Nonideality and Nonlinearity in Reaction-Diffusion Plasmas

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Abstract

Reaction and diffusion processes in dense plasmas are investigated on the basis of quantum statistical theory.

Many particle effects lead to nonlinear expressions for reaction and diffusion coefficients.

In the case of ambipolar diffusion and isobarity the plasma is described by only one reactiondiffusion equation. Travelling front solutions and droplet formation are investigated in the approximation of constant diffusion. The influence of nonlinearity of the diffusion on these solutions as well as the possibility of phase separation via spinodal decomposition and the formation of stable droplets are discussed.

Introduction

In this paper we would like to consider kinetic equations for reacting nonideal plasmas and the influence of the nonideality in a reaction-diffusion plasma. Of course the behaviour and the properties of a nonideal plasma are essentially determined by the Coulomb interaction. In many interesting systems the formation and the decay of bound states, that means reaction in connection with diffusion processes, can be observed. The simultaneous occurrence of these properties can be observed in many fields of science [1, 2], in physics especially in plasma physics as well as in chemistry and biology. From the phenomenological point of view such a reaction-diffusion system in the simplest cases can be described by a reaction-diffusion equation of the following type

$$\frac{\partial n_A}{\partial t} + V \boldsymbol{j}_A = W_A(n_i \dots n_f)$$

where $W_A(n_i \dots n_f)$ is the source function which describes the chemical reactions and j_A the particle current given in simple situations (ambipolar diffusion) by $\mathbf{j}_A = D_A \nabla n_A$ where D_A is the diffusion coefficient.

A very important problem is the quantum-statistical foundation of reaction-diffusion equations (r.d.eq.). This problem is connected with the derivation of a kinetic equation in which chemical reactions and nonideality effects [3-6] are included.

In the first part of this paper we will consider such a kinetic equation and explain the reaction term and the nonideality effects. In the second part we will derive the r.d.eq. Due to nonideality W_A and D_A are dependent on the density in nonlinear way. Therefore nonlinear phenomena like

- nonlinear diffusion and diffusion instability (phase separation)
- ionization fronts

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    dissipative structures
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- solitons
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and other effects may be expected [7].

I. Kinetic Equations for Nonideal Reacting Many Particle Systems

Usually the nonequilibrium properties of a many-particle system can be described by the Boltzmann equation. But in the case of a nonideal reacting plasma this equation must be generalized in many directions. Such generalizations can be found in many papers. Kinetic equations with chemical reactions are derived in papers of KLIMONTOVICH, KREMP [3], KLIMONTOVICH, KRAEFT, KREMP [4], MCLENNAN [6]. Nonideality contributions are taken into account in papers from SCHLANGES, BORNATH, KREMP [5, 8]. In the latter papers the powerful method of nonequilibrium Green's function is used in order to take into consideration many particle effects like [9]

- self energy;
- screening;
- Pauli blocking;

.

- influence of the plasma on the two particles spectrum (Mott effect).

The result of this consideration is the following kinetic equation for the distribution function $f_A(pRT)$ of the free particles

$$\left\{\frac{\partial}{\partial T} + \frac{\partial E_A}{\partial p_A}\frac{\partial}{\partial R} - \frac{\partial E_A}{\partial R}\frac{\partial}{\partial p_A}\right\}f_A(pRT) = \sum_B I_{AB} + \sum_{BC} I_{ABC}$$
(1)

Here E_A is the quasiparticle energy which is to be determined from the dispersion relation

$$E_A(\mathbf{p}) = \frac{\mathbf{p}_A^2}{2m_A} + \operatorname{Re} \Sigma(\mathbf{p}\omega \mathbf{R}T)$$
(2)

 $\Sigma(p \omega RT)$ is the nonequilibrium self energy. On the right hand side of (1) we have the collision integrals. I_{AB} is the well known two particle quantum Boltzmann collision term given by

$$I_{AB} = \frac{1}{\hbar V (2\pi\hbar)^9} \int \mathrm{d}\boldsymbol{p}_B \,\mathrm{d}\boldsymbol{\bar{p}}_A \,\mathrm{d}\boldsymbol{\bar{p}}_B |\langle \boldsymbol{p}_A \boldsymbol{p}_B | T_{AB} | \boldsymbol{\bar{p}}_B \boldsymbol{\bar{p}}_A \rangle|^2 \, 2\pi\delta(\boldsymbol{E}_{AB} - \boldsymbol{E}_{AB})$$
$$\{ \boldsymbol{\bar{f}}_A \boldsymbol{\bar{f}}_B (1 \pm f_A) \, (1 \pm f_B) - (1 \pm \boldsymbol{\bar{f}}_A) \, (1 \pm \boldsymbol{\bar{f}}_B) \, f_A f_B \} \tag{3}$$

with $E_{AB} = E_A + E_B$. I_{ABC} are the three-particle collision integrals containing the reaction terms. With the atomic distribution function $F_n(P_{AB})$ $(n_{AB}$ internal quantum number, P_{AB} center of mass momentum) this contribution has the form

