

Transient Continuum Mechanics and Chemomechanics

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A transient chemomechanical coupling formulation for solid continuum is presented. The second-order rate and the characterized time are introduced to include the transient effect through Taylor expansion. The transient Reynold's transport theorem is derived with the new products or material elimination considered. Based on conservation laws and the second law of thermodynamic, we state a consistent Helmholtz-energy-based framework. The transient field equations take mechanical and chemical contributions and microscopic time into account. Either microscopic time or chemical reactions leads to the unsymmetry of the stress tensor. The relationship of Helmholtz energy and constitutive properties, the evolution equations, and the entropy are consistent with the classical continuum thermodynamics and the constitutive theory in continuum mechanics. Further, the transient equations of thermal conduction and diffusion with finite velocity are naturally derived rather than postulated, and a comparison with the existing theories is discussed. [DOI: 10.1115/1.4054061]

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1 Introduction

There is now a great deal of interest in the study of the transient phenomenon, due to its many applications in modern science and technology, including integrated circuits, thermal protective systems, and lithium ion batteries. The transient behavior of complex materials systems often results from the simultaneously occurring coupling chemomechanical processes, such as heat transfer, mass diffusion, chemical reactions, and mechanical deformation. The applications of short-pulse lasers in the fabrication of sophisticated microstructures, syntheses of advanced materials, and measurements of the thin film properties are typical transient chemomechanical processes [1]. In the problems with microscopic time and size, the mass diffusion [2,3] and heat conduction [4,5] will propagate with finite velocity, and the transient effect should be considered.

Researches into this kind of phenomenon are traditionally based on the Fourier law of heat conduction and the Fick law of diffusion. The two laws were based on the statistical principle, and the propagation with an infinite velocity is assumed. Such traditional theory is precise enough for the conventional steady processes. However, for some transient phenomena, mass and heat transfer accompanied with chemical reaction under high temperature or extremely large diffusion flux, it will lead to errors to some extent, even contradict physical observations. Therefore, it is necessary to discuss the transient effects, diffusion [6,7], and heat conduction [8–12] with finite velocity.

These phenomena may induce irreversible deformations, mass and density changes (new products or materials elimination due to chemical reactions), and consistent variations of the local mechanical and chemical properties. So, the coupling of thermal-mechanical chemical processes is vital for the materials system. Thus, advanced understanding of the coupled chemomechanics is becoming crucial and is gaining momentum and attracting considerable research interest [13]. However, most of the existing coupling formulations are limited to steady processes [14–17]. In this paper, we will develop transient continuum mechanics that considers the microscopic time and coupling between chemistry and mechanics.

The structure of the paper is as follows. In Sec. 2, we introduce modified axioms in biomechanics and extend them to chemomechanics. Based on the Taylor expansion, we define the rate that depends on the characterized time t_c to consider the effect of microscopic time. Section 3 deals with the transient Reynold's transport theorem, which takes the effects of microscopic time and chemical reactions into account. Section 4 derives the transient field equations from fundamental conservation laws considering mechanical and chemical contributions and microscopic time. In Sec. 5, we consider the transient thermal conduction, and a comparison to the existing thermal conduction theory is given. In Sec. 6, the transient diffusion is described. Finally, we present the conclusions in Sec. 7.

2 Axioms of Continuum Mechanics

Biological phenomena are inhomogenous and multiscale (it actually is a chemical process), some of the classical conservation laws do not apply. Fung [18,19] thus modified the axioms of continuum mechanics to biomechanics as follows:

- (1) The system is inhomogenous and multiscale in space, so the definitions of stress and strain should depend on the length scale. Generally, higher-order stress and higher-order strain are introduced, such as strain gradients.
- (2) Material particles are varied. They can be new products or disappear due to growth or chemical reactions, and they can move and exchange neighbors.
- (3) The zero-stress state is often changed due to biological (chemical) processes.

For transient processes and chemomechanics, these modifications still apply. Moreover, in the temporal dimension, the process is inhomogenous and multiscale also. Hence, similar to axiom (i), the definition of the rate should depend on the characterized time t_c to consider the effect of the timescale, i.e., the second-order rate is introduced. Then, using the Taylor expansion, we define the rate as

$$\frac{Du}{Dt} = \lim_{\Delta t \rightarrow t_c} \frac{u(t + \Delta t) - u(t)}{\Delta t} = \frac{du}{dt} + \frac{1}{2} \frac{d^2u}{dt^2} t_c \quad (1)$$

when $t_c = 0$, the term including second-order rate d^2u/dt^2 disappears; Eq. (1) reduces to the classical definition of rate $Du/Dt = \lim_{\Delta t \rightarrow 0} \Delta u/\Delta t = du/dt$. Here, u is a scalar or vector.

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In this paper, we apply the above-mentioned axioms to transient processes and chemomechanics. Especially, we will derive Reynold's transport theorem based on Eq. (1) to consider the transient effect and the chemical reactions.

For simplicity and clear concepts, we limite this work to the simple material (i.e., excluding the higher-order strain) and infinite deformation.

For the description of the fully coupled chemomechanical system, we assume that Nt species construct a solid continuum. We denote the chemical species with index N ($N = 1, \dots, Nt$). The displacement of a particle in the system is denoted by $\mathbf{u}(\mathbf{x}, t)$, and the particle velocity is $\mathbf{v}(\mathbf{x}, t) = \partial \mathbf{u}(\mathbf{x}, t) / \partial t$.

The molar concentration of species N is denoted by c_N , and its molar mass is M_N ; then, we can define the partial density as

$$\rho_\alpha = c_\alpha M_\alpha \quad (2)$$

In this paper, the repeated Latin indices obey Einstein summation convention while the repeated Greek indices do not mean

summation. The density of the system is given as

$$\rho = \sum_{N=1}^{Nt} \rho_N = c_N M_N \quad (3)$$

The mole fractions should satisfy

$$\sum_{N=1}^{Nt} c_N = 1 \quad (4)$$

Due to the above-mentioned relation, only $(Nt-1)$ concentrations are independent.

