which plays an important role in charged systems, such as the ion channel in biological environment and electrodiffusion in capacitors/batteries. In this article, we propose a general framework to derive the transport equations with heat flow through the energetic variational approach. According to the first law of thermodynamics, the total energy is conserved and we can use the least action principle to derive the conservative forces. From the second law of thermodynamics, the entropy increases and the dissipative forces can be computed through the maximum dissipation principle. Combining these two laws, we then conclude with the force balance equations and a temperature equation. To emphasize, our method provides a self-consistent procedure to obtain the dynamical equations satisfying proper energy laws and it not only works for the charge systems but also for general systems.

Keywords. Electrokinetics; Electro-thermal Motion; Energetic Variation Approach.

AMS subject classifications. 35Q35; 35Q79; 76A02; 80A20.

1. Introduction

The inhomogeneous and time-dependent temperature could be of great importance in the electrodiffusion processes. It also plays a key role in many biological and chemical applications. For example, a number of ion channels are observed to be sensitive to the temperature changes [2,20]. These temperature-gated ion channels can detect the temperature; thus regulating the internal homeostasis and disease-related processes such as the thermal adaptation and the fever response. Also the electro-osmotic flow (EOF) in the microfluidic devices will cause the internal heat generation, which is known to be the Joule heating effects [13,14]. This inhomogeneous increase of the temperature will change the fluid dynamical properties, thus it is important in controlling the EOF and designing microfluidic devices.

The ionic transport can be modeled through the classical Poisson-Nernst-Planck (PNP) theory and its various modified versions [3,7,10,12,17,19,22,24], which are shown to be successful in describing various phenomena and properties. Through the energetic variational approach (EnVarA), C. Liu et al. derived the modified PNP equations with given free energy functional and the form of entropy production [9,11,23]. However, these models are all isothermal: the temperature is fixed as a constant.

To model the non-isothermal dynamic processes, we need to couple the mechanical equation and the thermal equation together. In [1], Bulíček *et al.* considered the

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incompressible homogeneous Newtonian fluids with temperature-dependent coefficients and obtained the long-time and large-data existence for a suitable weak solution. For the heat conducting compressible Newtonian fluid, Feireisl [5] developed a Navier-Stokes-Fourier system and derived a priori estimates and the weak stability based on variational weak formulation and the thermodynamic second law. Eleuteri *et al.* [4] studied the non-isothermal diffuse-interface model for two incompressible Newtonian fluids, resulting in a Cahn-Hilliard system. Also, many papers are devoted to real applications. For example, Xuan and Li [25] reported that the Joule heating effects in the electrokinetic flow could increase the current load, enhance the flow rate and reduce the separation efficiency. Sánchez *et al.* [21] analyzed the Joule heating effect on a purely electroosmotic flow of non-Newtonian fluids through a slit microchannel. In addtion, Gonzalez *et al.* [8] studied the electrothermal motion in microsystems generated by AC electrical field.

In this work, we adapt the EnVarA, aiming to propose an unified framework to self-consistently describe the electrothermal motion. With given form of the free energy functional and the entropy production, the conservative forces can be derived through the least action principle (LAP) and the dissipative forces are given by the maximum dissipation principle (MDP). For any open subset of the fluid region, the energy balance and the entropy increase lead to the mechanical and thermal equations. Here, we derive the model in Euler coordinates, in contrast to the classical approach in literature based on the Lagrange formalism. The reason is that the charged systems usually involve more than one ionic species, thus several velocity fields appear, employing the material derivative like previous papers might cause confusion and inconvenience.

To emphasize, our approach guarantees the resulting equations satisfying fundamental laws of thermodynamics and it can be generalized to a variety of complex fluid systems such as liquid crystal [6].

2. Theory of charge dynamics

Consider a closed system with N ionic species in domain Ω. Define the local density distribution for ith species as space dependent: $\rho_i(\mathbf{r},t)$, $i=1,2,\cdots,N$, and the charges are denoted by z_i respectively. The time evolution is usually modeled through the PNP equation:

$$\begin{cases} \dfrac{\partial}{\partial t}\rho_i = \nabla\cdot D_i\left(k_BT\nabla\rho_i+\rho_i z_i\nabla\phi\right), \\ -\nabla\cdot\epsilon\nabla\phi=\sum_{i=1}^N\rho_i z_i. \end{cases} \tag{2.1}$$

Here ϕ is the mean electrical potential, D_i is the mobility coefficient, k_B is the Boltzmann constant. T is the temperature, which is homogeneous and remains independent of time within the PNP model. The corresponding energy dissipation is known to be,

$$\frac{d}{dt}\int_\Omega\left(\frac{\epsilon}{2}|\nabla\phi|^2+\sum_{i=1}^N k_BT\rho_i(\log\rho_i-1)\right)d\mathbf{r} = -\sum_{i=1}^N\int_\Omega\frac{D_i}{\rho_i}|k_BT\nabla\rho_i+\rho_i z_i\nabla\phi|^2 d\mathbf{r}, \tag{2.2}$$

where the left integral is the Helmholtz free energy including the mean electrical energy and the entropic contribution. Since the classical PNP system is a mean field theory, the correlations between particles are neglected. The right hand side represents the energy dissipation. With the energy dissipation law (2.2), the PNP Equation (2.1) can be derived through the EnVarA [23]. In the PNP theory, the system entropy increases without affecting the temperature, which indicates that a specific amount of heat/energy must be transferred to the system. Through the second law of thermodynamics, it is straightforward to evaluate the heat absorption rate of the system,

$$\frac{dQ}{dt}=-\sum_{i=1}^{N}\int_{\Omega}\frac{D_i}{\rho_i}(k_BT\nabla\rho_i+\rho_iz_i\nabla\phi)\cdot\rho_iz_i\nabla\phi\ d\mathbf{r}. \tag{2.3}$$

When the heat conducting rate is very large or the total heat generated is negligible compared with the system heat capacitance, it is reasonable to assume that the temperature T is a constant. But more generally, we have to consider the temperature evolution with given heat sources.