$$I_{ABC} = \frac{1}{\hbar \overline{V}(2\pi\hbar)^6} \sum_C \sum_k \left\{ \int \mathrm{d}\boldsymbol{p}_B \,\mathrm{d}\boldsymbol{p}_C \,\mathrm{d}\overline{\boldsymbol{p}}|\langle \boldsymbol{p}_A \boldsymbol{p}_B \boldsymbol{p}_C | \, T^{ok} \, |k\overline{\boldsymbol{p}}\rangle|^2 \,\pi \delta(\boldsymbol{E}_0 - \boldsymbol{E}_k) \right. \\ \left. \times \left(\bar{f}_k N_0 - \overline{N}_k f_A f_B f_C \right) + \frac{1}{(2\pi\hbar)^3} \sum_{\boldsymbol{n}_{BC}} \int \mathrm{d}\overline{\boldsymbol{p}} \,\mathrm{d}\boldsymbol{P}_{BC} |\langle \boldsymbol{p}_A \boldsymbol{n}_{BC} \boldsymbol{P}_{BC} | \, T^{1k} \, |k\overline{\boldsymbol{p}}\rangle|^2 \\ \left. \times \,\pi \delta(\boldsymbol{E}_1 - \boldsymbol{E}_k) \, (\bar{f}_k N_1 - \overline{N}_k F \boldsymbol{n}_{BC} f_A) \right\}$$

$$(4)$$

Here $|pk\rangle$ are the asymptotic three-particle states. By the channel number k a classification of the states with respect to the asymptotic initial states (channel) is given. The

other observables which determine the three-particle state are denoted by p. Further explanations are given in the following table:

| k (channel) | kp angle | E _k | 1 _k | N _n |
|----------------------------|---------------------------------------|-------------------------|----------------|---------------------------------------|
| $\overline{0 \ A + B + C}$ | $\ket{p_A}\ket{p_B}\ket{p_C}$ | $E_A + E_B + E_C$ | tat btc | $(1 \pm f_A) (1 \pm f_B) (1 \pm f_C)$ |
| 1 A + (B + C) | $\ket{p_{A}}\ket{n_{BC}P_{BC}}$ | $E_A + E n_{BC} p_{BC}$ | $f_A F n_{BC}$ | $(1\pm f_A)$ $(1\pm Fn_{BC})$ |
| 2 B + (A + C) | $\ket{p_{B}}\ket{n_{AC}P_{AC}}$ | $E_B + En_{AC}p_{AC}$ | $f_B F n_{AC}$ | $(1 \pm f_B) (1 \pm Fn_{AC})$ |
| 3 C + (A + B) | $\ket{m{p}_{C}}\ket{n_{AB}m{P}_{AB}}$ | $E_{c}+En_{AB}p_{AB}$ | $f_C F n_{AB}$ | $(1 \pm f_c) (1 \pm F n_{AB})$ |

In order to discuss the properties of (4) is it useful to split up I_{ABC} into two parts

$$I_{ABC} = [I_{ABC}]_1 + [I_{ABC}]_2$$

where the first part $[I_{ABC}]_1$ is given by the terms with k = 0, 1 which means that we have bound states only between the particles BC and the following reactions

$$A + B + C \rightarrow A + B + C$$

$$A + (BC) \rightarrow A + B + C$$

$$A + B + C \rightarrow A + (BC)$$

$$A + (BC) \rightarrow A + (BC)$$

In all these processes the density n_A of particles of type A does not change. Therefore the collision integral has the important property

$$\int \mathrm{d}\boldsymbol{p}_A[I_A(\boldsymbol{p}_A,t)]_1 = 0.$$

Let us now consider $[I_{ABC}]_2$. We have the following reactions

$$A + B + C \rightarrow B + (AC)$$
$$A + (BC) \rightarrow B + (AC)$$
$$A + B + C \rightarrow C + (AB)$$
$$A + (BC) \rightarrow C + (AB).$$

As can be seen the four processes change the density of the free particles of species A. That means we have

$$\int \mathrm{d}\boldsymbol{p}_A[I_{ABC}]_2 = W_A \neq 0.$$

II. Nonideality Contribution in the Kinetic Equation

Now we would like to explain the many-particle effects in the kinetic equation. The quasiparticle energy may be obtained from the dispersion relation (2). In order to determine $E_A(p_A, R, T)$ we use the more simple concept of "rigid shift approximation" (see Zimmermann [16]). The quasiparticle energy is in this approximation given by a shift Δ_A which does not depend on the momentum

$$E_A(\mathbf{p}_A) \approx \frac{\mathbf{P}_A^2}{2m_A} + \Delta_A \tag{5}$$

If we assume local equilibrium Δ_A has to be determined from the condition

$$n_{A} = \int f_{A} \left(\frac{\mathbf{p}_{A}^{2}}{2m_{A}} + \operatorname{Re} \Sigma - \mu_{A} \right) d\mathbf{p}_{A} = \int f_{A} \left(\frac{\mathbf{p}_{A}^{2}}{2m_{A}} + \Delta_{A} - \mu_{A} \right) d\mathbf{p}_{A}$$
$$= \int f_{A} \left(\frac{\mathbf{p}_{A}^{2}}{2m_{A}} - \xi \right) d\mathbf{p}_{A}$$
$$\xi = \Delta_{A} - \mu_{A} = \mu_{A}^{id}$$

In first order with respect to $\operatorname{Re} \Sigma$ follows

$$\Delta_{A} = \int \mathrm{d}\boldsymbol{p}_{A} \frac{\partial f_{A}}{\partial \xi} \operatorname{Re} \boldsymbol{\varSigma} \left/ \int \mathrm{d}\boldsymbol{p}_{A} \frac{\partial f_{A}}{\partial \xi} \right. \tag{6}$$

and for the chemical potential

$$\mu_A = \mu_A^{id} + \Delta_A \tag{7}$$

But also in this simple approximation an analytical evaluation of (7) is possible only in the nondegenerate and strong degenerate case [9, 11]. In general situations numerical calculations are necessary [12]. Using the results for the limiting cases and the numerical results EBELING and RICHERT have found a Pade approximation [13] for the chemical potential and the quasiparticle shifts.

