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Aspects of Thermodynamic Equilibrium in Plasma

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Abstract

Investigation of various types of plasma for diagnosis involves the development of various plasma models. This article presents and compares various models of plasma in thermodynamic equilibrium. The comparative structure of models presentation allows quick selection of a suitable model for the type of investigated plasma.

Keywords: *thermodynamic equilibrium, plasma, Maxwell distribution, Boltzmann distribution, the Saha's ionization equation*

Introduction

The thermodynamic equilibrium (TE) is a state in which all species of particles (neutral atoms, molecules, ions, electrons) from the volume are considered at the same temperature or the velocity distribution of each species of particles present in the same volume corresponds to the same temperature T. In the case of thermodynamic equilibrium, there are valid the following relations: Maxwell distribution, Boltzmann distribution and the Saha's ionization equation [1].

Maxwell Distribution

The number of the free electrons with velocity in the range (v_e , $v_e + \mathrm{d}v_e$) is:

$$\mathrm{d}n_e = 4\pi n_e \left(\frac{m}{2\pi k T_e}\right)^{\frac{3}{2}} e^{-\frac{m v_e^2}{2kT_e}} v_e^2 \,\mathrm{d}v_e\,, \tag{1}$$

where n_e is the total electron density, T_e is the electrons temperature, k is the Boltzmann's constant, m is the electron mass.

Boltzmann Distribution

Particles in a plasma at TE are distributed by the energy given by the Boltzmann's distribution law

$$n_i = n_0 g_i A e^{-\frac{E_i}{kT}}\,, \tag{2}$$

where n_o is the total number of particles in unit volume, n_i is the energy level population with energy E_i and g_i is its statistical weight.

The Saha's Ionization Equation

In case of ionization and thermal equilibrium, $T_{gas} = T_e = T_i$ (T_i - the ions temperature), the Saha's ionization equation is obtained:

$$\frac{n_e^2}{n_g - n_e} = A' T_e^{\frac{3}{2}} e^{-\frac{E_i}{kT_e}} . \quad (3)$$

Complete Thermodynamic Equilibrium

In case of a complete TE (ideal case) there are implied both substance particles and radiation. Such radiation is called equilibrium radiation or black body radiation and it implies a balance between direct processes (emission, collisions type II, collisions of three particles) and inverse processes (absorption, collisions type I, ionization with electron) in the sense that each type of process should be directly compensated by a corresponding inverse process, see Table 1, where A_{ki}, $K_{i<k}$, $Q_{z,1/z-1,k}$ and $S_{z-1,k}$ represents the corresponding processes rates [2, 5].

Table 1. The equations that characterize the complete TE

Emission		*Absorption*
$\frac{n_k A_{ki}}{1 - e^{-\frac{h\nu}{kT}}}$	=	$n_i \frac{g_k}{g_i} \rho(\nu, T) \frac{c^3}{8\pi h \nu^3}$
Collisions type II (with electrons)		*Collisions type I (with electrons)*
$n_k n_e \frac{g_k}{g_i} K_{i<k} e^{\frac{E_k - E_i}{kT}}$	=	$n_e n_i K_{i<k}$
Collisions of three particles		*Ionization with electron*
$n_{k,1} n_e^2 Q_{z,1/z-1,k}$	=	$n_{z-1,k} n_e S_{z,k-1}$

The spectral density of radiation at equilibrium, characterized by the field of the equilibrium radiation, is $\rho(\upsilon, T)$, described by Planck's law:

$$\rho(\upsilon, T) = \frac{8\pi h \upsilon^3}{c^3} \frac{1}{e^{\frac{h\upsilon}{kT}} - 1} . \quad (4)$$

With the increase of temperature, radiation becomes more and more important and dominates the energy exchange. At high temperatures, that exceed 10^6 K, the thermodynamic properties of the plasma are completely determined by radiation and not by the collisions and in this case, in order to obtain the complete TE, all radiation emitted must be re-absorbed with same rate.

