PHYSICAL REVIEW VOLUME 131, NUMBER 3 1 AUGUST 1963

Validity of Local Thermal Equilibrium in Plasma Spectroscopy*

HANS R. GRIEM
University of Maryland, College Park, Maryland
and
U. S. Naval Research Laboratory, Washington, D. C.
(Received 18 March 1963)

Criteria for the existence of local thermal equilibrium in various classes of plasmas are derived. In addition to general criteria that should also be fulfilled for homogeneous and time-independent plasmas, special criteria must be imposed on inhomogeneous and/or transient plasmas. The influence of the imprisonment of resonance radiation on the establishment of thermal equilibrium is considered, and it is concluded that even then complete thermal equilibrium can usually not be achieved for multiply ionized species.

INTRODUCTION

IN dense plasmas ($N_e \geq 10^{16}$ cm^{-3}) of moderate temperature ($kT \leq 5$ eV), the velocity distribution of free electrons is almost always Maxwellian. This is true even though such plasmas are usually transient and/or spatially inhomogeneous. Electron-electron collision times and mean free paths are so small that only very small changes in the distribution function occur over times and distances of this order. The free electron component is, therefore, well described by a kinetic temperature, which depends, in general, both on time and the spatial coordinates. If now the distributions over the various bound states and ionization stages and the velocity distributions of atoms and ions are as in a thermodynamic equilibrium system of the same temperature, mass density, and chemical composition, then one speaks of complete local thermal equilibrium (LTE). Such systems can be characterized by a small number of parameters which, in turn, may be deduced from a few measurements of, e.g., spectral intensities of the emitted radiation. This circumstance makes LTE plasmas very valuable for the determination of atomic quantities like oscillator strengths, line broadening parameters, and continuous absorption coefficients, which are needed in the analysis of stellar atmospheres or the diagnostics of laboratory plasmas.

In laboratory plasmas the radiation field almost never resembles that of a blackbody except, perhaps, in the immediate neighborhood of some of the strongest spectral lines. Accordingly, LTE can only be expected if collisional processes are more important than radiative decay and recombination, and if the velocity distributions of the colliding particles are thermal so that the principle of detailed balancing can be used to find the steady-state solutions of the rate equations. Since most collisional excitations and ionizations and their inverses involve electrons, it is imperative for LTE to hold in the laboratory that the electron distribution be thermal. The velocity distributions of atoms and ions are of little consequence in this connection, as long as the velocities of these heavy particles are considerably smaller than those of the electrons, and as long as one is not interested in their contribution to the plasma pressure.

Whether or not the distribution over bound states and the degree of ionization of a *given* species is properly described by LTE relations involving the kinetic electron temperature, depends mainly on the electron density and, to a lesser extent, on the electron temperature, and, of course, also on cross sections and transition probabilities of the atoms and ions and on the spatial and time characteristics of the plasma. It is the purpose of the present paper to expose criteria for the existence of LTE within a certain precision in a given plasma and to discuss the limitations imposed by the corresponding requirements on applications of thermal light sources to measurements of atomic parameters.

To establish LTE, one needs some minimum electron density. On the other hand, Saha equations, etc., are formally derived in the limit of vanishing interactions, e.g., between electrons. For plasmas in which the mean Coulomb interaction energy is small compared to the thermal energy, a consistent set of high density corrections to these LTE relations exists.[1] If one wants the corresponding uncertainties for the various densities to stay in the percent range, it is necessary that the interaction energy remains below $\sim 10\%$ of the thermal energy. This imposes a theoretical limit on the electron density which is, however, usually less restrictive than practical limitations which rule out precision experiments at electron densities above $\sim 10^{18}$ cm^{-3}. Plasmas of higher densities are not only very difficult to produce but would also not be too useful, because then many spectral lines overlap so that detailed measurements of line oscillator strengths, line broadening parameters, and continuous absorption coefficients cannot be made.

PARTIAL LTE IN TIME-INDEPENDENT AND HOMOGENEOUS PLASMAS

The simplest model for a laboratory LTE plasma consists of a homogeneous layer which is thin enough so that all photons produced in it escape without further interactions, and whose properties also do not depend on time. The rate equations should in this case account for excitation and ionization by electron impacts, and

* Jointly sponsored by the Office of Naval Research and the National Science Foundation.

[1] H. R. Griem, Phys. Rev. **128**, 997 (1962).

for de-excitation and recombination both by collisional and radiative processes. (Radiative excitation and ionization are negligible in optically thin plasmas.) Another assumption, whose self-consistency must be checked later on, is that the free electrons have a thermal velocity distribution.

Steady-state solutions of these rate equations have been obtained for the density of ground-state atoms in hydrogen, hydrogenic ion, and pseudoalkali ion plasmas,[2] using cross sections[3] for the collisional rate coefficients which are probably correct to within a factor of 2, and hydrogen oscillator strengths, etc., for radiative rate coefficients which are, therefore, exact except for the pseudoalkali ions. The results indicate that the Saha equations relating ground-state densities and electron (ion) densities are almost never applicable for electron densities occurring in laboratory experiments. As will be seen in the next section, this is often no longer the case if resonance radiation is trapped in the plasma, at least not for the Saha equations describing first and second ionization. For model calculations, trapping of radiation can be accounted for by omitting the appropriate spontaneous decay rates.[4]

The situation is also different if Saha equations relating densities in excited states to electron and ion densities are considered. This has been shown in specific examples by finding the steady-state solutions of the appropriate rate equations[5,6] which indicate that such Saha equations may be used down to surprisingly low electron densities.

A criterion for the validity of the Saha equation relating the density of atoms or ions in some excited state n, the electron density, and the density in the ground state of the next higher ionization stage, results from the requirement that collision-induced transitions to bound states higher than n or into the continuum should be more frequent than radiative decay of atoms or ions in state n. If this is the case, also the collisional population rate from higher states or from the continuum (by three-body recombinations) is larger than the radiative decay rate. The steady-state population is then determined by collisional processes, a conclusion which is not seriously affected by the neglect of collision-induced transitions to or from lower levels than the level in whose population one is interested. (Because of the increase in the energy gaps and the decrease in the radial matrix elements occurring in the cross sections, transitions to or from lower levels are less important than those involving higher levels.)

As further simplification, one may first neglect all collision-induced transitions but that to the next higher level, because cross sections decrease rather rapidly even at principal quantum numbers as large as, say, 6 with increasing values of the difference in the principal quantum numbers of initial and final states. The energy gaps tend to be of the same order as the thermal energies of the electrons. Therefore, the Born approximation cannot be applied to estimate the relevant cross sections. Quite to the contrary, the interactions between atoms or ions and electrons must be considered as strong. Semiclassically, a transition will be induced when an electron comes within a distance ρ to the atomic or ionic system such that the interaction energy times the duration of the collision is of the order of $\hbar$. With the dipole approximation for the interaction energy, then the following criterion results for the maximum distance ρ for strong collisions, namely,

$$\frac{e^2}{\rho^2} r_{n'n}\left(\frac{\rho}{v}\right)=\frac{e^2 r_{n'n}}{\rho v}\approx\hbar\,, \tag{1}$$

where $r_{n'n}$ is the radial matrix element between initial state n and final state n' and v the velocity of the electron, i.e., ρ/v the duration of the collision. The corresponding cross section for the dominant collisional process is, thus, estimated by

$$\sigma_{n'n}\approx\pi\rho^2\approx\pi\frac{e^4(r_{n'n})^2}{\hbar^2 v^2}\,. \tag{2}$$

The radial matrix element is conveniently expressed in terms of absorption oscillator strength $f_{n'n}$ and energy values $E_{n'}$ and E_n. In this way the approximate cross section becomes

$$\sigma_{n'n}\approx\frac{\pi e^4 f_{n'n}}{(\frac{1}{2}mv^2)(E_{n'}-E_n)}\,. \tag{3}$$

This essentially agrees with cross sections for ions proposed by Seaton.[3] For atoms such rough estimates cannot be used, because here the threshold behavior is more complicated, but for ions Eq. (3) is appropriate for the most important transitions as long as the kinetic energy of the electron is not much larger than the energy gap $(E_{n'}-E_n)$. If this were not the case, cross sections would decrease somewhat slower as predicted by Eq. (3) with increasing electron energy.[7] That semiclassical considerations usually suffice for excited states follows from Eq. (1) and the estimate $r_{n'n}\approx n^2 a_0/z=n^2\hbar^2/me^2 z$ for the radial matrix elements, i.e., from realizing that the relevant angular momenta of the free electrons are of the order $\hbar n^2/z$, where z is the effective charge seen by the bound electron and n its principal quantum number. Also, the identification of the maximum distance with the impact parameter is not likely to cause

[2] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962).
[3] M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 11; see also M. Gryzinski, Phys. Rev. **115**, 374 (1959).
[4] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A270**, 155 (1962).
[5] R. W. P. McWhirter, Nature **190**, 902 (1961).
[6] R. W. P. McWhirter and A. G. Hearn (to be published).
[7] H. Bethe, Ann. Physik **5**, 325 (1930).

significant errors, even though the Coulomb attraction of the colliding electron by the ion will reduce the minimum separation below the impact parameter. This effect is as in Stark broadening[8] very nearly compensated by the reduction in the duration of the collision through the increase in the velocity.

From Eq. (3) follows for the collisional transition rate per atom in state n:

$$R_{n'n}{}^{c}=N_e\langle v\sigma_{n'n}\rangle_{\mathrm{av}}\approx N_e\frac{2\pi e^4 f_{n'n}}{m(E_{n'}-E_n)}\int_{v=[2(E_{n'}-E_n)/m]^{1/2}}^{\infty}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{m}{kT}\right)^{3/2} v\exp\left[-\left(\frac{mv^2}{2kT}\right)\right]dv$$
$$=N_e\frac{2e^4 f_{n'n}}{m(E_{n'}-E_n)}\left(\frac{2\pi m}{kT}\right)^{1/2}\exp\left(-\frac{E_{n'}-E_n}{kT}\right). \quad (4)$$

The dependence of this rate on the charge acting upon the bound electron ($z=1$ for neutrals, $z=2$ for singly ionized atoms, etc.) becomes evident if energy gaps and thermal energies are expressed in terms of the ionization energies of hydrogen or the corresponding hydrogenic ions $E_{\mathrm{H}}{}^z=z^2e^2/2a_0$, namely,

$$R_{n'n}{}^{c,z}\approx N_e\frac{8\pi^{1/2}a_0{}^{3/2}e}{m^{1/2}z^3}f_{n'n}\left(\frac{F_H{}^z}{E_{n'}-E_n}\right)\left(\frac{E_H{}^z}{kT}\right)^{1/2}\exp\left(-\frac{E_{n'}-E_n}{kT}\right)$$
$$=N_e\frac{8\pi^{1/2}\alpha a_0{}^2c}{z^3}f_{n'n}\left(\frac{E_H{}^z}{E_{n'}-E_n}\right)\left(\frac{E_H{}^z}{kT}\right)^{1/2}\exp\left(-\frac{E_{n'}-E_n}{kT}\right). \quad (5)$$

Here α is the fine structure constant $\alpha=e^2/\hbar c$.

As pointed out above, one mainly needs the rate for the transition from n to $n+1$. For higher values of n the hydrogen oscillator strengths can always be used, and transitions into higher levels can be accounted for by taking the sum of the oscillator strengths for all upward transitions. Survey of the tabulated values[9] suggests that this sum is of the order $\frac{1}{2}n$. The collisional rate thus becomes, omitting the usually insignificant exponential factor,

$$\sum_{n'}R_{n'n}{}^{c,z}\approx\frac{n^4}{z^3}N_e(2\pi^{1/2}\alpha a_0{}^2c)\left(\frac{E_H{}^z}{kT}\right)^{1/2}, \quad (6)$$

if one also replaces the energy difference in the denominator by the approximate value $2E_{\mathrm{H}}{}^z/n^3$. (The exponential is important for small n, but then collisional coupling with the ground state should be considered which causes a correction in the opposite direction.) This rate must be compared with the radiative decay rate of the nth level, which is for one-electron systems[9]

$$\sum_{n'<n}R_{n'n}{}^{r,z}\approx\frac{\alpha^4cz^4}{a_0n^{9/2}}. \quad (7)$$

For the population of the nth excited level to be in LTE with the higher levels and the continuum to, say, within 10%, the collisional rate should at least be 10 times larger than the radiative decay rate, i.e., according to Eqs. (6) and (7) the electron density should fulfill

$$N_e\geq\frac{10}{2\pi^{1/2}}\frac{z^7}{n^{17/2}}\left(\frac{\alpha}{a_0}\right)\left(\frac{kT}{E_H{}^z}\right)^{1/2}$$
$$\approx 7.4\times10^{18}\frac{z^7}{n^{17/2}}\left(\frac{kT}{E_H{}^z}\right)^{1/2}[\mathrm{cm}^{-3}]. \quad (8)$$