3 Transient Reynold's Transport Theorem

Considering a chemical or evolving process with the characterized time t_c , Reynold's transport theorem can be derived as

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} \mathbf{y} d\Omega \right) &= \lim_{\Delta t \rightarrow t_c} \frac{1}{\Delta t} \left[\int_{\Omega(\mathbf{x}, t+\Delta t)} \mathbf{y}(\mathbf{x}, t+\Delta t) d\Omega - \int_{\Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t) d\Omega \right] \\ &= \lim_{\Delta t \rightarrow t_c} \frac{1}{\Delta t} \left[\int_{\Omega(\mathbf{x}, t) + \Delta \Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t+\Delta t) d\Omega - \int_{\Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t) d\Omega \right] \\ &= \lim_{\Delta t \rightarrow t_c} \frac{1}{\Delta t} \left[\int_{\Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t+\Delta t) d\Omega - \int_{\Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t) d\Omega \right] + \lim_{\Delta t \rightarrow t_c} \frac{1}{\Delta t} \int_{\Delta \Omega(\mathbf{x}, t)} \mathbf{y}(\mathbf{x}, t+\Delta t) d\Omega \\ &= \int_{\Omega(\mathbf{x}, t)} \left[\frac{\partial \mathbf{y}(\mathbf{x}, t)}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \mathbf{y}(\mathbf{x}, t)}{\partial t^2} \right] d\Omega + \int_{\Gamma} \left(\mathbf{y} + t_c \frac{\partial \mathbf{y}}{\partial t} \right) [(v_k - V_k) n_k] d\Gamma \end{aligned} \quad (5)$$

The derivation of the above equation is similar to that in textbooks [20,21] but using the rate defined in Eq. (1) and taking into account the moving boundary due to chemical reactions or other processes. \mathbf{y} is a scalar or vector field defined on the domain $\Omega(\mathbf{x}, t)$. \mathbf{v} is the particle velocity, and \mathbf{V} is the velocity of the moving boundary Γ of the domain $\Omega(\mathbf{x}, t)$. $\Delta \Omega(\mathbf{x}, t)$ represents the variation of the volume $\Omega(\mathbf{x}, t)$ from mechanical and chemical contributions, which means, in addition to volume deformation, it also includes the new products (with positive direction \mathbf{V}) or material elimination (with negative direction \mathbf{V}) due to chemical reactions during time internal Δt . \mathbf{n} is normal vectors of the boundary Γ . The characterized time t_c represents the time scale that the transient process takes place on, which can be determined by experiments and molecular dynamics simulations. Generally, different process has different characterized time.

If there are no chemical reactions, that means no material is added or reduced, $\mathbf{V} = 0$, then we have

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} \mathbf{y} d\Omega \right) &= \int_{\Omega(\mathbf{x}, t)} \left[\frac{\partial \mathbf{y}(\mathbf{x}, t)}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \mathbf{y}(\mathbf{x}, t)}{\partial t^2} \right] d\Omega \\ &\quad + \int_{\Gamma} \left(\mathbf{y} + t_c \frac{\partial \mathbf{y}}{\partial t} \right) (v_k n_k) d\Gamma \end{aligned} \quad (6)$$

Moreover, if the characterized time t_c is zero, then Eq. (6) is reduced to the classical Reynold's theorem

$$\frac{d}{dt} \left(\int_{\Omega} \mathbf{y} d\Omega \right) = \int_{\Omega(\mathbf{x}, t)} \frac{\partial \mathbf{y}(\mathbf{x}, t)}{\partial t} d\Omega + \int_{\Gamma} \mathbf{y} (v_k n_k) d\Gamma$$

The transient Reynold's theorem (Eq. (5)) describes the non-equilibrium process. When the system evolves to the equilibrium state, the effect of characterized time can be omitted.

4 Conservation Laws and Field Equations

In this section, all the required field equations to describe the transient process in solid continua are derived from the conservation laws.

4.1 Conservation of Mass. For the balance of mass, all the chemical species ($N = 1, \dots, Nt$) are distinguished. To derive the balance of a single species N , the only change in mass of species N in that volume Ω occurs due to a mass source associated with chemical reactions and it can be written as

$$\frac{D}{Dt} \left(\int_{\Omega} c_N d\Omega \right) = \int_{\Omega} v_{Nr} \dot{w}_r d\Omega \quad (r = 1, 2, \dots, n_r) \quad (7)$$

where v_{Nr} is the stoichiometric coefficient of the r th reaction, \dot{w}_r is the r th reaction rate, and n_r is the total number of reactions. Using Reynold's transport theorem (Eq. (5)), one can get

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} c_\alpha d\Omega \right) &= \int_{\Omega} \left(\frac{\partial c_\alpha}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_\alpha}{\partial t^2} \right) d\Omega \\ &\quad + \int_{\Gamma} \left[\left(c_\alpha + t_c \frac{\partial c_\alpha}{\partial t} \right) (v_k^\alpha - V_k) \right] n_k d\Gamma \\ &= \int_{\Omega} \left\{ \left(\frac{\partial c_\alpha}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_\alpha}{\partial t^2} \right) + \nabla \left[\left(c_\alpha + t_c \frac{\partial c_\alpha}{\partial t} \right) (v_k^\alpha - V_k) \right] \right\} d\Omega \end{aligned} \quad (8)$$

where we introduced the mass flux with concentration c_α as

$$\mathbf{J}_\alpha = \left(c_\alpha + t_c \frac{\partial c_\alpha}{\partial t} \right) (\mathbf{v}^\alpha - \mathbf{V}) \quad (9)$$

Here, \mathbf{v}^α is the moving velocity of species α , and $\rho\mathbf{v} = \sum_{N=1}^{Nt} \rho_\alpha \mathbf{v}^\alpha$.

The second integral on the right-hand side of the first line of Eq. (8) denotes the mass flux \mathbf{J}_α through the boundary Γ . Here, we describe the mass flux of a species relative to the velocity of the boundary \mathbf{V} . That distinguishes our description from classical theory which usually does not consider the characterized time and moving of the boundary.