Local Thermodynamic Equilibrium

Among the methods of plasmas' diagnosis (optico-spectral, using microwaves, using lasers, electric and magnetic methods), diagnosis based on its own radiation inevitably involves an important loss of radiation by plasma. So the thermodynamic equilibrium cannot be fully achieved. However, the same laws that govern the total TE, excepting the one related to radiation, can describe the state of plasma. In other words, there is equilibrium in a weak radiation field, where T from the Maxwell distribution is equal to the temperature T from Saha ionization equation. This is the so-called plasma in local thermodynamic equilibrium (LTE).

Since radiation escapes from the plasma, the detailed equilibrium of emission and spectral lines absorption as well as that of photo-recombination processes is disturbed in the sense that the number of emission processes outstrips those of the photo-absorptions. This will reduce the number of excited particles and free electrons. These disturbances propagate by themselves and equilibrate the excitation and deexcitation processes produced by collisions with free electrons, excitation and deexcitation processes produced by heavy particles, ionization and recombination processes with electrons in collisions of three particles. So, the collision processes play a dominant role and their rate dominates the radiative emission and the recombination processes [4, 7].

To achieve this, it is necessary a minimum density of free electrons. According to Griem [3] the expression of electrons density required to obtain the LTE is:

$$n_e \geq 9 \cdot 10^{17} \left(\frac{E_2}{E_{ionizare}} \right)^3 \left(\frac{kT}{E_{ionizare}} \right)^{\frac{1}{2}}, \tag{5}$$

where E_2 is the first excited level, the higher resonance level.

The plasma parameters (T, n_e etc.) in the case of LTE can be determined by measuring the characteristic parameters of the radiation that escapes from the plasma.

Thus, the absorbed intensity of spectral lines emitted by plasma is:

$$I_{ki} = n_k A_{ki} h\nu_{ki} = cn_0 g_k A_{ki} h\nu_{ik} \mathrm{e}^{-\frac{E_k}{kT}}. \tag{6}$$

The Doppler width, in the case of interactions absence and with a small number of collisions (rarefied plasma), is:

$$\Delta\nu = 7{,}1 \cdot 10^{-7} \nu_0 \sqrt{\frac{T}{\mu}}, \tag{7}$$

where μ is the molecular weight.

To establish the existence of LTE in plasma, all determinations made to determine a parameter, regardless of the method used and in the case of minimum errors, should give the same values. Combining a large number of determinations of the same parameter (e.g. temperature) from different methods allows not only setting that parameter value with small errors but also the deviations from LTE.

Partial Local Thermodynamic Equilibrium

Electron densities necessary to obtain complete local thermodynamic equilibrium are not extremely high. These densities have much higher values than those obtained in the most experimental plasma and therefore, below the critical electron density, radiative transitions are very important, as they trigger overpopulation, especially that of the fundamental level. Electron density required for partial LTE is:

$$n_e \geq 7 \cdot 10^{18} \frac{Z^6}{n^{\frac{17}{2}}} \left(\frac{kT}{E_{ionizare}} \right)^{\frac{1}{3}} \mathrm{cm}^{-3}, \tag{8}$$

where n is the principal quantum number of the lowest level included in the partial LTE.

Local Thermodynamic Equilibrium in Transient and Homogeneous Plasmas

Transient and homogeneous plasmas are obtained in shock tubes, in which temperatures and densities along the absorption line, which is at an angle of 90° to the tube's axis, are constant (except for the border layers) [4, 7].

The time to establish kinetic equilibrium between electrons and heavy particles (ions and neutral atoms) is:

$$\tau_{cin} \cong \left[7,5 \cdot 10^{-7} \left(\frac{E_{ionizH}}{kT}\right)^{\frac{3}{2}} m_e\right]^{-1} \frac{n_0 m}{n^+ m_e} \text{ for atoms,} \tag{9}$$

$$\tau_{cin} \cong \left[7,5 \cdot 10^{-7} \left(\frac{Z^2 E_{ionizH}}{kT}\right)^{\frac{3}{2}}\right] \frac{m}{m_e} \text{ for ions,} \tag{10}$$

where $E_{ionizare}$ is the ionization energy of hydrogen, n_e the electron's concentration, n_g concentration of neutral atoms, n^+ concentration of ions, n_0 the total number of atoms within the volume unit, m_e electron's mass and m mass of atoms or ions.

