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On the Validity of Assumption of Local Thermodynamic Equilibrium

Hiroichi SHIMOODA
Department of Astronomy and Earth Science,
Aichi University of Education

Abstract

The validity of assumption of local thermodynamic equilibrium (LTE), particularly, astronomical local thermodynamic equilibrium (LTE-R) under LOS-Σ, the local production of radiant entropy and the flux of radiant energy in LTE-R are investigated.

It is concluded that it should be necessary for LTE-R to be a new parameter $\sigma = 1$ together with an asymptotic condition besides Thomas' criterion. In LOS-Σ, $\sigma = 1$ physically means that departure coefficients of energy levels of atom are all equal. It is moreover concluded that, in LTE-R, the local production of radiant entropy in a certain frequency, the total local production of radiant entropy and the divergence of the total flux of radiant energy under the influence of continuum are non-negative, respectively.

1. Introduction

The conditions for statistical equilibrium among atoms, electrons, and radiation, i.e., the necessary and sufficient conditions for thermodynamic equilibrium (TE) were first discussed by Dirac (1924) on the basis of principle of detailed balancing for unit mechanism.

The assumption of local thermodynamic equilibrium (LTE) is a necessary one to extend thermodynamics to non-equilibrium one. From a microscopic viewpoint, the validity of local equilibrium in thermodynamics was first discussed by Prigogine (1949), using Chapman-Enskog method. However it is not clear from his discussions whether or not such assumption of LTE is valid in the presence of a radiation field. Although a stellar atmosphere is not an enclosure in thermodynamic equilibrium, it is often assumed that Kirchhoff's law locally holds to a reasonable degree of approximation in a stellar atmosphere. Such assumption constitutes what Milne (1926) called an assumption of LTE. The equation of radiative transfer in LTE is obtained by substituting the Planck function for source function. The radiation field derived from this equation may be, in general, expected to be different from that described by the Planck function. It was however shown by Wildt (1956) that such practice under the strict radiative equilibrium contravenes the second law of thermodynamics.

On the basis of the LOS concept, a definition of an LTE configuration and a criterion for its validity were expressed by Thomas (1965). Recently Gebbie and Thomas (1968) have formulated a definition of astronomical local thermodynamic equilibrium (LTE-R) to make a distinction between LTE-R and LTE as follows: LTE implies that all distribution functions have their TE forms; LTE-R, all except that for photons.

On the other hand, Sampson (1965) studied another approach to LTE from the Boltzmann equation for photons and formulated a new definition for LTE, which requires only that the matter distribution functions entering the photon collision integral of the Boltzmann equation for photons can be approximated by those characteristic of thermal equilibrium at a local temperature. Let us call this definition LTE-S. As already demonstrated by Sampson (1965), the definition of LTE-R is more stringent than that of LTE-S, and of course, when scattering is negligible, the two definitions become equivalent. Accordingly, an approach to non-LTE from TE is described as follows:

TE $\longrightarrow$ LTE $\longrightarrow$ LTE-R $\longrightarrow$ LTE-S $\longrightarrow$ non-LTE.

However, Gebbie and Thomas (1968) have stated that there are circumstances where LOS is a necessary but not a sufficient condition for LTE, and that LOS-Σ in which LOS holds for all radiative transitions is a necessary and sufficient condition for LTE in all transitions. The LOS-Σ concept should not be wider than the LOS concept. However it is not clear whether or not the LOS-Σ concept coincides with LTE or LTE-R. In this paper, we investigate a necessary condition for LTE-R under LOS-Σ, the local production of radiant entropy and radiant energy in LTE-R.

2. A Condition Necessary for LTE-R under LOS-Σ

For simplicity, it is assumed that the kinetic temperature of gas is isothermal and the actual atom is described by the equivalent two-level atom representation. All net radiative brackets [NRB] are zero, since LOS-Σ is assumed. [NRB] is expressed in the form, following Thomas and Athay (1961)

$$[NRB] = \left[1 - \frac{\int \bar{I}_{\nu_{jk}} \Phi_{\nu_{jk}} d\nu}{S_{jk}}\right], \tag{1}$$

where $\bar{I}_{\nu_{jk}}$, $\Phi_{\nu_{jk}}$, and S_{jk} are the mean intensity of ν_{jk}-radiation, its line profile, and its source function, respectively.

