

Thermodynamic Coupling of Diffusion with Chemical Reaction¹

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On the basis of the nonlocal phenomenological relation between thermodynamic fluxes and forces in continuous systems, it is shown that the vectorial flux couples with the scalar force even in an isotropic system. This result has application to active transport in living organisms and to thermonuclear fusion research.

KEY WORDS: Nonlocal continuum thermodynamics; Curie-Prigogine theorem; active transport; nuclear fusion reaction; Lawson criterion.

1. INTRODUCTION

Thermodynamics of irreversible processes^(1,2) has been investigated extensively and applied successfully to many fields. Recently, nonlocal phenomenological equations were introduced,^(3,4) which is a fundamental contribution to the theories of continua such as elastic bodies and multicomponent fluids.

In the present paper, the concept of nonlocal coupling is applied to a continuous system where chemical reactions are taking place, and it is shown that the Curie-Prigogine theorem⁽¹⁾ does not necessarily hold even in an

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isotropic system. Consequently, vectorial fluxes such as diffusion flows can be driven by scalar forces such as affinities of chemical reactions in the isotropic system. Such a phenomenon may be related closely to the active transport (see, e.g., Ref. 5) in living organisms.

A straightforward consequence of the invalidity of the Curie–Prigogine theorem is that the loss rate of fuel particles from thermonuclear devices depends on the rate of the nuclear fusion reaction, or, inversely, that the reaction rate is influenced by the inhomogeneity of the temperature or particle densities in the device. Therefore, a reexamination must be made of the Lawson criterion⁽⁶⁾ on the power balance in thermonuclear reactors.

In the next section, the implication of the Curie–Prigogine theorem is explained. The nonlocal coupling of the reaction with diffusion is treated in Section 3 to show the invalidity of the Curie–Prigogine theorem.

2. DISSIPATION FUNCTION

The system to be considered is a two-component fluid. It is assumed that the temperature and the pressure are both uniform, and the state of thermal equilibrium is isotropic and homogeneous. In this system there occur two processes: chemical reaction and mutual diffusion. The generalization to multiprocess systems is straightforward.

The most fundamental quantity in the theory of irreversible processes is the entropy production σ , which is defined by the entropy created irreversibly in unit volume and unit time. In the present case where the temperature T is uniform, it is convenient to use instead of σ another quantity, $T\sigma$, called the dissipation function.

The dissipation function in the present system can be written in the form

$$T\sigma = X_0 Y_0 + X_1 \cdot Y_1 \quad (1)$$

where X is called the force and Y the flux, the subscript denoting the tensorial rank of the quantities. The scalar force X_0 is the affinity of the chemical reaction, and the conjugate flux Y_0 is the rate of the reaction. The vectorial force X_1 is the negative gradient of the chemical potential of one component, and the conjugate flux Y_1 is the diffusional flux of the component relative to the other. The choice of fluxes and forces is arbitrary to a certain extent.

The second law of thermodynamics requires that

$$\sigma \geq 0 \quad (2)$$

In addition to (2), the Curie–Prigogine theorem states that each term on the right side of (1) must separately be positive in isotropic systems:

$$X_0 Y_0 \geq 0, \quad X_1 \cdot Y_1 \geq 0 \quad (3)$$

That is, the scalar phenomena are independent of the vectorial phenomena.

In the present paper, however, it is shown that, even in the isotropic system, either $X_0 Y_0$ or $X_1 \cdot Y_1$ can be negative as long as σ is positive. For example, matter can be transported from dilute parts to dense parts, if the accompanying chemical reaction produces entropy sufficient to fulfill the requirement of the second law. Such a phenomenon is known as active transport⁽⁵⁾ in biological systems. However, active transport has been attributed to the anisotropy of the system.

3. NONLOCAL PHENOMENOLOGICAL EQUATION

In the case where the system is near thermal equilibrium, the fluxes are linearly related to the forces. The flux $Y_a(\mathbf{r}_1)$ at a position \mathbf{r}_1 may depend on the forces $X_b(\mathbf{r}_2)$ at different positions \mathbf{r}_2 , which is to be considered as a kind of cross-phenomenon. Therefore, the linear relation can be written in the form

$$Y_a(\mathbf{r}_1) = \sum_b \int l_{ab}(\mathbf{r}_1, \mathbf{r}_2) X_b(\mathbf{r}_2) d\mathbf{r}_2 \quad (4)$$

There is no reason to exclude this nonlocal cross-effect.

