

Nonequilibrium thermodynamics of nonlinear diffusion flux in a nonideal electrolyte solution

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The nonlinear diffusion-dispersion flux of the total mole concentrations in nonideal electrolyte solution is represented by a Korteweg–de Vries (KdV) type of equation in equilibrium. With small perturbations of the KdV equation's coefficients, we can obtain its nonequilibrium steady-state flux. One finding is that the nonequilibrium flux is separated into the nonlinear wave propagation and the diffusion process for entropy production. By means of the perturbation procedure, we further studied the individual chemical component fluxes. The major finding is that in the stationary state, the macroscaled space fluxes between individual components still remain in the no-total-flux system. From this finding, it follows that there is a hierarchy in the thermodynamical flux. Then we obtain Onsager's relations in the nonlinear form and the entropy production for each hierarchy of the flux.

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I. INTRODUCTION

Othmer has established the excess-free-energy theory in nonideal electrolyte solutions in closed systems [1]. Similarly, Caram and Scriven reported on the nonunique reaction equilibria in nonideal systems [2]. Thereafter, Li, Nicolis, and Frisch [3], and Li and Nicolis [4], extended the nonideal solution theory in the passage from equilibrium to nonequilibrium steady state. At present, the studies of not only nonideal chemical reactions in equilibrium but also nonideal chemical instability in nonequilibrium have been made possible on the basis of these theories. Furthermore, Horii derived the nonlinear diffusion flux from the excess free energy [1] via the chemical potential, and then, the nonlinear diffusion theory was introduced into chemical instabilities in nonideal systems [5]. As a consequence, the chemical instability due to the effects of its nonlinearity is almost that of the classic theories which have been established by Prigogine and Nicolis [6] and by Prigogine and Lefever [7] in ideal systems [8]. However, an important finding concerning the nonlinear diffusion-dispersion flux offered us the motivation to reconsider various relations in nonequilibrium thermodynamics from a different point of view. This study is started with the basic finding that the total mole concentration flux is represented by a Korteweg–de Vries (KdV) equation [9] in the absolutely equilibrium conditions. On the basis of this representation, the nonequilibrium steady-state flux is explored. This study may lead to the construction of theoretical connections between nonequilibrium thermodynamical relations and chemical instabilities [10,11].

Thus, the motivation of this study derives from the representation of the equilibrium thermodynamical flux. We consider that the nonlinear diffusion flux, which differs from Fick's law, is a good subject for construction of theories in nonlinear regions of nonequilibrium thermodynamics, which have been handled only in limited reviews [8,11]. This flux, first, poses the thermodynamical-

ly essential problem concerning the tight coupling of the diffusion to the nonlinear wave (soliton) propagation. The former is the irreversible process along with the entropy production, and the latter is the reversible one along with no entropy production. Secondly, therefore, the Lagrangian form of this flux in a velocity field introduced from a thermodynamical version becomes significant. Thirdly, from a more fundamental point of view, we consider that the study of this flux becomes closely connected with concrete understanding of the Onsager's relations between the flux and the force [12] in the nonlinear form. Fourth, the last problem of this flux is concerned with the fluctuations in nonlinear regions of nonequilibrium thermodynamics where Einstein's formula [13] is not satisfied. For the stochastic representation of this flux, the master equation will differ greatly from the classic formulation in an ideal system, which has been established by Lemarchand and Nicolis [14] and by Nicolis and Maleck Mansour [15]. However, only from a macroscopic point of view do we explore this flux. As the consequence, we found that the nonlinear diffusion primarily possesses the essential thermodynamical property for instability. This paper is organized as follows. In Sec. II, the total molar concentration flux in equilibrium is represented by a KdV equation. Section III reports that this total flux, which is perturbed slightly from equilibrium, can be separated into the diffusion and the soliton (nonlinear) wave propagation. In Sec. IV, we further explore the individual component fluxes by the perturbation procedures. Section V discusses the entropy production and the excess entropy production for this flux in relation to its hierarchy.

