Disturbed Bilateral Relations: a guide for plasma characterization and global models

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Abstract. The study of the competition between equilibrium disturbing and equilibrium restoring mechanisms, reveals that the various equilibrium departures as found in different plasmas, have much in common. They can be seen as disturbances of bilateral relation; relations effectuated by forward and corresponding backward processes in the sense of detailed balancing. The deviations from the equilibrium form of the atomic state distribution function and the electron energy distribution function of atomic plasmas, which are the result of the escape of photons and electron-ion pairs, can be given in a simple equation in which the escape per balance time plays a leading role. The same idea can be used to construct a characterisation method that relates external control parameters to average values of internal plasma properties such as the electron density, electron temperature and the gas temperature. The global discharge model presented here includes gas heating and is applicable to atomic plasmas for which convection can be neglected.

1. Introduction
The success of plasma technology with its steadily increasing applications is mainly due to the fact that the plasma state has virtually no limitation in creating fluxes of (strongly) non-equilibrium mixtures of photons and radicals. These fluxes leave the production zone towards the application region where use is made of their chemical nature, energy and/or momentum. If this outward transport is large compared to the internal activity of forward and backward processes, it will create deviations from equilibrium in the active plasma zone. A sketch of the active plasma zone can, in steady state (SS), be given by

\[ \phi \rightarrow \nu \rightarrow \phi \]

where the input and output side are denoted by \( \alpha \) and \( \beta \) respectively, while the fluxes are given by \( \phi \) and \( \phi \). If we deal with SS conditions we have \( \phi = \phi \).

The arrows in the \( \{\mathcal{A},\mathcal{B}\} \) system refer to the internal activity in the plasma and in order to produce the efflux at the \( \beta \)-side the arrow \( \alpha \rightarrow \beta \) must be larger than that in the opposite direction. The activities in the plasma are associated with frequencies of the forward \( (\nu) \) and backward \( (\nu) \) processes. The expression at the right hand side gives the balance for the output side \( \beta \), stating that in SS the efflux \( \phi = N_\beta \nu_\beta \), the product of a (generalized) density at the \( \beta \)-side and transport frequency, is responsible for and equal to the difference between the rates the forward \( \alpha \rightarrow \beta \) and backward process \( \beta \rightarrow \alpha \).

The presence of the effluxes on the global level (the plasma as a whole) will have consequences on various internal stages of the plasma. It may lead to an inequality of the temperatures of different

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plasma components or it may distort distribution functions such as the Atomic State Distribution Function (ASDF) or the Electron Energy Distribution Function (EEDF). In general we can say that the larger the efflux or leak, the larger the deviations from Local Thermal Equilibrium (LTE) will be. However, LTE has many aspects and therefore we need a precise description of the relation between LTE-deviations and the underlying effluxes.

In the past, several studies were devoted to the validity regions of LTE-conditions. Especially the effect of the leak of radiation on the ASDF was given much attention [1] but we have shown that under certain conditions the escape of charged particles is much more important [2]. One can also find several studies in literature on the relation between the external control parameters and the properties of the electron gas. These so-called global discharge models are especially well-known in the field of low electron density plasmas for IC fabrication [3] but they can also be used for atmospheric atomic plasmas [2].

In the present study we will give common bases to the LTE-validity-criteria and the global discharge models and show that they are special cases of a more general treatment of the competition between transport and equilibrium restoring processes. It will be shown that transport leads to disturbances of Bilateral Relations and that the global input-output picture sketched with Equation (1) can also be used on more elementary plasma levels. This method of disturbed Bilateral Relations (dBR) can be employed as a guide for the classification of equilibrium departures, as an assistant for the interpretation of plasma spectroscopy and to get insight in the relation between the external control parameters and internal conditions.

This paper is organized as follows; the general treatment of the dBR method, given in section 2, is followed in section 3 by an application to the escape of radiation, while section 4 deals with the efflux of electron-ion pairs. Section 5 gives a description of the departure of the EEDF from its equilibrium (Maxwell) form as a consequence of inelastic processes. In section 6 we deal with global models.

We will confine ourselves here to fluid-like atomic plasmas of low degree of ionization ruled by Electron Excitation Kinetics (EEK) [4] under steady state conditions. The method of dBR for transient strongly ionized plasmas will be dealt with in [5]. A method to solve the dBR-based global model will be given in [6], while [7] gives an application of dBR to microwave induced plasma in hydrogen under atmospheric conditions.

2. Disturbed bilateral relations

We start with the fictitious situation of full thermodynamic equilibrium (TE) for which the principle of DB is applicable. This states that in TE, equilibrium is present on each system-level in the sense that each forward process (irrespective its nature) is balanced by the corresponding backward process. This backward process acts along the same channel but in the opposite direction as the forward process. Consequently, plasma in TE can be seen as an ensemble of Bilateral Relations (BR): ‘generalized levels’ or system-parts linked up by forward and corresponding backward processes. Consequently, the departure from equilibrium can be described as a disturbance of one or more of these bilateral relations by one or more transport fluxes.

The macroscopic level of the plasma was already sketched in the introduction (Equation (1)) where the imbalance of the active plasma zone as a whole was discussed by considering the activity between the input and output side. Inspired by the principle of DB we will extrapolate this macroscopic picture to more elementary plasma levels.

The influence of transport on the departure from equilibrium can be visualized by disturbed bilateral relations dBR, each between two plasma levels or system parts, \( \alpha \) and \( \beta \). For such a two-fold structure the balance at the output-side \( \beta \) reads \( N_{\beta} V_{\beta} = N_{\alpha} V_{\alpha} - N_{\beta} V_{\beta} \).