In Fig. 1 are shown the isotherms of the chemical potential of free electrons and protons in hydrogen $\mu_e + \mu_p$. An important property of this isotherms is the van-der-Waalsloop. That means a region with

$$\frac{\partial \mu_e}{\partial n_e} + \frac{\partial \mu_p}{\partial n_p} \le 0$$
 occurs.

In the case of thermodynamic equilibrium the system is unstable in this region and a special phase transition is indicated. This plasma phase transition in H-plasmas was discussed in papers [14, 11, 13, 15]. The consequence for nonequilibrium systems will be investigated below.



Fig. 1. Isotherms of chemical potential of electrons and protons in hydrogen $\mu_e + \mu_p$, Padé approximation [13] in a version of [15] T = 8000 K (1), 10000 K (2), 12000 K (3), 14000 K (4), 16000 K (5). Dashed line — boundary of the region of negative diffusion

The second many particle effect is the influence of the plasma on the two and three particle problem. We cannot explain here the conplicated quantum statistical theory of this problem [16]. But the result is the following. We have to replace the Hamiltonian of the isolated two and three particle system by an effective two and three particle Hamiltonian H given by

$$H_{12} = \frac{p_1^2}{2m} + \Delta_1 + \frac{p_2^2}{2m} + \Delta_2 + N_{12} V^{\text{EFF}}$$

and

$$H_{123} = \frac{p_1^2}{2m} + \Delta_1 + \frac{p_2^2}{2m} + \Delta_2 + \frac{p_3^2}{2m} + \Delta_3 + N_{123}V_{123}^{\text{EFF}}$$

Here N_{12} and N_{123} are the Pauli blocking factors given by the distribution function f_A in the following way

$$N_{12} = 1 - f_1 - f_2;$$
 $N_{123} = 1 - f_1 - f_2 - f_3$

The particle spectrum then follows from an effective wave equation

$$H_{12}|\alpha \mathbf{P}\rangle = E_{\alpha \mathbf{P}}|\alpha \mathbf{P}\rangle.$$

We obtain a shift of the continuum edge given by $\Delta_1 + \Delta_2$, that means the continuum edge moves down rapidly. The bound state energy shifts downwards only slightly. In this way the ionization energy $I = E_1 + \Delta_0 - \Delta_1 - \Delta_2$ vanishes at the Mott density $I(n_{\text{MOTT}}, T_{\text{MOTT}}) = 0$ and bound states are not possible, cf. Fig. 2. The next problem is the determination of the scattering quantities. We obtain for T_{AB} the effective Lippman-Schwinger equation [5, 8]

$$T_{12} = V_{12} + i V_{12} G_{12} V_{12}, \qquad G_{12} = -i \frac{N_{12}}{z - H_{12}^{\text{EFF}}}$$

and for the many channel T-operator

$$T_{123}^{kk'} = V_{123}^{k} + i^{2} V_{123}^{k} G_{123} V_{123}^{k'}, \qquad G_{123} = -\frac{N_{123}}{z - H_{123}^{\rm EFF}}.$$

It is important to remark that now the scattering quantities are dependent on the distribution functions f_A and have to be determined self-consistently with the kinetic equation [5, 8].



Fig. 2. Lowering of the ionization gap in a dense plasma (qualitatively).

III. Reaction-Diffusion Equation. Rate Coefficients

Let us now consider the macroscopic consequences of the kinetic equation [17]. We introduce macroscopic observables. The density is given by

$$n_{A}(\mathbf{R}T) = \int \frac{\mathrm{d}\mathbf{p}_{A}}{(2\pi\hbar)^{3}} f_{A}(\mathbf{p}_{A}\mathbf{R}T)$$
(8)

and the mean velocity u_A by

$$\boldsymbol{u}_{A}(\boldsymbol{R}T) \ \boldsymbol{n}_{A} = \int \frac{\mathrm{d}\boldsymbol{p}_{A}}{(2\pi\hbar)^{3}} \frac{\boldsymbol{p}_{A}}{m_{A}} f_{A}(\boldsymbol{p}_{A}\boldsymbol{R}T)$$
(9)

We obtain an equation for $n_A(\mathbf{R}T)$ by integration of the kinetic equation with respect to p_A

$$\frac{\partial n_A}{\partial T} + \nabla n_A(\mathbf{R}T) \, \boldsymbol{u}_A(\mathbf{R}T) = \boldsymbol{W}_A \tag{10}$$

where W_A is the source function given by [3, 4, 16]

$$W_A = \sum_{BC} \int \mathrm{d}\mathbf{p}_A \, \frac{[I_{ABC}]_2}{(2\pi\hbar)^3} \tag{11}$$

For purpose of simplification we consider a three-component system A, B, AB and assume that bound states are possible only between different species. Furthermore we neglect all exchange reactions. Then the source function can be written as

$$W_A = \sum_{C=A,B} (\alpha_C n_{AB} n_C - \beta_C n_A n_B n_C)$$
(12)

with the rate coefficients

$$\alpha_{C} = \frac{2\pi}{\hbar V (2\pi\hbar)^{15}} \int \mathrm{d}\boldsymbol{p}_{A} \,\mathrm{d}\boldsymbol{p}_{B} \,\mathrm{d}\boldsymbol{p}_{C} \,\mathrm{d}\overline{\boldsymbol{P}}_{AB} \,\mathrm{d}\overline{\boldsymbol{p}}_{C} \left|\langle \boldsymbol{p}_{A} \boldsymbol{p}_{B} \boldsymbol{p}_{C} \right| \mathbf{T}^{02} \left|n_{AB} \overline{\boldsymbol{P}}_{AB} \overline{\boldsymbol{p}}_{C}\rangle\right|^{2} \quad (13)$$