II. NONLINEAR DIFFUSION FLUX IN EQUILIBRIUM

The excess free energy in nonideal solution is given by [1]

$$G_e = \sum_{\substack{i,j \\ i \leq j}} \omega_{ij} \frac{n_i n_j}{n}, \quad (2.1)$$

where ω_{ij} is a parameter characterizing the nonideal interchange energy between components i and j , and n_k is the mole number of component k . It follows from (2.1) that the composition-dependent activity coefficients $\gamma_k(n)$ are obtained by [1,3]

$$k_B T \ln \gamma_k(n) = \sum_{\substack{i,j \\ i \leq j}} \omega_{ij} (\delta_{jk} X_i + \delta_{ik} X_j - X_i X_j), \quad (2.2)$$

where X_k denotes the mole fraction of component k ($X_k = n_k/n$), and k_B , T , and δ_{jk} represent, respectively, the Boltzmann constant, temperature (K), and the Kronecker delta. From (2.1) and (2.2), we explore the phenomenological relationship between the diffusion flux, denoted by \mathbf{J}_{X_i} for component i , and the diffusion force, $\nabla(\mu_i/T)$ (μ_i denotes the chemical potential), under an isothermal and isobaric condition [16],

$$\mathbf{J}_{X_i} = -L_{ij} \left[\nabla \frac{\mu_i}{T} \right]_{T,P}, \quad (2.3)$$

where L_{ij} is Onsager's coefficient, so that we obtain [5]

$$\mathbf{J}_{X_i} = \sum_j D_{ij}(X_i) \nabla X_j + D_i^*(X_j) \nabla X_i, \quad (2.4)$$

where

$$D_{ij}(X_i) = \xi_{ij} X_i, \quad (2.5)$$

$$D_i^*(X_j) = \sum_j \xi_{ij} X_j - \xi_{ij} \delta_{ij}, \quad (2.6)$$

and

$$\begin{aligned} \xi_{ij} &= -\frac{L_{ij}}{T} \frac{\partial \mu_i}{\partial X_j} \\ &= -\frac{L_{ij}}{T} \frac{\partial^2 G_e}{\partial X_i \partial X_j} \left[\frac{\partial^2 G_e}{\partial X_i \partial X_j} > 0 \right] \end{aligned} \quad (2.7)$$

for thermodynamical stability in equilibrium. Thus, in a nonideal system with excess free energy, the diffusion flux is represented by the two kinds of nonlinear diffusion terms [5].

For exploring the diffusion-dispersion relation in a nonideal system [5], introducing the dispersion term $\nabla^4 X_i$, Eq. (2.4) is now cast into

$$\mathbf{J}_{X_i} = \sum_j D_{ij}(X_i) \nabla X_j + D_i^*(X_j) \nabla X_i - \Lambda_i \nabla^2 \nabla X_i. \quad (2.8)$$

In the absolutely equilibrium conditions for Onsager's reciprocity [12], we now give the values to the coefficients in (2.5) and (2.6); $\xi_{ij} = -\xi^0$ and $\xi_{ii} = D_i = D^0$ for all i and j , and also $\Lambda_i = \Lambda^0$ in (2.8). Then, it follows from inserting the modified relations of (2.5) and (2.6) into (2.8) that

$$\mathbf{J}_{X_i} = -\xi^0 \sum_j (X_i \nabla X_j + X_j \nabla X_i) - D^0 \nabla X_i - \Lambda^0 \nabla^2 \nabla X_i. \quad (2.9)$$

Now, introducing another notation of $\sum_k X_k = U$, the total flux of \mathbf{J}_{X_i} reads

$$\mathbf{J} = \sum_i \mathbf{J}_{X_i} = -\xi^0 U \nabla U - D^0 \nabla U - \Lambda^0 \nabla^2 \nabla U. \quad (2.10)$$

For exploring the stationary flux, we take the transform of $|r| - ct = \rho$. It follows from inserting (2.10) into the continuum equation, $\partial_t U + \text{div} \mathbf{J} = 0$, that the flux reads

$$cU + (\xi^0 U + D^0) \partial_\rho U + \Lambda^0 \partial_\rho^3 U = 0, \quad (2.11)$$

where $\mathbf{J} = \mathbf{0}$ in equilibrium.

In the case of $\xi^0 = 0$, Eq. (2.11) represents the linear form of \mathbf{J} in an ideal system. Obviously, in an ideal system the spatial distribution of the total mole concentration U is homogeneous. Alternatively, if $D^0 = \epsilon^2$, then (2.11) is the stationary form of the KdV equation [9]. In equilibrium where no gradient of U exists ($\partial_\rho U = 0$), the spatial distribution of the total concentrations is also homogeneous in the nonideal system. However, (2.11) indicates that any small deviation from equilibrium gives rise to the inhomogeneous spatial distribution in the perturbed system.