For \( \phi=0 \) (or \( \nu_t=0 \)) the principle of DB states that

\[ \text{with the nature of a process we refer to whether the transition is induced by electron collision, heavy particle collisions, the emission or absorption of a photon etc.} \]
\[ N_\alpha^{eq} v_f = N_\beta^{eq} v_b; \quad \phi_\alpha = 0 \quad \phi_\beta = 0 \quad \alpha \rightarrow v_f \quad v_b \leftarrow \beta \]  

(2)

Dividing Equation (1) by Equation (2) gives:

\[ y(\alpha) = y(\beta)[1 + \nu t \tau_b] \]  

(3)

where \( \nu t \tau_b = \nu f \nu b^{-1} \) is the escape per balance time \( \tau_b = \nu b^{-1} \). Here we introduced the parameter \( y = N/N^{eq} \) to express the densities in units of the corresponding equilibrium values. Due to the unidirectionality of \( \phi \) and \( \phi \) the density of level \( \alpha \) (the input side) will be pushed up while \( \beta \) (the leak side) will pulled down. That is indeed in accordance with Equation (3) which shows that the deviations from the equilibrium densities are in a linear way related to the dimensionless quantity \( \nu t \tau_b \). Note that it is assumed that the equilibrium departure does not change the frequencies \( \nu f \) and \( \nu b \) [2].

In the subsequent sections we will find various examples in which system parts \( \alpha \) and \( \beta \) can play various roles; such as that of 1) two atomic levels, 2) two subsequent ion stages, 3) two energy intervals in the electron energy space or on an even higher stage 4) \( \alpha \) can refer to the group of electrons \{e\} and \( \beta \) to that of the heavy particles \{h\}. The transport leak \( \phi \) can be realized by the escape of 1) photons, 2) electron-ion pairs 3) tail electrons (removed due to inelastic collisions) or 4) by the heat loss from \{h\} to the environment.

**Particles, energy and momentum**

The quantity \( N \) in Equation (2) may refer to a number density; for instances the density of atomic (or ionic) states. However, it can also be used for the energy density or momentum density. In section 6.3 we will give an example where the energy variant is used. In this study we will not deal with situations in which \( N \) refers to a momentum density.

**Equilibrium criterion and distribution functions.**

The simple Equation (3) can in many cases be used to predict (parts of) distribution functions and serves as a general formulation for equilibrium criteria: There is equilibrium provided

\[ \nu t \tau_b < < 1 \quad \text{or} \quad \nu t \tau_b < 0.1 \]  

(4)

In words: equilibrium is (almost) established if the number of leaks per balance time is much less than unity (or less than 0.1). In this way a general (quantitative) boundary criterion is introduced. This general criterion covers the existing ones but we will also introduce novel applications of (4).

**Small or severe departures: Proper and improper balances.**

If the leak can be neglected we have a so-called proper balance; an equilibrium balance of forward and corresponding backward processes \( (N_\alpha^{eq} v_f = N_\beta^{eq} v_b) \), whereas if the leak dominates (in steady state) a so-called improper balance is present in which the number of processes arriving at the leak-side \( \beta \) equals that of the ‘outward’ processes leaving this \( \alpha \beta \) system (thus \( N_\alpha v_f = N_\beta v_b \)) [4].

**Maxwell, Saha, Boltzmann and Planck**

Depending on the nature of the equilibrium restoring process, we can distinguish between proper balances of the Boltzmann (de)excitation), Saha (ionization/recombination), Maxwell (elastic energy transfer), and Planck (absorption/emission) type. It is very well possible that a proper balance of a certain type is (almost) in equilibrium whereas others are not. We then speak of partial equilibria. For instance pLSE (partial Local Saha equilibrium) refers to the situation in which (usually) an upper part of the atomic system is ruled by a Saha balance (ionization/recombination in equilibrium) and in that case the density obeys the Saha formula [8].
\[ \eta^s(p) = \left( n_e/2 \right) \left[ \frac{n_+/g_+}{(2\pi n_e kT_e)^{3/2}} \right] \exp \left( \frac{I_p}{kT_e} \right) \]  

(5)
in which \( \eta(p) = n(p)/g(p) \) is the number density of an atomic state, that is the number density \( n(p) \) of a level ‘\( p \)’ per statistical weight \( g(p) \); \( n_e \) and \( g_+ \) are the number density and the statistical weight of the ion ground-level respectively (e.g. \( g_+(H) = 1 \) and \( g_+(Ar) = 6 \)), whereas \( I_p \) is the ionization energy of the level in question.

3. The escape of radiation: departure from Boltzmann equilibrium

The escape of radiation: will cause deviations from equilibrium. Especially for plasmas with relatively low \( n_e \) values this can modify the ASDF considerably. In order to study the degree of the equilibrium departure and its dependence on plasma properties we start with a case-study in which \( \alpha \) and \( \beta \) play the role of the ground state and the first excited resonant level; say \( \{ \alpha, \beta \} = \{1,2\} \).

\[
\begin{array}{c|c|c}
\alpha = 1 & \rightarrow & \beta = 2 \\
| \begin{array}{c} n(1) \ n, K(1,2) \\
\end{array} & n(2) \ n, K(2,1) & \leftarrow \\
\begin{array}{c}
\leq \equiv \\
| \begin{array}{c}
\leq \equiv \\
\end{array}
\end{array} & n(2) A^*(2,1) \\
\end{array}
\]  

(6)
The underlying proper balance is the so-called Boltzmann balance formed by forward and backward processes of electron-induced transitions. If this balance is in equilibrium the Boltzmann relation between the densities of atoms in state ‘\( 1 \)’ and ‘\( 2 \)’ is applicable:

\[ \eta^B(2) = \eta^B(1) \exp \left( -E_{12}/kT_e \right) \]  

(7)
where \( E_{12} \) is the energy distance between the levels ‘\( 1 \)’ and ‘\( 2 \)’. The superscript ‘\( B \)’ refers to Boltzmann. The leak disturbing Boltzmann Equilibrium (BE) is formed by the escape of radiation generated by radiative decay of the upper level ‘\( 2 \)’. It creates an ‘outward’ flux \( \phi \) for level ‘\( 2 \)’ which in the same time serves as an inward flux \( \phi \) for level ‘\( 1 \)’; thus indeed \( \phi = \phi \). The transport frequency at the leak side equals \( \nu = A^*(2,1) \), the modified radiative transition probability, in which the asterisk (the modification) accounts for the fact that re-absorption may occur. The frequency of the equilibrium restoring process at the leak side \( \beta \) equals \( \nu_b = n_e K(2,1) \) where \( K(2,1) \) is the rate coefficient for the de-excitation 1 \( \leftarrow \) 2 induced by electron impact. Thus, according to Equation (3) the departure from equilibrium is given by

\[ y(1) = y(2) \left[ 1 + \left[ \nu, \tau \right]^B \right] \quad \text{with} \quad \left[ \nu, \tau \right]^B = A^*(2,1)/n_e K(2,1) \]  

(8)
the number of leaks per balance time. Again the superscript “\( B \)” refers to Boltzmann while \( y = \eta/\eta^B \).

The Corona balance: If \( \left[ \nu, \tau \right]^B \) in Equation (8) is much larger than unity, which happens if \( n_e \) is small enough\(^4\), we say that the density of level ‘\( 2 \)’ is determined by the corona balance (CB): a balance for level ‘\( 2 \)’ formed by the population by electron excitation (1 \( \rightarrow \) 2) and depopulation by means of radiative decay (1 \( \leftarrow \) 2). This clearly is an improper balance since the forward and backward processes are not each other inverse process. The density \( n(2) \) can, in good approximation be found using \( \left[ \nu, \tau \right]^B \) as a correction on the Boltzmann value \( n^B(2) \) (Equation (7)).

\(^3\) The level indicated by ‘\( 2 \)’ is the second level (first excited); not necessarily the level with principle quantum number 2. Sometimes ‘\( 2 \)’ can even refer to a group of levels such as the 4s group of Ar.

\(^4\) The \( K(2,1) \) is a de-excitation rate and thus only weakly temperature dependent; note that the value of \( A^*(2,1) \) depends on the ground state density, since the modification (\( \ast \)) depends on re-absorption process 1 \( \leftarrow \) 2.
For plasmas with sufficiently small $n_e$-values we can apply the same dBR procedure to higher levels and get a relation between the ground state ‘1’ and level ‘3’, between ‘1’ and ‘4’ and so on. Each dBR (thus $\{\alpha, \beta\} = \{1, 2\}, \{1, 3\}, \{1, 4\}$...) gives a relation between the density of the ground state and the excited states ‘2’, ‘3’ and so on. In this way the CB-part of the ASDF can be constructed.

Some fine-tuning can be used to correct for the population of excited levels due to contribution of other levels than the ground state. Most important is the (radiative) cascade contribution giving corrections in the order of 20% [4]. After that (fixed) correction we get an analytical description of the corona part of the ASDF that was found to be rather accurate [9]. Constructing a numerical model that takes all other population processes into account is only useful if the underlying rate coefficients are accurately known5. At this moment there is no atomic (or ionic) system for which this is the case.

**Diagnostic implications.** The preceding shows that due to the escape of radiation the ASDF will deviate from the equilibrium form as predicted by Boltzmann. It is therefore not allowed to determine the electron temperature from the slope of the ASDF. However, the equilibrium departure is (mainly) given by the factor $[\nu, \tau_b]^B$ and these can be determined using simple analytical Collisional Radiative Models (CRM). With this knowledge we can modify the measured ASDF and determine $T_e$ and $n_e$ out this modified plot.

**The equilibrium criterion; the boundary level $p_{cr}$**

Following the general form of the equilibrium criterion as given by Equation (4) one could define a criterion like: $[\nu, \tau_b]^B (p) = A^*(p, I) / n_e K(p, I) < 0.1$. The densities of levels $p$ satisfying this condition are not affected by radiative decay. However, it is preferable to work with the (total) radiative escape per (total) collisional live-time

$$[\nu_{tot}, \tau_{tot}]^B (p) = A^*(p) / \{n_e K(p)\} = 10^{23} \left(\frac{\hat{T}_e + 2}{\hat{T}_e^{0.5}}\right) p^9 n_e^{-1} Z^6$$

where $A(p)$ and $n_e K(p)$ are respectively the total probability of radiative and collisional depopulation, $\hat{T}_e$ the electron temperature in eV, $Z$ the charge number of the core and $p$ the effective quantum number

$$p = Z (Ry/L_p)^{1/2}$$

Now we can introduce the collision radiation (CR) boundary level $p_{cr}$ for which $[\nu_{tot}, \tau_{tot}]^B (p_{cr}) = 1$.

Due to the high exponent of $p$ in Equation (9) we get a sharp position of $p_{cr}$ and a clear transition between levels that are radiative $p < p_{cr}$ and collisionally $p > p_{cr}$ dominated. The rather strong dependence of $p_{cr}$ on $Z$ is due the fact that for increasing $Z$ the radiative transition probability increases with $Z^2$ whereas the collision frequency decreases with $Z^{-2}$ [4, 9].

As can be seen, the role of the electron temperature $T_e$ is not important; instead the degree of equilibrium departure for an atomic (or ionic) system is predominantly prescribed by the $n_e$-value. If $n_e$ is relatively small we get a lower part of the ASDF determined by the corona balance CB. The plasmas, for which the lower part of the (dominant) system is ruled by the CB, are denoted by CB-plasmas. For sufficiently high $n_e$ -values $p_{cr}$ will lie below the first excited level; i.e. $p_{cr} < '2'$ (cf. note b). The system is said to be full collisional (shortly: full-C).