In order to satisfy LOS-Σ, we have for every pair (j,k) each source function:

$$S_{jk} = \int \bar{I}_{\nu_{jk}} \Phi_{\nu_{jk}} d\nu. \tag{2}$$

Now, assuming that the kinetic temperature T of gas is equal to the electron temperature, and following Thomas' notations (1965), we can write the source function $B_\nu[T_{ex}]$ in the equivalent two-level atom representation as follows:

$$B_\nu[T_{ex}] = \frac{\int \bar{I}_\nu \Phi_\nu d\nu + \epsilon B_{\nu_0}[T] + \theta}{1 + \epsilon + \Delta}, \tag{3}$$

where

$$\epsilon = \left[1 - e^{-h\nu_0/kT}\right] C_{UL}/A_{UL}, \tag{4}$$

$$\theta = \frac{2h\nu_0^3}{c^2} \cdot \frac{g_L}{g_U} \cdot \frac{\delta_1}{A_{UL}} \cdot \frac{\mathcal{F}_U}{\mathcal{F}_L + \mathcal{F}_U}, \tag{5}$$

$$\Delta = \frac{g_L}{g_U} \cdot \frac{\delta_1}{A_{UL}} \cdot \frac{\mathcal{F}_U}{\mathcal{F}_L + \mathcal{F}_U} \left[\frac{\mathcal{F}_L}{\mathcal{F}_U} \cdot \frac{g_U}{g_L} \cdot \frac{\delta_3}{\delta_1} - 1\right], \tag{6}$$

and further, we introduce a new parameter σ and the grouping of terms:

$$\sigma = \frac{e^{h\nu_0/kT} - 1}{\frac{\mathcal{F}_L}{\mathcal{F}_U} \frac{g_U}{g_L} \frac{\delta_3}{\delta_1} - 1}, \tag{7}$$

$$\left.\begin{aligned}
\delta_1 &= \sum_{L<j\neq U} C_{Lj}[NCB]_{L,j} + \sum_{L>i} A_{Li}[NRB]_{L,i} + J_{Lc}, \\
\delta_2 &= \sum_{L<j\neq U} n_j A_{jL}[NRB]_{j,L} + \sum_{L>i} n_i C_{iL}[NCB]_{i,L}, \\
\delta_3 &= \sum_{U>k\neq L} A_{Uk}[NRB]_{U,k} + \sum_{U<\ell} C_{U\ell}[NCB]_{U,\ell} + J_{Uc}, \\
\delta_4 &= \sum_{U>k\neq L} n_k C_{kU}[NCB]_{k,U} + \sum_{U<\ell} n_\ell A_{\ell U}[NRB]_{\ell,U},
\end{aligned}\right\} \tag{8}$$

$$\mathcal{F}_L = R_{cL} + \delta_2 , \qquad \mathcal{F}_U = R_{cU} + \delta_4 ,$$
$$n_L[C_{LU} + B_{LU}\int \bar{I}_\nu \phi_\nu d\nu + \delta_1] - n_U[A_{UL} + B_{UL}\int \bar{I}_\nu \phi_\nu d\nu + C_{UL}] = \mathcal{F}_L,$$
$$- n_L[C_{LU} + B_{LU}\int \bar{I}_\nu \phi_\nu d\nu] + n_U[A_{UL} + B_{UL}\int \bar{I}_\nu \phi_\nu d\nu + C_{UL} + \delta_3] = \mathcal{F}_U,$$

C_{LU} and C_{UL} are the collisional rates and a net interchange between bound state and continuum is $P[\text{Rad};c,j] - R[\text{Rad};j,c] = R_{cj} - n_j J_{jc}$. Then θ is rewritten as follows:

$$\theta = \sigma \cdot \Delta \cdot B_{\nu_0}[T]. \tag{9}$$

From equations (3) and (9) under LOS-Σ (cf. equation (2)), we have

$$B_\nu[T_{ex}] = \left[1 + \frac{(\sigma - 1)\Delta}{\epsilon + \Delta}\right] B_{\nu_0}[T]. \tag{10}$$

According to Thomas' criterion for the validity of LTE, ϵ, θ and $\epsilon B_{\nu_0}[T]$ are homogeneous in the region where LOS-Σ holds. Therefore the coefficient $\left[1 + \frac{(\sigma-1)\Delta}{\epsilon+\Delta}\right]$ of the Planck function $B_{\nu_0}[T]$ on the right-hand side of equation (10) is a constant in the region where LOS-Σ holds. In order that the source function $B_\nu[T_{ex}]$ is equal to the Planck function $B_{\nu_0}[T]$, it is necessary to be $\sigma = 1$ together with LOS-Σ.

