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Phenomenological Equations for Reacting Fluids

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Abstract

A nonlocal phenomenological equation is introduced for a multicomponent fluid where chemical or nuclear reactions are taking place. The reciprocity between the nonlocal linear-coefficients is examined closely. An approximation reduces the nonlocal equation to the ordinary phenomenological relation with correction terms which show clearly a coupling of the reaction with the diffusion and the thermal conduction in an isotropic system.

1. Introduction

As was pointed out in a previous paper[1), thermodynamic forces of scalar character may drive vectorial fluxes even in an isotropic system. Therefore, the chemical reaction does couple thermodynamically with the diffusion, a result which will explain the phenomena of active transport[2) observed in living organisms. Such a coupling is due to a nonlocal phenomenological relation[3) between the forces and the fluxes.

In the present paper, we examine the reciprocity between the nonlocal phenomenological coefficients. The system to be considered is a multicomponent fluid where chemical or nuclear reactions are taking place. We assume that the system is isolated, and that all the components in the system have a common temperature.

The following two sections summarize several concepts necessary to derivation of the phenomenological equation[4). In Section 4, the forces and fluxes are defined, and a linear phenomenological equation is introduced in the nonlocal form. The reciprocal relation between the nonlocal coefficients is obtained in Section 5. The final section treats of a local approximation to the nonlocal equation.

The concept of nonlocal coupling may be applied to the phenomena of energy and particle losses from thermonuclear fusion devices as well as the active transport. Examples will be given elsewhere of the effect of reactions on the vectorial phenomena.

2. Conservation laws

We consider a plasma or an electrolyte solution where nuclear or chemical reactions are taking place. The total energy of the system consists of the internal energy and kinetic energy of the fluid motion. If conservative forces such as electrostatic force are present, we include their potential energies in the internal energy. The differential of the total energy density u* is given by[3)]

$$du^* = du + \Sigma d(\frac{1}{2} m_i n_i v_i^2), \tag{2.1}$$

where u is the internal energy per unit volume, and m_i, n_i and v_i denote the mass, the number density and the velocity of the fluid motion of the component i, respectively.

The first law of thermodynamics can be expressed in a local form as

$$\dot{u}^* + \mathrm{div}\, \mathbf{q}^* = 0 \tag{2.2}$$

where q^* is the total energy flux per unit area and unit time. In the isolated system, the total energy U*

$$U^* = \int u^* d\mathbf{r} \tag{2.3}$$

is conserved.

In the system where chemical or nuclear reactions take place, the rate J_c of reaction c is defined by

$$\dot{n}_i + \mathrm{div}\, n_i \mathbf{v}_i = \sum_c \nu_{ic} J_c, \qquad (2.4)$$

where ν_{ic} denotes the stoichiometric coefficient. The mass conservation law during the reaction c leads to the relation

$$\sum_i m_i \nu_{ic} = 0. \qquad (2.5)$$

Therefore, the total mass M_c

$$M_c = \int \Sigma\, m_i n_i \, d\mathbf{r} \qquad (2.6)$$

is conserved, where the summation is taken over the species participating in the reaction c. The total mass of each nonreactive component is of course conserved.

Since the total force on the system is assumed to vanish, the total momentum $\mathbb{P}$

$$\mathbb{P} = \int \Sigma m_i n_i \mathbf{v}_i \, d\mathbf{r} \qquad (2.7)$$

is independent of time. The total angular momentum $\mathbb{M}$ is also conserved:

$$\mathbb{M} = \int (\mathbf{r} - \mathbf{r}_0) \times \Sigma m_i n_i \mathbf{v}_i \, d\mathbf{r}, \qquad (2.8)$$

where $\mathbf{r}_0$ denotes the center of mass of the whole system.

3. Equilibrium state

In the continuous system, the Gibbs relation can be expressed as[2)]

$$du = Tds + \Sigma\mu_i dn_i, \tag{3.1}$$

where T is the temperature, s is the entropy density, ar˥ μ_i is the chemical potential of the component i. Inserting eq. (2.1), we obtain [3)]

$$Tds = du^* - \Sigma\mu_i^* dn_i - \Sigma n_i m_i \mathbf{v}_i . d\mathbf{v}_i, \tag{3.2}$$

where

$$\mu_i^* = \mu_i + \frac{1}{2} m_i v_i^2 . \tag{3.3}$$

From eq. (3.2), we see that the state variables are the energy density u*, number density n_i and the velocity $\mathbf{v}_i$ of each component.