Strictly speaking, this criterion only applies to ionized helium, etc. But comparison with detailed calculations for hydrogen indicates that it is essentially correct for hydrogen as well. It should also be appropriate for higher excited states of other light atoms or ions, because most of these levels are quite close to the corresponding hydrogenic levels, and because the radiative decay rates of such levels are not too drastically affected by omitting the transitions to $n=1$ and perhaps $n=2$ to account for closed shells. The assumption of a thermal distribution for the free electrons is justified if the electron density is large enough to fulfill Eq. (8) for at least one level below the reduced ionization limit,[1] i.e., for $n\approx(\rho_DE_H{}^z/ze^2)^{1/2}$, where ρ_D is the Debye radius. Additional conditions for real plasmas are that electron-electron collision times should be much shorter than the times characterizing confinement and heating or cooling of the plasma.[10]

[8] H. R. Griem and K. Y. Shen, Phys. Rev. **122**, 1490 (1961).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Springer-Verlag, Berlin; Academic Press Inc., New York, 1957), pp. 264–266.

[10] R. Wilson, J. Quant. Spectr. Radiative Transfer **2**, 477 (1962).

COMPLETE LTE IN TIME-INDEPENDENT AND HOMOGENEOUS PLASMAS

The electron densities required for LTE down to the first excited state according to Eq. (8) are $N_e=6\times10^{15}$ cm^{-3} for hydrogen and $N_e=7\times10^{17}$ cm^{-3} for singly ionized helium at temperatures of 1 eV and 4 eV, respectively. These examples suggest that in most optically thin laboratory plasmas complete LTE, including the ground-state populations, cannot be expected. In such plasmas it would be necessary that the radiative population rate of the ground state be negligible against the corresponding collisional rate. Near LTE, the latter is practically equal to the collisional depopulation rate of this state, which is usually reasonably estimated by the partial rate leading into the upper state of the resonance line. In analogy to Eq. (4) one has for this rate

$$\left.\frac{dN_2}{dt}\right|_{21}^{c}\approx N_eN_1\frac{2e^4f_{21}}{m(E_2-E_1)}\left(\frac{2\pi m}{kT}\right)^{1/2}\exp\left(-\frac{E_2-E_1}{kT}\right). \quad (9)$$

Similarly, the radiative population rate of the ground state can be estimated from the radiative decay rate of the upper level of the resonance line, namely,

$$\left.\frac{dN_2}{dt}\right|_{12}^{r}=-A_{12}N_2=-\frac{2\alpha^2a_0(E_2-E_1)^2f_{21}}{\hbar^2c}\frac{g_1}{g_2}N_2, \quad (10)$$

if the spontaneous transition probability is expressed in terms of absorption oscillator strength, statistical weights, and energies.

In LTE the collisional rate should be about 10 times larger than the radiative rate. With Eqs. (9) and (10) this results in the following criterion for LTE in optically thin plasmas down to the ground state:

$$N_e\geq\frac{5}{8\pi^{1/2}}z^7\left(\frac{\alpha}{a_0}\right)^3\left(\frac{kT}{E_H{}^z}\right)^{1/2}\left(\frac{E_2-E_1}{E_H{}^z}\right)^3$$
$$=9.2\times10^{17}z^7\left(\frac{kT}{E_H{}^z}\right)^{1/2}\left(\frac{E_2-E_1}{E_H{}^z}\right)^3[\text{cm}^{-3}]. \quad (11)$$

Excitation energies and thermal energies are again expressed in terms of the ionization energy of hydrogen ($E_H{}^1$) or the corresponding hydrogenic ion ($E_H{}^z$). Clearly, the electron densities required by Eq. (11) are prohibitively large even for typical singly ionized atoms ($z=2$). Already for hydrogen, $N_e\geq10^{17}$ cm^{-3} is necessary at an electron temperature of 1 eV. Complete LTE will, therefore, usually not prevail in plasmas where radiative decay is balanced solely by collisional processes.

