



# Heat transfer theory for thermal non-equilibrium, quasi-equilibrium, and equilibrium



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## ABSTRACT

Heat transfer is one of the fundamental and veiled energy transfer processes. The complex characteristics of heat transfer in a thermal process are far from being understood entirely. We here propose a statistical thermodynamic transport theory which is applicable to the heat transfer mechanisms for non-equilibrium, quasi-equilibrium, and equilibrium to overcome limits on the heat diffusion equation. The heat transfer theory adopts a postulate that temperature, time, and displacement are independent and orthogonal variables in extended phase spaces. The solutions of the heat transfer theory are obtained for thermal non-equilibrium, quasi-equilibrium, and equilibrium and the heat fluxes are expressed as the functions of temperature, time, and displacement. The heat transfer theory demonstrates that there are heat flux gaps and broken discrete symmetries at the activation temperature, time, and displacement. The theory is consistent with statistical thermodynamics. The kinetic theory is the unification of conduction and internal convection heat transfer, a non-equilibrium generalization beyond quasi-equilibrium theories for isothermal and isentropic processes, and the integration of internal equilibrium and internal non-equilibrium.

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## 1. Introduction

Energy transfer from one body to another is central to life in the universe. Heat transfer is a discipline of thermal science and engineering that concerns the exchange of thermal energy [1–11]. It is one of the most fundamental subjects dealing with thermodynamic energy transfer processes of heat, work, and chemical energy. Boiling, condensation, melting, and solidification are exact examples of heat transfer during phase transitions.

Even though heat transfer as one of three energy transfer processes has been comprehensively studied since its inception, its entire understanding is challenging due to the very complex characteristics [12–23]. Heat transfer is classified into the three modes of heat conduction, convection, and radiation in addition to equilibrium. The heat diffusion theory for conductive heat transfer is well established, but a rigorous theory for thermal internal convective heat transfer does not exist. As a consequence, reliable theoretical methods are still lacking, and the extrapolation beyond experiments plays the major role at the present state of the art. However, design, operation, and optimization of involved devices require accurate predictions of heat transfer between a solid surface and a fluid.

There are limitations on the Fourier–Biot equation for heat diffusion [9]

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

It deals with incompressible mediums, accounts for only the heat conduction without internal heat convection, and shows no expression for the internal heat generation per unit length  $q'_i$ . The convective term ( $-\rho c_p \mathbf{v}_a \cdot \nabla T$ ) can be added to the left hand side of the above equation, but it is only the convective heat contribution. We are here interested in the internal convective heat generation depending on temperature difference as well as the external conductive and convective heat transfer.

In this paper, we propose a systematically unified theory for the heat transfer mechanisms of internal convection and internal equilibrium beyond overcoming intrinsic limits on the heat diffusion equation. In the heat transfer theory, the heat fluxes are described as functions of temperature, time, and displacement simultaneously under a postulate that temperature, time, and displacement are independent and orthogonal variables in extended phase spaces. This is the first rigorous microscopic kinetic theory for internal equilibrium and internal convective heat transfer.

The theory unifies conduction and internal convection heat transfer, it leads to a non-equilibrium theory beyond quasi-equilibrium theories for the isothermal and isentropic processes, it works on non-equilibrium and equilibrium dynamics, and it integrates conduction and convection mechanisms. The heat transfer theory can be applied to the internal convective thermal processes at a solid–liquid boundary as an illustration [3,4].

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Fig. 1 shows the hierarchy for internal energy transfer which consists of heat, work, and chemical energy transfer. Each energy transfer is composed of three modes of conduction (or diffusion), convection, and radiation in addition to equilibrium. Apart from radiation, this paper addresses the internal convection and external conduction as well as internal equilibrium and external convection of heat transfer.

## 2. Heat transfer theory

A statistical thermodynamic kinetic theory for heat transfer mechanisms is proposed based on the thermal energy conservation and statistical thermodynamics. The heat transfer theory is generally applicable to heat transfer mechanisms of non-equilibrium, quasi-equilibrium, and equilibrium. It has a close analogy to the kinetic theory of electrochemical reactions [1,2]. A total system containing reactants and products is thermally isolated from its surroundings and is in thermal non-equilibrium while the two phases of reactants and products are in mechanical and chemical isolation. For the system in thermal non-equilibrium, the physical mechanisms of energy transfer can be described in terms of physical parameters in local thermodynamic equilibrium [5]. The heat flux in thermodynamic non-equilibrium is characterized by the intensive variable of temperature.

### 2.1. Motivation of internal energy transfer in thermodynamics

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 dependence of intensive state variables for internal energy transfer is addressed.

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

$$dU(T, S, P, V, \mu, N) = (TdS - PdV + \mu dN) + (SdT - VdP + Nd\mu), \quad (2)$$

where

$$\delta Q(T, S) = TdS + SdT,$$

$$\delta W(P, V) = PdV + VdP,$$

$$\delta G(\mu, N) = \mu dN + Nd\mu.$$

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

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

which is the fundamental thermodynamic relation.

Comparing Eq. (2) with the above equation, 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. (2). 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. (2), we can specifically classify non-equilibrium, quasi-equilibrium, and equilibrium processes. We utilize the definitions of the thermodynamic potentials:

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

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

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

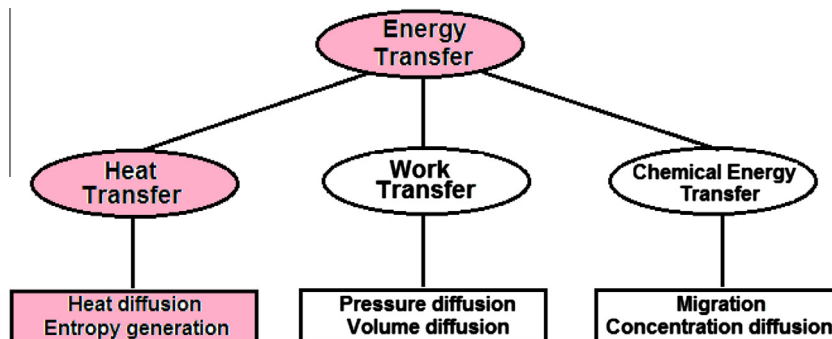


Fig. 1. Hierarchy for energy transfer mechanisms.

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