It is a misconception that the demand $p_{cr} < '2'$ is a sufficient criterion for the presence of Boltzmann-Saha equilibrium. The reason is that, apart from the escape of photons also the efflux of charged particles creates deviations from equilibrium. This will be dealt with in next section.

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5 Numerical models for the CB can be useful if non-EEK processes like Penning ionisation are important
4. The efflux of charged particles: Departures from Saha equilibrium

The distortion of the ASDF as created by the efflux of electron-ion pairs (e-i) is especially important for the case of small-sized plasma parts with relatively large $n_e$-values. Due to large gradients, (e-i) pairs will diffuse towards plasma-wall, where recombination takes place. In the active plasma zone, where these (e-i) pairs are being created, the Saha balance of ionization and recombination will be out of equilibrium. The effective ionization is mainly formed by a stepwise excitation flow through the excitation space: the system of excited levels. Especially the first excited levels are ruled by electron impact (de)excitation, and the production/destruction balance of excited levels is denoted by the Excitation Saturation Balance (ESB). Here we will study the effect of the ESB on the ASDF for the case that the escape of radiation can be ignored; thus the first excited level lies below the $p_{cr}$-value as predicted by Equation (9); the system is so to say full-C. We start by applying the method of dBR to the main atomic system: $\{\alpha, \beta\} = \{1,+\}$; the roles of $\alpha$ and $\beta$ are thus played by the ground states of the atom (‘1’) and ion (‘+’) of the main gas in an active plasma zone.

\[
\phi_t \rightarrow \begin{array}{c}
\alpha = 1 \\
n_1 \nu_f
\end{array} \quad \begin{array}{c}
\beta = + \\
n_+ \nu_b
\end{array} \quad \rightarrow \begin{array}{c}
\phi = n_+ \nu_i = \nabla \cdot n_+ \mathbf{w}_+
\end{array} \quad (11)
\]

The underlying proper balance is the Saha balance formed by forward (ionization) and backward ($2e$-recombination$^6$) electron induced transitions; the frequency of the equilibrium restoring process at the leak side $\beta$ equals $\nu_b = n_e^2 K(+,1)$ where $K(+,1)$ is the rate coefficient for $2e$- recombination. If this balance is in equilibrium the Saha relation between the atomic and ionic ground state is applicable (cf. Equation (5)). The leak disturbing Saha Equilibrium (SE) is formed by the efflux $\phi_t = \nabla \cdot n_+ \mathbf{w}_+$, which equals the divergence of the ion flux density ($\mathbf{w}_+$ is the ion drift velocity). This can be written as $\phi_t = n_+ \nu_i$; i.e. the ion density, $n_+$, times a transport frequency, $\nu_i$. We assume that only one type of singly ionized species is present so that due to charge neutrality, $n_e = n_+$ and $\mathbf{w}_+ = \mathbf{w}_+$. Employing the general formula (cf. Equation (3)) we find the following relation between the ground state and the ion state

\[
y(1) = y(+)(1 + [\nu_i \tau_b]^S) \quad \text{or} \quad \delta b(1) \equiv b(1) - 1 = [\nu_i \tau_b]^S. \quad (12)
\]

In the expression we introduced $b \equiv n/n^S = y/y(+)$ with $n^S$ as prescribed by the Saha formula (cf. Equation (5)) (thus $N_{eq}^{n^S} = n(1)$). It is clear that the Saha-normalized overpopulation $\delta b(1)$ equals the escape per balance time $[\nu_i \tau_b]^S = \nu_i [n_e^2 K(+,1)]^{1/2}$. The frequency of the backward, equilibrium restoring, process can be found via the application of detailed balancing

\[
n_+ \nu_b = n_e^2 K(+,1) = n_e n^S(1) K_{ion} \quad \text{so that} \quad \delta b(1) = \nu_i [(n_+/n_e)^{} n^S(1) K_{ion}]^{1/2}. \quad (13)
\]

For the rate coefficients $K_{ion}$ we can use an Arrhenius-type expression [2] which reads

\[
K_{ion} = C_i(S) \left[8kT_e/(\pi n_e)\right]^{1/2} \left[4\pi a^2\right] \left(R/I^*\right)^2 \exp(-I^*/kT_e), \quad (14)
\]

The symbol $I^*$ stands for the effective ionization potential; it is more or less equal to the excitation energy of the first level above $p_{cr}$. The idea is that excitation to level $p_{cr} + 1$ in fact implies ionisation, since it is immediately followed by stepwise excitation towards the ionisation continuum. Radiative processes during this ladder-like ionisation are not important. In the case of a full-C plasma we have

\footnote{This reverse process of electron ionisation: $A^+ + e^+ e \rightarrow A + e$ is usually denoted by 3 particle recombination. However, to distinguish between other three particle processes like $A^+ + e^+ A \rightarrow A + A$ we prefer the nomenclature $2e$-recombination. This should not be confused with dielectronic recombination.}
\( I^* = E^*_{12} \) and \( K_{ion} \) is almost equal to the rate of the first excitation step \((1 \rightarrow 2)\); i.e. \( K_{ion} = K_{1,2} \) (cf. [2]).

The general structure of this and subsequent equations makes it possible to switch easily to atomic plasmas of other chemical compositions (cf. [2]). The value of atomic-system dependent adjustment parameters \( C_i(S) \) and \( I^* \) can best be obtained by casting the rate coefficients as found in literature in an Arrhenius form as given in Equation (14). In [2] we have found for a full-C argon plasma that \( E_{12}(\text{Ar}) = 12.06 \, \text{eV} \) and \( C_i(\text{Ar}) = 0.244 \) and for helium \( E_{12}(\text{He}) = 19.38 \, \text{eV} \) and \( C_i(\text{He}) = 0.315 \).

For decreasing \( n_e \), more levels will enter the CB-domain, the CR boundary \( p_{cr} \) will increase while the value of \( I^* \) will approach the ionization potential; the value of \( C_i(S) \) has to be adjusted accordingly.

