PHYSICAL REVIEW A VOLUME 38, NUMBER 4 AUGUST 15, 1988

Rate coefficients in reacting strongly coupled plasmas

M. Schlanges, Th. Bornath, and D. Kremp
Sektion Physik der Wilhelm-Pieck-Universität Rostock, DDR-2500 Rostock, German Democratic Republic

(Received 30 November 1987)

A kinetic approach is derived to take into account nonideality effects in the rate coefficients of plasmas. First results are given for a reacting hydrogen plasma.

The time dependence of the densities in a reacting plasma is determined by rate equations. The coefficients in these equations describe the different elementary processes, e.g., ionization by external pumping, impact ionization, and recombination processes. Usually these coefficients are considered to be independent of the density.[1-4] The corresponding rate equation then describes an ideal plasma. At higher densities one may expect nonideality effects which lead to a density dependence of the rate coefficients.

It is known that explicit expressions for the rate coefficients cannot be given by phenomenological theories. The properties of the coefficients and especially nonideality effects are essentially determined by the microscopic interaction between the particles. That requires a strong foundation of the rate equation on the basis of quantum kinetic theory.[5-8]

In our paper we will give a first calculation of nonideality effects in the rate coefficients of plasmas.[9] We assume the plasma to be dense enough that radiation processes can be neglected.[10]

We start from quantum kinetic equations for chemically reacting systems which we have derived using the method of nonequilibrium Green's functions.[11,12] In comparison with kinetic equations given in the literature[5-8,13,14] our equations take into account many particle effects, such as quasiparticle energies, medium dependent scattering, and phase-space occupation effects. The kinetic equations were derived for systems with two-particle bound states in the case of short-range potentials. Nevertheless, because the effective interaction in a Coulomb system is short range due to screening we will apply them to plasmas.

As an example we consider a spatially homogeneous hydrogen plasma, consisting of electrons and protons with densities n_e, n_p and hydrogen atoms in the states j with the densities n_j with $n_H = \sum_j n_j$. In order to get a rate equation for the densities one has to integrate the corresponding kinetic equation with respect to the momentum. A source term results from collision integrals due to the reactions

$$(e+p) + \left\{ \begin{matrix} e \\ p \end{matrix} \right\} \leftrightarrow \bar{e} + \bar{p} + \left\{ \begin{matrix} \bar{e} \\ \bar{p} \end{matrix} \right\} . \tag{1}$$

Then the rate equation for the electrons can be written as

$$\frac{dn_e}{dt} = \sum_j (\alpha_j n_j n_e - \beta_j n_e^2 n_p) . \tag{2}$$

The ionization coefficients are given by

$$\alpha_j = \frac{1}{\hbar V} \sum_{a=e,p} \int \frac{d\mathbf{P}}{(2\pi\hbar)^3} \int \frac{d\mathbf{p}_a}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{P}}}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{p}}}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{p}}_a}{(2\pi\hbar)^3} 2\pi\delta(\varepsilon_{123}^3 - \bar{\varepsilon}_{123}^0) \left| \langle j\mathbf{P} | \langle \mathbf{p}_a | T_{123}^{33} | \bar{\mathbf{p}}_a \rangle | \bar{\mathbf{P}}\bar{\mathbf{p}} + \rangle \right|^2 \times \frac{f_a(\mathbf{p}_a, t)}{n_a} \frac{F_j(\mathbf{P}, t)}{n_j} . \tag{3}$$

For the recombination coefficients we have

$$\beta_j = \frac{1}{\hbar V} \sum_{a=e,p} \int \frac{d\mathbf{P}}{(2\pi\hbar)^3} \int \frac{d\mathbf{p}_a}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{P}}}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{p}}}{(2\pi\hbar)^3} \int \frac{d\bar{\mathbf{p}}_a}{(2\pi\hbar)^3} 2\pi\delta(\varepsilon_{123}^3 - \bar{\varepsilon}_{123}^0) \left| \langle j\mathbf{P} | \langle \mathbf{p}_a | T_{123}^{33} | \bar{\mathbf{p}}_a \rangle | \bar{\mathbf{P}}\bar{\mathbf{p}} + \rangle \right|^2 \times \frac{f_a(\bar{\mathbf{p}}_a, t)}{n_a} \frac{f_e(\tilde{\mathbf{p}}_e, t)}{n_e} \frac{f_p(\tilde{\mathbf{p}}_p, t)}{n_p} . \tag{4}$$

Here $f_a(p_a,t)$ $(a=e,p)$ are the distribution functions of the charged particles, $F_j(P,t)$ is the distribution function of atoms in the state j, and V is the volume. The three-particle states are given by that of free particles $|p_a\rangle$, atoms $|P_j\rangle$, and ionized atoms $|\bar{\mathbf{P}}\bar{\mathbf{p}}+\rangle$, where

$$\bar{\mathbf{p}}=\frac{m_p\bar{\mathbf{p}}_e-m_e\bar{\mathbf{p}}_p}{m_e+m_p}\ ,\quad \bar{\mathbf{P}}=\bar{\mathbf{p}}_e+\bar{\mathbf{p}}_p\ .$$

The T matrices in (3) and (4) describe the corresponding three-particle reaction processes in the nonequilibrium medium. In general the different three-particle T matrices are determined by

$$T_{123}^{KK'}(z)=V_{123}^{K}+i^2V_{123}^{K}G_{123}(z)V_{123}^{K'}\ . \tag{5}$$

According to scattering theory[15] the channel numbers K,K' denote the different initial and final (asymptotic) three-particle states. The scattering potentials are

$$V_{123}^{0}=V_{12}+V_{13}+V_{23}\ ,\quad V_{123}^{1}=V_{12}+V_{13}\ ,$$

etc., and the resolvent for three interacting quasiparticles is given by

$$G_{123}(z)=(H_{123}^{\text{eff}}-z)^{-1}\ .$$

For the scattering energies, e.g., in the channels $K=0,1$, we have

$$\varepsilon_{123}^{0}=\sum_a\varepsilon_a(\mathbf{p}_a,t)\ ,\quad \varepsilon_{123}^{1}=\varepsilon_a(\mathbf{p}_a,t)+\varepsilon_j(\mathbf{P},t)\ , \tag{6}$$

where the energies of the free and bound particles are quasiparticle energies. They are given by

$$\varepsilon_a(\mathbf{p}_a,t)=\frac{p_a^2}{2m_a}+\Delta_a(\mathbf{p}_a,t)\quad (a=e,p)\ , \tag{7a}$$

$$\varepsilon_j(\mathbf{P},t)=\frac{P^2}{2M}+E_j+\Delta_j(\mathbf{P},t)\ . \tag{7b}$$

Here Δ_a and Δ_j are the energy shifts due to the influence of the surrounding medium (E_j bound state energy).

In order to avoid the dependence on the momentum in the shifts we will use thermally averaged quantities $\Delta_a(t)$ and $\Delta_j(t)$ in a first approximation.[16,17] The electron distribution function is assumed to be Maxwellian. If reactions due to proton impact are neglected[18] and the adiabatic approximation ($m_p \gg m_e$) is used the ionization coefficients are given by

$$\alpha_j=\frac{2\pi}{\hbar}\Lambda_e^3\int\frac{d\mathbf{p}_e}{(2\pi\hbar)^3}\int\frac{d\bar{\mathbf{p}}_e}{(2\pi\hbar)^3}\int d\bar{p}\,\delta\left[E_j+\Delta_j+\frac{p_e^2}{2m_e}-\frac{\bar{p}_e^{\,2}}{2m_e}-\frac{\bar{p}^{\,2}}{2m_e}-\Delta_e-\Delta_p\right]$$
$$\times\left|\langle j|\ \langle\mathbf{p}_e|T_{123}^{33}|\bar{\mathbf{p}}_e\rangle\ |\bar{\mathbf{p}}+\rangle\right|^2\exp\left[-\frac{p_e^2}{2m_ek_BT}\right]\ , \tag{8}$$

with

$$\Lambda_e=\left[\frac{2\pi\hbar^2}{m_ek_BT}\right]^{1/2}\ .$$

If energy conservation is used one gets the following relation between α_j and β_j:

$$\beta_j=\Lambda_e^3\exp[(-E_j-\Delta_j+\Delta_e+\Delta_p)/k_BT]\alpha_j\ . \tag{9}$$

In the following only ionization from the ground-state level shall be considered ($j=1$).

After introduction of the cross section the expression for the ionization coefficient reads

$$\alpha_1=\frac{8\pi m_e}{(2\pi m_ek_BT)^{3/2}}\int_I^\infty d\left[\frac{p_e^2}{2m_e}\right]\frac{p_e^2}{2m_e}\exp\left[-\frac{p_e^2}{2m_ek_BT}\right]\sigma_1^{\text{ion}}(p_e)\ , \tag{10}$$

with $I=-E_1-\Delta_1+\Delta_e+\Delta_p$ being the effective ionization energy. σ_1^{ion} is the cross section for ionization from the ground level and is given by

$$\sigma_1^{\text{ion}}=\int_0^{(p_e^2-2m_eI)^{1/2}}d\bar{p}\,\bar{p}^{\,2}\int d\Omega_{\bar{p}}\int d\Omega_{p_e}\frac{\bar{p}_e}{p_e}\frac{m_e^2}{4\pi^2\hbar^7}\left|\langle 1|\ \langle\mathbf{p}_e|T_{123}^{33}|\bar{\mathbf{p}}_e\rangle\ |\bar{\mathbf{p}}+\rangle\right|^2_{\bar{p}_e^{\,2}=p_e^2-\bar{p}^{\,2}-2m_eI}\ . \tag{11}$$

The calculation of the cross section is a difficult task because it involves the three-body problem. Therefore we make some simplifications: the T matrix is considered in the first Born approximation using Coulomb potentials instead of screened potentials and for the ground state and the scattering wave functions Coulombic ones are used. Thus it is possible to follow the method of Bethe[19] but additionally the quasiparticle energies shall be taken into account.

On the basis of the Bethe-Born approximation we propose the following formula:

$$\sigma_1^{\text{ion}}=2.5\pi a_B^2\frac{|E_1|}{p_e^2/2m_e}\ln\frac{\frac{p_e^2}{2m_e}-(\Delta_e+\Delta_p-\Delta_1)}{|E_1|} \tag{12}$$

(a_B is the Bohr radius). If the many-particle effects condensed in the shifts are neglected ($\Delta_a=0$, $\Delta_1=0$) this formula coincides with one formula of Biberman *et al.*,[20] which is in good agreement with experimental results.

Inserting (12) into Eq. (10), one can perform the integration with the result

$$\alpha_1=\frac{10\pi a_B^2}{(2\pi m_e k_B T)^{1/2}}E_1\mathrm{Ei}\left[-\frac{|E_1|}{k_BT}\right]\times\exp[(\Delta_1-\Delta_e-\Delta_p)/k_BT]$$

$$=\alpha_1^{\text{ideal}}\exp[(\Delta_1-\Delta_e-\Delta_p)/k_BT]\ , \qquad (13)$$

where $\mathrm{Ei}(x)$ is the exponential integral function

$$\mathrm{Ei}(x)=\int_{-\infty}^{x}\frac{e^t}{t}dt\ .$$

An expression for the recombination coefficient follows immediately from (9),

$$\beta_1=\Lambda_e^3\exp\left[\frac{|E_1|}{k_BT}\right]\alpha_1^{\text{ideal}}=\beta_1^{\text{ideal}}\ . \qquad (14)$$

Therefore nonideality has only an effect on the ionization coefficient whereas the recombination coefficient remains unaffected in our approximation.

In order to calculate the ionization coefficient α_1 from the generalized expression (13) the quasiparticle shifts must be known. Explicit results for these shifts were derived on the basis of Green's-function techniques for Coulomb systems.[21,17] It was shown that the bound-state shift is only small and can be neglected in a first approximation. For the thermally averaged quasiparticle shift of the free particles the following expression can be derived in lowest order (nondegenerate case):

$$\Delta_a=-\frac{\kappa e^2}{2}\quad(a=e,p)\ , \qquad (15)$$

with κ being the inverse Debye radius

$$\kappa^2=4\pi\sum_a n_a e_a^2/k_BT\ .$$

In this approximation the ionization coefficient is given by

$$\alpha_1=\alpha_1^{\text{ideal}}\exp(\kappa e^2/k_BT)\ . \qquad (16)$$

Thus nonideality leads to a density dependence of the ionization coefficient. The ionization coefficient is increasing with growing density because of the lowering of the effective ionization energy. In Fig. 1 the ionization coefficient is shown as a function of the density for different temperatures.

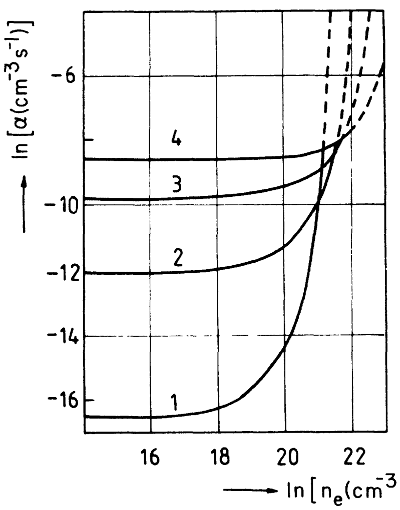

FIG. 1. Ionization coefficient for the ionization of hydrogen atoms from the ground state as a function of the electron density for different temperatures: (1) $T=8000$ K, (2) $T=10\,000$ K, (3) $T=32\,000$ K, (4) $T=64\,000$ K. The dashed lines indicate the region where bound states cannot exist because of the shifting into the continuum (Mott effect) (Ref. 17).