By combining Eqs. (7) and (8), one can obtain the local form of the balance of species mass

$$\frac{\partial c_N}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_N}{\partial t^2} + \nabla \cdot \mathbf{J}_N = v_{Nr} \dot{w}_r \quad (10)$$

Compared to the classical mass balance equation for the irreversible process with chemical reactions [22], Eq. (10) includes the second-order rate of concentration shown in the second term of the left-hand side which is due to the transient effect of the irreversible process, maybe it can be called concentration acceleration. This term is very similar to the inertial concentration which is introduced by Kuang [7,11] to remedy that Fick diffusion theory cannot explain the transient diffusion with finite speed. This work describes naturally the transient diffusion with finite velocity, which we will discuss in Sec. 6.

4.2 Conservation of Linear Momentum. To state the balance of linear momentum, the rates of the partial linear momenta of all species are summed and equate with body forces \mathbf{b} and tractions \mathbf{t} acting on the system, and one obtains

$$\frac{D}{Dt} \left(\int_{\Omega} \rho \mathbf{v} d\Omega \right) = \int_{\Omega} \mathbf{b} d\Omega + \int_{\Gamma} \mathbf{t} d\Gamma \quad (11)$$

By applying Reynold's transport theorem (Eq. (5)), the left-hand side of Eq. (11) can be written as

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} \rho \mathbf{v} d\Omega \right) &= \int_{\Omega} \left\{ \frac{\partial \rho \mathbf{v}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \rho \mathbf{v}}{\partial t^2} \right\} d\Omega \\ &+ \int_{\Gamma} \left[\left(\rho \mathbf{v} + t_c \frac{\partial \rho \mathbf{v}}{\partial t} \right) (v_k - V_k) \right] n_k d\Gamma \end{aligned} \quad (12)$$

The second integral of the right-hand side of Eq. (12) can be expressed as

$$\int_{\Gamma} \left[\left(\rho \mathbf{v} + t_c \frac{\partial \rho \mathbf{v}}{\partial t} \right) (v_k - V_k) \right] n_k d\Gamma = \int_{\Gamma} \sigma_{ik}^V n_k d\Gamma = \int_{\Omega} \nabla \cdot \boldsymbol{\sigma}^V d\Omega \quad (13)$$

where we introduce $\sigma_{ik}^V = \left(\rho v_i + t_c \frac{\partial \rho v_i}{\partial t} \right) (v_k - V_k)$, which can be thought as the residual stress or body stress due to the convective diffusion [23] and chemical reactions. This supports the axiom (iii), i.e., the zero-stress state is often changed. The traction on the boundary can be balanced by the stress, i.e.,

$$\int_{\Gamma} \mathbf{t} d\Gamma = \int_{\Gamma} \boldsymbol{\sigma} \cdot \mathbf{n} d\Gamma = \int_{\Omega} \nabla \cdot \boldsymbol{\sigma} d\Omega \quad (14)$$

Thus, the balance of the linear momentum is expressed as

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \rho \mathbf{v}}{\partial t^2} = \nabla \cdot (\boldsymbol{\sigma} - \boldsymbol{\sigma}^V) + \mathbf{b} \quad (15)$$

If the timescale t_c approaches 0, then

$$\frac{\partial \rho \mathbf{v}}{\partial t} = \nabla \cdot (\boldsymbol{\sigma} - \boldsymbol{\sigma}^V) + \mathbf{b}$$

Moreover, if the boundary is static, the above equation returns to the classical equilibrium equation.

4.3 Conservation of Angular Momentum. The conservation of angular momentum states that the rate of the angular momentum is equal to the total torque, i.e.,

$$\frac{D}{Dt} \left(\int_{\Omega} \mathbf{x} \times \rho \mathbf{v} d\Omega \right) = \int_{\Omega} (\mathbf{x} \times \mathbf{b}) d\Omega + \int_{\Gamma} (\mathbf{x} \times \mathbf{t}) d\Gamma \quad (16)$$

The rate of the angular momentum is derived as

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} \mathbf{x} \times \rho \mathbf{v} d\Omega \right) &= \int_{\Omega} \left\{ \frac{\partial (\mathbf{x} \times \rho \mathbf{v})}{\partial t} + \frac{t_c}{2} \frac{\partial^2 (\mathbf{x} \times \rho \mathbf{v})}{\partial t^2} \right\} d\Omega \\ &+ \int_{\Gamma} \left[(\mathbf{x} \times \rho \mathbf{v}) + t_c \left(\frac{\partial (\mathbf{x} \times \rho \mathbf{v})}{\partial t} \right) \right] (v_k - V_k) n_k d\Gamma \\ &= \int_{\Omega} \mathbf{x} \times \left\{ \frac{\partial \rho \mathbf{v}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \rho \mathbf{v}}{\partial t^2} \right\} d\Omega \\ &+ \int_{\Gamma} \mathbf{x} \times \left\{ \left[\rho \mathbf{v} + t_c \left(\frac{\partial \rho \mathbf{v}}{\partial t} \right) \right] (v_k - V_k) \right\} n_k d\Gamma \\ &= \int_{\Omega} \mathbf{x} \times (\nabla \cdot (\boldsymbol{\sigma} - \boldsymbol{\sigma}^V) + \mathbf{b}) d\Omega + \int_{\Omega} (\boldsymbol{\delta} \times \boldsymbol{\sigma}^V + \mathbf{x} \times \nabla \cdot \boldsymbol{\sigma}^V) d\Omega \end{aligned} \quad (17)$$

Here, we utilized the balance of linear momentum of Eq. (15) and the following derivation

$$\begin{aligned} \int_{\Gamma} \mathbf{x} \times \left\{ \left[\rho \mathbf{v} + t_c \left(\frac{\partial \rho \mathbf{v}}{\partial t} \right) \right] (v_k - V_k) \right\} n_k d\Gamma &= \int_{\Gamma} e_{ijk} x_j \sigma_{km}^V n_m d\Gamma \\ &= \int_{\Omega} \nabla \cdot (\mathbf{x} \times \boldsymbol{\sigma}^V) d\Omega = \int_{\Omega} (\boldsymbol{\delta} \times \boldsymbol{\sigma}^V + \mathbf{x} \times \nabla \cdot \boldsymbol{\sigma}^V) d\Omega \end{aligned}$$

where e_{ijk} is the permutation tensor.