$$* \,\delta(E_{ABC} - \widetilde{E}_{(AB),C}) \,\frac{\widetilde{f}_{AB} \widetilde{f}_{C}}{n_{AB} n_{C}}$$

and

$$\beta_{C} = \frac{2\pi}{\hbar V (2\pi\hbar)^{15}} \int \mathrm{d}\boldsymbol{p}_{A} \, \mathrm{d}\boldsymbol{p}_{B} \, \mathrm{d}\boldsymbol{p}_{C} \, \mathrm{d}\overline{\boldsymbol{P}}_{AB} \, \mathrm{d}\overline{\boldsymbol{p}}_{C} \, |\langle \boldsymbol{p}_{A} \boldsymbol{p}_{B} \boldsymbol{p}_{C} | \, \mathbf{T}^{02} \, |n_{AB} \overline{\boldsymbol{P}}_{AB} \overline{\boldsymbol{p}}_{C} \rangle|^{2} \quad (14)$$

$$* \, \delta(E_{ABC} - \overline{E}_{(AB),C}) \, \frac{\overline{f}_{A} \overline{f}_{B} \overline{f}_{C}}{n_{A} n_{B} n_{C}}$$

Eq. (10) is not closed. In addition we must derive an equation of motion for the diffusion current $\mathbf{j}_A{}^D = n_A(\mathbf{u}_A - \mathbf{u})$ where $\mathbf{u} = 1/\varrho \sum_A u_A \varrho_A$ is the mass average velocity. By standard methods, that means: Grad method in first approximation, and taking into account only elastic collisions we obtain neglecting pressure gradients in the nondegenerate limit [17]

$$\boldsymbol{j}_{A}{}^{D} = \sum_{C} D_{AC} \left\{ \boldsymbol{\nabla}_{\boldsymbol{R}} \boldsymbol{n}_{C} + \frac{\boldsymbol{n}_{C}}{\boldsymbol{k}_{B}T} \boldsymbol{\nabla}_{\boldsymbol{R}} \boldsymbol{\Delta}_{C}(\boldsymbol{n}_{C}T) \right\}$$
(15)

where by D_{AC} are denoted the multicomponent diffusion coefficients given by the elastic collision integrals (3).

Let us now again consider the ionization and recombination coefficients. For their calculation according to (13) and (14) we assume local equilibrium distribution functions given by

$$f_A = \exp\left(-\left(E_A - \mu_A^{id}(\mathbf{R}T)\right)/k_BT\right);$$

 $F_n = \exp\left(-\left(E_n + \frac{P^2}{2M} - \mu^{id}(\mathbf{R}T)\right)/k_BT\right)$

Using the energy conservation expressed by the δ -function we obtain the following relation between α and β [18]

$$\beta = \frac{\alpha \Lambda_A{}^3 \Lambda_B{}^3}{\Lambda_{AB}{}^3} \exp\left[-(E_n + \Delta_0 - \Delta_A - \Delta_B)/k_BT\right]$$
(16)

 Λ_c denotes the thermal wavelength.

It is interesting to consider the thermodynamic equilibrium case, then $W_A = 0$ and therefore

$$\frac{n_{AB}}{n_A n_B} = \frac{\beta}{\alpha} = \frac{\Lambda_A{}^3 \Lambda_B{}^3}{\Lambda_{AB}{}^3} \exp\left[-(E_n + \Lambda_0 - \Lambda_A - \Lambda_B)/k_BT\right]$$
(17)

(17) is just the mass action law for a nonideal system with reaction $A + B \rightarrow (AB)$ and the effective ionization energy

$$I^{\text{EFF}} = |E_n| - \Delta_0 + \Delta_A + \Delta_B$$

This behaviour is consistent with the picture for the two particle spectrum explained in Fig. 2.

V. Nonideality Effects on Ambipolar Diffusion

We consider a partially ionized plasma consisting of electrons, ions and atoms with the densities n_e , n_i and n_A , respectively. We shall neglect the formation of molecules [15] as well as multiple charged ions [19].

We will study reaction and diffusion processes affected by nonideality (due to particle interactions) which leads to density dependence of the reaction and diffusion coefficients. We focus on ionization and recombination reactions in the ambipolar diffusion regime.

As we have shown from kinetic theory a system of coupled reaction-diffusion equations (10) can be derived.

For the source functions of electrons, ions and atoms follows

$$W_e = W_i = -W_A \equiv W.$$

In the case of electroneutrality, i.e. ambipolar diffusion regime $n_e(\mathbf{r}, t) = n_i(\mathbf{r}, t)$ and $\mathbf{j}_e^{\ D} = \mathbf{j}_i^{\ D}$ for the diffusion currents $\mathbf{j}_C^{\ D} = n_C(\mathbf{u}_C - \mathbf{u})$ one obtains neglecting pressure gradients (for details cf. [20])

$$\boldsymbol{j}_{e}{}^{D} = \boldsymbol{j}_{i}{}^{D} = D_{AMB}^{e}(n_{e}, n_{A}, T) \left[\frac{\partial \mu_{e}}{\partial n_{e}} + \frac{\partial \mu_{i}}{\partial n_{i}} \right] n_{e} \nabla n_{e}$$

$$\boldsymbol{j}_{A}{}^{D} = D_{AMB}^{A}(n_{e}, n_{A}, T) \frac{\partial \mu_{A}}{\partial n_{A}} n_{A} \nabla n_{A}$$
(18)

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Another result is the Gibbs-Duhem relation, cf. [21]

$$\sum_{C} n_{C} \frac{\partial \mu_{C}}{\partial n_{C}} \nabla n_{C} = 0.$$
⁽¹⁹⁾

 $D^{\bullet,A}_{AMB}$ are complicated functions of the densities depending on the collision integrals. Only under very restrictive conditions they are constants and connected only with the ion-atom diffusion coefficient.