2.1. Energy functional. To study the effects of temperature, we use $T(\mathbf{r},t)$ to describe the temperature distribution at time t. We write the general form of the free energy $F(V,t)$ for the system in any subdomain $V\subset\Omega$, which is a functional of the temperature and particle densities,

$$\begin{aligned}F(V,t)=&\sum_{i=0}^{N}\int_V\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))d\mathbf{r}+\sum_{i,m=0}^{N}\frac{z_iz_m}{2}\iint_V\rho_i(\mathbf{r},t)\rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'\\&+\sum_{i=0}^{N}z_i\int_V\rho_i(\mathbf{r})\left(\psi(\mathbf{r},t)+\sum_{m=0}^{N}z_m\int_{\Omega\backslash V}\rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}'\right)d\mathbf{r}.\end{aligned} \tag{2.4}$$

The first term Ψ_i is a local function of density $\rho_i(\mathbf{r},t)$ and temperature $T(\mathbf{r},t)$, representing the free energy density from the entropy contribution. It should be noted that one can include the steric effect, ionic correlation and the variable dielectrics into proper form of Ψ_i. The index $i=0$ stands for the solvent particles, which is imcompressible with constant density ρ_0, and index $1,\cdots,N$ represents the solute species. The second term in (2.4) represents the potential energy from the Coulomb interaction $z_iz_mv(\mathbf{r},\mathbf{r}')$, and the kernel v satisfies $-\nabla\cdot\epsilon\nabla v(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r},\mathbf{r}')$. The last term is the potential energy from the external field, including the external electrical potential ψ and the contribution from particles outside domain V. Since the negative local entropic density is the derivative of the free energy density with respect to the temperature, the entropy,

$$S(V,t)=-\sum_{i=0}^{N}\int_V\frac{\partial\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))}{\partial T(\mathbf{r},t)}d\mathbf{r}. \tag{2.5}$$

Then the corresponding internal energy is given by the Legendre transform of the Helmholtz free energy with respect to the temperature,

$$U(V,t)=F(V,t)-\sum_{i=0}^{N}\int_V T(\mathbf{r},t)\frac{\partial\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))}{\partial T(\mathbf{r},t)}d\mathbf{r} \tag{2.6}$$

For each species, the velocity field is denoted as $u_i(\mathbf{r},t)$, then their densities satisfy the mass conservation: $\frac{\partial}{\partial t}\rho_i+\nabla\cdot(\rho_iu_i)=0$. Each velocity field $u_i(\mathbf{x_i}(\mathbf{X},t),t)$ determines a unique flow map $\mathbf{x_i}(\mathbf{X},t)$ for the corresponding particle species through $\frac{\partial}{\partial t}\mathbf{x_i}(\mathbf{X},t)=u_i(\mathbf{x_i}(\mathbf{X},t),t)$. Introduce the mass m_i of each species and the kinetic energy $K(V,t)=\frac{1}{2}\sum_{i=0}^{N}\int_V m_i\rho_i(\mathbf{r},t)u_i^2(\mathbf{r},t)d\mathbf{r}$. Then the total action of the whole system is $A=\int_0^T[K(\Omega,t)-F(\Omega,t)]\,dt$. According to LAP, the conservative force on each species can be obtained through the variation of the action with respect to the flow map,

$$f_i^{\mathrm{con}}(\mathbf{x},t)=\frac{\delta A}{\delta\mathbf{x_i}(\mathbf{X},t)}=-m_i\rho_i\left(\frac{\partial}{\partial t}u_i+u_i\nabla u_i\right)-\nabla P_i-\rho_iz_i\nabla\phi, \tag{2.7}$$

where $\phi(\mathbf{r},t)=\psi(\mathbf{r},t)+\sum_{i=1}^{N} z_i\int_{\Omega}\rho_i(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}'$ is the mean electrical potential, $P_i(\mathbf{r},t)=\rho_i^2(\mathbf{r},t)\frac{\partial}{\partial\rho_i(\mathbf{r},t)}\left(\frac{\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))}{\rho_i(\mathbf{r},t)}\right)$ is the thermal pressure [23] for $i=1,\cdots,N$. Since the solvent is incompressible, the thermal pressure P_0 appears as a Lagrange multiplier and is undetermined.

Remark 2.1. Define the entropic density: $\eta_i(\mathbf{r},t)=-\frac{1}{\rho_i(\mathbf{r},t)}\frac{\partial\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))}{\partial T(\mathbf{r},t)}$ and the internal energy density: $e_i^{\mathrm{int}}(\rho_i(\mathbf{r},t),\eta_i(\mathbf{r},t))=\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))+T(\mathbf{r},t)\rho_i(\mathbf{r},t)\eta_i(\mathbf{r},t)$. According to the property of Legendre transform, the definition of thermal pressure is equivalent to $P_i(\mathbf{r},t)=\rho_i^2(\mathbf{r},t)\frac{\partial}{\partial\rho_i(\mathbf{r},t)}\left(\frac{e_i^{\mathrm{int}}(\rho_i(\mathbf{r},t),\eta_i(\mathbf{r},t))}{\rho_i(\mathbf{r},t)}\right)$, which is used in literature [5].

