



Internal energy transfer theory for thermodynamic non-equilibrium, quasi-equilibrium, and equilibrium



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ABSTRACT

Internal energy transfer is one of the most principal processes in the dynamic universe, but its exact thermodynamic processes have not been completely unveiled. We here propose an internal energy transfer theory for thermodynamic non-equilibrium, quasi-equilibrium, and equilibrium as a new paradigm for internal energy transfer, based on the first and the second laws of thermodynamics. The internal generation mechanisms of heat, work, and chemical energy transfer are considered. The internal energy fluxes are obtained as functions of temperature, pressure, chemical potential, time, and displacement under a postulate that the intensive variables are independent and orthogonal in extended phase spaces. The internal energy transfer theory is applicable to exploring the internal equilibrium, internal convection, external convection, and diffusion (or conduction) transfer mechanisms of heat, work, and chemical energy. The theory is a statistical thermodynamic generalization of thermal, mechanical, and chemical energy transfer as well as the conventional convection energy transfer. Six phase spaces consist of three intensive property dimensions of temperature, pressure, and chemical potential and three extensive property dimensions of entropy, volume, and particle number. The theory is a non-equilibrium generalization beyond the quasi-equilibrium theories of isothermal, isentropic, isobaric, isochoric, migration, and diffusion processes.

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1. Introduction

Energy transfer deals with the transfer of energy from one body to another and is one of the central processes to life in the universe. Thermodynamics is the science of energy conversion which has application areas including phase transition, fluid flow, chemical reaction, corrosion, thermal devices, microscopic organisms, physics, cosmology, fluid mechanics, and chemical cells. Chemicals, metals, and other materials in nature are produced by means of thermodynamic processes. Such thermodynamic processes have attracted attention in the multidisciplinary fields, and intensive and extensive research has been conducted for developing a reliable theory to describe thermodynamic processes, which include heat, work, and chemical energy transfer [1–22].

However, the exact mechanisms of thermodynamic non-equilibrium, quasi-equilibrium, and equilibrium have not been completely understood, despite numerous investigations [23–25], even though the mechanisms for thermodynamic equilibrium have been relatively well established. The current thermodynamics provides the macroscopic relationships between thermodynamic

properties without detailed microscopic views of systems. It only interrelates the macroscopic variables which describe physical systems. A microscopic understanding of thermodynamic processes may become an indispensable issue to get attention from interdisciplinary fields since the systems found in nature are mostly in thermodynamic processes.

Energy is transferred through the mechanisms of heat, work, and chemical energy transfer. There are limitations on the heat diffusion equation [26,27]:

$$\nabla \cdot (\kappa \nabla T) - \rho c_p (\partial T / \partial t + \mathbf{v}_a \cdot \nabla T) + q'_i = 0. \quad (1)$$

It deals with incompressible mediums, takes into account only external heat conduction and convection, and shows no expression for the internal heat generation per unit length q'_i . Analogous limitations are on the concentration equation for mass transfer [26,27]:

$$\partial C / \partial t + \mathbf{v}_a \cdot \nabla C = D_0 \nabla^2 C + C'_i. \quad (2)$$

They are closely related to chemical reactions or electrochemical reactions which account for the internal concentration generation per unit time C'_i . The exact form of C'_i is not explicitly clarified yet. Here, we are interested in the internal convective energy generation for heat, chemical energy, and work transfer as well as convective

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energy transfer. The internal generation or destruction terms of heat, work, and chemical energy can be established by considering internal energy transfer of heat and chemical energy. Therefore, a unified theory for internal energy transfer during thermodynamic processes is demanded.

In this paper, we propose a systematically unified transport theory for the three internal energy transfer mechanisms of non-equilibrium, quasi-equilibrium, and equilibrium thermodynamics based on the first law of thermodynamics. It predicts the detailed characteristics of transport parameters in thermodynamic processes. The theory is a thermodynamic generalization of conventional convective energy transfer. It is the thermodynamic generalization beyond thermodynamic quasi-equilibrium and equilibrium. The transport theory may become a new paradigm for the non-equilibrium processes of three internal energy transfer mechanisms.

In the internal energy transfer theory, the energy fluxes are described as functions of temperature, pressure, chemical potential, time, and space simultaneously under a postulate that the thermodynamic intensive variables are independent and orthogonal in extended phase spaces. This is the first rigorous microscopic kinetic theory for internal convective energy transfer.

