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Energy and entropy equations in coupled nonequilibrium thermal mechanical diffusive chemical heterogeneous system

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Abstract In this paper we give an appropriate energy equation considering the diffusion and the energy production contributions of species for a complex coupled system with chemical reaction. It is shown that the contribution of the mass diffusion on the internal energy is the same whether it is introduced by the mass flow through the outer boundary or by the inner chemical reaction. In addition, the diffusion is a purely irreversible process and does not produce reversible entropy or entropy flow. Based on this theory a new entropy production rate equation is derived for the coupled thermal diffusive chemical heterogeneous system. The evolution equations of the heat conduction and the mass diffusion derived from this theory are fully consistent with the Fourier and Fick's laws.

Keywords Energy equation · Mass diffusion · Chemical reaction · Entropy production rate · Gibbs equation · Evolution equation

1 Introduction

In modern science and technology there are large coupling effects among transports of mass, heat, electric charge and chemical reactions in a complex heterogeneous system. The nonequilibrium thermodynamics together with modern continuum mechanics allow us to construct an efficient theory to understand the coupling multi-field phenomena. There have been extensive studies to discuss the coupling problem in a complex heterogeneous system [1–10]. In the current textbooks and literatures, the energy equation is shown as

$$\begin{aligned} &\rho\dot{u} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \nabla \cdot \boldsymbol{q}, \quad \varepsilon_{ij} = (u_{i,j} + u_{j,i})/2; \quad \text{or} \\ &\mathrm{d}U = \int_V \rho \mathrm{d}u \mathrm{d}V = \mathrm{d}W + \mathrm{d}Q, \\ &\mathrm{d}W = \int_V \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{u} \mathrm{d}V + \int_a \boldsymbol{T} \cdot \mathrm{d}\boldsymbol{u} \mathrm{d}\boldsymbol{a}, \\ &\mathrm{d}Q = -\int_a \boldsymbol{q} \cdot \boldsymbol{n} \mathrm{d}a, \end{aligned} \tag{1}$$

where $\mathrm{d}U$ is the internal energy rate, $\mathrm{d}W$ is the external work rate done on the medium, $\mathrm{d}Q$ is the heat rate supplied by the environment, u is the internal energy density, $\boldsymbol{f}$ is the mechanical body force, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, $\boldsymbol{\varepsilon}$ is the strain tensor, $\boldsymbol{q}$ is the heat flow vector, $\boldsymbol{T} = \boldsymbol{\sigma} \cdot \boldsymbol{n}$ is the surface traction, and $\boldsymbol{n}$ is the external normal of the surface. In Eq. (1), a comma in the subscript followed by index i indicates partial differentiation with respect to x_i, such as $u_{i,j} = \partial u_i / \partial x_j$. Though it is usually assumed that the total mass is constant in a chemical reaction process, the energy exchange with environment is occurred. The mass of each species of the system can be varied. In other words, each subsystem consisted of a species is an open subsystem, with its own mass diffusion and energy production phenomena. For different species the corresponding chemical potential is different, so the total diffuse energy and energy production of the system, which are the sum of all the species, are varied. Therefore the mass exchange and energy exchange in the subsystems as well as the whole system should be considered. However, Eq. (1) does not include the diffusion energy and the energy production produced by the species of the complex system. Therefore

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the corresponding entropy production rate equation and evolution equation based on Eq. (1) are also not fully appropriate.

In this paper we give an energy conservation equation, which considers the mass exchange and energy exchange of the species in the system, and derive the new entropy production rate equation and evolution equation for a system with internal chemical reaction. A systematic discussion of the nonequilibrium thermodynamics in coupled thermal mechanical diffusive chemical heterogeneous system is presented.

2 A general form of the conservation equation

Why the diffuse energy and energy production produced by the species in the chemical reaction system have not been considered in the energy conservation equation in the previous literatures? The reason may be that the internal boundary introduced by the chemical reaction was not addressed. In this section we emphasize the internal boundary and discuss the general case for the conservation equation.