III. NONLINEAR DIFFUSION-DISPERSION FLUX IN NONEQUILIBRIUM

In this section we explore the nonlinear diffusion-dispersion flux in nonequilibrium. Onsager's conditions for nonequilibrium, $\xi_{ij} \neq \xi_{ji}$ [12], admit variations of the nonlinear diffusion coefficients ξ . The primary purpose is to understand the distinctions between equilibrium flux and nonequilibrium steady-state flux. For this purpose we explore the total concentration flux in the perturbed system under the condition of small deviations from equilibrium values, ξ^0 , D^0 , and Λ^0 . Since the individual component fluxes are perturbed slightly from equilibrium, the total flux is represented by small deviation of U in (2.10). The flux reads

$$\begin{aligned} \mathbf{J} &= -(\xi^0 + \delta\xi)(U^0 + \delta U) \nabla(U^0 + \delta U) \\ &\quad - (D^0 + \delta D) \nabla(U^0 + \delta U) - (\Lambda^0 + \delta\Lambda) \nabla^2 \nabla(U^0 + \delta U), \end{aligned} \quad (3.1)$$

where $\delta\xi$, δD , and $\delta\Lambda$ are, respectively, the average of deviations $\delta\xi_{ij}$, δD_i , and $\delta\Lambda_i$ in the individual component fluxes, and U^0 is the equilibrium value. \mathbf{J} in (3.1) is divided into \mathbf{J}_0 , which is the same as (2.10), and its deviation part,

$$\begin{aligned} \delta\mathbf{J} &= -(\xi^0 + \delta\xi)(U^0 + \delta U) \nabla \delta U - (D^0 + \delta D) \nabla \delta U \\ &\quad - (\Lambda^0 + \delta\Lambda) \nabla^2 \nabla \delta U. \end{aligned} \quad (3.2)$$

Our concern is thus the deviation flux $\delta\mathbf{J}$ in the nonequilibrium steady state. First of all, we explore the total flux of U in nonequilibrium by the following procedure:

$$\partial_t (\partial_t U + \text{div} \mathbf{J}) = 0, \quad (3.3)$$

$$\nabla (\partial_t U + \text{div} \mathbf{J}) \mathbf{e} = \mathbf{0}, \quad (3.4)$$

where

$$\mathbf{J} = -\xi U \nabla U - D \nabla U - \Lambda \nabla^2 \nabla U \quad (3.5)$$

with the eigenvector \mathbf{e} . It follows from inserting (3.5) into the linear combination of (3.3) and (3.4) that

$$\nabla \cdot \left[\partial_t U \mathbf{e} + \frac{1}{\tau} (\mathbf{J} + \xi U \nabla U + D \nabla U + \Lambda \nabla^2 \nabla U) \right] + \partial_t^2 U + \nabla^2 \mathbf{J} \cdot \mathbf{e} = 0, \quad (3.6)$$

where ∂t is replaced by $1/\tau$ (the inverse of the mean free passage time and $t \gg \tau$). Inserting (3.5) into (3.6), again, it is now cast by

$$\frac{1}{\tau} \nabla \cdot [\tau \partial_t U \mathbf{e} + \xi U \nabla U + \Lambda \nabla^2 \nabla U] + \frac{1}{\tau} [-\partial_t U + D \nabla^2 U] + \partial_t^2 U - \nabla^2 (\xi U \nabla U + D \nabla U + \Lambda \nabla^2 \nabla U) \cdot \mathbf{e} = 0. \quad (3.7)$$

Equation (3.7) represents the three kinds of dynamics for U . First, if we set $\tau^{-1}[\] = 0$ in the first term, then with the transform of ∇ to $\partial_\rho \mathbf{e}$, we obtain the Korteweg–de Vries equation of a soliton. The second term, setting $[\] = 0$, represents obviously the linear diffusion. The others represent a phenomenon like nonlinear wave propagation. The first and second square brackets for $\partial_t U$ and the remaining parts for $\partial_t^2 U$ indicate that the changes in the total molar concentrations U are the soliton propagation, the diffusion obeying Fick's law, and the nonlinear wave propagation. If $\xi = 0$ and $\Lambda = 0$, then (3.7) represents simply the diffusion in an ideal system.