The torque of the tractions computes to

$$\begin{aligned} \int_{\Gamma} \mathbf{x} \times \mathbf{t} d\Gamma &= \int_{\Gamma} \mathbf{x} \times (\boldsymbol{\sigma} \cdot \mathbf{n}) d\Gamma = \int_{\Omega} \nabla \cdot (\mathbf{x} \times \boldsymbol{\sigma}) d\Omega \\ &= \int_{\Omega} (\boldsymbol{\delta} \times \boldsymbol{\sigma} + \mathbf{x} \times \nabla \cdot \boldsymbol{\sigma}) d\Omega \end{aligned} \quad (18)$$

Then, by combining Eqs. (16)–(18), one can reach

$$\int_{\Omega} [\boldsymbol{\delta} \times (\boldsymbol{\sigma} - \boldsymbol{\sigma}^V)] d\Omega = 0 \quad (19)$$

The above equation results in the symmetry condition

$$[\boldsymbol{\sigma} - \boldsymbol{\sigma}^V] = [\boldsymbol{\sigma} - \boldsymbol{\sigma}^V]^T \quad (20)$$

From Eq. (20), one can find that either of the transient effect and chemical reactions results in $(\boldsymbol{\sigma}^V)^T \neq \boldsymbol{\sigma}^V$ and the unsymmetry of the stress tensor $\boldsymbol{\sigma}$. Conversely, without the characterized time t_c and boundary motion ($\mathbf{V} = 0$), $(\boldsymbol{\sigma}^V)^T = \boldsymbol{\sigma}^V$, then $\boldsymbol{\sigma}^T = \boldsymbol{\sigma}$, this aligns with the standard result, i.e., symmetrical stress tensor.

4.4 Conservation of Energy. For the balance of energy, the change of total internal energy U , as well as kinetic energy K , is equal to the power supply in body Ω due to heat Q and the work W done by the external force, i.e.,

$$\frac{D}{Dt} (U + K) = W + Q \quad (21)$$

The left-hand side of Eq. (21) describes the rate of internal energy density e_N and kinetic energy density of each species

$$U = \int_{\Omega} \rho_N e_N d\Omega, \quad K = \int_{\Omega} \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} d\Omega \quad (22)$$

we have to again apply Reynold's transport theorem through Eq. (5) and obtain

$$\begin{aligned}
 \frac{D}{Dt} U &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\frac{\partial(\rho_{\alpha} e_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} e_{\alpha})}{\partial t^2} \right] d\Omega + \int_{\Gamma} \left[\rho_{\alpha} e_{\alpha} + t_c \frac{\partial(\rho_{\alpha} e_{\alpha})}{\partial t} \right] (v_k^{\alpha} - V_k) n_k d\Gamma \right\} \\
 &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\frac{\partial(\rho_{\alpha} e_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} e_{\alpha})}{\partial t^2} \right] d\Omega + \int_{\Omega} M_{\alpha} (\nabla e_{\alpha} \cdot \mathbf{J}_{\alpha} + e_{\alpha} \nabla \mathbf{J}_{\alpha}) d\Omega + \int_{\Omega} t_c \nabla(\rho_{\alpha} \mathbf{e}_v^{\alpha}) d\Omega \right\} \\
 &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\left(\frac{\partial(\rho_{\alpha} e_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} e_{\alpha})}{\partial t^2} \right) + M_{\alpha} \nabla e_{\alpha} \cdot \mathbf{J}_{\alpha} - M_{\alpha} e_{\alpha} \left(\frac{\partial c_{\alpha}}{\partial t} - \frac{t_c}{2} \frac{\partial^2 c_{\alpha}}{\partial t^2} \right) + M_{\alpha} v_{ar} \dot{w}_r \right] d\Omega + \int_{\Omega} t_c \nabla(\rho_{\alpha} \mathbf{e}_v^{\alpha}) d\Omega \right\} \quad (23)
 \end{aligned}$$

where we have utilized the conservation of mass of Eq. (10) and

$$\begin{aligned}
 & \int_{\Gamma} \left[\rho_{\alpha} e_{\alpha} + t_c \frac{\partial(\rho_{\alpha} e_{\alpha})}{\partial t} \right] (v_k^{\alpha} - V_k) n_k d\Gamma \\
 &= \int_{\Gamma} \left[\rho_{\alpha} e_{\alpha} + t_c \frac{\partial \rho_{\alpha}}{\partial t} e_{\alpha} \right] (v_k^{\alpha} - V_k) n_k d\Gamma + \int_{\Gamma} \left[t_c \left(\rho_{\alpha} \frac{\partial e_{\alpha}}{\partial t} \right) (v_k^{\alpha} - V_k) \right] n_k d\Gamma \\
 &= \int_{\Omega} \nabla(M_{\alpha} e_{\alpha} \mathbf{J}_{\alpha}) d\Omega + \int_{\Gamma} \left[t_c \left(\rho_{\alpha} \frac{\partial e_{\alpha}}{\partial t} \right) (v_k^{\alpha} - V_k) \right] n_k d\Gamma \\
 &= \int_{\Omega} M_{\alpha} (\nabla e_{\alpha} \cdot \mathbf{J}_{\alpha} + e_{\alpha} \nabla \mathbf{J}_{\alpha}) d\Omega + \int_{\Omega} t_c \nabla(\rho_{\alpha} \mathbf{e}_v^{\alpha}) d\Omega
 \end{aligned}$$

with $\int_{\Gamma} \left[\rho_{\alpha} \left(\frac{\partial e_{\alpha}}{\partial t} \right) (v_k^{\alpha} - V_k) \right] n_k d\Gamma = \int_{\Omega} \nabla(\rho_{\alpha} \mathbf{e}_v^{\alpha}) d\Omega$