3. A Physical Meaning of $\sigma = 1$

In order that $\sigma = 1$, it is necessary to be from equation (7) and the Boltzmann law

$$\frac{\mathcal{F}_L}{\mathcal{F}_U} \cdot \frac{\delta_3}{\delta_1} = \frac{g_L}{g_U} e^{h\nu_0/kT} = \frac{n_L^*}{n_U^*}, \tag{11}$$

where n_L^* and n_U^* are respectively the equilibrium occupation numbers in the lower level, L, and upper level, U involved in the transition producing the spectral line ν_{UL} which are defined by means of the Boltzmann-Saha equation, according to Kalkofen

(1968). The actual occupation number n_i of atom in ith energy level is related to n_i^* according to $n_i = b_i\, n_i^*$, (12) where b_i is the departure coefficient as defined by Menzel (1937). From equations (8), (11), and (12) under LOS-Σ, a following equation is derived in Appendix:

$$\left(1-\frac{b_U}{b_L}\right)\left\{1+\frac{C_{LU}}{\sum\limits_{L<j\neq U} C_{Lj}\left(1-\frac{b_j}{b_L}\right)+J_{LC}}+\frac{C_{UL}}{\sum\limits_{U<\ell} C_{U\ell}\left(1-\frac{b_\ell}{b_U}\right)+J_{UC}}\right\}=0, \qquad (13)$$

where

$$\delta_1=\sum_{L<j\neq U} C_{Lj}[NCB]_{L,j}+J_{LC}=\sum_{L<j\neq U} C_{Lj}\left(1-\frac{b_j}{b_L}\right)+J_{LC},$$

and

$$\delta_3=\sum_{U<\ell} C_{U\ell}[NCB]_{U,\ell}+J_{UC}=\sum_{U<\ell} C_{U\ell}\left(1-\frac{b_\ell}{b_U}\right)+J_{UC}. \qquad (14)$$

In order to hold equation (13), it should be necessary to be

$$b_U/b_L = 1, \qquad (15)$$

or

$$1+\frac{C_{LU}}{\sum\limits_{L<j\neq U} C_{Lj}\left(1-\frac{b_j}{b_L}\right)+J_{LC}}+\frac{C_{UL}}{\sum\limits_{U<\ell} C_{U\ell}\left(1-\frac{b_\ell}{b_U}\right)+J_{UC}}=0. \qquad (16)$$

If this representation is reduced to that of the two-level plus continuum atom, the left-hand side of equation (16) is not zero. If not so, however, unknown numbers such as b_ℓ/b_U in equation (16) are too many to decide whether or not the left-hand side of equation (16) becomes zero. Hence in order to hold equation (13), it should be necessary to be at least $b_U/b_L = 1$. Since suffices U and L denote the energy levels refered to a spectral line under consideration, equation (15) should hold for any pair (U,L) as long as LOS-Σ is assumed, i.e.,

$$b_i = b_j = \text{-----------------} = b_k . \qquad (17)$$

Assuming an asymptotic condition that we have equipartition of the upper-level population with the electron continuum due to collisional ionization, we have

$$\lim_{k\to\infty} b_k = 1. \tag{18}$$

From equations (17) and (18), we obtain

$$b_i = b_j = \text{----------} = b_k = \text{-----} = 1. \tag{19}$$

The state of such a gas is then in LTE-R in the sense of Gebbie and Thomas (1968).

4. Local Production of Radiant Entropy and Radiant Energy in LTE-R

The equation for local production of radiant entropy of frequency x including the effect of continuum was derived by the author (1968) as follows:

$$\operatorname{div}\left(\Delta\nu_D \cdot \mathbf{E}_\nu / k\right) = \mathcal{X}\,(1+\gamma_x)\,\Psi_x, \tag{20}$$

where

$$\left.\begin{aligned} \mathcal{X} &= n_L B_{L\sigma} B_{\nu_0}(T)\,(1-e^{-\xi^*}), \\ \Psi_x &= \phi_x \int \left(S_x^* - j_x(\mathbf{n})\right) \xi_x(\mathbf{n}) \frac{d\Omega}{4\pi}, \end{aligned}\right\} \tag{21}$$

and the dimensionless quantities

$$\xi^* = h\nu_0/kT_{ex}, \quad \xi_x(\mathbf{n}) = h\nu_0/kT_\nu(\mathbf{n}), \quad S_x^* = S_\nu^*/B_{\nu_0}(T), \quad j_x(\mathbf{n}) = I_\nu(\mathbf{n})/B_{\nu_0}(T),$$

and the dimensionless absorption profile $\phi_x = \Delta\nu_D \phi_\nu$ ($\int \phi_x dx = 1$, $\Delta\nu_D$:the Doppler width) are defined.

The source function S_ν including the effect of continuum is expressed in the form

$$S_\nu = \frac{S_l + \gamma_\nu S_c}{1+\gamma_\nu}, \tag{22}$$

where

$$S_\ell = \frac{\int \bar{I}_\nu \phi_\nu d\nu + \epsilon B_{\nu_0}(T) + \theta}{1+\epsilon+\Delta}, \tag{23}$$

$$S_c = \frac{B_\nu(T) + q_\nu \bar{I}_\nu}{1+q_\nu}, \quad B_\nu(T) \approx B_{\nu_0}(T), \tag{24}$$

$$q_\nu = \frac{\sigma_c}{\varkappa_c} \equiv q_x, \quad \text{and} \quad \frac{d\tau_c}{d\tau_\ell} = r_\nu \equiv r_x. \tag{25}$$

In LOS-Σ, we have from equation (23)

$$S_\ell = \int \bar{I}_\nu \phi_\nu d\nu = \left[1 + \frac{(\sigma-1)\,\Delta}{\epsilon+\Delta}\right] B_{\nu_0}(T). \tag{26}$$

Since $\sigma = 1$ and the scattering coefficient for continuum $\sigma_c = 0$ ($q_\nu = 0$), we obtain from equation (24) and (26) $S_c = B_\nu(T) \approx B_{\nu_0}(T)$ and $S_\ell = B_{\nu_0}(T)$. Hence we have $S_\nu = B_{\nu_0}(T)$. Thus the state of this gas is in LTE-R.

Then $S_x^* = S_\nu / B_{\nu_0}(T) = 1$ and $j_x(n) \leqq 1$, as derived by the author (1968), since $\sigma = 1$.

From equation (20), therefore, we have div $(\Delta\nu_D E_\nu/k) \geqq 0$

$$\text{and} \quad \text{div}\,(E/k) = \int \text{div}\,(\Delta\nu_D E_\nu/k)\,dx \geq 0, \tag{27}$$

since $r_x = \frac{d\tau_c}{d\tau_\ell} > 0$.

The equation for the divergence of the flux of radiant energy of frequency ν was derived by the author (1968) as follows:

$$\text{div}\, F_\nu = k_0 \phi_\nu (1 + r_\nu)(S_\nu - \bar{I}_\nu), \tag{28}$$

where $k_0 = h\nu_0 (n_L B_{LU} - n_U B_{UL})$ and $\frac{k_0}{4\pi}\phi_\nu$ is the isotropic absorption coefficient.