To come to a numerical expression for the escape per balance time we need an expression for the efflux. In cases that the efflux is diffusive we have \( n^+ \w + \mathbb{D} \n^+ \), so that the approximation \( \nu t \approx D_a \Lambda e^{-2} \) holds in which \( \Lambda e \) is the gradient length of the electron density whereas \( D_a \) is the ambipolar diffusion coefficient given by

\[
D_a = 2/(3 \sigma_{ia} n_a) (kT_h/\pi M_i)^{1/2} (1 + T_e/T_h) = 2/(3 \hat{\sigma}_{ia} \hat{n}_a) (kT_h/\pi M_i)^{1/2} (1 + T_e/T_h)
\]

(15a)

where \( T_h \) is the heavy particle temperature while \( \sigma_{ia} \) is the ion-atom cross section for momentum transfer and \( M_i \) the ion mass. In Equation (15a) we introduced \( \hat{n}_a = n_a/(10^{20} \, \text{m}^{-3}) \) and \( \hat{\sigma}_{ia} = \sigma_{ia}/(10^{-20} \, \text{m}^2) \). Defining \( \hat{D}_a = D_a \hat{n}_a \) (the \( D_a \)-value for \( n_a = 10^{20} \, \text{m}^{-3} \)) we get numerically

\[
\hat{D}_a = 2/(3 \hat{\sigma}_{ia} (kT_h/\pi M_i)^{1/2} (1 + T_e/T_h) = 5.521 \times 10^{11} \, (\hat{\sigma}_{ia} A^{1/2})^{-1} \, F(T_e, T_h)
\]

(15b)

with \( A \) the ion mass number and \( F_1(T_e, T_h) = \hat{T}_e^{-1/2} (1 + T_e/T_h) \). Combining Equations (13-15) we find that

\[
\delta b(1) = \left[ \nu_1 \tau_1 \right]^{1/2} = 1.30 \times 10^7 \, C_b \, \hat{D}_a \left( \hat{n}_a \hat{\Lambda}_e^{-1} \hat{T}_e^{-3/2} \exp(-I^*_2/kT_e) \right) \]

(16)

where \( I^*_2 = I^* - I_1 \) and \( C_b(S) = (2g_i/g_f) \, C_i(S) \, (I^*/R)^{2} \) while \( \hat{n}_e, \hat{n}_a, \) are \( n_e \) and \( n_a \) expressed in \( 10^{20} \, \text{m}^{-3} \) and \( \hat{\Lambda}_e \) is given in mm.

This equation clearly shows that large \( \delta b(1) \)-values are obtained for small plasmas with low \( n_e \), low \( n_a \) and large \( \hat{D}_a \) values\(^7\). Examples of adjustment parameters are \( C_b(\text{Ar}) = 39 \) and \( C_i(\text{He}) = 26 \).

Diffusion induced equilibrium departures were studied for different plasmas sources in [2] and two main gases (Ar and He). It was found that replacing Ar by He leads to larger Saha-departures. Due to the 10 times larger mobility of He ions, He plasmas will not easily be kept in equilibrium.

The Excitation Saturation Balance (ESB)

The structure of the ASDF of CB-plasmas was studied by taking the atomic ground state as reference and applying the method of dBR on the couples \{1,2\}; \{1,3\}; \{1,4\} etc.. Here the ESB effect on the ASDF will be investigated by taking the ionic ground state as reference and analyzing the dBR couples \{1, +\}; \{2, +\}; \{3, +\} and so on.

For a full-C plasma the ionization is mainly realized by means of a stepwise excitation flow that propagating from \( I \rightarrow + \), has first to pass the excited level ‘2’ then ‘3’ and so on. This means that we have on each position in the chain the same influx, \( \phi_0 = \phi \) (see Equation (17)). Thus the dependence of

\(^7\) We use the *-symbol for ‘modification’ (like for \( I^* \)) and ^ for normalisation, like \( \hat{n}_e \) and \( \hat{T}_e \).
\( \delta b(p) \) on the effective principal quantum number \( 'p' \) can be obtained by constructing a dBR for the \( \{ \alpha, \beta \} = \{ p, + \} \) system which has the same leak-side as the dBR \( \{ l, + \} \) whereas the role of the influx is played by the (effective) rate of the \( (p-1) \rightarrow p \) excitation process and equals \( \phi \). So for instance we get the following dBR of \( \{ 2, p \} \):

\[
\begin{align*}
\phi & \rightarrow l \\
\phi & \rightarrow \alpha = 2 \\
\beta & = + \\
\phi & \rightarrow \phi = n_+ v_t
\end{align*}
\]

Replacing in Equations (13&17) the ground level \( 'l' \) by level \( 'p' \) and the forward frequency \( n_e K(1, 2) \) by \( n_e K(p, p+1) \) we get \( \delta b(p) = v_f / [ (n_e/n_+) \ n'(p) \ K(p,p+1) ] \). Inserting the hydrogenic approximation [2, 4]

\[
K(p,p+1) = 2.6 \times 10^{-14} p^4 T_e^{0.5} \exp\left( -\frac{I_{p'} - I_{p+1}}{kT_e} \right)
\]

we get:

\[
\delta b(p) = [ v_f \ \tau_b f^f(p) ] = 1.2 \times 10^7 \ \hat{D}_a \ \left[ \hat{n}_e^2 \hat{n}_a^2 \hat{l}^p \ p^6 \ \hat{T}_e \ \exp\left( -I_{p'} / kT_e \right) \right]
\]