However, in many plasmas for which LTE is according to Eq. (8) expected down to the second excited state ($N_e\geq2\times10^{14}$ cm^{-3} and $N_e\geq2.5\times10^{16}$ cm^{-3} for hydrogen and ionized helium, respectively, at the usual temperatures), the resonance lines will be considerably reabsorbed. Near LTE the radiation field in the frequency range of these lines is then close to that of a blackbody whose temperature equals that of the electrons, and the rate of radiative excitation of the ground state or radiative population of the upper state of the resonance line becomes practically equal to the radiative decay of this state. Now decay from higher states must be considered, which is typically an order of magnitude less important than the radiative decay through optically thin resonance lines. The condition imposed by Eq. (11) for LTE between ground state and first excited state populations can, therefore, be relaxed by about a factor of 10 if the resonance line is optically thick. Now also the condition on the electron density imposed by Eq. (8) for LTE of the first excited state with respect to all higher levels is too restrictive, because it is rather populated by radiative processes from above than depopulated by downward transitions. Electron densities required for LTE down to the second excited state are well below the reduced limit for LTE between ground-state and first excited state populations if the resonance radiation is trapped, and it is, therefore, rather safe to say that complete LTE should exist if the electron density fulfills

$$N_e\geq10^{17}z^7\left(\frac{kT}{E_H{}^z}\right)^{1/2}\left(\frac{E_2-E_1}{E_H{}^z}\right)^3[\text{cm}^{-3}], \quad (12)$$

and if the plasma is optically thick for the resonance line, homogeneous, and time-independent.

Some further reduction in the electron density would be permissible, if also the next line in the resonance series is self-absorbed. But its transition probability is usually much smaller so that this reduction is not very substantial. It should also be noted that the oscillator strengths cancelled in the derivation of Eqs. (11) and (12), which are, therefore, not only applicable to hydrogenic ions, even though the remarks on the minimum densities for LTE of the lower levels only pertain to such ions. Except for some uncertainties due to entirely different level structures in complex systems, Eqs. (11) or (12) can accordingly be used to estimate minimum electron densities for complete LTE regardless of the chemical species involved.

TRANSIENT PLASMAS

Plasmas of sufficiently high density for LTE to hold are hardly ever both homogeneous in space and independent of time. Examples of transient but essentially homogeneous plasmas are those produced in shock tubes. In addition to fulfillment of the criteria in Eqs. (8), (11), or (12), it is then necessary that changes in electron temperatures, etc., are small over times characterizing the establishment of excitation and ionization equilibrium. One is tempted to assume that the appropriate relaxation time is of the order of the lifetime of ground-state atoms or ions against ionizing collisions. However, if the plasma goes through a sequence of quasistationary near LTE states, most ionizations occur via intermediate excited states, mainly through the upper state of the resonance line. The relevant time constant is, therefore, of the order of the time which is required to establish LTE between upper and lower states of the resonance line.

This time is given by the inverse collisional excitation rate of ground state "atoms," multiplied with the fraction of atoms or ions that must be excited, i.e., with Eq. (9) and N^+ and N as total "atom" or "ion" densities by

$$\tau_1 \approx \left(\frac{N^+}{N^+ + N}\right)\left(\frac{1}{N_1}\frac{dN_2}{dt}\bigg|_{21}^{c}\right)^{-1} \approx \frac{m(E_2-E_1)N^+}{2e^4 f_{21}N_e(N^+ + N)}\left(\frac{kT}{2\pi m}\right)^{1/2} \exp\left(\frac{E_2-E_1}{kT}\right)$$
$$= z^3(8\pi^{1/2}\alpha a_0^2 c f_{21} N_e)^{-1}\left(\frac{N^+}{N^+ + N}\right)\left(\frac{E_2-E_1}{E_H^z}\right)\left(\frac{kT}{E_H^z}\right)^{1/2} \exp\left(\frac{E_2-E_1}{kT}\right)$$
$$= \frac{1.15\times 10^7 z^3 N^+}{f_{21}N_e(N^+ + N)}\left(\frac{E_2-E_1}{E_H^z}\right)\left(\frac{kT}{E_H^z}\right)^{1/2} \exp\left(\frac{E_2-E_1}{kT}\right)[\text{sec}]. \quad (13)$$