Conditions for the thermal equilibrium state are derived from maximizing the total entropy of the system with respect to the state variables which depend on each other through the laws of conservation. With the help of Lagrange's method of undetermined multipliers, we obtain the equilibrium conditions as[3)]

$$T = T^o, \tag{3.4}$$

$$\mu_i = \lambda_i m_i + \frac{1}{2} m_i v_o^2 + \frac{1}{2} m_i[\omega \times (\mathbf{r} - \mathbf{r}_o)]^2, \tag{3.5}$$

$$\mathbf{v}_i = \mathbf{v}_o + \omega \times (\mathbf{r} - \mathbf{r}_o), \tag{3.6}$$

where T^o, $\mathbf{v}_o$, ω and λ_i are constants independent of position.

The condition (3.4) shows that the temperature becomes uniform as expected. The second condition (3.5) means that the chemical potential plus the potential energy of the centrifugal force is uniform at equilibrium. The constant λ_i is common to all the components participating in the same reaction. The third condition (3.6) shows that all components flow with the same velocity, and that the system performs the uniform translation and rotation. Hereafter, we take such a frame of reference as translates and rotates with the system.

For later use, several expressions are mentioned here. From eq. (3.2), we can see the statistical averages$^{5)}$

$$\langle u^*(\mathbf{r}_1)\ \Delta \frac{1}{T(\mathbf{r}_2)} \rangle = -k\ \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{3.7}$$

$$\langle n_i(\mathbf{r}_1)\ \Delta \frac{\mu_j^*(\mathbf{r}_2)}{T(\mathbf{r}_2)} \rangle = k\delta_{ij}\ \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{3.8}$$

$$\langle m_i v_i^{\alpha}(\mathbf{r}_1)\ \Delta \frac{n_j(\mathbf{r}_2) v_j^{\beta}(\mathbf{r}_2)}{T(\mathbf{r}_2)} \rangle = k\delta_{\alpha\beta}\ \delta_{ij}\ \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{3.9}$$

where Δ denotes the deviation of the quantity from its equilibrium value, and k is the Boltzmann constant. As a result of the property of time reversal invariance of the equation of motion for individual particles in the system, the state variables x and y satisfy the relation$^{4)}$

$$\langle \dot{x}y \rangle = \pm \langle x\dot{y} \rangle, \tag{3.10}$$

where the positive or negative sign is taken when xy is an even or odd function of $\mathbf{v}_i$, respectively.

4. Phenomenological equations

The relation (3.2) means that the rate of change of the entropy density is given by

$$\dot{s} = (\dot{u}^* - \Sigma\mu_i{}^*\dot{n}_i - \Sigma n_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i)/T. \tag{4.1}$$

Using eqs. (2.2) and (2.4), we have

$$\begin{aligned}\dot{s} = &- \mathrm{div}(\mathbf{q}T^{-1} + \Sigma n_i \mathbf{v}_i s_i)\\ &+ \mathbf{q}.\nabla T^{-1} + \Sigma J_c A_c{}^* T^{-1}\\ &- \Sigma[m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i.\nabla\mathbf{v}_i) + (\nabla\mu_i)_T]\cdot n_i \mathbf{v}_i T^{-1}.\end{aligned} \tag{4.2}$$

Here s_i is the entropy per one particle of component i, and

$$\mathbf{q} = \mathbf{q}^* - \Sigma n_i \mathbf{v}_i h_i{}^* \tag{4.3}$$

$$A_c{}^* = -\Sigma_i \nu_{ic}\mu_i{}^*, \tag{4.4}$$

$$(\nabla\mu_i)_T = \nabla\mu_i - s_i T^2 \nabla T^{-1}. \tag{4.5}$$

where $h_i{}^*$ defined by $h_i{}^* = \mu_i{}^* + Ts_i$ is the enthalpy per one particle. The quantity $A_c{}^*$ is a 'chemical' affinity, and $\mathbf{q}$ is the reduced heat flux. In a rotating system, the quantities with * include the potential energy of the centrifugal force.

From eq. (4.2), we may define a set of forces and fluxes. That is, the forces are

$$X_t = \nabla T^{-1}, \tag{4.6}$$

$$X_c = A_c{}^* T^{-1}, \tag{4.7}$$

$$X_i = n_i \mathbf{v}_i T^{-1}, \tag{4.8}$$

and the fluxes are

$$Y_t = \mathbf{q}, \tag{4.9}$$

$$Y_c = J_c, \tag{4.10}$$

$$Y_i = - m_i(\dot{\mathbf{v}}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) - (\nabla \mu_i)_T. \tag{4.11}$$

In terms of the forces and fluxes defined above the entropy production is given by

$$\dot{S} = \int (X_t . Y_t + \Sigma X_c Y_c + \Sigma X_i . Y_i) d\mathbf{r}, \tag{4.12}$$

where the integration is taken over the whole system.

