

Basics of Irreversible Thermodynamics

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December 23, 2005

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1 Introduction

The conventional thermodynamic theory is, practically speaking, a macroscopically-static theory. Most of the theory is dedicated to the macroscopic state representation of a system which is in equilibrium state and then explaining relationships between various intensive and extensive equilibrium-state-variables. Thermodynamics does give some insight into dynamics as well – but in a very restrictive sense. Mostly the dynamic insight comes in two forms - 1) knowing the initial equilibrium state and the final equilibrium state one can authoritatively say whether change from initial state to final state is possible spontaneously or not; and 2) if the change from initial state to final state is so slow that process can be assumed to be proceeding through a series of closely spaced quasi-equilibrium states then such a process is called reversible process and the entire path of time evolution of each of the state variables can be obtained from the conventional theory of thermodynamics.

On the other hand almost all the processes that we are interested in are irreversible processes and hence most of the time system is not in an equilibrium state as system evolves in time. A general theory of non-equilibrium thermodynamics is not existing. Its a heavily researched area. But the thermodynamics of steady state processes is relatively well established at least when the system does not deviate substantially from equilibrium. Here I am briefly explaining about the basic structure of this theory as its quite important for device physicists to have a solid understanding of steady state irreversible process (like electric current and heat conduction) in semiconductor, metals and other solid state systems.

In classical physics we mostly use kinetic theory and in quantum physics we mostly use statistical quantum theories with open systems to describe motion of systems in non-equilibrium. Purpose of non-equilibrium or irreversible thermodynamics is to explain meaning of those system properties that we typically associate with equilibrium states but when system is in non-equilibrium state. For example how do we define temperature when system is not in equilibrium? Can we define local temperatures? Does this assume that locally system is in thermal equilibrium¹? These things are covered in non-equilibrium thermodynamics.

For understanding basics of equilibrium thermodynamics from statistical and quantum mechanical point of view please see other articles on [Equilibrium Quantum Statistical Mechanics](#) and [Non-Equilibrium Quantum Statistical Mechanics / Statistical QFT](#). Second article on [Non-Equilibrium Quantum Statistical Mechanics / Statistical QFT](#) also explains

¹These particular questions are debated in article on [Equilibrium Quantum Statistical Mechanics](#). Interested reader might want to check that article. In this article I would just focus on basic setup of the subject.

how to analyze open quantum systems. This is, in some senses, equivalent to quantum kinetic theory.

2 Basic postulates and definitions

To formulate irreversible thermodynamics, it seems, from statistical mechanical point of view, only time reversibility assumption is needed apart from the two basic postulates of conventional statistical mechanics (i.e. the fundamental assumption and the assumption about the profile of $\sigma - U$ curve²). But from thermodynamic point of view, I think, at least three more postulates are needed :- Local Equilibrium, Time Reversibility, and form of Phenomenological Equation.

- Locally and instantaneously its possible to represent the state of system using the same state variables as we did in equilibrium. Moreover, one should note that its not possible for some variables to become independent or constrained when one moves in or out of equilibrium. What I mean is this. If V is treated as a variable parameter for a system in equilibrium then it would remain so even in non-equilibrium. Hence instantaneous, local entropy can always be written as a single valued continuous, differentiable, monotonic, zero-starting function of extensive variables of the system. Hence the fundamental relation would remain same as that in equilibrium situation of the same infinitesimally small volume. Sometimes fundamental relation and the form of $\sigma - U$ is considered as an additional assumption of statistical mechanics. So that assumption should still remain true even in dynamic situation.
- Fundamental assumption of statistical mechanics still makes sense.
- For studying irreversible processes we need at least one more postulate. Its called time symmetry of physical laws. All laws of physics remain unaltered if we replace t by $-t$ everywhere. This postulate can be used to prove that $L_{ij} = L_{ji}$ where L_{nm} is the phenological tensor coefficient as we would discuss below.
- Affinities are defined as the gradient of all the intensive parameters (actually the gradients of coefficients in the expansion of $d\sigma$) in the entropy representation. Fluxes are defined as the flux of flow density vector of any of the extensive property.

²See article on [Equilibrium Quantum Statistical Mechanics](#).

- Further it is assumed that system is a Markoffian system. In the Markoffian system instantaneous local fluxes depends only on the instantaneous local affinities (and coefficient of proportionality would depend on instantaneous local intensive properties). Further for small perturbations (near equilibrium problems) one can assume the relationship to be linear. **But remember that one type of flux can in general depend on all affinities and not only on its own affinity.**

So for small perturbations one can write

$$j_k = \sum_p L_{k,p} F_p$$

Where $L_{k,p}$ is a tensor and F_p and j_k are affinity and flux vectors respectively. Note that the one type of flux is assumed, for generality, to depend on all types of affinities.

3 Entropy flux density vector and continuity equation for entropy

Let us assume that the system has the following fundamental relation :-

$$U = U(\sigma, N, V, q, \text{ etc.})$$

Hence,

$$dU = \tau d\sigma + \mu dN + p dV + \phi dq + \text{ etc.}$$

This equation can be integrated to obtain :-

$$U = \tau \sigma + \mu N + pV + \phi q + \text{ etc.}$$

Which can be inverted to obtain :-

$$\sigma = \frac{1}{\tau} U - \frac{\mu}{\tau} N - \frac{p}{\tau} V - \frac{\phi}{\tau} q + \text{ etc.}$$

Using this we can define what we mean by **entropy flux density vector** :-

$$j_\sigma = \frac{1}{\tau} j_U - \frac{\mu}{\tau} j_N - \frac{p}{\tau} j_V - \frac{\phi}{\tau} j_q + \text{ etc.}$$

Also one invert the differential relation to obtain,

$$d\sigma = \frac{1}{\tau}dU - \frac{\mu}{\tau}dN - \frac{p}{\tau}dV - \frac{\phi}{\tau}dq + \text{etc.}$$

Hence we can write,

$$\frac{d\sigma}{dt} = \frac{1}{\tau} \frac{dU}{dt} - \frac{\mu}{\tau} \frac{dN}{dt} - \frac{p}{\tau} \frac{dV}{dt} - \frac{\phi}{\tau} \frac{dq}{dt} + \text{etc.}$$

Using the continuity equations for energy, particles, volume and charge we can obtain (for all quantities written as per unit volume),

$$\frac{d\sigma}{dt} = -\frac{1}{\tau}\nabla \cdot j_U + \frac{\mu}{\tau}\nabla \cdot j_N + \frac{p}{\tau}\nabla \cdot j_V + \frac{\phi}{\tau}\nabla \cdot j_q + \text{etc.}$$

Which is same as,

$$\frac{d\sigma}{dt} + \nabla \cdot j_\sigma = +j_U \cdot \nabla \left(\frac{1}{\tau} \right) - j_N \cdot \nabla \left(\frac{\mu}{\tau} \right) - j_V \cdot \nabla \left(\frac{p}{\tau} \right) - j_q \cdot \nabla \left(\frac{\phi}{\tau} \right) + \text{etc.}$$

Which can be recognized as the **continuity equation for entropy**.

$$\Phi = j_U \cdot \nabla \left(\frac{1}{\tau} \right) - j_N \cdot \nabla \left(\frac{\mu}{\tau} \right) - j_V \cdot \nabla \left(\frac{p}{\tau} \right) - j_q \cdot \nabla \left(\frac{\phi}{\tau} \right) + \text{etc.}$$

is called the entropy production function. Which contains the summation of dot products of all fluxes and corresponding affinities.

4 Further Resources

- Background Material

- Some useful [mathematical background](#) can be found in one of the articles [?] written by the author.
- A good discussion on [equilibrium quantum statistical mechanics](#) can be found in reference[?].
- For a brief review of postulatory nature of [quantum mechanics](#) see another article [?].
- Elementary review of [quantum field theory \(QFT\)](#) can be found in the reference[?] while for introductory treatment of [statistical quantum field theory \(QFT\)](#) and

- details of density matrix formalism can be found in the article[?].
- A quick review of [classical optics](#) and calculation of classical orthonormal modes can be found in the reference [?].
 - List of all related articles can be found at [author's homepage](#).

References