**Figure 1.** The ASDF of ionizing plasma: 1) In steady state an outward flux of ions has to be compensated by a net ionization flow through the atomic system and an inward flux of ground state atoms. 2) Due to the drain of ions and the source of ground state atoms the lower lying states are overpopulated with respect to Saha, i.e. \( \eta > \eta_s \). This overpopulation \( (b = \eta / \eta_s) \) decreases with increasing effective quantum number \( 'p' \) i.e. decreasing ionization potential \( I_p \). Only the highest levels are in partial Local Saha Equilibrium (pLSE). For strongly ionizing plasma regions this part is not observable with optical emission spectroscopy.
So that, retaining the main p-dependency (that is taking \( \exp{-Ip/kTe} = 1 \)), it is found that:

\[
\delta b(p) = \nu_t \tau_b = b_o p^{-x} \quad \text{or} \quad \delta b(I_p) = \beta_o I_p^{x/2} \quad \text{with} \quad x = 6.
\]

This expression shows that large values of \( b(p) >> 1 \) can be found for lower levels in ionizing plasma parts (cf. Figure 1). However, for highly excited states the rates of ionization and recombination processes can be so large that equilibrium disturbing processes (associated with \( \nu_t \)) will have less influence on the equilibrium restoring Saha balance since \( \nu_b \) increases for approaching the ionization continuum. Thus \( \delta b(p) = \nu_t \tau_b \rightarrow 0 \) for \( I_p \rightarrow 0 \) and pLSE will be settled high in the system.

This dBR approach gives a reasonable description and some fine-tuning can be used to correct for other processes like direct ionisation. In [4] the ASDF was studied by constructing and solving the continuity equation in the excitation space. The result has the same structure as that of Equation (19) but the exponent \( x \) (\( x = 6 \) was proposed in [10]) was found to be variable and somewhere in the range between \( x = 5 \) and \( x = 6.5 \), thus slightly dependent on plasma conditions [11, 12].

**Diagnostic implications.** Thus, the fact that the system has to generate a stepwise ionization flow leads to a drastic change in the ASDF. The slope is variable and the slope-temperature \( kT_s = I_p/3 \) (if \( x = 6 \)); a value which is independent of \( T_e \) [2]! This means that equating \( T_e \) to the temperature found from the slope \( T_s \) of the lower part of the ASDF (as usually done) often gives wrong results.

However, the insights in the nature of the ESB can be used in the interpretation of spectroscopic data. Moreover the ASDF can be modified such that the value of the exponent \( x \) and the electron temperature \( T_e \) can be obtained out of that modified Boltzmann plot. This method was used in [11,12].

**The equilibrium criterion: the boundary level \( p_{ES} \).** Following the general equilibrium criterion (cf. Equation (3)), one can define a criterion like: \( \left[ \nu_t \tau_b \right]_{S}(p) = \delta b(p) = \nu_t / [n_1 \nu_1 (p,p+1)] < 0.1 \). The levels for which this criterion is fulfilled are in pLSE. It is also instructive to introduce the level \( p_{ES} \) on the boundary between ESB and pLSE. This is the level for which \( \delta b(p_{ES}) = \left[ \nu_t \tau_b \right]_{S}(p_{ES}) = 1 \).

### 5. The influence of fluxes on the EEDF: departures from Maxwell equilibrium

The escape of photons and effluxes of (e-i)-pairs will not only distort the ASDF but also the Electron Energy Distribution Function (EEDF). The reason is that inelastic collisions like \( I \rightarrow 2 \) are not compensated by the corresponding reverse super-elastic collisions \( 1 \leftarrow 2 \). This can, under certain conditions, also be studied by applying the method of dBR. To that end the EEDF has to be divided in a bulk and tail (with \( E_{12} \) on the boundary). The dBR \( /\alpha /\beta \) couple is then formed by \{Bulk, Tail\}. Thus the tail is the output side and the degree of equilibrium departure is established by computing for the tail electrons the number of ‘transport’ processes (tail removal by excitation) per equilibration (Maxwellization) time, giving \( (\nu_t \tau_b)^{Mbr} \). The tail population can be related to a tail temperature \( T_t \). By taking the bulk as reference and realizing that \( y(tail)/y(bulk) = T_t/T_e \) Equation (3) gets the form

\[
T_t/T_e = [1 + (\nu_t \tau_b)^{Mbr}]^{-1} \quad \text{with} \quad (\nu_t \tau_b)^{Mbr} = C_s(A) (n_1/n_e) (kT_e/E_{12})^x/2 \ln \lambda_c
\]

for the ratio of the tail \( T_t \) and electron \( T_e \) or bulk temperature [13]. Here \( \ln \lambda_c \) is the Coulomb logarithm and \( C_s(A) \) is the same adjustment parameter as that in Equation (15). Note that the form of the tail of the (EEDF) is thus established by the competition of the interactions between tail electrons and bound electrons (excitation = tail removal) on the one hand and tail and bulk electrons (Maxwellization) on the other hand. Since the bound electrons are ‘stored’ in ground state atoms, their density equals \( n_1 \) and it can be understood that the \( (\nu_t \tau_b)^{Mbr} \) is proportional to \( n_1/n_e \), the inverse of the ionization ratio. More details of this approach can be found in [13].
Note that this is an example of the application of dBR to higher system parts, namely the bulk and the tail of the electron energy space. In next section we will even go further by applying the dBR concept to the relation between the group of electrons \(\{e\}\) and heavy particles \(\{h\}\).

6. Global discharge models

The set of Equations (9, 16, 19, 21) gives a recipe to compute the deviations from equilibrium as manifested in the EEDF and ASDF. It provides the position of the boundary levels \(p_{cr}\) and \(p_{ES}\) and the degree of equilibrium departure \(\delta_{b}(1) = (\nu \tau_{b})^{S}\) and \((\nu \tau_{b})^{M_{b}t}\). These formulas are of great help for the characterization of plasmas and the interpretation of plasma diagnostics. However, we need the values of \(n_e\) and \(T_e\) in order to be able to compute the various \(\nu \tau\)-values. These can be obtained experimentally or by using a plasma-transport model.