The reaction rate Y_c should vanish at equilibrium, because of the principle of detailed balance. With the help of the equilibrium conditions, we can show that the other forces and fluxes vanish at equilibrium$^{3)}$. We may, therefore, assume a linear relation between the forces and fluxes as$^{3)}$

$$Y_a(\mathbf{r}_1) = \int \sum_b L_{ab}(\mathbf{r}_1, \mathbf{r}_2) \cdot X_b(\mathbf{r}_2) d\mathbf{r}_2 . \tag{4.13}$$

Here the integration is performed over the whole system, and the suffixes a and b denote the suffixes t, c and i of the forces (4.6) (4.7) (4.8) and the fluxes (4.9) (4.10) (4.11).

5. Reciprocity

It is proved in this section that the linear coefficients appearing in eq. (4.13) obey the relations

$$\sum_{\alpha\beta} \frac{\partial}{\partial r_1^{\alpha}} \frac{\partial}{\partial r_2^{\beta}} L_{tt}^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\alpha\beta} \frac{\partial}{\partial r_1^{\alpha}} \frac{\partial}{\partial r_2^{\beta}} L_{tt}^{\beta\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.1}$$

$$\sum_{\alpha} \frac{\partial}{\partial r_1^{\alpha}} L_{tc}^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\alpha} \frac{\partial}{\partial r_1^{\alpha}} L_{ct}^{\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.2}$$

$$\sum_{\alpha} \frac{\partial}{\partial r_1^{\alpha}} L_{ti}^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = -\sum_{\alpha} \frac{\partial}{\partial r_1^{\alpha}} L_{it}^{\beta\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.3}$$

$$L_{cd}(\mathbf{r}_1,\mathbf{r}_2) = L_{dc}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.4}$$

$$L_{ci}^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) = -L_{ic}^{\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.5}$$

$$L_{ij}^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = L_{ji}^{\beta\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.6}$$

where the Greek indices denote the tensorial component. The complicated relations (5.1, 2, 3) are a reflection of the fact that only the divergence of the heat flux $\mathbf{q}$ has a physical meaning$^{6)}$. The suffixes c and d indicate the reactions, and i and j the chemical species.

By the use of eqs. (2.2) with (4.3) and (2.4), the phenomenological equation (4.13) is transformed into

$$-\dot{u}^* - \mathrm{div}\,\Sigma n_i \mathbf{v}_i h_i^* = \sum_b \int \nabla_1 \cdot L_{tb}(\mathbf{r}_1,\mathbf{r}_2)\cdot X_b(\mathbf{r}_2)d\mathbf{r}_2, \tag{5.7}$$

$$\dot{n}_i + \mathrm{div}\, n_i \mathbf{v}_i = \sum_{c,b} \int \nu_{ic} L_{cb}(\mathbf{r}_1,\mathbf{r}_2)\cdot X_b(\mathbf{r}_2)d\mathbf{r}_2, \tag{5.8}$$

$$-m_i\dot{\mathbf{v}}_i - [(\nabla\mu_i)_T + m_i v_i\cdot\nabla v_i]$$

$$= \sum_b \int L_{ib}(\mathbf{r}_1,\mathbf{r}_2)\cdot X_b(\mathbf{r}_2)d\mathbf{r}_2, \tag{5.9}$$

where the quantities on the left sides take the values at the position $\mathbf{r}_1$, and ∇_1 denotes the gradient with respect to $\mathbf{r}_1$.

The second terms on the left sides of the above three equations may be written as

$$\mathrm{div}\, n_i \mathbf{v}_i = \mathrm{div}\, T^o X_i, \tag{5.10}$$

$$\mathrm{div}\, \Sigma n_i \mathbf{v}_i h_i^* = \mathrm{div}\, \Sigma h_i^o\, T^o X_i, \tag{5.11}$$

$$(\nabla\mu_i)_T + m_i \mathbf{v}_i\cdot\nabla\mathbf{v}_i = T^o\, \nabla\frac{\mu_i^*}{T} - h_i{}^o T^o\, \nabla\frac{1}{T}\,, \tag{5.12}$$

where index o denotes the equilibrium value, and the higher order terms of the small deviations from the equilibrium values have been disregarded.