According to the first law of thermodynamics, the internal energy is conserved with the work done and the heat absorbed. The rate of work is given by,

$$\frac{d}{dt}W(V,t)=\sum_{i=0}^{N} z_i\int_V \rho_i(\mathbf{r},t)\frac{\partial}{\partial t}\left[\psi(\mathbf{r},t)+\sum_{m=0}^{N} z_m\int_{\Omega\backslash V}\rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}'\right]d\mathbf{r}$$
$$+\sum_{i=0}^{N}\int_{\partial V}\mathbb{T}_i(\mathbf{r},t)u_i(\mathbf{r},t)\cdot d\mathbf{r}. \tag{2.8}$$

Here the first integral is due to the time-dependent external field, including the contribution from the ions in domain $\Omega\backslash V$. The second term is from the work of the stress tensor $\mathbb{T}_i$ on the boundary ∂V, which includes the contribution from the thermal pressure P_i and the dissipative force. The form of $\mathbb{T}_i(\mathbf{r},t)$ will be specified when we have the dissipative force in Equation (2.14). The rate of heat transfer is given by the heat flux j and body heat source q,

$$\frac{d}{dt}Q(V,t)=-\int_{\partial V} j\cdot d\mathbf{r}+\int_V q d\mathbf{r}. \tag{2.9}$$

We should notice here that the control volume V does not move along with the velocity field as different solute species have different flow maps. At the boundary ∂V, the mechanical flux will also introduce a total energy flux, which should be considered,

$$J_E(V,t)=\sum_{i=0}^{N}\int_{\partial V} u_i\left[\frac{1}{2}m_i\rho_i u_i^2+e_i^{\mathrm{int}}(\rho_i,\eta_i)+z_i\rho_i\phi\right]d\mathbf{r}. \tag{2.10}$$

So, the energy conservation is expressed as,

$$\frac{d}{dt}[U(V,t)+K(V,t)]+J_E(V,t)=\frac{d}{dt}W(V,t)+\frac{d}{dt}Q(V,t). \tag{2.11}$$

With (2.6) and (2.8)-(2.11), and using the fact that the control volume V is arbitrarily chosen, we then obtain a differential equation (see Appendix for more details),

$$\sum_{i=0}^{N}\left(-T\frac{\partial^2\Psi_i}{\partial T^2}\right)\left(\frac{\partial T}{\partial t}+u_i\cdot\nabla T\right)+\sum_{i=1}^{N}\left(\Psi_i-\rho_i\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial\Psi_i}{\partial T}+\rho_i T\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot u_i$$
$$+\sum_{i=0}^{N}[\rho_i u_i z_i\nabla\phi-\nabla\cdot(\mathbb{T}_i u_i)]+\sum_{i=0}^{N} m_i\rho_i(\frac{\partial}{\partial t}u_i+u_i\nabla u_i)\cdot u_i=q-\nabla\cdot j. \tag{2.12}$$

This equation provides a relation between the temperature evolution and the mechanical velocities. In order to form a closed PDE system, we need another relation which can be given by the entropy production.

2.2. Entropy production. The second law of thermodynamics states the fact that the entropy increase of any closed system must not be less than the heat absorbed from the environment, and the equality only holds for reversible process. We choose the entropy production density to be,

$$\widetilde{\Delta}(\mathbf{r},t)=\sum_{i=1}^{N}\frac{\nu_i\rho_i|u_i-u_0|^2+\xi_i|\nabla\cdot u_i|^2}{T}+\sum_{i=0}^{N}\frac{\lambda_i|\nabla u_i|^2}{T}+\frac{1}{k}|\frac{j}{T}|^2. \tag{2.13}$$

Then the entropy production rate in arbitrary domain V is $\Delta(V,t)=\int_V\widetilde{\Delta}(\mathbf{r},t)d\mathbf{r}$. Here ξ_i is the bulk viscosity, λ_i is the shear viscosity coefficient for ith species, ν_i describes the viscosity between the ith particle and the solvent, j represents the heat flux, k is a constant relating with the heat conductance. It should be noted that all of these coefficients can depend on the concentration distribution and the temperature. Here we only consider the relative drag between the solvent and the solute while neglecting the friction between different solvent species. This is generally true for dilute solutions, and the correction can be made following the argument in [10]. Compared with the entropy production in the classical fluid dynamic equations, we have one extra term from the heat flux. Then the dissipative force is given by the MDP,

$$f_i^{\text{dis}}(\mathbf{r},t)=\frac{1}{2}\frac{\delta\int_\Omega T\widetilde{\Delta}d\mathbf{r}}{\delta u_i(\mathbf{r},t)}=\begin{cases}\nu_i\rho_i(u_i-u_0)-\nabla(\xi_i\nabla\cdot u_i)-\nabla\cdot\lambda_i\nabla u_i, & i=1,\cdots,N.\\ \sum_{m=1}^{N}\nu_m\rho_m(u_0-u_m)-\nabla\cdot\lambda_0\nabla u_0, & i=0.\end{cases} \tag{2.14}$$