Secondly, for the further exploration of the nonlinear diffusion-dispersion flux of U , we introduce the velocity field \mathbf{c} in nonequilibrium. In this case, by means of the Lagrangian differential, the continuum equation reads

$$\frac{DU}{Dt} - (\mathbf{c} \cdot \nabla) U + \text{div} \mathbf{J}^D = 0, \quad (3.8)$$

where \mathbf{c} is the velocity of the center of the total mass. In (3.8), the term $(\mathbf{c} \cdot \nabla) U$ is the reversible process. It follows from inserting (3.5) into (3.8) that the Lagrangian differential form of U is

$$\frac{DU}{Dt} = (\mathbf{c} \cdot \nabla) U + [\xi \nabla \cdot (U \nabla U) + D \nabla^2 U + \Lambda \nabla^4 U]. \quad (3.9)$$

By the transforms of ∇ to $\partial_\rho \mathbf{e}$ and \mathbf{c} to \mathbf{c}' ($\mathbf{e} \cdot \mathbf{e}' = \mathbf{e}' \cdot \mathbf{e} = 1$), Eq. (3.9) is cast by

$$J_{(\rho)} = [cU + \xi U \partial_\rho U + \Lambda \partial_\rho^3 U] + D \partial_\rho U, \quad (3.10)$$

where $J_{(\rho)}$ denotes the Lagrangian differential form of the flux in the transformed coordinate ρ . The nonlinear part in square brackets in (3.10) is the KdV equation, and then $\text{div} \mathbf{J}^D$ in (3.8) represents the diffusion and the soliton propagation. Thus, we conclude that the nonlinear diffusion-dispersion flux of U in nonequilibrium is sorted into the reversible process due to the soliton propagation and the irreversible process due to the diffusion.

Thirdly, for understanding the nonlinear diffusion-dispersion flux in a nonequilibrium steady state, we explore the small deviations from the equilibrium flux (2.10) by the perturbation procedure. The coefficients of the individual component fluxes are given by the sets of $\{\xi_{ij}\}$, $\{D_i\}$, and $\{\Lambda_i\}$ which are deviated slightly from the equilibrium values ξ^0 , D^0 , and Λ^0 in (2.10). Only small variations of these coefficients are admitted for the individual component fluxes in nonequilibrium. Under these condi-

tions, the perturbation to the total flux is also limited to the small deviations from the equilibrium values, ξ^0 , D^0 , and Λ^0 . We now define a small parameter ϵ by the characteristic correlation length l and the characteristic length scale [17]. In the mean concentration field, ϵ is defined by $\epsilon = l/L \ll 1$.

For the precise representation of (3.1), the deviations of ξ , D , and Λ are expanded by the ϵ -power series, so that the total concentration U is also expanded by the ϵ -power series. Then, the nonequilibrium steady-state flux read

$$\begin{aligned} \mathbf{J} = & -(\xi^0 + \epsilon \delta \xi)(U^0 + \epsilon \delta U) \nabla(U^0 + \epsilon \delta U) \\ & - (D^0 + \epsilon \delta D) \nabla(U^0 + \epsilon \delta U) \\ & - (\Lambda^0 + \epsilon \delta \Lambda) \nabla^3(U^0 + \epsilon \delta U). \end{aligned} \quad (3.11)$$

To $O(\epsilon^0)$, we find $\mathbf{J}_0 = 0$ in the stationary state, where the flux \mathbf{J}_0 is the same as (2.10) in equilibrium. To $O(\epsilon^1)$, we find the deviation flux

$$\mathbf{J}_1 = -2\xi^0 \delta U \nabla \delta U - \Lambda^0 \nabla^3 \delta U - D^0 \nabla \delta U - 2\xi^0 U' \nabla \delta U, \quad (3.12)$$

where $\nabla \cdot \mathbf{J}_1 = 0$ in stationary state and then, $\nabla U^0 = 0$ ($U' = U^0 - \delta U$). The deviations δU are not Gaussian white noise obeying the Einstein formula [13] because of the nonlinearity, so that not necessarily $\langle \delta U \rangle \neq 0$. In conclusion, the small deviation flux still exists in the nonequilibrium stationary state.