Similarly, by applying Reynold's transport theorem through Eq. (5) to the kinetic energy, we obtain

$$\begin{aligned}
 \frac{D}{Dt} K &= \frac{1}{2} \int_{\Omega} \left\{ \frac{\partial \rho \mathbf{v}^2}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \rho \mathbf{v}^2}{\partial t^2} \right\} d\Omega + \frac{1}{2} \int_{\Gamma} \sum_{\alpha=1}^{Nt} \left\{ \left[\rho_{\alpha} \mathbf{v}^2 + t_c \left(\frac{\partial \rho_{\alpha} \mathbf{v}^2}{\partial t} \right) \right] (v_k^{\alpha} - V_k) \right\} n_k d\Gamma \\
 &= \frac{1}{2} \int_{\Omega} \left\{ M_N \nabla \mathbf{v}^2 \cdot \mathbf{J}_N + M_N \mathbf{v}^2 v_{Nr} \dot{w}_r + 2\rho \mathbf{v} \left(\frac{\partial \mathbf{v}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \mathbf{v}}{\partial t^2} \right) \right\} d\Omega \\
 &\quad + \frac{1}{2} \int_{\Omega} t_c \left\{ 2\nabla \rho \mathbf{K}_v + \left[\frac{\partial \rho}{\partial t} \frac{\partial \mathbf{v}^2}{\partial t} + \rho \left(\frac{\partial \mathbf{v}}{\partial t} \right)^2 \right] \right\} d\Omega \quad (24)
 \end{aligned}$$

with $\int_{\Gamma} \sum_{\alpha=1}^{Nt} \left[\left(\rho_{\alpha} \mathbf{v} \frac{\partial \mathbf{v}}{\partial t} \right) (v_k^{\alpha} - V_k) \right] n_k d\Gamma = \int_{\Gamma} \left[\left(\rho \mathbf{v} \frac{\partial \mathbf{v}}{\partial t} \right) (v_k - V_k) \right] n_k d\Gamma = \int_{\Omega} \nabla(\rho \mathbf{K}_v) d\Omega$

In another way, we can utilize the Reynold's transport theorem Eq. (5) and the balance of linear of momentum Eq. (15) to get

$$\begin{aligned}
 \frac{D}{Dt} K &= \frac{1}{2} \int_{\Omega} \left[\left(\frac{\partial \rho \mathbf{v}^2}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \rho \mathbf{v}^2}{\partial t^2} \right) + \nabla(\boldsymbol{\sigma}^v \cdot \mathbf{v}) \right] d\Omega + \frac{1}{2} \int_{\Gamma} \left[t_c \left(\rho \mathbf{v} \frac{\partial \mathbf{v}}{\partial t} \right) (v_k - V_k) \right] n_k d\Gamma \\
 &= \frac{1}{2} \int_{\Omega} \left\{ \rho \mathbf{v} \left(\frac{\partial \mathbf{v}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 \mathbf{v}}{\partial t^2} \right) + \frac{t_c}{2} \left(2 \frac{\partial \rho \mathbf{v}}{\partial t} \frac{\partial \mathbf{v}}{\partial t} \right) + t_c \nabla(\rho \mathbf{K}_v) + (\nabla \otimes \mathbf{v}) : \boldsymbol{\sigma}^v + \mathbf{v} \cdot (\nabla \boldsymbol{\sigma} + \mathbf{b}) \right\} d\Omega \quad (25)
 \end{aligned}$$

By combining Eqs. (24) and (25), we can obtain

$$\begin{aligned}
 \frac{D}{Dt} K &= \int_{\Omega} \left\{ (\nabla \otimes \mathbf{v}) : \boldsymbol{\sigma}^v + \mathbf{v} \cdot (\nabla \boldsymbol{\sigma} + \mathbf{b}) - \frac{1}{2} (M_N \nabla \mathbf{v}^2 \cdot \mathbf{J}_N + M_N \mathbf{v}^2 v_{Nr} \dot{w}_r) \right\} d\Omega \\
 &\quad + \frac{1}{2} \int_{\Omega} t_c \left\{ \left[\frac{\partial \rho}{\partial t} \frac{\partial \mathbf{v}^2}{\partial t} + 3\rho \left(\frac{\partial \mathbf{v}}{\partial t} \right)^2 \right] \right\} d\Omega \quad (26)
 \end{aligned}$$

In terms of heat, we treat energy production due to heat sources and heat fluxes

$$Q = \int_{\Omega} r d\Omega - \int_{\Gamma} \mathbf{q} \cdot \mathbf{n} d\Gamma = \int_{\Omega} (r - \nabla \mathbf{q}) d\Omega \quad (27)$$

where r and q_k are the external body heat source strength and the heat flow, respectively. It is noted that heat generated due to chemical reactions is an internal process of conversion and dissipation within the internal energy.

The rate of the work done by tractions is written as

$$W = \int_{\Omega} \mathbf{b} \cdot \mathbf{v} d\Omega + \int_{\Gamma} \mathbf{t} \cdot \mathbf{v} d\Gamma = \int_{\Omega} [\mathbf{b} \cdot \mathbf{v} + \nabla(\mathbf{v} \cdot \boldsymbol{\sigma})] d\Omega \quad (28)$$

Combining Eqs. (23) and (26)–(28), we obtain the transient form for the balance of energy

$$\begin{aligned} \sum_{\alpha=1}^{Nt} \left[\frac{\partial(\rho_{\alpha}e_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha}e_{\alpha})}{\partial t^2} \right] &= (r - \nabla \mathbf{q}) + (\nabla \otimes \mathbf{v}) : (\boldsymbol{\sigma} - \boldsymbol{\sigma}^v) - \sum_{\alpha=1}^{Nt} \left[M_{\alpha} \nabla \left(e_{\alpha} - \frac{1}{2} \mathbf{v}^2 \right) \cdot \mathbf{J}_{\alpha} \right] \\ &+ \sum_{\alpha=1}^{Nt} \left[M_{\alpha} e_{\alpha} \left(\frac{\partial c_{\alpha}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_{\alpha}}{\partial t^2} \right) - M_{\alpha} \left(e_{\alpha} - \frac{1}{2} \mathbf{v}^2 \right) v_{ar} \dot{w}_r \right] - t_c \left\{ \nabla(\rho_N \mathbf{e}_v^N) + \frac{1}{2} \left[\frac{\partial \rho}{\partial t} \frac{\partial \mathbf{v}^2}{\partial t} + 3\rho \left(\frac{\partial \mathbf{v}}{\partial t} \right)^2 \right] \right\} \\ &= (r - \nabla \mathbf{q}) + (\nabla \otimes \mathbf{v}) : \boldsymbol{\sigma} - \sum_{\alpha=1}^{Nt} \left[M_{\alpha} \nabla e_{\alpha} \cdot \mathbf{J}_{\alpha} - M_{\alpha} e_{\alpha} \left(\frac{\partial c_{\alpha}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_{\alpha}}{\partial t^2} \right) + M_{\alpha} e_{\alpha} v_{ar} \dot{w}_r \right] \\ &- t_c \left\{ \nabla(\rho_N \mathbf{e}_v^N) + \frac{1}{2} \left[\frac{\partial \rho}{\partial t} \frac{\partial \mathbf{v}^2}{\partial t} + 3\rho \left(\frac{\partial \mathbf{v}}{\partial t} \right)^2 \right] + (\nabla \otimes \mathbf{v}) : \left[\rho \frac{\partial \mathbf{v}}{\partial t} \otimes (\mathbf{v} - \mathbf{V}) \right] \right\} \end{aligned} \quad (29)$$

where we utilized $M_{N^v N_r} = 0$ for each chemical reaction r .

4.5 Balance of Entropy. Similarly, we proceed with the balance of entropy. We assume the entropy density η_{α} of each species and the temperature T of the system and obtain

$$\frac{D}{Dt} \int_{\Omega} \rho_N \eta_N d\Omega = \int_{\Omega} \frac{r}{T} d\Omega - \int_{\Gamma} \frac{\mathbf{q}}{T} \cdot \mathbf{n} d\Gamma + \int_{\Omega} \frac{d_u}{T} d\Omega \quad (30)$$

where d_u is the rate of dissipation energy density. Applying Reynold's theorem through Eq. (5) on the left-hand side of Eq. (30) gives

$$\begin{aligned} \frac{D}{Dt} \left(\int_{\Omega} \rho_N \eta_N d\Omega \right) &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} \eta_{\alpha})}{\partial t^2} \right] d\Omega + \int_{\Gamma} \left[\rho_{\alpha} \eta_{\alpha} + t_c \frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} \right] (v_k^{\alpha} - V_k) n_k d\Gamma \right\} \\ &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} \eta_{\alpha})}{\partial t^2} \right] d\Omega + \int_{\Gamma} \left[M_{\alpha} c_{\alpha} \eta_{\alpha} + t_c \frac{\partial(M_{\alpha} c_{\alpha} \eta_{\alpha})}{\partial t} \right] (v_k^{\alpha} - V_k) n_k d\Gamma \right\} \\ &= \sum_{\alpha=1}^{Nt} \int_{\Omega} \left\{ \left[\frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} \eta_{\alpha})}{\partial t^2} \right] + (M_{\alpha} \nabla \eta_{\alpha} \cdot \mathbf{J}_{\alpha} + M_{\alpha} \eta_{\alpha} \nabla \mathbf{J}_{\alpha}) + t_c \nabla(\rho_{\alpha} \eta_{\alpha}^{\alpha}) \right\} d\Omega \\ &= \sum_{\alpha=1}^{Nt} \left\{ \int_{\Omega} \left[\left(\frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} \eta_{\alpha})}{\partial t^2} \right) + M_{\alpha} \nabla \eta_{\alpha} \cdot \mathbf{J}_{\alpha} - M_{\alpha} \eta_{\alpha} \left(\frac{\partial c_{\alpha}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_{\alpha}}{\partial t^2} \right) \right. \right. \\ &\quad \left. \left. + M_{\alpha} \eta_{\alpha} v_{ar} \dot{w}_r \right] d\Omega + \int_{\Omega} t_c (\rho_{\alpha} \eta_{\alpha}^{\alpha}) d\Omega \right\} \end{aligned} \quad (31)$$

Then, applying divergence theorem on the right-hand side of Eq. (30) and combining Eqs. (30) and (31) reaches an expression for the rate of total entropy as

$$\begin{aligned} \sum_{\alpha=1}^{Nt} \left[\frac{\partial(\rho_{\alpha} \eta_{\alpha})}{\partial t} + \frac{t_c}{2} \frac{\partial^2(\rho_{\alpha} \eta_{\alpha})}{\partial t^2} \right] &= \frac{d_u}{T} + \frac{r}{T} - \left(\frac{\nabla \mathbf{q}}{T} - \frac{\mathbf{q} \cdot \nabla T}{T^2} \right) - \sum_{\alpha=1}^{Nt} \left[M_{\alpha} \nabla \eta_{\alpha} \cdot \mathbf{J}_{\alpha} \right. \\ &\quad \left. - M_{\alpha} \eta_{\alpha} \left(\frac{\partial c_{\alpha}}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_{\alpha}}{\partial t^2} \right) + M_{\alpha} \eta_{\alpha} v_{ar} \dot{w}_r + t_c \nabla(\rho_{\alpha} \eta_{\alpha}^{\alpha}) \right] \end{aligned} \quad (32)$$

This equation is a transient representation of the Clausius-Duhem inequality [25].

4.6 The Second Law of Thermodynamics. Denoting the total Helmholtz energy H and the species Helmholtz energy density h_N , we utilize the Legendre transformation of the internal energy density e_N to obtain

$$H(\mathbf{e}, \boldsymbol{\gamma}, c_N, T) = \rho_N h_N = \rho_N (e_N - T \eta_N) \quad (33)$$

Here, the strain rate tensor $\dot{\mathbf{e}}$ which is symmetrical and the vorticity $\dot{\boldsymbol{\gamma}}$ which is skew-symmetrical are defined, respectively, as

$$\dot{\mathbf{e}} = \frac{1}{2} (\nabla \otimes \mathbf{v} + \mathbf{v} \otimes \nabla) = \dot{\mathbf{e}}^{(r)} + \dot{\mathbf{e}}^{(i)} \quad (34)$$

$$\dot{\boldsymbol{\gamma}} = \frac{1}{2} (\nabla \otimes \mathbf{v} - \mathbf{v} \otimes \nabla) = \dot{\boldsymbol{\gamma}}^{(r)} + \dot{\boldsymbol{\gamma}}^{(i)} \quad (35)$$

This is because the stress is unsymmetrical as we discussed in Sec. 4.3. Here, the superscript (r) represents the reversible part, and the superscript (i) represents the irreversible part. The stress tensor is decomposed as symmetric stress $\boldsymbol{\tau}$ and skew stress \mathbf{m}

$$\boldsymbol{\tau} = \frac{1}{2} (\boldsymbol{\sigma} + \boldsymbol{\sigma}^T), \quad \mathbf{m} = \frac{1}{2} (\boldsymbol{\sigma} - \boldsymbol{\sigma}^T) \quad (36)$$

Then, we have

$$\boldsymbol{\sigma}:(\nabla \otimes \mathbf{v}) = (\boldsymbol{\tau} + \mathbf{m}):(\dot{\boldsymbol{\varepsilon}} + \dot{\boldsymbol{\gamma}}) = \boldsymbol{\tau}:\dot{\boldsymbol{\varepsilon}} + \mathbf{m}:\dot{\boldsymbol{\gamma}} \quad (37)$$

Thus, combining Eqs. (29), (32), and (33), making use of Eq. (37), and solving for d_u , the so-called full dissipation inequality, also known as the Clausius-Planck inequality, is obtained as

$$\begin{aligned} d_u = & \left(-\rho_N \eta_N - \frac{\partial H}{\partial T} \right) \frac{\partial T}{\partial t} + \left(\boldsymbol{\tau} - \frac{\partial H}{\partial \boldsymbol{\varepsilon}^{(r)}} \right) : \dot{\boldsymbol{\varepsilon}}^{(r)} \\ & + \left(\mathbf{m} - \frac{\partial H}{\partial \boldsymbol{\gamma}^{(r)}} \right) : \dot{\boldsymbol{\gamma}}^{(r)} + \sum_{\alpha=1}^{Nt} \left(M_\alpha h_\alpha - \frac{\partial H}{\partial c_\alpha} \right) \frac{\partial c_\alpha}{\partial t} \\ & - \left(\frac{\mathbf{q}}{T} - \sum_{\alpha=1}^{Nt} M_\alpha \eta_\alpha \mathbf{J}_\alpha \right) \cdot \nabla T + \boldsymbol{\tau}:\dot{\boldsymbol{\varepsilon}}^{(i)} + \mathbf{m}:\dot{\boldsymbol{\gamma}}^{(i)} \\ & - \sum_{\alpha=1}^{Nt} M_\alpha \nabla h_\alpha \cdot \mathbf{J}_\alpha - \sum_{\alpha=1}^{Nt} M_\alpha h_\alpha v_{ar} \dot{w}_r + t_c A \end{aligned} \quad (38)$$

Here, we let A to denote the sum of terms multiplied by characterized time t_c , and its detail expression is omitted. Based on the second law of thermodynamics, the dissipation must be greater than zero for the irreversible transformation, while it is equal to zero for reversible transformations, i.e., $d_u \geq 0$. Following the Coleman-Noll argument [24], the rates of $\boldsymbol{\varepsilon}$, $\boldsymbol{\gamma}$, c_N , T are assumed to be independent. Therefore, the parenthetical terms in Eq. (38) are required to vanish. This yields the consistency conditions

$$s = \rho_N \eta_N = -\frac{\partial H}{\partial T}, \quad \boldsymbol{\tau} = \frac{\partial H}{\partial \boldsymbol{\varepsilon}^{(r)}}, \quad \mathbf{m} = \frac{\partial H}{\partial \boldsymbol{\gamma}^{(r)}}, \quad \hat{\mu}_\alpha = M_\alpha h_\alpha = \frac{\partial H}{\partial c_\alpha} \quad (39)$$

where s is the total entropy, and the chemical potential (per mole) of species α is introduced as $\hat{\mu}_\alpha = M_\alpha h_\alpha$. Due to the relation Eq. (4), only $(Nt-1)$ concentrations are independent, we denote the driving force μ_N to be the chemical potential difference $\mu_N = \hat{\mu}_N - \hat{\mu}_{Nt}$ ($N = 1, 2, \dots, Nt-1$). In the rest of the paper, we call μ_N the chemical potential for convenience. Hence, the total Helmholtz energy of Eq. (33) is the sum of the chemical potentials of all the components

$$H = \rho_N h_N = c_N \mu_N \quad (40)$$

The affinity of the r th reaction is defined as

$$A_r = -v_{Nr} \mu_N \quad (41)$$

And the entropy flow vector is

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} - \sum_{\alpha=1}^{Nt} M_\alpha \eta_\alpha \mathbf{J}_\alpha \quad (42)$$

We continue to evaluate the dissipation inequality (38). Since the term $t_c A$ is the high order small quantity and all equations of Eq. (39) are fulfilled, Eq. (38) reduces to

$$0 \leq \boldsymbol{\tau}:\dot{\boldsymbol{\varepsilon}}^{(i)} + \mathbf{m}:\dot{\boldsymbol{\gamma}}^{(i)} - \nabla T \cdot \mathbf{J}^s - \nabla \mu_N \cdot \mathbf{J}_N + A_r \dot{w}_r \quad (43)$$

$$0 \leq t_c A \approx 0 \quad (44)$$

Equation (43) constitutes a thermodynamic constraint for irreversible strains, the entropy flux \mathbf{J}^s , the species fluxes \mathbf{J}_N , and the reaction rate \dot{w}_r . According to the linear irreversible thermodynamics, the irreversible flows are proportional to the irreversible forces, and the evolving equations (this relation is also called the second constitutive equation) can be obtained from Eq. (43). It should be noted that there is no relation between the irreversible force and flow tensor with different rank for isotropic materials, according to the requirements of Curie's symmetry principles [25]; i.e., the corresponding Onsager interference coefficient must necessarily

be zero. For anisotropic materials, the relation between the irreversible force and flow tensor with different rank exists, as discussed in Refs. [26].