Splitting up the chemical potentials again in an ideal and an interaction part (7), one can simplify (19) for the case of nondegenerate plasma with $\mu_c^{ID} = k_B T \ln \Lambda_c^3 n_c$

$$\mathbf{j}_{e}^{D} = D^{e}_{ID}(n_{e}, n_{A}, T) \left\{ 1 + \frac{n_{e}}{k_{B}T} \left[\frac{\partial \Delta_{e}}{\partial n_{e}} + \frac{\partial \Delta_{i}}{\partial n_{i}} \right] \right\} \nabla n_{e} = D^{e}_{NONID} \nabla n_{e}$$
(20)

Of course, for given n_s the density n_A can be found from (19). If the plasma is nondegenerate and nonideality can be neglected the shifts in (20) vanish and the Gibbs-Duhem relation gives a simple connection between the densities:

$$2n_{s}(\boldsymbol{r},t) + n_{A}(\boldsymbol{r},t) = \text{const.}$$
⁽²¹⁾

As an example we consider a hydrogen plasma. The chemical potential of electrons and protons was shown in Fig. 1. Due to interaction effects the diffusion coefficients $D_{NONID}^{e,A}$ are highly nonlinear functions of the densities. This leads to new effects in comparison with the case of constant diffusion (neglecting for a moment chemical reactions):

- 1. Stationary density profile (e.g. in the case of fixed boundary concentrations and constant diffusion coefficient it is a straight line) remains monotonous, however it deforms in such a way that the diffusion coefficient in each point is as great as possible.
- 2. Propagation of diffusion fronts becomes possible even if there are no chemical reactions going on [22]. Using an automodal-ansatz $n_e = n_e(r - tv)$ one obtains the profil of such fronts, which can propagate if special time-dependent boundary conditions depending on the diffusion coefficient are satisfied. In the case of linear diffusion fronts are not possible (velocity goes to infinity).
- 3. Negative diffusion (cf. also [21]). Fig. 1 shows the electron density region of negative derivative of the free particle chemical potential, i.e. of negative diffusion coefficient: $D_{NONID}^e \sim \partial/\partial n_e(\mu_e + \mu_i) < 0$. The boundary of this region (the spinodal curve, cf. [23]) is marked with the dashed line. In Fig. 3 it is shown once more, however in the density-temperature plane. Inside the spinodal curve, below a critical temperature $T_{CR} \sim 17500$ K the diffusion coefficient becomes negative.

Let us discuss the meaning of negative diffusion. If the system is in thermodynamic equilibrium this effect cannot occure because it is equivalent to mechanical instability (if $\partial n_e/\partial n > 0$):

$$0 > \frac{\partial}{\partial n_e} \left(\mu_e + \mu_i \right) \frac{\partial n_e}{\partial n} = -\frac{V}{n^2} \frac{\partial p}{\partial V}, \qquad n = n_e + n_A$$
[11]

In the nonequilibrium situation states with D < 0 are of course unstable too. They lead to rapid increase of density fluctuations until free electron densities below or beyond the spinodal curve are reached. That means phase separation (spinodal decomposition), formation of droplets of high electron concentration in a weakly ionized background plasma or vice versa. So we think that eqs. (18, 19, 20) can help to find a quantum kinetic description of the dynamics of those phase transitions in a nonideal plasma.



Fig. 3. Spinodal curve of hydrogen (Approximation like fig. 1). Negative diffusion possible for $T < T_{CR} = 17\,500$ K

V. Nonideality Effects in Ionization and Recombination Processes

The changes of the particle concentrations due to chemical reactions (the source function W) have been derived from kinetic equations above. Taking into account only three particle interactions like $e + i + e \rightleftharpoons A + e$ one obtains in the case of electroneutrality from (12)

$$W(n_e, n_A, T) = \alpha n_e n_A - \beta n_e^3$$
(22)

The expressions for the rate coefficients (13, 14) for hydrogen in the nondegenerate limit are [17]

$$\alpha = \alpha_{ID} \exp\left[\left(\Delta_e + \Delta_i - \Delta_A\right)\right] / k_B T \tag{23}$$

$$\beta = \alpha_{ID} \mathcal{\Delta}_{e^{3}} \exp\left(E_{1}/k_{B}T\right) \tag{24}$$

$$\alpha_{ID} = 10\pi a_B^2 (2\pi m k_B T)^{-1} / {}^2E_1 E_i (-|E_1| / k_B T)$$

Here E_1 is the ground state energy of the atom, a_B the Bohr radius, $\Delta_C \sim \mu_C^{INT}$ the one particle shifts (6, 7). In an ideal plasma $\alpha = \alpha_{ID}$, however with increasing density due to increasing screening effects the exponential factor in (24) becomes important (see above).

Let us discuss the most simple case — Debye approximation for the screening effects:

$$\Delta_e = \Delta_i = -\varkappa e^2/2, \quad \Delta_A \approx 0$$
^[9]

with \varkappa the inverse Debye radius.