IV. INDIVIDUAL COMPONENT FLUXES IN NONEQUILIBRIUM STATIONARY STATE

In the preceding section we explored the total mole concentration flux under the condition of small deviations from equilibrium. In short, we studied the nonequilibrium steady-state flux in the small perturbation system from equilibrium. In this section we, furthermore, explore the mole fraction flux of the individual components in the system as in (3.11). While the total mole concentration U is spatially homogeneous, there is a possibility that the individual mole fractions are still inhomogeneous in the no-total-flux system. From a thermodynamical point of view [17], we consider that the spatial inhomogeneities give rise to flowing fluxes in the nonequilibrium stationary state. The fluxes are generated owing to the interactions between the individual components as is, in fact, suggested by (3.12). The spatial disorder of the chemical component distributions and their corresponding excess-free-energy distribution can alter ξ_{ij} to be space-dependent coefficients.

We explore the linear and nonlinear diffusion flux \mathbf{J}_i in (2.4), where the coefficients ξ_{ij} and D_i are now space dependent. For the perturbation scheme, we introduce δx_i (deviation from equilibrium \bar{X}_i), ϵ (the smallness parameter $\epsilon = l/L$ [17]), $t = \epsilon^2 T$, and $\mathbf{r} = \epsilon \mathbf{R}$ (the transforms to the macroscaled variables T and \mathbf{R}) by [18]

$$X_i = \bar{X}_i + \epsilon \delta x_i^{(1)} + \epsilon^2 \delta x_i^{(2)}, \quad (4.1)$$

$$\nabla_{\mathbf{r}} \rightarrow \nabla_{\mathbf{r}} + \epsilon \nabla_{\mathbf{R}},$$

$$\partial_t \rightarrow \epsilon^2 \partial_T. \quad (4.2)$$

The linear and nonlinear diffusion coefficients are

$$D_i = D_i^0 + \epsilon \delta D_i, \quad (4.3)$$

$$\xi_{ij} = \xi_{ij}^0 + \epsilon \delta \xi_{ij}. \quad (4.4)$$

To $O(\epsilon^0)$, obviously $\mathbf{J}^{(0)} = \mathbf{0}$. To $O(\epsilon^1)$, we find

$$\begin{aligned} \mathbf{J}_i^{(1)} = & - \sum_j \xi_{ij}^0 \bar{X}_i \nabla_{\mathbf{R}} \bar{X}_j - D_i^0 \nabla_{\mathbf{R}} \bar{X}_i \\ & - \sum_j \delta \xi_{ij} \bar{X}_i \nabla_{\mathbf{r}} \delta x_j^{(1)} - D_i^0 \nabla_{\mathbf{r}} \delta x_i^{(1)}. \end{aligned} \quad (4.5)$$

It follows from $\text{div}_{\mathbf{r}} \mathbf{J}^{(1)} = 0$ that

$$\nabla^2 \delta \mathbf{x}^{(1)} = \mathbf{0}. \quad (4.6)$$

To $O(\epsilon^2)$, we find

$$\begin{aligned} \mathbf{J}_i^{(2)} = & - \sum_j \delta \xi_{ij} \bar{X}_i \nabla_{\mathbf{R}} \bar{X}_j - \delta D_i \nabla_{\mathbf{R}} \bar{X}_i \\ & - \sum_j \xi_{ij}^0 \bar{X}_i \nabla_{\mathbf{r}} \delta x_j^{(2)} - D_i^0 \nabla_{\mathbf{r}} \delta x_i^{(2)}. \end{aligned} \quad (4.7)$$

It follows from

$$\partial_T X_i + \text{div}_{\mathbf{R}} \mathbf{J}_i^{(1)} + \text{div}_{\mathbf{r}} \mathbf{J}_i^{(2)} = 0 \quad (4.8)$$

that

$$\begin{aligned} \partial_T \bar{X}_i - \nabla_{\mathbf{R}} \left[\sum_j \xi_{ij}^0 \bar{X}_i (\nabla_{\mathbf{R}} \bar{X}_j) \right] \\ - D_i^0 \nabla_{\mathbf{R}}^2 \bar{X}_i - \sum_j (\nabla_{\mathbf{r}} \delta \xi_{ij} \bar{X}_i) \cdot \nabla_{\mathbf{R}} \bar{X}_j \\ - (\nabla_{\mathbf{r}} \delta D_i) \cdot \nabla_{\mathbf{R}} \bar{X}_i - f_i^{(2)} = 0, \end{aligned} \quad (4.9)$$

where the fluctuations in the second order $f_i^{(2)}$ are

$$f_i^{(2)} = \sum_j \xi_{ij}^0 \bar{X}_i \nabla_{\mathbf{r}}^2 \delta x_j^{(2)} + D_i^0 \nabla_{\mathbf{r}}^2 \delta x_i^{(2)}. \quad (4.10)$$