It is the aim of this section to show that these plasma properties can also be obtained directly from the values of the control parameters. A systematic treatment will be given of the relation between external control-parameters (pressure, power-density and plasma size\(^8\)) on the one hand and the plasma properties \((n_e, T_e, T_h)\) on the other hand. For this relation we use the set formed by the balance equations for the electron density, the electron energy and the heavy particle energy. They will be presented as dBR’s. The relations are now acting on higher structures; not between atomic levels but between the groups of electrons and heavy particles. The electron particle balance will be used for the \(T_e\)-determination whereas the two energy balances will give the value of \(n_e\) and \(T_h\).

In literature these models are known as global discharge models [3]. As far as we know they were until now mainly used for non-thermal plasmas, thus neglecting gas heating. Here and in [6] we will incorporate gas-heating as well.

6.1. The electron particle balance: the electron temperature

We confine ourselves to diffusive plasmas in SS where the ionization is balanced by outward diffusion in such a way that the inverse process of ionization, i.e. \(2e\)-recombination, is unimportant. This implies that the electron particle balance becomes an improper balance \((\nu \tau >> 1)\) and reads (cf. Equation (15))

\[
\tag{22}
\frac{n_e n_1 K_{ion}(T_e)}{\text{ionization}} = n_e D_a A_n^{-2} \quad \text{so that} \quad K_{ion}(T_e) = \hat{D}_a I(\hat{n}_a n_1 A^2)
\]

This is based on the same dBR as that given in Equation (11). By employing Equations (14) and (15) we get

\[
\hat{T}_e = \frac{\hat{I}^*}{\ln[C(S)\hat{D}_a^{-1}(R/\hat{I}^*)^2(\hat{n}_a \hat{n}_u \hat{A}_n^2 T_e^{0.5})] + 0.854}
\]

This expression shows that \(T_e\) in first instance depends on the value of \(I^*\) and that the influence of the atomic structure as expressed by \(C(S)(R/I)^2\), is reduced due to the logarithm. Low \(T_e\)-values are found for high-density plasmas with large gradient lengths, operating in a gas of low intrinsic diffusion.

This equation gives a rather good approximation tool to estimate the \(T_e\)-value. One should however keep eye on the various assumptions made in the derivation (cf. [6]). Note that in the simple case of a mono-atomic gas of low ionization degree we can replace \([\hat{n}_1 \hat{n}_u]\) by \(\hat{n}_1 \hat{n}_u\). However, in the

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\(8\) One can select another triad of control parameters such as gas-density, power per unit length and plasma size.
case of a fluorescence lamp we see a clear distinction between \( n_1 \) and \( n_a \). The first is the ionization supplier (Hg) the second the diffusion obstructer (bugger gas, e.g. Ar).

An important and remarkable result of this derivation is that the electron particle balance in SS does not give the electron density but the electron temperature. Moreover, although \( T_e \) is the internal energy parameter it is not (directly) determined by the power, the important external parameter controlling the energy content of the plasma. The \( T_e \)-value primarily depends on \( I^* \) and the shape of the \( n_e \)-profile (as typified by \( A_e \)) (not the magnitude of \( n_e \)) and via the diffusion coefficient on the value of \( n_1 \).

However, there are two slight indirect power-dependences of \( T_e \). Firstly, for plasmas with relative low \( n_e \)-values (CB-plasmas) we will find that increasing the power leads to lower \( T_e \)-values!! The reason of this counter-intuitive trend is that increasing the power (density) leads to higher \( n_e \) values (cf. section 6.2) which on its turn will lead to a lowering of \( I^* \) and thus (via Equation (23)) to a lower \( T_e \)-value. The physics behind the lowering of \( I^* \) is that for large \( n_e \)-values, direct ionization will lose importance; the creation of electron-ion pairs is ruled by stepwise ionization which can be done at lower \( T_e \)-values. For instance, as discussed in section 4 in the case of full-C plasma, (almost) any \( 1 \rightarrow 2 \) transition will eventually lead to ionization.

Secondly, for full-C plasmas (for these plasmas \( I^* = E_{12} \) can not be lowered) we can get an opposite trend. If the power increases while the pressure is kept constant (as usually done), this will lead to an increase of \( T_h \) and thus a decrease of \( n_1 \). This, on its turn, will enhance the diffusion coefficient so that \( T_e \) will increase. Such a moderate increase of \( T_e \) for increasing powers has been observed in atmospheric plasmas [14].

We conclude this subsection with a remark on the influence of convection. Usually, convection is much less important than diffusion but, at relatively high gas velocities, convection can indeed change the \( T_e \)-value. This can be a direct effect; namely, convective transport of electron-ion pairs can increase the transport frequency (\( \nu_t \) in Equation (3)), which leads to an increase of the \( \nu_t \)-value and thus an increase of \( T_e \). But most importantly is the decrease of \( T_h \) by which the formation and destruction of molecular ions can be enhanced. In [2] we found that this can lead to a dramatic increase of the leak frequency of electron-ion pairs, which can result in an enhancement of \( T_e \) by a factor of 2. Thus, although convective cooling of the plasma indeed leads to a decrease of \( T_h \) we see the counter-intuitive trend that convective cooling enhances \( T_e \), the temperature of the most active species!

6.2. The electron energy balance: the electron number density

The electron energy balance in simplified form

\[
\varepsilon = n_e n_h K_{heat} (k_BT_e - k_BT_h) + n_e n_1 K_{crea} (E) (I^* + 3/2 k_BT_e)
\]

shows that power density \( \varepsilon = P/V_{ac} \) (\( P \) is the power and \( V_{ac} \) the volume of the active plasma zone) is divided over two channels; the heat channel and the plasma creation channel.

In the heat channel kinetic energy is transferred from the electron to the heavy particles (by means of elastic collisions) whereas the plasma creation channel guides the energy flow associated with excitation and ionization (thus inelastic) processes.