Fig. 1 shows the hierarchy for internal energy transfer. Internal energy transfer is comprised of heat, work, and chemical energy transfer [28–34]. Each internal energy transfer may contain the three modes of diffusion (or conduction), convection, and radiation in addition to equilibrium. Except for radiation, this paper focuses on the modes of internal convection, diffusion, internal equilibrium, and convection.

2. Internal energy transfer

A rigorous internal energy transfer theory is proposed for the transfer mechanisms of heat, work, and chemical energy. A total system containing reactants and products is thermodynamically isolated from its surroundings, and has thermodynamic energy transfer due to thermal, mechanical, and chemical non-equilibrium between reactants and products. The physical mechanisms of internal energy transfer can be described by physical parameters [35] of local thermodynamic equilibrium. The local thermodynamic non-equilibrium process is characterized by the intensive variables of temperature, pressure, and chemical potential.

2.1. Motivation of internal energy transfer

The internal energy transfer theory is motivated from the thermodynamic point of view in which internal energy transfer depends on intensive state variables as well as extensive state variables. Internal energy transfer in a quasi-equilibrium (quasi-static) process is conventionally described only by extensive state variables, but internal energy in a non-equilibrium process can be stated by including intensive state variables. Here, the

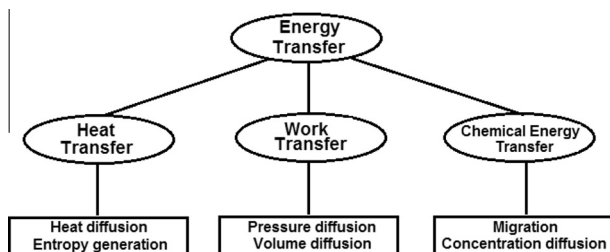


Fig. 1. Hierarchy for internal energy transfer mechanisms.

dependence of intensive state variables for internal energy transfer is addressed [28–34].

Euler's equation of thermodynamics for the internal energy is $U(T, S, P, V, \mu, N) = TS - PV + \mu N$.

From Euler's equation, we have the first law of thermodynamics:

$$dU = \delta Q - \delta W + \delta G.$$

Rewriting the first law, we obtain

$$dU(T, S, P, V, \mu, N) = (TdS - PdV + \mu dN) + (SdT - VdP + Nd\mu), \quad (3)$$

where

$$\begin{aligned} \delta Q(T, S) &= TdS + SdT, \\ \delta W(P, V) &= PdV + VdP, \\ \delta G(\mu, N) &= \mu dN + Nd\mu. \end{aligned}$$

For a quasi-equilibrium process, the fundamental equation of thermodynamics is given by

$$dU(S, V, N) = TdS - PdV + \mu dN,$$

where the Gibbs–Duhem equation is observed:

$$SdT - VdP + Nd\mu = 0.$$

On the other hand, for a non-equilibrium or equilibrium process, we have

$$dU(S, V, N) < TdS - PdV + \mu dN.$$

Combining non-equilibrium, quasi-equilibrium, and equilibrium processes, we can rewrite

$$dU(S, V, N) \leq TdS - PdV + \mu dN, \quad (4)$$

which is the fundamental thermodynamic relation.

Comparing Eq. (3) with Eq. (4), we can analyze that

$$SdT - VdP + Nd\mu \geq 0.$$

From the above equation, we have the conditions of distinct thermodynamic processes:

For a quasi-equilibrium process, it reduces to the Gibbs–Duhem equation

$$SdT - VdP + Nd\mu = 0.$$

For a non-equilibrium or equilibrium process, it holds the inequality condition

$$SdT - VdP + Nd\mu > 0.$$

Distinction between non-equilibrium and equilibrium depends on whether temperature, pressure, and chemical potential are larger than their corresponding activation temperature, activation pressure, and activation chemical potential.

In summary, we analyze that there are two contributions in internal energy transfer in Eq. (3). The first contribution originates from external variable changes, and the second contribution comes from the internal variable changes. The Gibbs–Duhem relation holds only for the quasi-equilibrium process.

Based on Eq. (3), we can specifically classify non-equilibrium, quasi-equilibrium, and equilibrium processes. We utilize the definitions of the thermodynamic potentials:

$$\text{Gibbs free energy, } G = U - TS + PV = \mu N,$$

$$\text{Heat potential, } Q = U + PV - \mu N = TS,$$

$$\text{Grand potential, } W = U - TS - \mu N = PV.$$

We also employ the activation points of intensive variables from equilibrium to non-equilibrium:

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