Integrating equation (28) over the whole spectral line, we obtain as the divergence of the total flux of radiant energy

$$\text{div}\,F = \int \text{div}\,F_\nu\, d\nu = k_0 \int \phi_\nu r_\nu \left[B_{\nu_0}(T) - \bar{I}_\nu\right] d\nu$$

$$= k_0 B_{\nu_0}(T) \int \Phi_x \Upsilon_x (1 - \bar{j}_x)\, dx, \quad \left(\int j_x(n) \frac{d\Omega}{4\pi} \equiv \bar{j}_x \right) \tag{29}$$

since $S_\nu = B_{\nu_0}(T) = \int \bar{I}_\nu \Phi_\nu \, d\nu$, when $\sigma_c = 0$.
From equation (29), we have div $F \geqq 0$, since $\bar{j}_x \leqq 1$ is obtained from $j_x \leqq 1$.
In order that div F $= 0$, it should be necessary that $\bar{j}_x = 1$, since $\Phi_x \Upsilon_x > 0$. Then Φ_ν should be a delta-function in order that $\bar{I}_\nu = B_{\nu_0}(T)$ and further $S_\nu = B_{\nu_0}(T) = \int \bar{I}_\nu \Phi_\nu \, d\nu$ on account of LOS-Σ. If so, we have div $F_\nu = 0$ from equation (28). Hence it follows that the radiation field is in monochromatic radiative equilibrium. If not so, it follows that div F > 0, i.e., such gas is in self-exciting state.

5. Concluding Remark

The criterion for validity of LTE in the sense of Thomas (1965) is unsufficient even for that of LTE-R in the sense of Gebbie and Thomas (1968). As the criterion for validity of LTE-R, it should be necessary to be a new parameter $\sigma = 1$ besides Thomas' criterion. $\sigma = 1$ physically means that $b_U = b_L$, where b_U and b_L are the departure coefficients of two energy levels U and L related to a spectral line under consideration. Hence the departure coefficients of energy levels of atom should be all equal, since LOS-Σ is assumed. If an asymptotic condition that we have equipartition of the upper-level population with the electron continuum due to collisional ionization is assumed, we have $\lim_{k \to \infty} b_k = 1$. Then the state of such gas is in LTE-R in the sense of Gebbie and Thomas (1968). The local production of radiant entropy in a certain frequency and the total local production of radiant entropy under the influence of continuum are non-negative. The divergence of the total flux of radiant energy under the influence of continuum is also non-negative. Hence such gas that the divergence of the total flux of radiant energy is positive is in self-exciting state. If the line profile is expressed by a delta-function, the radiation field is in monochromatic radiative equilibrium which is more stringent than radiative equilibrium. If the line profile is not so, the gas is in self-exciting state.

Appendix

From equation (8), we have

$$\left.\begin{aligned} \mathcal{F}_L &= n_L^* b_L \delta_1 + n_L^* b_L C_{L\sigma} [NCB]_{L,\sigma} \\ \text{and} \quad \mathcal{F}_\sigma &= n_\sigma^* b_\sigma \delta_3 + n_\sigma^* b_\sigma C_{\sigma L} [NCB]_{\sigma,L}, \end{aligned}\right\} \tag{A.1}$$

where

$$\left.\begin{aligned} [NCB]_{L,\sigma} &= 1 - \frac{b_\sigma}{b_L}\frac{g_\sigma}{g_L}\frac{C_{\sigma L}}{C_{L\sigma}} e^{-\chi_{L\sigma}} \\ \text{and} \quad [NCB]_{\sigma,L} &= 1 - \frac{b_L}{b_\sigma}\frac{g_L}{g_\sigma}\frac{C_{L\sigma}}{C_{\sigma L}} e^{\chi_{L\sigma}}. \end{aligned}\right\} \tag{A.2}$$

In LTE, the electronic velocity distribution is of course the Maxwellian distribution. So if under some non-LTE conditions, its velocity distribution is still Maxwellian, then we have

$$[NCB]_{L,\sigma} = 1 - \frac{b_\sigma}{b_L}, \quad \text{and} \quad [NCB]_{\sigma,L} = 1 - \frac{b_L}{b_\sigma}. \tag{A.3}$$

Substituting equations (A.1) and (A.3) into equation (11), and using equations (14), we obtain after some calculations

$$\left(1 - \frac{b_\sigma}{b_L}\right)\left\{1 + \frac{C_{L\sigma}}{\sum\limits_{L<j\neq\sigma} C_{Lj}\left(1 - \frac{b_j}{b_L}\right) + J_{Lc}} + \frac{C_{\sigma L}}{\sum\limits_{\sigma<\ell} C_{\sigma\ell}\left(1 - \frac{b_\ell}{b_\sigma}\right) + J_{\sigma c}}\right\} = 0. \tag{13}$$

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