If the nonlocal coefficients $l_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ vanish rapidly as the distance $|\mathbf{r}_2 - \mathbf{r}_1|$ of the two points increases, they can be approximated by

$$l_{ab}(\mathbf{r}_1, \mathbf{r}_2) = L'_{ab}(\mathbf{r}) \delta(\mathbf{r}_2 - \mathbf{r}_1) \quad (5)$$

The customary phenomenological equation is based on this local approximation. Only when this approximation is valid does the Curie-Prigogine theorem hold true.

Since the system is uniform and isotropic, the linear coefficients have the forms

$$\begin{aligned} l_{00}(\mathbf{r}_1, \mathbf{r}_2) &= \lambda_{00}(r) \\ l_{01}(\mathbf{r}_1, \mathbf{r}_2) &= \lambda_{01}(r)\mathbf{r} \\ l_{10}(\mathbf{r}_1, \mathbf{r}_2) &= \lambda_{10}(r)\mathbf{r} \\ l_{11}(\mathbf{r}_1, \mathbf{r}_2) &= \lambda'_{11}(r)\mathbf{1} + \lambda''_{11}(r)\mathbf{r}\mathbf{r} \end{aligned} \quad (6)$$

where the functions $\lambda(r)$ are scalars, $\mathbf{1}$ is the unit tensor, and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. If the local approximation (5) holds, then $l_{01} = l_{10} = 0$: hence the Curie-Prigogine theorem.

In general, the scalar functions $\lambda(r)$ may be assumed to decrease rapidly as r increases. Therefore, the force $X_b(\mathbf{r}_1 + \mathbf{r})$ in the integrand of (4) may be expanded and retained up to the second-order terms with respect to \mathbf{r} :

$$X_b(\mathbf{r}_2) = X_b(\mathbf{r}_1) + \mathbf{r} \cdot \frac{\partial}{\partial \mathbf{r}_1} X_b(\mathbf{r}_1) + \frac{1}{2} \mathbf{r}\mathbf{r} : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} X_b(\mathbf{r}_1) \quad (7)$$

On substitution of this expression together with (6) into (4), we can perform the integral to give

$$Y_0 = L_{00}X_{00} + \Lambda_{00} \operatorname{div} \operatorname{grad} X_0 + \Lambda_{01} \operatorname{div} X_1 \quad (8)$$

$$Y_1 = L_{11}X_1 + \Lambda_{10} \operatorname{grad} X_0 + \Lambda'_{11} \operatorname{div} \operatorname{grad} X_1 + \Lambda''_{11} \operatorname{grad} \operatorname{div} X_1 \quad (9)$$

Here, the coefficients L are the customary local phenomenological coefficients, and the coefficients Λ are given by

$$\Lambda_{10}\mathbf{1} = \int \lambda_{10}(r)\mathbf{r}\mathbf{r} \, dr, \quad \text{etc.} \quad (10)$$

$\mathbf{1}$ being the unit tensor.

Since Λ_{10} and Λ_{01} do not necessarily vanish, the fluxes are coupled thermodynamically with the forces of different tensorial rank. Therefore, it is possible that

$$X_0 Y_0 < 0 \quad \text{or} \quad X_1 \cdot Y_1 < 0 \quad (11)$$

as long as $\sigma \geq 0$. Hence, the inequalities (3) do not always hold even in an isotropic system.

The physical meaning of (8) may be understood as follows. The forces X_1 and X_0 depend on the concentration. The existence of the concentration inhomogeneity makes the energy distribution of the molecules deviate from the Maxwellian distribution. The reaction is dependent on the energy of the interacting molecules. In this manner, the reaction rate is influenced by the inhomogeneity of the concentration, which is a driving force of the diffusion flow. Equation (9) shows the effect reciprocal to (8). Thus the diffusion is coupled with the chemical reaction in the isotropic system.

Examples will be given elsewhere of the effect of the nuclear fusion reaction on the heat conduction, thermal diffusion, and ordinary diffusion in a plasma. It is also desirable to investigate the effect of the inhomogeneity of the density and the temperature on the rate of the nuclear fusion reaction in connection with the Lawson criterion⁽⁶⁾ of the power balance.

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