The terms related with the relative velocity u_i-u_0 between the solvent and the solute species are the body forces and they do not provide work to the system. The terms $\nabla\xi_i\nabla\cdot u_i$ and $\nabla\cdot\lambda_i\nabla u_i$ represents the surface forces, which can be expressed into the divergence form: $\nabla\cdot(\xi_i\nabla\cdot u_i\mathbb{I}+\lambda_i\nabla u_i)$. Since the stress tensor $\mathbb{T}_i$ is symmetric, by noticing $\nabla\cdot\lambda_i\nabla^T u_i=\nabla(\lambda_i\nabla\cdot u_i)$, we should have $\mathbb{T}_i=[-P_i+(\xi_i-\lambda_i)\nabla\cdot u_i]\mathbb{I}+2\lambda_i\mathcal{D}u_i$, for $i=1,\cdots,N$, where $\mathbb{I}$ is a 3-by-3 identity matrix, $\mathcal{D}u_i=[\nabla u_i+(\nabla u_i)^T]/2$ is the symmetric part of ∇u_i. For the imcompressible solvent, $\mathbb{T}_0=-P_0\mathbb{I}+2\lambda_0\mathcal{D}u_0$. Similarly, we should take into account the entropic flux at the boundary ∂V,

$$J_S=-\sum_{i=0}^{N}\int_{\partial V}\frac{\partial\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t))}{\partial T(\mathbf{r},t)}u_i\cdot d\mathbf{r}. \tag{2.15}$$

So the second law of thermodynamics is expressed as,

$$\frac{d}{dt}S(V,t)+\int_{\partial V}\frac{j}{T}\cdot d\mathbf{r}-\int_V\frac{q}{T}d\mathbf{r}+J_S=\Delta(V,t)\geq 0, \tag{2.16}$$

where q is the heat source. Combining (2.5), (2.13) and (2.16), we then obtain (see Appendix for more details),

$$-\sum_{i=0}^{N}\left[\frac{\partial^2\Psi_i}{\partial T^2}\left(\frac{\partial T}{\partial t}+u_i\cdot\nabla T\right)+\left(\frac{\partial\Psi_i}{\partial T}-\rho_i\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot u_i\right]=\widetilde{\Delta}+\frac{q}{T}-\nabla\cdot\frac{j}{T}. \tag{2.17}$$

This equation provides another relation between the temperature evolution and the velocity fields.

2.3. Governing equations. Multiply Equation (2.17) by the local temperature $T(\mathbf{r},t)$ and then subtracting Equation (2.12) gives,

$$\sum_{i=0}^{N} u_i \cdot (f_i^{\text{con}} - f_i^{\text{dis}}) = j \cdot \left(\frac{j}{kT} + \frac{\nabla T}{T} \right). \tag{2.18}$$

Here, we have used the definition of the conservative force (2.7) and the dissipative force (2.14). The right hand side of Equation (2.18) is about the heat flux which is invariant under any inertial frames of reference, while the left hand side is about the particle velocities which depend on the reference frame we choose. So it is reasonable to claim their coefficients must vanish, thus the Onsager Principle holds, $f_i^{\text{con}} = f_i^{\text{dis}}$, for $i=0,\cdots,N$. The heat flux: $j=-k\nabla T$, which is the Fourier law. Finally, the dynamic equations for the solute particles become,

$$\begin{cases} \dfrac{\partial}{\partial t}\rho_i + \nabla\cdot(\rho_i u_i) = 0, \\ m_i\rho_i(\dfrac{\partial u_i}{\partial t} + u_i\nabla u_i) + \nabla P_i + \rho_i z_i \nabla\phi = \nu_i\rho_i(u_0 - u_i) + \nabla(\xi_i \nabla\cdot u_i) + \nabla\cdot\lambda_i\nabla u_i, \\ -\nabla\cdot\epsilon\nabla\phi = \sum_{m=0}^{N}\rho_m z_m + \rho_f. \end{cases} \tag{2.19}$$

Here, we use the fact that $-\nabla\cdot\epsilon\nabla v(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$. Together with proper boundary conditions, $\rho_f = -\nabla\cdot\epsilon\nabla\psi$ describes the external field ψ. For the imcompressible solvent,

$$\begin{cases} m_0\rho_0\left(\dfrac{\partial}{\partial t}u_0 + u_0\nabla u_0\right) + \nabla P_0 + \rho_0 z_0\nabla\phi = \displaystyle\sum_{i=1}^{N}\nu_i\rho_i(u_i - u_0) + \nabla\cdot\lambda_0\nabla u_0, \\ \nabla\cdot u_0 = 0. \end{cases} \tag{2.20}$$

And the temperature equation,

$$\begin{aligned} &\sum_{i=0}^{N}\left(-T\frac{\partial^2\Psi_i}{\partial T^2}\right)\left(\frac{\partial T}{\partial t} + u_i\cdot\nabla T\right) + \left(\sum_{i=1}^{N}\frac{\partial P_i}{\partial T}\nabla\cdot u_i\right)T \\ =&\nabla\cdot k\nabla T + \sum_{i=1}^{N}\nu_i\rho_i|u_i - u_0|^2 + \xi_i|\nabla\cdot u_i|^2 + \sum_{i=0}^{N}\lambda_i|\nabla u_i|^2 + q. \end{aligned} \tag{2.21}$$

In Equation (2.21), $\sum_{i=0}^{N}\left(-T\frac{\partial^2\Psi_i}{\partial T^2}\right)$ can be viewed as the weighted average heat capacitance of the system. The second term represents the work of thermopressure transfer into heat. On the right hand side, $\nabla\cdot k\nabla T$ describes the heat diffusion. We should notice that the entropy production from mechanical viscosity appears as an internal heat source.

Together with proper boundary conditions, the Equations (2.19), (2.20) and (2.21) form a closed PDE system to describe the non-isothermal electro-thermal flow.

REMARK 2.2. For real physical systems, we usually have $\frac{\partial^2\Psi_i}{\partial T^2} < 0$, corresponding to a positive heat capacitance. For example, $\Psi = k_B T\rho(\log\rho - C\log T)$ describes the ideal gas system, $\frac{\partial^2\Psi}{\partial T^2} = -\frac{C\rho}{T}$. Thus $\frac{\partial T}{\partial t}$ and $\nabla\cdot k\nabla T$ in (2.21) have the same sign as in the heat equation.