We show here a proof of the relation (5.5). Multiplying both sides of eq. (5.8) by $m_j v_j{}^{\alpha}(r_3)$, and taking statistical average, we have, from eq. (3.9),

$$<m_j v_j{}^{\alpha}\,(r_3)\dot{n}_i(r_1)> + kT^o\delta_{ij}\,\frac{\partial}{\partial r_1{}^{\alpha}}\,\delta(r_1 - r_3) = \Sigma\ \nu_{ic}L_{cj}{}^{\alpha}(\mathbf{r}_1,\mathbf{r}_3)k, \tag{5.13}$$

where k is the Boltzmann constant. Similarly, we have from eqs. (5.9) and (3.8)

$$-\ <n_i(r_1)m_j\dot{v}_j{}^{\alpha}(r_3)> - kT^o\delta_{ij}\,\frac{\partial}{\partial r_3{}^{\alpha}}\,\delta(r_1 - r_3) = -\ \Sigma L_{jc}{}^{\alpha}(\mathbf{r}_3,\mathbf{r}_1)\nu_{ic}k, \tag{5.14}$$

Using eq. (3.10), we have

$$\Sigma\ \nu_{ic}L_{cj}{}^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) = -\ \Sigma\ \nu_{ic}L_{jc}{}^{\alpha}(\mathbf{r}_2,\mathbf{r}_1), \tag{5.15}$$

which reduces to the relation (5.5), as the reactions are independent. The other reciprocities can be obtained similarly.

Inserting the linear relation (4.13) into the expression (4.12), we have the entropy production in terms of the forces:

$$\dot{S} = \sum_{a,b} \iint X_a(\mathbf{r}_1)\cdot L_{ab}(\mathbf{r}_1,\mathbf{r}_2)\cdot X_b(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2. \tag{5.16}$$

Accoding to the second law of thermodynamics, the right hand side must not be negative for any values of the forces. This fact limits the coefficient $L_{ab}(\mathbf{r}_1,\mathbf{r}_2)$ to a positive semidefinite 'matrix'. The reciprocities (5.3) and (5.5) show that the terms containing these coefficients cancel each other in eq. (5.16), when the system is not rotating. Therefore, these coefficients may take any values.

6. Local form

In the present section, we regard the system to be homogeneous and isotropic, and apply a short-range approximation to the linear coefficients, in order to make the phenomenological equation (4.13) convenient for practical use. As the distance between $\mathbf{r}_1$ and $\mathbf{r}_2$ of eq. (4.13) increases, the coefficient should vanish rapidly. Therefore, we may assume the coefficient to be of the form

$$L_{ab}(\mathbf{r}_1,\mathbf{r}_2) = \Lambda_{ab}\ \delta(\mathbf{r}). \tag{6.1}$$

where L_{ab} is a tensor or a scalar, Λ_{ab} is a diagonal tensor or a scalar constant, and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. This local approximation is taken for granted in ordinary theories[4). On account of homogeneity and isotropy of the system, we may write the vectorial coefficient as

$$L_{ab}(\mathbf{r}_1,\mathbf{r}_2) = \ell_{ab}(r)\ \mathbf{r}, \tag{6.2}$$

where L_{ab} is a vector, and ℓ_{ab} is a scalar. The local approximation to the vectorial coefficients makes them vanish, a fact which is known as the Curie theorem[4).

Taking into account that $L_{ab}(\mathbb{r})$ is rapidly decreasing function of r, we may expand the force $X_b(\mathbb{r}_2)$ in eq. (4.13) around $\mathbb{r}_1$ in terms of $\mathbb{r}$, and keep up to the first order terms with respect to $\mathbb{r}$. After straightforward calculations, the phenomenological equation (4.13) are reduced to the form

$$Y_t = \Lambda_{tt}X_t + \Sigma\Lambda_{tc}\,\nabla X_c + \Sigma\Lambda_{ti}X_i, \tag{6.3}$$

$$Y_c = \Lambda_{ct}\,\nabla.X_t + \Sigma\Lambda_{cd}X_d + \Sigma\Lambda_{ci}\,\nabla.X_i, \tag{6.4}$$

$$Y_i = \Lambda_{it}X_t + \Sigma\Lambda_{ic}\,\nabla X_c + \Sigma\Lambda_{ij}X_j, \tag{6.5}$$

where all the coefficients are scalar constants. The reciprocal relations

$$\Lambda_{ct} = -\Lambda_{tc},$$

$$\Lambda_{it} = -\Lambda_{ti},$$

are obtained from the reciprocity in the previous section, and the other coefficients are symmetric.

The terms containing ∇ on the right sides of the above phenomenological equations do not appear in the ordinary theory[4]. The existence of such terms is due to the nonlocal coupling, and is closely related to the active transport.

The higher oder terms in the expansion of X_b may be significant in some cases. For example, the second order term of X_j gives the effect of the viscosity, as was pointed out in a previous paper[3]. Adding such a term to the right side of eq. (6.5), we have a hydrodynamic equation of motion for each component of the multicomponent viscous fluid.

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