The rate of heat exchange is given by

\[
K_{heat} = 3 (m_e/M) K_{mom} \quad \text{with} \quad K_{mom} = \sigma_{eh} (8 kT_e/m_e)^{1/2}
\]

9 In the general case we should take as many types of collisions into account as there are different heavy species; in the case of low degree of ionization (to which we confine ourselves here) we can replace \( n_h \) by \( n_1 \).
the rate for momentum transfer between electrons and heavy particles for which we assume that it can be approximated with the product of an (average) electron-atom cross section and the thermal velocity of the electrons. The rate for inelastic collisions $K_{crea}$ can be replaced by $K_{ion}$ (cf. Equation (14)) that handles the efflux of ion-electron pairs. But in CB-plasmas we have to deal with the inelastic collisions that lead to the creation and escape of photons and radicals. This will change $K_{crea}$ although the Arrhenius expression with a exponent based on the excitation energy $E_{12}$ (like in $K_{ion}$ for ESB-plasmas) still gives a good approximation. Here we will confine ourselves to the simple case of ESB-plasmas for which $K_{crea} = K_{ion}$.

Note that expression (24) shows that both terms are (in first order) proportional to $n_e$ so that it is useful to introduce the power per electron defined as $\theta = \epsilon/n_e$. The $\theta$-value can be determined theoretically or by means of experiments [15]; and if $\theta$ is known, it can be employed to estimate $n_e$ using $\epsilon$ that, on its turn, can be deduced from the driving power and the (estimated) value of $V_{dc}$.

6.3. The heavy particle energy balance

As discussed above, the creation term in Equation (24) is closely related to the electron particle balance that can be seen as a dBR. In a comparable way the heat term is associated with the energy balance of the heavy particles and again a dBR representation is very instructive. It can be depicted as follows

$$\{e\} = \alpha n_e n_h K_{heat}(k_B T_e - k_B T_h) = \nabla \cdot \lambda \left( \nabla T_h \right)$$

(26)

showing that part of the heat flux from the electrons $\{e\}$ to the heavy particles $\{h\}$ is returned in the backward processes whereas the rest is transported to the environment. Below the dBR in Equation (26) the corresponding energy balance of the heavy particle is given for the case that the transport is conductive. In this way we recognise the same structure as that of Equation (3) and we find

$$[\nu \tau]^{Meh} = \lambda [A_h^2 n_h n_{th} K_{heat}]^{-1} \text{ or } [\nu \tau]^{Meh} = (m_h u_{th}^h/(m_e u_{th}^e)) (6 n_e n_h \sigma_{hh} \sigma_{eh} \Lambda_h^2)^{-1}$$

(27)

where $A_h$ is the gradient length of the heavy particles temperature. The coefficient for heat conduction is approximately given by $\lambda = u_{th}^h k_p/(2 \sigma_{hh})$ where $\sigma_{hh}$ is the cross section for atom-atom collisions. The meaning of ‘y’ (cf. Equation (3)) can be established by taking $T_e$ as the norm so that $y(\{e\}) \equiv 1$. Since in the limit of $\phi = 0$ we have $T_h = T_{eq} = T_e$ we obtain the following temperature ratio

$$\frac{T_h}{T_e} = \left[ 1 + 7.1 \times 10^6 \frac{T_h}{T_e} \frac{\sqrt{A}}{n_e n_h \nabla_{hh} \sigma_{hh} \nabla_{bh} \Lambda_h^2} \right]^{-1}$$

(28)

This formula gives a reasonable estimation for situations not too far from $T_e = T_{h eq}$-equilibrium. For plasmas with low $T_h$-values the temperature of the environment $T_{env}$ should be taken into account. This can be done by multiplying the constant $7.2 \times 10^6$ with $(T_p-T_{env})/T_h$ (cf. [6]).

Expression (28) shows that especially plasmas with low $n_e^*$ values, low $n_{rh}^*$ values and/or small sizes, $A_h$, will be far from thermal equilibrium. In these cases we find $T_e >> T_h$; the temperature of the heavy particle temperature will stay close to that of the environment. So CB-plasmas are plasmas that are far from Temperature Equilibrium. These plasmas are known as non-thermal plasmas. They are usually typified by low $\epsilon$-values (which keep $n_e$ low).

10 It is assumed that the heat conduction of the neutral gas is dominant and that the reactive part can be neglected.
By increasing \(\varepsilon\)-values and thus \(n_e\) we will enter the realm of thermal plasmas the \(\nu \tau\) will go down and the heavy particle temperature \(T_h\) will approach \(T_e\).

The system of three Equations (23), (24) and (28) can be solved so that a relation between external control-parameters (pressure, power-density and plasma size) on the one hand and the plasma properties \((n_e, T_e\) and \(T_h)\) on the other hand can be obtained. This will be the topic of paper [6].

7. Conclusions

In this paper we introduced the method of disturbed Bilateral Relation (dBR). A method that follows the competition between equilibrium disturbing (transport fluxes) and equilibrium restoring processes from the global down to elementary plasma-level. On the global level the dBR-method can serve as a tool to construct global-discharge-models. These give recipes to compute internal plasma parameters, such as the electron density and temperatures of the electrons and heavy particles as functions of external plasma control parameters. More elementary the method gives validity criteria for the presence of the equilibrium form of the ASDF and EEDF. In this way, the dBR-method can be used as a guide in the interpretation of plasma diagnostics.

The method of dBR was in past used for the characterization of microwave-induced plasmas and inductively coupled plasmas [2]. In the present Journal, studies are published of the application of the dBR-method on highly transient EUV emitting plasmas [5] on microwave plasma created in an atmospheric hydrogen flow [7] and on the construction of global models for plasmas for which gas-heating [6] is important. In the future we plan to apply the dBR method to construct global models for strongly convective plasmas.

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