REMARK 2.3. The heat source term $\sum_{i=1}^{N}\nu_i\rho_i|u_i - u_0|^2$ in Equation (2.21) takes the form of ionic flux square times the resistance. If the temperature and densities are all homogeneous in space, then the electrical current as well as the ionic fluxes $\rho_i(u_i - u_0)$ are proportional to the local electrical field. Thus the energy dissipation is equivalent to the well known Joule heating effect, which states the current square times the resistance becomes heat in a circuit. For more general situation, our model suggests to use fluxes of each ionic species instead of the total electrical current.

3. Examples

With given free energy density Ψ_i and entropy production Δ, the above approach can be applied and generalized to a wide variety of systems, such as the modified PNP equations with ionic correlation, size effects and relative drags. In this section, we consider two examples.

3.1. Incompressible Navier-Stokes-Fourier system. By setting the number of ionic species to zero, we can also investigate the solvent system alone. Consider the fluid in a confined domain Ω and at the boundary $\partial\Omega$ there is neither mechanical nor heat flux. Suppose the solvent is charge-neutral and incompressible, the free energy functional is just,

$$F(V,t) = -C\int_V T(\mathbf{r})\log T(\mathbf{r})d\mathbf{r}. \tag{3.1}$$

Here C is a constant. The entropy production takes the form,

$$\Delta(V,t) = \int_V \left(\frac{\lambda|\nabla u|^2}{T} + \frac{1}{k}|\frac{j}{T}|^2\right) d\mathbf{r}. \tag{3.2}$$

We also take into account the kinetic energy $K(V,t) = \frac{1}{2}\int_V mu^2(\mathbf{r},t)d\mathbf{r}$. So the governing equations become,

$$\begin{cases} \nabla\cdot u = 0, \\ m\left(\dfrac{\partial}{\partial t}u + u\nabla u\right) + \nabla P = \nabla\cdot\lambda\nabla u, \\ C\left(\dfrac{\partial T}{\partial t} + u\cdot\nabla T\right) = \nabla\cdot k\nabla T + \lambda|\nabla u|^2 + q. \end{cases} \tag{3.3}$$

This set of equations satisfy the thermodynamic laws automatically,

$$\begin{cases} \dfrac{d}{dt}[U(\Omega,t) + K(\Omega,t)] = \displaystyle\int_\Omega q(\mathbf{r},t)d\mathbf{r}, \\ \dfrac{d}{dt}S(\Omega,t) = \displaystyle\int_\Omega \left(\frac{q}{T} + \frac{\lambda|\nabla u|^2}{T} + \frac{1}{k}|\frac{j}{T}|^2\right) d\mathbf{r}, \end{cases} \tag{3.4}$$

where the entropy is $S(\Omega,t) = C\int_\Omega(\log T(\mathbf{r}) + 1)d\mathbf{r}$ and the internal energy is given by $U(\Omega,t) = C\int_\Omega T(\mathbf{r})d\mathbf{r}$. Note that the diffusion coefficients λ and k can depend on space and the state variables.

3.2. Poisson-Nernst-Planck-Fourier system. Consider a system in a confined domain Ω and there is no flux at the boundary. The free energy density function Ψ_i is given by,

$$\Psi_i(\rho_i(\mathbf{r},t), T(\mathbf{r},t)) = k_B T(\mathbf{r},t)\rho_i(\mathbf{r},t)\left[\log\rho_i(\mathbf{r},t) - C_i\log T(\mathbf{r},t)\right], \tag{3.5}$$

Remark 3.1. In the classical PNP system, the temperature is a constant, so there is only the $\rho\log\rho$ term. Here Equation (3.5) uses the complete form of the ideal gas free energy density as a function of both density and temperature. C_i is a constant related to the heat capacitance of each species.

The entropy production rate is,

$$\Delta(V,t)=\int_V \widetilde{\Delta}(\mathbf{r},t)d\mathbf{r}=\int_V\left(\frac{\lambda_0|\nabla u_0|^2}{T}+\sum_{i=1}^N\frac{\nu_i\rho_i|u_i-u_0|^2}{T}+\frac{1}{k}|\frac{j}{T}|^2\right)d\mathbf{r}. \tag{3.6}$$

Neglecting the kinetic energy, the governing equations for the ionic species become,

$$\begin{cases}\dfrac{\partial}{\partial t}\rho_i+\nabla\cdot(\rho_i u_i)=0,\\ \nu_i\rho_i(u_i-u_0)=-k_B\nabla(\rho_i T)-z_i\rho_i\nabla\phi,\\ -\nabla\cdot\epsilon\nabla\phi=\sum_{m=1}^N\rho_m z_m+\rho_f.\end{cases} \tag{3.7}$$

Here $\rho_f(\mathbf{r},t)=-\nabla\cdot\epsilon\nabla\psi(\mathbf{r},t)$ describes the external field $\psi(\mathbf{r},t)$. For the solvent,

$$\begin{cases}\nabla\cdot u_0=0,\\ \nabla P_0+\sum_{i=1}^N\nu_i\rho_i(u_0-u_i)-\nabla\cdot\lambda_0\nabla u_0=0.\end{cases} \tag{3.8}$$

And the temperature equation,

$$\begin{aligned}&\left(\sum_{i=0}^N k_B C_i\rho_i\right)\frac{\partial T}{\partial t}+\left(\sum_{i=0}^N k_B C_i\rho_i u_i\right)\cdot\nabla T+\left(\sum_{i=1}^N k_B\rho_i\nabla\cdot u_i\right)T\\ =&\nabla\cdot k\nabla T+\lambda_0|\nabla u_0|^2+\sum_{i=1}^N\nu_i\rho_i|u_i-u_0|^2+q.\end{aligned} \tag{3.9}$$