Introducing dimensionless time and concentration variables

$$\tau = t/t_0, \quad c = n_s/n_0, \quad c_A = n_A/n_0, \quad t_0 = (\alpha_{ID}n_0)^{-1}$$

$$n_0 = V^{-1} \int n \, \mathrm{d}\mathbf{r}, \quad c(\mathbf{r}, t) + c_A(\mathbf{r}, t) = n/n_0, \quad c_T, \quad n = n_s + n_A$$
(25)

the source function reads

$$W(c, n, T) = c \left\{ \exp\left(\gamma \sqrt{c}\right) (1-c) - \lambda c^2 \right\}$$
(26)

where

$$\gamma = 2 e^{3} (k_{B}T)^{-1} (2\pi n/k_{B}T)^{1/2}, \qquad \lambda = A e^{3} n_{0} \exp (E_{1}/k_{B}T)$$

In the homogeneous case of course $n(\mathbf{r}, t) = n_0$.



Fig. 4. Source function of hydrogen in Debye approximation. T = 20500 K, $n = 7.35 \cdot 10^{21}$ cm⁻³ (Dashed line) and the corresponding potential U (full line). The horizontal line corresponds to zero.

In Fig. 4 the source function is drawn for T = 20500 K and $n = 7.35 \cdot 10^{21}$ cm⁻³. The zeros of W are the stationary electron concentrations:

1. $c_0 = 0$

corresponds to an atomic gas, this state is always unstable

2.
$$c_M^2 (1 - c_M)^{-1} = \lambda^{-1} \exp\left[\gamma \sqrt[n]{c_M}\right]$$
 (27)

is the Saha equation (17) (mass action law) for a nonideal plasma.

Fig. 4 shows that for certain values of temperature and density the Saha equation obeys 3 solutions $c_1 \leq c_2 \leq c_3$. Linear stability analysis shows that c_1 and c_3 are stable $(dW/dc(c_{1,3}) < 0)$ with respect to small fluctuations and c_2 is unstable. Hence bistable behaviour can be observed. This is a well known phenomenon in chemical kinetics [1, 2], however in our case it does not as usual come from complicated many particle reactions but from microscopic interaction in a nonideal plasma.

In Fig. 5 the bifurcation diagram $c_{\mathcal{M}}(n)$ is given. For $n_I(T) < n < n_{II}(T)$ we observe bistability. The stationary degrees of ionization are the zeroes of the source function (Fig. 4). The values $n_I(T)$ and $n_{II}(T)$ are defined by

$$W(c, n_{I,II}, T) = \frac{\mathrm{d}W}{\mathrm{d}c} (c, n_{I,II}, T) = 0$$
(28)

The critical point (T_{CR}, n_{CR}) satisfies the equations

$$W(c, n_{CR}, T_{CR}) = \frac{\mathrm{d}W}{\mathrm{d}c} (c, n_{CR}, T_{CR}) = \frac{\mathrm{d}^2 W}{\mathrm{d}c^2} (c, n_{CR}, T_{CR}) = 0$$
(29)

Only for $T < T_{CR}$ bistability is possible.

Fig. 6 shows the corresponding region in the n - T plane. In Fig. 7 is drawn the bistability region corresponding to the Padé approximation for the chemical potentials, (cf. Fig. 1).



Fig. 5. Isotherm of the degree of ionization in the bistability region T = 20500 K (Approximation like Fig. 4). Dashed line corresponds with the zeroes of the source function from Fig. 4.



Fig. 6. Bistability region of hydrogen in Debye approximation. Dashed line corresponds with density-temperature values satisfying (38). $T_{CR} = 23\,886$ K.

VI. Reaction and Diffusion in a Nonideal Plasma

Taking into account (10), (18) and (19) we can now write down the reaction-diffusion equations for a nonideal plasma in the approximation of electroneutrality, $n_e(\mathbf{R}, t) = n_i(\mathbf{R}, t)$ in the isobar situation

$$\frac{\partial}{\partial \tau} c = V_x D^s_{NONID}(c, n, T) V_x c + W(c, n, T)$$

$$\frac{\partial}{\partial \tau} c_A = V_x D^A_{NONID}(c, n, T) V_x c_A - W(c, n, T)$$
(30)

In addition to the dimensionless parameters (25) we introduced a dimensionless length $\boldsymbol{x} = \boldsymbol{R}/l_0, \ l_0^2 = D_{ID}/t_0$ is the diffusion length.

$$W = c(c_T - c) \alpha(c, n, T) \{1 - \exp[(\mu_e + \mu_i - \mu_A)/k_B T]\}$$
(31)
$$\mu a = \mu a^{ID} + \Delta a, \qquad a = e, i, A$$



Fig. 7. Bistability region of hydrogen in Padé approximation for the chemical potentials [13] in a version of [15]. $T_{CR} = 13800$ K.

The key quantities in (30) are the chemical potentials, indeed diffusion coefficient and rate coefficients have to be determined simultaneously.

If we account for $j_e = -j_A$ then (30) has an integral – the total electron density: $n(\mathbf{r}, t) = n(\mathbf{r}, 0)$.

Let us investigate a simple situation where the diffusion coefficient is constant and the total electron density is approximately homogeneous. After it we will discuss the influence of nonlinear diffusion on the results.

From (25) then follows $D_{NONID} = 1$ and $c_T \equiv 1$

$$\frac{\mathrm{d}c}{\mathrm{d}\tau} = \Delta c + W(c, n, T) \tag{32}$$

This equation can be derived from a variational principle:

$$\delta \int L(c, \dot{c}) \, \mathrm{d} X = 0$$

with

$$L = c\dot{c} - \frac{1}{2}(Vc)^{2} + U(c, n, T), \qquad W = \frac{\delta U(cnT)}{\delta c(x, \tau)}$$
(33)

The potential U is drawn in Fig. 4.