Arguments that Eq. (13) is an overestimate because the density N_2 is only a small fraction of N_1, i.e., because only very few atoms or ions need be excited, are false, since most of these excitations are followed by collision-induced transitions into higher levels and the continuum. Also self-absorption of the resonance line does not lead to a reduction in the equilibration time, as it does not cause any net change in the excitation in an isolated and homogeneous plasma.

For electron densities just fulfilling Eq. (12), the times characterizing the approach to LTE are about 3 μsec for hydrogen ($N_e \approx 10^{16}$ cm^{-3}, $kT \approx 1$ eV) and 0.3 μsec for ionized helium ($N_e \approx 10^{18}$ cm^{-3}, $kT \approx 4$ eV). To obtain these numbers, Eq. (13) and the appropriate Saha equations were employed, assuming pure hydrogen or pure helium. In typical experiments with electromagnetic shock tubes,[11,12] lifetimes of the shock-heated plasmas are of the same order, and LTE could not be established sufficiently fast by collisions or radiation generated in the shock-heated plasma. It was, therefore, proposed that the ambient gas is pre-excited by the much more intense radiation from the discharge driving the shock wave.[11–13] Energy considerations suggested that a significant fraction of the atoms would at least be in the first excited state,[11,12] so that the equilibration time will now be only of the order of the inverse collisional excitation rate of atoms in excited states.

Relaxation times for relative populations of excited (hydrogenic) states are estimated from Eq. (6) as

$$\tau_n \approx \Big(\sum_{n'>n} R_{n'n}{}^{c,z}\Big)^{-1}$$
$$\approx \frac{z^3}{n^4}(2\pi^{1/2}\alpha a_0^2 c N_e)^{-1}\left(\frac{kT}{E_H^z}\right)^{1/2} \exp\left(\frac{E_{n+1}-E_n}{kT}\right) = \frac{4.6\times 10^7 z^3}{n^4 N_e}\left(\frac{kT}{E_H^z}\right)^{1/2} \exp\left(\frac{E_{n+1}-E_n}{kT}\right)[\text{sec}]. \quad (14)$$

(Here approximate exponential factors were reinstated.) Because the density in the nth excited state is always relatively small, there is now no reduction factor corresponding to $N^+/(N^+ + N)$ in Eq. (13). For the above examples, the characteristic times τ_2, etc., are below 10^{-3} μsec, and are, therefore, much shorter than the times in which macroscopic changes occur. These extremely short times imply that the transient nature of a plasma only rarely causes deviations from LTE between excited-state populations, if the same partial LTE would exist otherwise.

However, times for establishment of complete LTE can be relatively long, at least if initially most of the atoms or ions are in the ground state. If one instead observes a decaying plasma, Eq. (13) may well be too pessimistic, because the relevant recombination times are extremely short and because radiative decay into the ground state must now also be considered. Besides, in the existence of quasistationary LTE excitation and ionization, one might also be interested in the kinetic temperatures of electrons and atoms or ions. Depending on heating and energy loss rates for the various plasma components, their temperatures can be different from each other, but for densities and temperatures at which excitation and ionization equilibrium prevails, the relaxation times for kinetic temperatures are so small[14] that there is no need to discuss these deviations in the present context. This is quite different from the situation in high-energy nonthermal plasmas.[10]

All preceding estimates were based on the assumption that the electron density had already a certain value, i.e., the difficulties connected with the establishment of

[11] E. A. McLean, C. E. Faneuff, A. C. Kolb, and H. R. Griem, Phys. Fluids **3**, 843 (1960).
[12] W. Wiese, H. F. Berg, and H. R. Griem, Phys. Rev. **120**, 1079 (1960).
[13] W. Wiese, H. F. Berg, and H. R. Griem, Phys. Fluids **4**, 250 (1961).
[14] L. Spitzer, *Physics of Ionized Gases* (Interscience Publishers Inc., New York, 1956), p. 76.