It follows from $\partial_T \bar{X}_i = 0$ in the stationary state that (4.9) is cast in the simple representation

$$\text{div}_{\mathbf{R}} \mathbf{J}_i^{(1)} + \mathbf{J}_i^{*(2)} + f_i^{(2)} = 0, \quad (4.11)$$

where the scalar flux $\mathbf{J}_i^{*(2)}$ is the convection,

$$\mathbf{J}_i^{*(2)} = - \sum_j (\nabla_{\mathbf{r}} \delta \xi_{ij} \bar{X}_i) \cdot \nabla_{\mathbf{R}} \bar{X}_j - \nabla_{\mathbf{r}} \delta D_i \cdot \nabla_{\mathbf{R}} \bar{X}_i.$$

Equation (4.11) represents the flux, which is divided into $\text{div}_{\mathbf{R}} \mathbf{J}_i^{(1)}$ and $f_i^{(2)}$ in the irreversible process and $\mathbf{J}_i^{*(2)}$ in the reversible process in the macroscaled coordinates (\mathbf{R}, T) . It follows from (4.11) that only the slow scaled fluxes of individual components exist in the nonequilibrium stationary state.

We consider that this study is significant for approaching chemical instabilities far from equilibrium. In other words, our present purpose is to explore the relationships between each hierarchical flux in nonequilibrium and chemical instability. First of all, if $\Lambda_i \neq 0$, then the soliton propagation occurs in the flux $\mathbf{J}^{(0)}$, because the chemical concentrations are constantly supplied by reactions far from equilibrium. On the other hand, chemical oscillations evolve from the fluctuations' enhancement near the critical point. We need to clarify the relationships between the fluctuations' enhancement and the soliton propagation, in particular, in the case of chemical oscillations represented by the Kuramoto-Sivashinsky equation

[19,20]. Secondly, with respect to the fluxes $\mathbf{J}^{(1)}$ and $\mathbf{J}^{(2)}$, the situations of (3.11) change along with chemical reactions, so that the fluxes may damp. During a long range of period of time T , the concentrations' change in chemical X_i can be represented by nearly zero or $-\kappa X_i$.

To $O(\epsilon^3)$, we find

$$\partial_T^2 \bar{X}_i + \text{div}_{\mathbf{R}} \mathbf{J}_i^{(2)} = 0, \quad (4.12)$$

so that the nonlinear wave part is

$$\epsilon \partial_T^2 X_i - \sum_j [(\delta \xi_{ij} \bar{X}_i + \delta D_i) \partial_{\mathbf{R}}^2 \bar{X}_j] = 0. \quad (4.13)$$

Equation (4.13) represents the small wave propagation and, in short, the standing wave because of $\epsilon \ll 1$. If the wave is thermodynamically stable, then the concentration valley and the free-energy potential wells are very significant in biological systems.

V. ONSAGER'S RELATION FOR THE NONLINEAR DIFFUSION AND ITS ENTROPY PRODUCTION

Transport phenomena such as diffusion have been treated satisfactorily by linear thermodynamics, where the conjugate force is a gradient of the chemical potential. Then, the problems that require an extension of the linear thermodynamical theory to the nonlinear range have been concerned with, for example, a realistic description of chemical reactions. However, from the results in Secs. III and IV, we are confronted with the problem that the nonlinear diffusion, in the coupling between dissipative and convection processes, cannot be described by the methods of linear thermodynamical theory [11]. From (2.3) it follows that the force conjugate to the nonlinear diffusion is derived from the excess free energy, which participates in interactions in nonideal electrolyte solution. Therefore, we identify the force with a gradient of its chemical potential.

Near equilibrium, the entropy production due to the variation of this force, denoted by $d_t P_x$, is computed by [11]

$$\begin{aligned} d_t P_x &= \int dV \sum_i \nabla \cdot \mathbf{J}_i d_t (\mu_i / T) \\ &= \frac{1}{T} \int dV \sum_i \nabla \cdot \mathbf{J}_i d_t \left[\sum_j \omega_{ij} X_i X_j \right] \\ &= - \frac{1}{T} \int dV \sum_{\substack{i,j \\ i < j}} d_t X_i d_t (\omega_{ij} X_i X_j) \\ &= - \frac{1}{T} \int dV \sum_{i,j} \omega_{ij} [X_i d_t X_i d_t X_j + X_j (d_t X_i)^2] \leq 0, \end{aligned} \quad (5.1)$$

where the entropy production due to chemical reactions is ignored.