1. Stationary states

Time independent solutions follow from

$$\frac{\mathrm{d}^2 c}{\mathrm{d}x^2} = -\frac{\partial U}{\partial c} \tag{34}$$

(We focus on the 1-dimensional case: $a \le x \le b$)

Eq. (34) is well known from classical mechanics: substituting $c \rightarrow r$, the coordinate, and $x \rightarrow t$, the time, it describes the movement of a particle with mass equal to 1 in the potential U [24]. (34) has a first integral — the "energy":

$$\frac{1}{2}(dc/dx)^2 + U(c) = E = \text{const.}$$
(35)

Integrating (35) one obtains the inverse function of the stationary density profile

$$x(c) = \int \left[2(E - U(c)) \right]^{-1/2} dc.$$
(36)

This solution of course essentially depends on the boundary conditions. A stability analysis shows [24] that monotonous solutions or in special cases those with a single extremum are stable. Of special interest are profils which can be formed in an isolated system, when the boundary conditions have to coincide with the stable concentrated values of the spatially homogeneous system:

$$c(a) = c_1, \qquad c(b) = c_3.$$
 (37)

Under these conditions the volume is separated into two parts with the degree of ionization equal to c_1 and c_3 , respectively.

In an infinite system one obtains the so called kink solutions, when

$$\lim_{x \to \pm \infty} \frac{\mathrm{d}c}{\mathrm{d}x} = 0.$$

These special solutions are possible only if $U(c_1) = U(c_3)$ or, in terms of the source function

$$\int_{c_1}^{c_2} W(c) \, \mathrm{d}c) = 0 \tag{38}$$

2. Ionization fronts

Front solutions of reaction-diffusion-like equations were first investigated by KOLMO-GOROFF et al. [25]. Introducing an automodal-ansatz $c(z) = c(x - V\tau)$ in (32) one comes to an eigenvalue equation for the profile of an ionization front c(z) and the velocity V. Analytical results can be found if the source function is approximated by a polynomial with the same zeroes [7, 26]

$$\begin{split} W(c, n, T) &= -A(c - c_1) (c - c_2) (c - c_3), \qquad 0 < c \le 1, \qquad A > 0 \quad (39) \\ c(-\infty) &= c_1, \qquad c(\infty) = c_3. \end{split}$$

The result is well known:

$$c(x - V\tau) = \frac{c_3 - c_1}{2} \tanh\left\{\frac{c_3 - c_1}{2} A(x - V\tau)\right\} + \frac{c_1 + c_3}{2}$$
$$V = (A/2)^{1/2} (c_1 + c_3 - 2c_2)$$

Indeed for V = 0 one comes back to the stationary solution discussed above.

In a plasma in the assumed approximations standing fronts are possible only for certain values of total electron density and temperature for which (38) is satisfied. The corresponding line lies inside the bistability region near its lower edge. For the Debye approximation it is marked in Fig. 6 with a dashed line.

Above this line the state c_3 is more stable than c_1 , e.g. if $c(-\infty) = c_1$, and $c(\infty) = c_3$ the ionization fronts move against the x-axis, else they move in opposite direction.

Of course, ionization fronts are possible for arbitrary boundary values of the concentrations, e.g. if at one boundary we have an atomic gas (c = 0), then ionization fronts always propagate towards this boundary. In particulary two fronts can follow one another, the first leading to a homogeneous state with $c \equiv c_1$, the second with $c \equiv c_3$ [7].

3. Nucleation

In a bistable reaction-diffusion system (plasma) with a certain stable degree of ionization local electron density fluctuations can lead to the formation of droplets of the other stable concentration. This droplets are unstable if their radius is less than a critical value. If we assume droplets of constant density, i.e. density changes only in a thin boundary layer, much smaller than the radius, approximate results can be found [27]. We consider a spherical droplet: $c(0, \tau) = c_3$, $c(\infty, \tau) = c_1$, $c(R(\tau)) = c_2$ with c_1, c_3 being the stable zeros and c_2 the unstable one of the source function and R the dimensionless droplet radius. The temporal growth then is governed by

$$\frac{\mathrm{d}R(\tau)}{\mathrm{d}\tau} = 2\left[\frac{1}{R_{CR}} - \frac{1}{R}\right] \tag{40}$$

with the critical radius

$$R_{CR} = 2 \int_{0}^{\infty} (\mathrm{d}c/\mathrm{d}x)^2 \,\mathrm{d}x / \int_{c_1}^{c_2} W(c) \,\mathrm{d}c$$

cf. [28]. Only droplets with $R > R_{CR}$ are overcritical and grow further. Spherical fluctuations less than R_{CR} decay. If the condition for standing fronts (38) is fulfilled we obtain stationary droplets. However they are structurally unstable.