Under the assumption of each process being independent for isotropic materials, the first and second terms on the right-hand side of Eq. (43) relate irreversible strains to stresses. The last term guides the direction of chemical reactions. The third and fourth terms lead to Fourier's law of thermal conduction and Fick's law of diffusion, respectively, as

$$\mathbf{J}^s = -\boldsymbol{\lambda} \cdot \nabla T \quad (45)$$

$$\mathbf{J}_N = -\mathbf{D} \cdot \nabla \mu_N \quad (46)$$

where coefficients of thermal conduction $\boldsymbol{\lambda}$ and coefficients of diffusion \mathbf{D} are symmetrical.

The constitutive relations of the materials can be derived from Eq. (39). We can also introduce internal variables in energy function to describe other irreversible processes.

5 Transient Thermal Conduction

The development of the hyperbolic temperature wave equation (such as Eq. (10)) instead of the parabolic thermal equation is mainly based on two reasons: the paradox of infinite thermal wave velocity and the Landau second sound speed observed by experiments in liquid helium and in solids at low temperatures [4,5]. This is called non-Fourier effect of thermal conduction.

By combining Eqs. (32) and (38), the entropy balance equation can be rewritten as

$$\begin{aligned} \frac{\partial s}{\partial t} + \frac{t_c}{2} \frac{\partial^2 s}{\partial t^2} = & \frac{r}{T} - \frac{\nabla \mathbf{q}}{T} + \frac{1}{T} \sum_{\alpha=1}^{Nt} (M_\alpha \eta_\alpha \mathbf{J}_\alpha) \cdot \nabla T \\ & + \sum_{\alpha=1}^{Nt} \left[M_\alpha \eta_\alpha \left(\frac{\partial c_\alpha}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_\alpha}{\partial t^2} \right) \right] \\ & + \frac{1}{T} (\boldsymbol{\tau}:\dot{\boldsymbol{\varepsilon}}^{(i)} + \mathbf{m}:\dot{\boldsymbol{\gamma}}^{(i)}) \\ & - \sum_{\alpha=1}^{Nt} M_\alpha \nabla \left(\frac{1}{T} h_\alpha + \eta_\alpha \right) \cdot \mathbf{J}_\alpha - \sum_{\alpha=1}^{Nt} M_\alpha \left(\frac{1}{T} h_\alpha + \eta_\alpha \right) v_{ar} \dot{w}_r \end{aligned} \quad (47)$$

If we consider only the pure thermal conduction, the previous equation reduces to

$$\frac{\partial s}{\partial t} T + \frac{t_c}{2} \frac{\partial^2 s}{\partial t^2} T = r - \nabla \mathbf{q} \quad (48)$$

This equation is similar to the inertial entropy theory proposed by Kuang [7,11,12] where an inertial entropy is introduced in the equation of entropy balance. In a pure thermal conduction case, $T \frac{\partial s}{\partial t} = C \frac{\partial \theta}{\partial t}$, where we denote $\theta = T - T_0$, with T_0 is a reference temperature, and C is the specific heat per volume, by means of Fourier's law (Eq. (45)), Eq. (48) can be written as

$$C \frac{\partial \theta}{\partial t} + \frac{C t_c}{2} \frac{\partial^2 \theta}{\partial t^2} = r + \lambda_{ij} \theta_{,ij} \quad (49)$$

This is a hyperbolic heat transfer equation with a finite propagation speed. This theory is useful in problem with the microscopic size and time under shock loadings, for an example, applying a short-pulse laser beam to a thin gold films.

For an isotropic thermal conduction problem, $\lambda_{ij} = \lambda \delta_{ij}$. Eq. (49) is same as Cattaneo-Vernotte's (C-V) theory [8,9] if heat source $r = 0$, but the physical meaning is total different. In C-V theory, they modified the Fourier's law (Eq. (45)) by introducing a relaxation time to get a hyperbolic heat transfer equation.

The temperature wave equation with finite velocity can be derived by the transient theory naturally in this paper.

6 Transient Diffusion

The transient mass transfer can be defined as the random walk of an ensemble of particles, from regions of high concentration to regions of lower concentration. For transient diffusion, the propagation speed of mass transfer is finite and the concentration field has a wave-like behavior. This was called non-Fick effect. During the past few years, considerable attention has been paid to the non-Fick effect. Combining the Maxwell model [2] and mass conservation equation, non-Fick mass transfer equation can be derived.

In this section, the diffusion of finite speed can be treated naturally. For simplicity, we consider the isotropic pure diffusion, $\mu_N = RT \ln c_N$ and $\mathbf{J}_N = -D c_N / RT \nabla \mu_N$. Then, by combining the balance of mass Eq. (10) and Fick's law, we can obtain a hyperbolic diffusion equation

$$\frac{\partial c_N}{\partial t} + \frac{t_c}{2} \frac{\partial^2 c_N}{\partial t^2} = D \nabla^2 c_N \quad (50)$$

This is just the famous non-Fick theory, when $t_c/2$ is taken to be the diffusion relaxation time.

7 Conclusions

In this paper, we presented a rigorous formulation of chemomechanics for solid continuum. The effects of transient and the coupling between chemistry and mechanics are considered. For the transient or microscopic time, the second-order rate and the characterized time are introduced through Taylor expansion. Then, the transient Reynold's transport theorem is derived, where the new products or material elimination due to chemical reactions are considered as well. The transient field equations with second-order rates are derived from fundamental conservation laws considering mechanical and chemical contributions and microscopic time. Either microscopic time or chemical reactions leads to the unsymmetry of the stress tensor. Based on the second law of thermodynamics, the relationship between Helmholtz's energy and constitutive properties, the evolution equations and the entropy are described, which is consistent with the classical continuum thermodynamics and consistent with the constitutive theory in continuum mechanics. From the balances of entropy and mass, the transient equations of thermal conduction and diffusion with finite velocity are naturally derived rather than postulated.

The theory can reduce to the classical continuum theory or steady-state case by simply letting the characterized time approach zero, which means the transient non-equilibrium approaching to the equilibrium state. The formulation introduced in this paper is exact, and the physical meaning is clear. This work can be undertaken to model the entire process within the framework of irreversible thermodynamics, bridge the molecular dynamics to the continuum mechanics, and thus correctly reproduce the physics.

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Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The data sets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request. The authors attest that all data for this study are included in the paper. Data provided by a third party are listed in Acknowledgment. No data, models, or code were generated or used for this paper.

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