Equation (5.1) is now cast by

$$\begin{aligned} d_t P_x &= - \frac{1}{T} \int dV \sum_{i,j} \omega_{ij} X_i \delta X_i \delta X_j \leq 0 \\ &= 0 \quad (\text{in the steady state}). \end{aligned} \quad (5.2)$$

The inequality (5.2), while it is in the nonlinear form, is as general as local thermodynamics [8]. Thus, beyond the nonlinearity, we can conclude that $d_t P_x$ satisfies a general inequality extending the theorem of minimum entropy production [10]. Then, the thermodynamical stability for the nonlinear diffusion is given in the nonlinear form:

$$\sum_{i,j} \omega_{ij} X_i \delta X_i \delta X_j \geq 0. \quad (5.3)$$

The evolution criterion by the excess entropy production in linear range indicates that the stability in nonequilibrium is represented by the excess entropy balance equation. We notice that in the entire linear range where the local formulation of thermodynamics remains valid, the quadratic form $\delta^2 S$ has the same structure as in equilibrium [8]. Then, from the result of (5.2) obtained by an extension of the linear theory it follows that in the nonlinear range the excess entropy is

$$\delta^2 S = -\frac{1}{T} \int dV \sum_{i,j} \omega_{ij} X_i \delta X_i \delta X_j. \quad (5.4)$$

The time derivative of $\delta^2 S$ with respect to the nonlinear diffusion is computed, by neglecting chemical reactions term,

$$\begin{aligned} d_t \frac{1}{2} (\delta^2 S) &= -\frac{1}{T} \int dV \left[\sum_{i,j} \delta J_i \cdot \nabla (\omega_{ij} X_i) \delta X_j \right] \\ &= \frac{1}{T} \int dV \left[-\sum_i \delta J_i \cdot \delta (\nabla \xi_{ij} X_i X_j) \right] \\ &= \int dV \sum_i \delta J_i \cdot \delta \chi_i \\ &= \delta_{\chi} P|_{\text{diff}}. \end{aligned} \quad (5.5)$$

It follows from (5.5) that the nonequilibrium steady state becomes unstable as soon as the excess entropy production $\delta_{\chi} P$ becomes negative [10].

From the results in Sec. IV, the conjugate forces to $\mathbf{J}^{(0)}$ and $\mathbf{J}^{(1)}$ are defined as

$$\begin{aligned} \chi_{ij}^{(0)} &= X_i \nabla_r X_j \quad \text{for } k=0, \\ \chi_{ij}^{(1)} &= X_i \nabla_R X_j \quad \text{for } k=1, \end{aligned} \quad (5.6)$$

where k symbolizes a hierarchy. The relations in (5.6) represent the thermodynamical hierarchy where the generalized forces are defined in space \mathbf{r} and in space \mathbf{R} . The flux $\mathbf{J}^{(0)}$ and the force $\chi^{(0)}$ satisfy (5.2), so that the theorem of minimum entropy production holds apparently for $k=0$. Alternatively, because of $\mathbf{J}^{(1)} \neq \mathbf{0}$ in the stationary state, the theorem is no longer valid for $k=1$, and then, (5.5) is applied to the flux and the force for $k=1$ by the linearization.

This thermodynamical conclusion in our paper suggests that since it becomes $\delta_{\chi} P < 0$ (unstable) for $k=1$ far from equilibrium, the flux $\mathbf{J}^{(1)}$ in the macroscaled space \mathbf{R} can play an important role for the system to undergo an instability. Thus, it follows that the nonlinear diffusion possesses primarily a thermodynamical property as a transport phenomenon for instability. In nonideal electrolyte solution, the excess free energy generates the nonlinear diffusion, and furthermore, the spatial disorder of chemicals concentration (and its corresponding excess free-energy inhomogeneity) gives rise to the hierarchy in the thermodynamical flux in nonequilibrium. Through this study we clarified that the methods of an extension of linear thermodynamics to nonlinear range is valid for the nonlinear transport phenomenon.

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