Using the same polynomial approximation for the source function (39) one obtains Montroll's solution for plane wave fronts [29]

$$c(x,\tau) = c_1 + (c_3 - c_1) \{1 + \exp\left[B(x - R(\tau))\right]\}^{-1}$$

with

$$B = (c_3 - c_1) (A/2)^{1/2}, \qquad R_{CR} = 2A^{-1/2}(c_3 + c_1 - 2c_2)^{-1}.$$

Now we shall summarize the influence of nonlinear diffusion on the discussed effects. In (32) another term occurs:

$$\frac{\partial c}{\partial \tau} = D_{NONID}(c, c_T, T) \, \Delta c + \frac{\mathrm{d} D_{NONID}}{\mathrm{d} c} \, (\nabla c)^2 + W(c, c_T, T) \tag{41}$$

- i) Eq. (41) is "dissipative", there exists no potential which it can be derived from, cf. (33).
- ii) The condition of standing fronts changes. Depending on D_{NONID} the front profile can become steeper or smoother. The front velocity changes too (see below).
- iii) The growth velocity of droplets and the critical radius change essentially, cf. (40)

$$\frac{\mathrm{d}R}{\mathrm{d}\tau} = \frac{\int\limits_{0}^{c_{1}} W(c) \,\mathrm{d}c \,-\,\frac{1}{2} \int\limits_{0}^{\infty} D'(c) \left(\frac{\partial c}{\partial x}\right)^{2} \,\mathrm{d}x \,-\,\frac{2}{R} \int\limits_{0}^{\infty} D(c) \left(\frac{\partial c}{\partial x}\right)^{3} \,\mathrm{d}x}{\int\limits_{0}^{\infty} \left(\frac{\partial c}{\partial x}\right)^{2} \,\mathrm{d}x} \tag{42}$$

(40) follows for D = 1.

 iv) The case of negative diffusion has been discussed above. In the presence of chemical reactions it again is connected with phase transitions via spinodal decomposition. Moreover, as it can be seen from (42) negative diffusion can lead to the formation of stable droplets.

References

- [1] EBELING, W., Strukturbildung bei irreversiblen Prozessen, Leipzig 1976 (in German).
- [2] NICOLIS, G., PRIGOGINE, I., Self Organization in Nonequilibrium Systems, New York 1977.
 [3] KLIMONTOVICH, YU. L., KREMP, D., Physica 109 A (1981) 517.
- [4] KLIMONTOVICH, YU. L., KREMP, D., KRAEFT, W. D., Advances of Chem. Phys. LXVIII (1987) 175.
- [5] SCHLANGES, M., Thesis, Rostock 1985; BORNATH, T., Thesis, Rostock 1987.
- [6] MCLENNAN, J. A., J. Stat. Phys. 28 (1982) 521.
- [7] EBELING, W., FÖRSTER, A., KREMP, D., SCHLANGES, M., Physica (1989) in press.
- [8] KREMP, D., SCHLANGES, M., BORNATH, T., Proceedings of the International Conference on the Dynamics of Systems with Chemical Reactions, Swidno 1988.
- [9] KRAEFT, W. D., KREMP, D., EBELING, W., RÖPKE, G., Quantum Statitistics of Charged Particle Systems, Akademie-Verlag, Berlin 1985, Plenum Press, New York 1985, Mir Publishers, Moscow 1988 (in Russian).
- [10] ZIMMERMANN, R., Many Particle Theory of Highly Exited Semiconductors, Teubner, Leipzig 1988.
- [11] EBELING, W., KRAEFT, W. D., KREMP, D., Theory of Bound States and Ionization Equilibrium, Berlin 1970, Moscow 1978.
- [12] KRAEFT, W. D., STOLZMANN, W., Physica A 79 (1979) 306.
- [13] EBELING, W., RICHERT, W., Ann. Phys. 39 (1982) 362; phys. stat. sol. (b) 128 (1985) 467.
- [14] NORMAN, H. E., STAROSTIN, A. N., TBT 6 (1968) 410.
- [15] HARONSKA, P., KREMP, D., SCHLANGES, M., Wiss. Z. WPU, Naturwiss. Reihe Heft 1 (1987) 98.
- [16] ZIMMERMANN, R., KILIMANN, K., KRAEFT, W. D., KREMP, D., RÖPKE, G., phys. stat. sol. (b) 90 (1978) 175.
- [17] KLIMONTOVICH, YU. L., SCHLANGES, M., BORNATH, T., in preparation.
- [18] BORNATH, T., SCHLANGES, M., KREMP, D., Contr. Plasmaphys. 1 (1988) 56; SCHLANGES, M., BORNATH, T., KREMP, D., Phys. Rev. A 38 (1988) 2174.
- [19] EBELING, W., et al., in this volume.
- [20] SCHLANGES, M., BORNATH, T., in this volume.
- [21] EBELING, W., et al., Transport Properties of Dense Plasmas, Birkhäuser Verlag Basel, Stuttgart 1984.
- [22] ŽELDOVICH, YA. B., KOMPANEEC, A. S., K teorii rasprostranenija tepla pri teploprovodnosti savisjaschej ot temperatury. Sbornik k 70-letiju A. F. Joffe. Moskva, Isd. vo AN SSSR 1950, 61-71.
- [23] CAHN, J. W., HILLIARD, J. E., J. Chem. Phys. 28 (1958) 258.
- [24] JETSCHKE, G., Phys. Lett. 72 A (1979) 265.
- [25] KOLMOGOROFF, A. N., PETROVSKIJ, I. G., PISKUNOV, N. S., Bul. MGU, Sekz. A. 1, 6 (1937) 1-26.
- [26] VASILIEV, V. A., ROMANOWSKI, YU. M., CHERNAVSKI, D. S., YACHNO, V. G., Autowave Processes in Kinetic Systems, Deutscher Verlag der Wissenschaften 1987.
- [27] SCHLÖGL, F., Z. Physik 253 (1972) 147.
- [28] [1] Russian Edition, Mir, Moscow 1979.
- [29] MONTROLL, E. W., in: RICE, S. A. et al. 1972, zitiert nach H. MALCHOW, L. Schimansky-Geier: Noise and Diffusion in Bistable Nonequilibrium Systems, Teubner, Leipzig 1985.