Remark 3.2. Equation (3.7) is the modified PNP equation, where particles are driven by the pressure gradient and the mean electrical potential. The chemical potential of ith ion species is given by, $\mu_i(\mathbf{r},t)=\frac{\delta F(\Omega,t)}{\delta\rho_i(\mathbf{r},t)}=k_B T(\mathbf{r},t)\left[\log\rho_i(\mathbf{r},t)+1-C_i\log T(\mathbf{r},t)\right]+z_i\phi(\mathbf{r},t)$. Thus the equations in (3.7) are not equivalent to $\frac{\partial}{\partial t}\rho_i=\nabla\cdot\frac{\rho_i}{\nu_i}\nabla\mu_i$, indicating that when temperature is a variable, we should use pressure instead of using chemical potential.

Remark 3.3. Here we cannot simply assume u_0 is a constant, since the solvent energy and entropy are included. This is different from the original PNP equation where the velocity, energy and entropy of the solvent are not considered. Equation (3.8) might not be solvable without the solvent viscosity λ_0.

Equation (3.7), (3.8), (3.9) form a closed PDE system, which we call Poisson-Nernst-Planck-Fourier (PNPF). We can also check that they satisfy the thermodynamic laws,

$$\begin{cases}\dfrac{d}{dt}U(\Omega,t)=\displaystyle\int_\Omega\left(q+\sum_{i=0}^N\rho_i z_i\frac{\partial\psi(\mathbf{r},t)}{\partial t}\right)d\mathbf{r},\\ \dfrac{d}{dt}S(\Omega,t)=\displaystyle\int_\Omega\left(\frac{q}{T}+\frac{\lambda_0|\nabla u_0|^2}{T}+\sum_{i=1}^N\frac{\nu_i\rho_i|u_i-u_0|^2}{T}+\frac{1}{k}|\frac{j}{T}|^2\right)d\mathbf{r}.\end{cases} \tag{3.10}$$

Here the entropy and internal energy are given by,

$$\begin{cases} S(\Omega,t) = -\displaystyle\sum_{i=0}^{N}\int_{\Omega} k_B\rho_i(\mathbf{r},t)\left[\log\rho_i(\mathbf{r},t) - C_i\log T(\mathbf{r},t) - C_i\right]d\mathbf{r}, \\ U(\Omega,t) = \displaystyle\sum_{i,m=1}^{N}\frac{z_iz_m}{2}\iint_{\Omega}\rho_i(\mathbf{r},t)\rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}' + \sum_{i=0}^{N}k_BC_i\int_{\Omega}\rho_i(\mathbf{r},t)T(\mathbf{r},t)d\mathbf{r}. \end{cases}$$

Note that only for the isothermal system, we can combine the above two thermodynamic laws together, obtaining the free energy dissipation,

$$\frac{d}{dt}F(\Omega,t) = \frac{d}{dt}[U(\Omega,t) - TS(\Omega,t)] = \int_{\Omega}\sum_{i=1}^{N}\rho_iz_i\frac{\partial\psi(\mathbf{r},t)}{\partial t}d\mathbf{r} - T\Delta(\Omega,t). \tag{3.11}$$

When the external field ψ is independent of time, this is equivalent to (2.2),

4. Numerical results

In this section, we present the numerical results of the PNPF equations. Consider a one-dimensional channel with $100mM$ $NaCl$ water solution at room temperature $T_0 = 25^{\circ}C = 298.15K$, so that $N = 2$, $z = \pm e$, where e is the elementary charge. The water velocity vanishes due to the incompressible condition. We choose the parameters from the real experimental data. The diffusion coefficients for Na^+ is $1.334nm^2/ns$ and for Cl^- is $2.032nm^2/ns$ [15]. Water mass density is $10^3kg/m^3$, dielectric permittivity is 78.3 [18] and the specific heat capacity is $75.375J/(mol\cdot K)$ [16]. For an ion, we choose $C_{\pm} = 3$. After nondimensionalizing with $\ell = 1nm$, $\tau = 1ns$, $T_0 = 298.15K$, the whole set of dimensionless equations becomes,

$$\begin{cases} \dfrac{\partial}{\partial t}\rho_i + \nabla\cdot(\rho_iu_i) = 0, \\ \nu_i\rho_iu_i = -\nabla(\rho_iT) - z_i\rho_i\nabla\phi, \\ -\nabla\cdot\epsilon\nabla\phi = 4\pi l_B\displaystyle\sum_{i=\pm}\rho_iz_i, \\ \displaystyle\sum_{i=0,\pm}C_i\rho_i\frac{\partial T}{\partial t} + \sum_{i=\pm}C_i\rho_iu_i\cdot\nabla T + \sum_{i=\pm}\rho_iT\nabla\cdot u_i = \nabla\cdot k\nabla T + \sum_{i=\pm}\nu_i\rho_i|u_i|^2, \end{cases} \tag{4.1}$$

with initial conditions, $\rho_{\pm}(x,0) = \rho_0 = 0.06$ and $T(x,0) = 1$.The dimensionless parameters are, $z_{\pm} = \pm 1$, $C_0\rho_0 = 302$, $1/\nu_+ = 1.334$, $1/\nu_- = 2.032$, $\epsilon = 1$, $l_B = 0.714$. In order to highlight the contribution from the temperature, we choose a relatively small heat conductance $k = 100$. The computational domain is $L = 10$. The boundary conditions for ion density and temperature are Dirichlet, i.e. $\rho_i(0,t) = \rho_i(L,t) = \rho_0$, $T(0,t) = T(L,t) = 1$.

The initial concentration and temperature distribution are all constants in space. Then we apply constant electrical voltage on the boundary, $\phi(0) = 0$ and $\phi(L) = V$, so that the ions immigrate under the electrical field. Under the same setup, for the classical PNP system, where the temperature is a constant, there is no temperature equation; thus we can derive its analytical solution: $\rho_{\mathrm{Na}}^{\mathrm{PNP}}(x,t) = \rho_{\mathrm{Cl}}^{\mathrm{PNP}}(x,t) = 1$, $\phi^{\mathrm{PNP}}(x,t) = \frac{xV}{L}$ and the VI relation is linear.

However, from panel (a) and (b), we can see the ionic distributions from the PNPF model become nonhomogeneous. Both the Na^+ and Cl^- have lower concentrations in between the boundaries. This is related with the local temperature enhanced by the electrodiffusion, as shown in panel (c). With higher voltage applied, the entropy

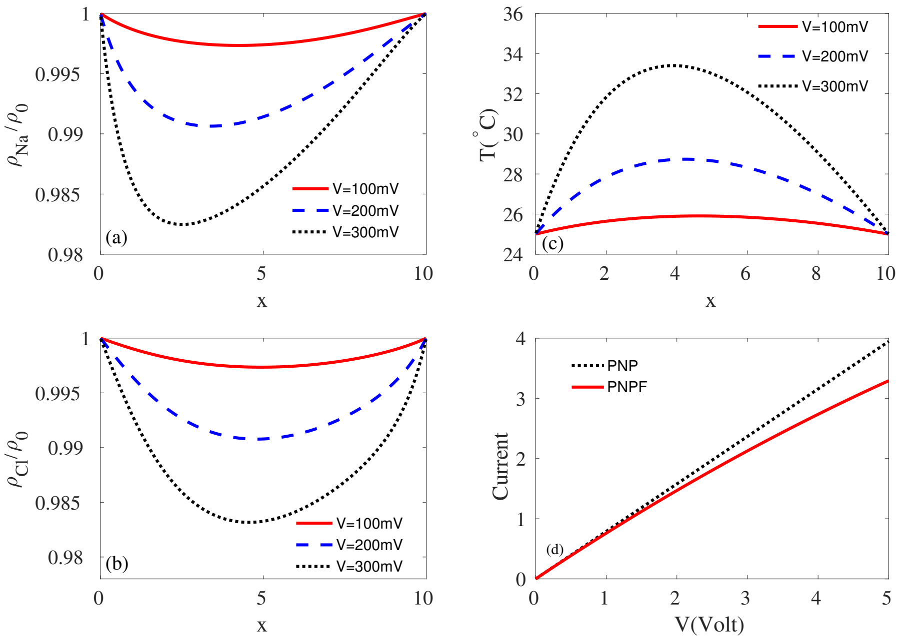

FIG. 4.1. *The steady state properties of the system. (a) Na$^+$ density distribution. (b) Cl$^-$ density distribution. (c) Temperature distribution. (d) Voltage-Current relation of the system. PNP stands for the classical Poisson-Nernst-Planck model, PNPF stands for the Poisson-Nernst-Planck-Fourier system with the temperature effect.*

production or we say the Joule heating effect becomes more significant, so that we have higher temperature distribution and lower ionic concentrations. As a consequence, although the diffusion efficiency increases with the temperature, the overall ionic current reduces as shown in panel (d).

5. Conclusion

The temperature diffusion and mechanical diffusion are coupled for a non-isothermal fluid. We have proposed a self-consistent framework to derive the equations for electrothermal diffusion, which can also be applied and generalized to many other systems with different kinds of inter-molecular interaction. When applied to the imcompressible Navier-Stokes system, we obtain the Navier-Stokes-Fourier equations; when applied to the classical Poisson-Nernst-Planck system, we obtain the Poisson-Nernst-Planck-Fourier equations. Our approach is consistent with the laws of thermodynamics. The constitutive relation for the mechanical fluxes are governed by the force balance equations, where we use the pressure instead of the chemical potential. The thermal distribution is given by the heat equation with additional heat convection and heat sources. Within the framework, all the diffusion coefficients can depend on the space, time and even state variables.

Appendix. In the appendix, we present the mathematical details of Equation (2.11) and Equation (2.17).

Derivation of Equation (2.11). We first compute the time derivative of the internal energy and the kinetic energy. Here, we use Ψ_i to represent $\Psi_i(\rho_i(\mathbf{r},t),T(\mathbf{r},t)$ for short,