sufficient initial ionization were ignored. The latter can be quite important in conventional shock tubes.[15,16]

INHOMOGENEOUS PLASMAS

Time-dependent LTE plasmas normally possess spatial gradients in electron temperature and density, because a considerable fraction of the energy transfer occurs by electron heat conduction. In addition to the fulfillment of the validity criteria for LTE in time-independent and spatially-homogeneous plasmas, it must then be required that the gradients of the electron temperature are so small that a given atom does not diffuse over regions of significantly different temperatures in times of the order of the equilibration times estimated in the preceding section. This additional criterion should especially be applied to stabilized arcs as thermal light sources.

Time-independent LTE plasmas usually contain a significant fraction of neutrals and, ignoring molecules, the additional validity criterion should be most restrictive for atoms in the ground state. Elastic cross sections for such atoms are of the order πa_0^2 and charge-exchange cross sections tend to be an order of magnitude larger than this.[17] The mean free path becomes, therefore,

$$\lambda \approx [\pi a_0^2(N+10N^+)]^{-1}, \tag{15}$$

assuming for simplicity that only atoms and ions of one chemical species are present. The mean time between elastic or charge-exchange collisions is accordingly, with $v \approx (kT/M)^{1/2}$,

$$\tau = (\lambda/v) \approx (M/kT)^{1/2}[\pi a_0^2(N+10N^+)]^{-1}. \tag{16}$$

These times are always considerably shorter than the excitation and ionization equilibration time τ_1 in Eq. (13), i.e., atoms diffuse on the average over distances of the order

$$d \approx \lambda\left(\frac{\tau_1}{\tau}\right)^{1/2} = (v\lambda\tau_1)^{1/2} \approx (2a_0^2)^{-1}(2\pi)^{-3/4}\left(\frac{m}{M}\right)^{1/4}\left(\frac{kT}{E_H^1}\right)^{1/2}\left(\frac{E_2-E_1}{f_{21}E_H^1}\right)^{1/2}\exp\left(\frac{E_2-E_1}{2kT}\right)[(N+10N^+)(N+N^+)]^{-1/2}$$

$$= \frac{7\times10^{14}}{A^{1/4}}\left(\frac{kT}{E_H^1}\right)^{1/2}\left(\frac{E_2-E_1}{f_{21}E_H^1}\right)^{1/2}\exp\left(\frac{E_2-E_1}{2kT}\right)[(N+10N^+)(N+N^+)]^{-1/2}[\mathrm{cm}] \tag{17}$$

in the time needed for the establishment of excitation and ionization equilibrium. Here kinetic energies of the atoms of mass M (atomic weight A) and excitation energies E_2-E_1 for the upper level of the resonance line were expressed in terms of the ionization energy of hydrogen E_H^1, and use was made of the near-equality of electron and ion densities.

Temperature changes in the percent range are quite common over the radial distances given by Eq. (17), even near the axis of stabilized arcs. This implies that, e.g., the degrees of excitation and ionization on the axis would correspond to a temperature that is a few percent below the local electron temperature or, vice versa, that temperatures inferred from measurements of excitation (line intensities) or ionization (continuum intensities) are too low by the same amount. One might again think that inclusion of radiative energy transfer in optically thick resonance lines would diminish such deviations from LTE. However, as in case of transient plasmas, this does not necessarily happen because no net increase in excitation occurs near the axis, i.e., in the region of maximum temperature, but rather only exchanges of excitation energy between different atoms. In other words, the atom which gives its excitation energy to an incoming "cold" atom takes in a sense the place of the latter, and it or some other atom must eventually be excited by electron impact to maintain LTE. Details would, of course, depend on the actual flow pattern. For the cooler outer layers the situation may be different. Here radiation from hotter zones can indeed speed up the excitation of ground-state atoms. This is analogous to the influence of intense radiation from the discharge region in electromagnetic shock tubes on the equilibration rates in the plasma behind the shock front. A further reduction in the length over which equilibration can be expected in the outer layers is due to the influx of excited atoms or of ions from the inner zones. The analogous effect in transient plasmas is the very fast relaxation from energetic to less energetic plasmas.