Having reached the kinetic equilibrium between particles will lead to a distribution of energy to the excited states of atoms, in agreement with the Boltzmann law. Most excitements lead to the superior part of the resonance spectral line. The time to achieve equilibrium is the inverse of the collision rate that leads to excitement and ionization. So the time to establish LTE depends decisively on the electron density. The time needed to achieve balance between the fundamental and the first excited level (the level of the resonance line) is:

$$\tau_1^{z-1} \cong 1,1 \cdot 10^7 \frac{z^3}{f_{1,2} n_e} \frac{n_z}{n_z + n_{z-1}} \left(\frac{E_{z-1,2}}{Z^2 E_{ionizare}}\right)\left(\frac{kT}{Z^2 E_{ionizH}}\right)^{\frac{1}{2}} e^{\frac{E_{z-1,2}}{kT}}, \tag{11}$$

where $Z = 1$ represents the neutral atoms and $Z = 2$ the first order ionized atoms.

If the electron densities are so high they meet LTE validity conditions, in a stationary and homogeneous plasma, and provided that the plasma parameters such as temperature and density are constant over time, by the equilibrium time order given by equation (11), $0,1\mu s$, are high enough, a complete LTE in transient plasmas is to be expected in a few situations.

Local Thermodynamic Equilibrium in Inhomogeneous Stationary Plasmas

Stationary and inhomogeneous plasmas are obtained in stabilized electrical discharges; within these discharges the conditions vary along any axis of the discharge column. In these plasmas LTE is likely to occur if the criteria for achieving LTE in stationary and homogeneous plasmas are satisfied and, moreover, the spatial variations of electrons temperature must be small over distances comparable to those that a given particle can diffuse on, in the time of the order for the above-discussed equilibrium time [5].

The expression for the average distance traveled by a particle between collisions that leads to equilibrium is:

$$d_1^{0,a} \cong 6\cdot 10^{14}\left(\frac{m_H}{m}\right)\left(\frac{kT}{E_{ionizH}}\right)^{\frac{1}{2}}\left(\frac{E_2^{0,a}}{f_2 E_{ionizH}}\right)^{\frac{1}{2}}\left[\left(n_o+n_a^+\right)\left(n_o+10n_a^+\right)\right]^{\frac{-1}{2}} E^{\frac{E_2^{0,a}}{2kT}}, \qquad (12)$$

where a refers to the chemical species; this distance refers to neutral atoms (0) in the fundamental state (1).

Equation (12) refers to the distance along which the temperature T must be constant and it can be successfully applied in zones near the discharge axis. For peripheral regions, where the temperature is much smaller and the temperature gradient is high, formula (12) gives less accurate estimations.

Corona Equilibrium

A special case of equilibrium is the corona equilibrium [6]. This equilibrium occurs when the electron densities of plasma are too small to achieve the complete LTE. In this case, the relative populations of high energy levels are controlled by the collisions between particles.

Conclusions

The equilibrium model types discussed here: complete thermodynamic equilibrium, local thermodynamic equilibrium and partial local thermodynamic equilibrium, local thermodynamic equilibrium in transient and homogeneous plasmas, local thermodynamic equilibrium in inhomogeneous stationary plasmas and corona equilibrium are presented with characteristic conditions.

In many applications (chemical analysis, arc depositions, surface cleaning, plastics processing, gas treatment, spraying of materials, high-efficiency lighting, semiconductor production, TVs and electronics, medical sterilization and surgery etc., [8]) are involved phenomena connected to plasma, that require an adequate model to increase the efficiency of these applications.

These comparisons for the models mentioned in this paper are useful to choose the best one for different investigated plasmas.

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Aspecte privind echilibrul termodinamic în plasmă

Rezumat

Investigarea diverselor tipuri de plasme în vederea diagnosticării acestora presupune elaborarea diverselor modele de plasmă. În acest articol sunt prezentate şi comparate diverse modele de plasmă la echilibru termodinamic. Această structurare comparativă a modelelor permite alegerea rapidă a unui model potrivit pentru tipul de plasmă investigată.