The conservation equation of a continuous single value physical variable A in V can be derived as follows. Figure 1 shows an open system with the volume V, the fixed outer boundary a^0 and inner boundary a^{I}. Let $\boldsymbol{v}$ be the motion velocity vector of A and the production rate of A is $\dot{\eta}(P)$ at a point P in V. Under theses conditions, the conservation equation of A is

$$\int_V (\partial A/\partial t)\mathrm{d}V = -\int_a A\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a + \int_V \dot{\eta}\mathrm{d}V, \quad a = a^0 + a^{\mathrm{I}}. \tag{2}$$

When A is a continuous single value function in V, the Gauss divergence theorem can be expressed as

$$\int_a A\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a = \int_V \nabla\cdot(A\boldsymbol{v})\mathrm{d}V, \tag{3}$$

where ∇ is the vector differential operator delta. Since the volume is arbitrary in Eq. (2), we obtain the local conservation equation of A:

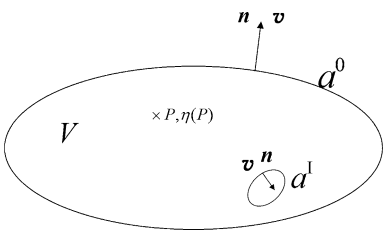

Fig. 1 The stretch for derivation of the mass equation

$$\partial A/\partial t + \nabla\cdot(A\boldsymbol{v}) = \dot{\eta}. \tag{4}$$

When a^{I} approaches zero, the mass flow through its boundary is nonzero, i.e., $\lim_{\max\, l\to 0}\oint_a A\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a \neq 0$, where l is the inner size of a^{I}. In the limit it represents a point source or sink of A. Consider a contour surrounding a point of distributed source A, the conservation equation of the variable A is still expressed by Eq. (4). This concept is extensively used in the physics, mathematics and engineering.

3 The mass conservation equation

In this section we show that the usual mass conservation equation is still valid when the internal boundaries are considered. For a complex thermal mechanical diffuse chemical reaction heterogeneous system with N species, the mass conservation equation can be obtained by using the theory given in Sect. 2. In this case for a species i, A represents the partial mass $m^{(i)}$ or partial density $\rho^{(i)}$. From Eq. (4), we get

$$\begin{aligned}
&\partial\rho^{(k)}/\partial t + \nabla\cdot\left(\rho^{(k)}\boldsymbol{v}^{(k)}\right) = \dot{\eta}^{(k)}; \quad \text{or}\\
&\dot{\rho}^{(k)} + \rho^{(k)}\nabla\cdot\boldsymbol{v}^{(k)} = \dot{\eta}^{(k)}; \quad k = 1-N,\\
&\rho^{(k)} = \frac{M^{(k)}}{V} = \rho c^{(k)}, \quad M = \sum_{k=1}^{N} M^{(k)},\\
&\rho = \sum_{k=1}^{N}\rho^{(k)} = \frac{M}{V},\\
&c^{(k)} = \frac{\rho^{(k)}}{\rho} = \frac{M^{(k)}}{M}, \quad \sum_{k=1}^{N} c^{(k)} = 1,
\end{aligned} \tag{5}$$

where $M^{(k)}$, $\rho^{(k)}$, $c^{(k)}$ and $\dot{\eta}^{(k)}$ are the mass, partial density, the mass (density) fraction or the (mass) concentration and the mass or density production rate of the species k, respectively, M is the total mass, V is the total volume. Note throughout this paper, we use superscript to denote the number of the species and the number of the chemical reaction and the summation notation is written in evidence, i.e., the summation rule for the repeated indices is not used, such as in Eq. (5).

Let $\boldsymbol{v}$ be the centroid velocity of an element, and let $\boldsymbol{w}^{(k)}$ and $\boldsymbol{J}^{(k)}$ be the diffuse velocity and the mass flow or the mass diffusion flux of the species k, respectively. It is noted that the velocity of a species k is $\boldsymbol{v}^{(k)}$, but the velocity of an element is $\boldsymbol{v}$, so when we discuss the entire behavior of an element, for the species k the diffuse velocity is $\boldsymbol{w}^{(k)} = \boldsymbol{v}^{(k)} - \boldsymbol{v}$ and the mass flow is $\boldsymbol{J}^{(k)} = \rho^{(k)}(\boldsymbol{v}^{(k)} - \boldsymbol{v})$, i.e. [5–8]: