§ 17. Non-Equilibrium Thermodynamics of Highly Charged Ion Plasmas

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Atomic non-local thermodynamic equilibrium (NLTE) has significant effects on ionization, excited-state populations, and the emission of radiation in astrophysics (solar corona) and laboratory plasma physics (tokamak plasmas, pinches, laser hohlraums, and laser-produced plasmas). When LTE prevails, we usually combine atomic physics, equilibrium thermodynamics, and statistical mechanics to develop an *ab initio* treatment of the free electron, ion, and radiation field system. When LTE assumption breaks down, the situation is a little bit confused, because no definite and well-settled theoretical framework exists to describe our system[1]. How to calculate a NLTE equation of state for a consistent numerical simulation of laser plasma hydrodynamic motion? How energy-transfers between electrons and radiation field occur during the transient evolution of a non-equilibrium ion? How to treat the huge number of atomic levels when their *a priori* probabilities are unknown? What about entropy and entropy production? These questions are still unsolved.

Yet, various approaches have been presented to attack the problem. Near equilibrium, we can employ the Onsager and Kubo linear response methods. Far from equilibrium, we often use *ad-hoc* kinetic equations combined with semi-classical radiative transfer equation. We can also adopt the point of view of Prigogine's thermodynamics of irreversible processes. However, one can seriously question the internal consistency of these approaches, wonder how they are related to each other, and ask for relevant and pertinent experiments to test theory.

Following a seminal work establishing a connection between atomic kinetics and non-equilibrium thermodynamics to calculate the net emission from a NLTE response matrix[2], we prove that the thermodynamics of irreversible processes is valid for the system of ions, described by Maxwell-Boltzmann statistics and rate equations, radiation field, described by Bose-Einstein statistics and radiative transfer equation, and free electrons, described by Fermi-Dirac statistics and assumed to be in LTE. The key elements are the statistical interpretation and expression of entropy, the smallness of interactions between ions, electrons, and photons, the balance-type structure of kinetic equations, and the use of conjugate variables. In short, entropy production of this system can be written as a sum of positive products of two factors, i.e., flux and force (affinity) that are zero if and only if the system is in LTE: this is the 2nd law of thermodynamics statement. Near equilibrium, the steady state is a state of minimum entropy production: this is the famous Prigogine's theorem of minimum entropy production. Moreover, an H or Lyapounov function exists for the ion subsystem in constant environment without assuming the detailed balance principle. Finally, our work is consistent with previous results concerning the response matrix notion.

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1. R.M. More and T. Kato (to be published)
2. R.M. More and T. Kato, Phys. Rev. Lett. **81**, 814 (1998)