$$
\begin{aligned}
&\frac{d}{dt}[U(V,t)+K(V,t)]=\sum_{i=1}^{N} z_i\int_V \frac{\partial \rho_i(\mathbf{r},t)}{\partial t}\left(\psi(\mathbf{r},t)+\sum_{m=1}^{N} z_m\int_\Omega \rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}'\right)d\mathbf{r}\\
&+\sum_{i=1}^{N} z_i\int_V \rho_i(\mathbf{r},t)\frac{\partial}{\partial t}\left(\psi(\mathbf{r},t)+\sum_{m=1}^{N} z_m\int_{\Omega\backslash V} \rho_m(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')d\mathbf{r}'\right)d\mathbf{r}\\
&+\sum_{i=0}^{N}\int_V\left[\left(\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}+\frac{1}{2}m_iu^2\right)\frac{\partial\rho_i}{\partial t}-T\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}+m_i\rho_iu_i\frac{\partial u_i}{\partial t}\right]d\mathbf{r}, \qquad (5.1)\\
=&\sum_{i=0}^{N}\int_V\left[-\left(\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}+\frac{1}{2}m_iu^2+z_i\phi\right)\nabla\cdot(\rho_iu_i)-T\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}+m_i\rho_iu_i\frac{\partial u_i}{\partial t}\right]d\mathbf{r}\\
&+\frac{dW(V,t)}{dt}-\sum_{i=0}^{N}\int_{\partial V}\mathbb{T}_iu_i d\mathbf{r}, \qquad (5.2)\\
=&\sum_{i=0}^{N}\int_V\left[\rho_iu_i\left(m_i\frac{\partial u_i}{\partial t}+\nabla(\frac{m_iu_i^2}{2}+z_i\phi)\right)-\nabla\cdot\left(\rho_iu_i(\frac{1}{2}m_iu_i^2+z_i\phi)\right)\right.\\
&\left.-\left(\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot(\rho_iu_i)-T\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}-\nabla\cdot(\mathbb{T}_iu_i)\right]d\mathbf{r}+\frac{dW(V,t)}{dt}, \qquad (5.3)\\
=&\sum_{i=0}^{N}\int_V\left[\rho_iu_i\left(m_i(\frac{\partial u_i}{\partial t}+u_i\nabla u_i)+z_i\nabla\phi\right)-\left(\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot(\rho_iu_i)\right.\\
&\left.+\nabla\cdot\left(u_i(\Psi_i-T\frac{\partial\Psi_i}{\partial T})\right)-T\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}-\nabla\cdot(\mathbb{T}_iu_i)\right]d\mathbf{r}+\frac{dW(V,t)}{dt}-J_E(V,t), \qquad (5.4)\\
=&\sum_{i=0}^{N}\int_V\left[\rho_iu_i\left(m_i(\frac{\partial u_i}{\partial t}+u_i\nabla u_i)+z_i\nabla\phi\right)-T\frac{\partial^2\Psi_i}{\partial T^2}\left(\frac{\partial T}{\partial t}+u_i\cdot\nabla T\right)-\nabla\cdot(\mathbb{T}_iu_i)\right.\\
&\left.+\left(\Psi_i-\rho_i\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial\Psi_i}{\partial T}+\rho_iT\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot u_i\right]d\mathbf{r}+\frac{dW(V,t)}{dt}-J_E(V,t). \qquad (5.5)
\end{aligned}
$$

Equation (5.1) to (5.2) uses the mass conservation, the definition of the mean electrical potential (2.7) and the work (2.8). Equation (5.3) to (5.4) uses the form of the energy flux (2.10). Comparing with Equation (2.11), we can see,

$$
\begin{aligned}
&\int_V\sum_{i=0}^{N}\left[\rho_iu_i\left(m_i(\frac{\partial u_i}{\partial t}+u_i\nabla u_i)+z_i\nabla\phi\right)-T\frac{\partial^2\Psi_i}{\partial T^2}\left(\frac{\partial T}{\partial t}+u_i\cdot\nabla T\right)-\nabla\cdot(\mathbb{T}_iu_i)\right.\\
&\left.+\left(\Psi_i-\rho_i\frac{\partial\Psi_i}{\partial\rho_i}-T\frac{\partial\Psi_i}{\partial T}+\rho_iT\frac{\partial^2\Psi_i}{\partial T\partial\rho_i}\right)\nabla\cdot u_i\right]d\mathbf{r}=\int_V(q-\nabla\cdot j)d\mathbf{r}. \qquad (5.6)
\end{aligned}
$$

Since the control volume V is arbitrary, we then conclude with Equation (2.11).

Derivation of Equation (2.17)**.** Similarly, we first compute the time derivative of the entropy (2.5),

$$\frac{d}{dt}S(V,t)=-\sum_{i=0}^{N}\int_V\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}\frac{\partial\rho_i}{\partial t}+\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}d\mathbf{r}, \qquad (5.7)$$

$$=\sum_{i=0}^{N}\int_V \frac{\partial^2\Psi_i}{\partial\rho_i\partial T}\nabla\cdot(\rho_i u_i)-\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}d\mathbf{r}, \tag{5.8}$$

$$=\sum_{i=0}^{N}\int_V \rho_i\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}\nabla\cdot u_i+u_i\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}\nabla\rho_i-\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}d\mathbf{r}, \tag{5.9}$$

$$=\sum_{i=0}^{N}\int_V \rho_i\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}\nabla\cdot u_i+u_i\nabla\frac{\partial\Psi_i}{\partial T}-u_i\frac{\partial^2\Psi_i}{\partial T^2}\nabla T-\frac{\partial^2\Psi_i}{\partial T^2}\frac{\partial T}{\partial t}d\mathbf{r}, \tag{5.10}$$

$$=-J_S+\sum_{i=0}^{N}\int_V \left[\left(\rho_i\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}-\frac{\partial\Psi_i}{\partial T}\right)\nabla\cdot u_i-\frac{\partial^2\Psi_i}{\partial T^2}\left(\frac{\partial T}{\partial t}+u_i\nabla T\right)\right]d\mathbf{r}. \tag{5.11}$$

Comparing with Equation (2.16), we can see,

$$\sum_{i=0}^{N}\int_V \left[\left(\rho_i\frac{\partial^2\Psi_i}{\partial\rho_i\partial T}-\frac{\partial\Psi_i}{\partial T}\right)\nabla\cdot u_i-\frac{\partial^2\Psi_i}{\partial T^2}\left(\frac{\partial T}{\partial t}+u_i\nabla T\right)\right]d\mathbf{r}=\widetilde{\Delta}+\frac{q}{T}-\nabla\cdot\frac{j}{T}. \tag{5.12}$$

Taking into account that the control volume V is arbitrary, we then conclude with Equation (2.17).

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