For the more important zones near the axis, Eq. (17) must be used in conjunction with the radial temperature profile to estimate deviations of excitation and ionization from LTE. The restriction to neutrals is not serious. For excitation of ions and second ionization, deviations from LTE due to only marginal fulfillment of the criteria for time-independent and spatially homogeneous plasmas are usually much more important, because mean free paths for ions are short. This compensates for the increase in the equilibration length by the small-excitation cross sections.

Besides deviations from LTE excitation and ionization, there is also the possibility of deviations between kinetic temperatures of electrons and ions. An upper limit for the difference of these temperatures in arcs can be obtained by equating the resistive heating rate

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[16] R. A. Alpher and D. R. White, Phys. Fluids 2, 162 (1959).
[17] D. R. Bates, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 14.

of the electron component with the energy-transfer rate to the ions.[18] Usually the difference will be smaller because, e.g., electrons also lose energy by heat conduction to the walls. These kinetic temperatures hardly ever differ by more than, say, 5% for arc plasmas that are in LTE otherwise. Since the kinetic ion temperature enters only linearly into the relations describing the plasma, namely, into the equation for the pressure, such deviations are usually negligible, or at least not more important than uncertainties in the gas pressure which are connected with the momentum flux accompanying the heat flux from the central columns of high-current arcs.[19] This should be contrasted with the relations for excitation and ionization, which depend exponentially on the electron temperature. Furthermore, there is little question that kinetic temperatures of atoms and ions will be the same for all practical purposes in plasmas where excitation and ionization are governed by LTE relations.

SUMMARY

From the discussion in the preceding section follows as the most important additional validity criterion for LTE in inhomogeneous plasmas

$$\left|\frac{T(r)-T(r+d)}{T(r)}\right|=\epsilon\ll 1, \tag{18}$$

where $T(r)$ is the radial distribution of the electron temperature and d the equilibration length as estimated by Eq. (17). The corresponding criterion for the validity of LTE in transient plasmas is

$$\left|\frac{T(t+\tau_1)-T(t)}{T(t)}\right|=\delta\ll 1, \tag{19}$$

with the temporal electron temperature distribution $T(t)$ and the equilibration time τ_1 from Eq. (13). The quantities ϵ and δ in these criteria give a measure of the relative deviations between local or instantaneous electron temperatures and the effective excitation and ionization temperatures.

These two criteria are often more restrictive than the criterion for complete LTE in homogeneous and time-independent plasmas as expressed by Eq. (11), which can usually be relaxed by about an order of magnitude if the resonance line is self-absorbed. All criteria for complete LTE with respect to excitation and ionization, i.e., Eqs. (11) or (12), and/or (18) and (19), can only be met at rather high electron densities, especially if one is also interested in excitation of ions and second ionization. The rapid increase of the minimum electron densities with further ionization appears to rule out the establishment of complete LTE in laboratory plasmas containing multiply ionized species.

However, partial LTE between excited states can exist at much lower electron densities. The validity criteria are then given by Eq. (8) and by relations corresponding to Eqs. (18) and (19) in which τ_1 is replaced by τ_n from Eq. (14) or the length d calculated from Eq. (17) using τ_n instead of τ_1. Such partial LTE is of considerable value in applications of plasmas for the determination of atomic parameters, e.g., for the measurement of relative oscillator strengths from relative line intensities.

If electron densities barely fulfill Eqs. (8) or (11), the latter being corrected for self-absorption of the resonance line, if necessary, one can expect LTE relations for excitation and ionization to hold within about 10%. These deviations will decrease by the same factor by which the criteria might be overfulfilled, as long as the errors due to the transient and/or inhomogeneous nature of the plasma do not dominate. Finally, it must not be overlooked that such estimates may well be uncertain by a factor of 2 or 3, because cross sections even for hydrogenic ions are not known with much better accuracy than this, and because rate equations, etc., were only treated in a rather schematic manner.

[18] W. Finkelnburg and H. Maecker, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 22, Sec. II, p. 306.

[19] V. V. Yankov, Zh. Tekhn. Fiz. **31**, 1324 (1961) [translation: Soviet Phys.—Tech. Phys. **6**, 965 (1962)].