In a similar manner ionization coefficients may be given for ionization processes from excited levels. Then we have

$$\alpha_j=\alpha_j^{\text{ideal}}\exp(\kappa e^2/k_BT)\ , \qquad (17)$$

where for the calculation of α_j^{ideal} scaled cross sections can be used.[20,3]

If we neglect excited states using (14) and (16) the rate equation reads

$$\frac{dn_e}{dt}=\alpha_1^{\text{ideal}}\exp(\kappa e^2/k_BT)n_en_H-\beta_1^{\text{ideal}}n_e^2n_p\ . \qquad (18)$$

There are two effects in the rate equation caused by nonideality. The velocity of the reaction as well as the properties of the stationary states are changed. The stationary states follow from (18) and can be calculated from

$$\frac{n_H}{n_en_p}=\Lambda_e^3\exp[(|E_1|-\kappa e^2)/k_BT]\ . \qquad (19)$$

In thermodynamic equilibrium (19) is a Saha equation for a nonideal plasma.[22] An interesting feature is that corrections due to nonideality can lead to new properties of the stationary states (e.g., bistability). A reasonable discussion of such effects requires further improvements in the description of the strongly coupled plasma.

---

[1] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. London, Ser. A **270**, 155 (1962).

[2] H. W. Drawin and F. Emard, Physica **85C**, 333 (1977).

[3] L. M. Biberman, V. S. Vorobev, and I. T. Yakubov, *Kinetics of the Nonequilibrium Low-Temperature Plasma* (Nauka, Moscow, 1982).

[4] T. Fujimoto, J. Phys. Soc. Jpn. **54**, 2905 (1985).

[5] Y. L. Klimontovich, *Kinetic Theory of Nonideal Gases and*

Nonideal Plasmas (Pergamon, New York, 1982).

[6] Y. L. Klimontovich and D. Kremp, Physica **109A**, 517 (1981).

[7] Y. L. Klimontovich, D. Kremp, and M. Schlanges, in *Transport Properties of Dense Plasmas,* edited by W. Ebeling (Birkhäuser, Basel, 1984).

[8] S. Lagan and J. A. McLennan, Physica **128A**, 188 (1984).

[9] Th. Bornath, M. Schlanges, and D. Kremp, Contrib. Plasma Phys. **28**, 57 (1988).

[10] L. D. Landau and E. M. Lifshitz, *Theoretical Physics X* (Akademie-Verlag, Berlin, 1983).

[11] M. Schlanges, Ph.D. thesis, Universität Rostock, 1985; Th. Bornath, Ph.D. thesis, Universität Rostock, 1987.

[12] D. Kremp, M. Schlanges, and Th. Bornath, in *Selforganization by Nonlinear Irreversible Processes,* edited by W. Ebeling and H. Ulbricht (Springer-Verlag, Berlin, 1987).

[13] S. W. Peletminski, Zh. Teor. Mat. Fiz. **6**, 123 (1971).

[14] S. J. Vashukov, V. V. Marusin, Zh. Teor. Mat. Fiz. **29**, 255 (1976).

[15] J. R. Taylor, *Scattering Theory* (Mir, Moscow, 1975) (in Russian).

[16] D. Kremp, W. D. Kraeft, and A. J. D. Lambert, Physica **127A**, 2 (1984).

[17] W. D. Kraeft, D. Kremp, W. Ebeling, and G. Röpke, *Quantum Statistics of Charged Particle Systems* (Plenum, New York, 1986).

[18] M. E. Rudd, Y.-K. Kim, D. H. Madison, and J. W. Gallagher, Rev. Mod. Phys. **57**, 965 (1985).

[19] H. Bethe, Ann. Phys. (Leipzig) **5**, 325 (1930).

[20] L. M. Biberman, Yu. N. Toropkin, and K. N. Uljanov, Zh. Tekh. Fiz. **32**, 817 (1962) [Sov. Phys.—Tech. Phys. **7**, 598 (1963).

[21] R. Zimmermann, K. Kilimann, W. D. Kraeft, D. Kremp, and G. Röpke, Phys. Status Solidi B **90**, 175 (1978).

[22] W. Ebeling, W. D. Kraeft, and D. Kremp, *Theory of Bound States and Ionization Equilibrium in Plasmas and Solids* (Akademie-Verlag, Berlin, 1976).