

# Ion recombination in dense gases

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**Abstract.** Ion recombination is considered in a wide range of medium properties in dense gases. A dependence of the ion recombination rate on background gas density is found. Three ranges of different recombination kinetics regimes are defined: collisional, diffusion and intermediate. Their borders are defined. A dependence of the recombination rate on the ion Coulomb nonideality is established, contrary to the idea that there is no such dependence, though it is weaker than in the collisional regime. The dependence can be interpolated as exponentially drop-down curves in the whole range the nonideality parameter values. The slope of the decay decreases with an increase of the background gas density, in other words, with the decrease of the ion free path. Extrapolation of this trend to high densities permits to suggest that the dependence is of no importance in liquids. However, the effect can be remarkable in the range of gas pressures from one up to several dozen atmospheres.

## 1. Introduction

Non-equilibrium plasma is formed in lasers with nuclear pumping at the interaction of high energy charged particles with matter [1]. Kinetics of subsequent elementary processes defines efficiency of the atom excitation which results in inverse population. Recombination of electrons and negative ions with positive ions [1] are important elementary processes. Ion recombination processes are essential at discharges in air [2, 3], at the dielectric strength restoration after electrical breakdown in high-voltage equipment, etc.

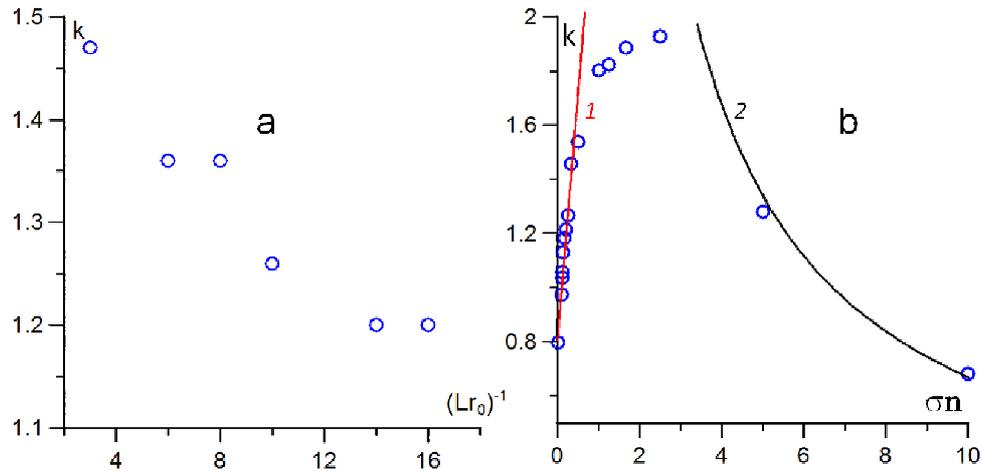
The non-equilibrium media with high number densities of charged particles are created at relatively low temperatures. Therefore, Coulomb non-ideality effects become important. To take them into account, classical molecular dynamics (MD) can be applied. It is effective at modeling of liquids [4], electrolytes, ion solvation [5, 6], molecular and ion-molecular clusters [7–11] and nonideal plasmas [12–14].

MD approach is applied in the paper to treat ion recombination. Section 2 presents plasma model developed and methods used. Dependence of the ion recombination rate on the background gas pressure is obtained in section 3. Evolution of the ion recombination rate with increase of the Coulomb non-ideality in diffusive regime is described in section 4, as well as the background gas influence.

## 2. Model

The concentration of neutral molecules in ion plasmas is many orders of magnitude higher than the concentration of ions. It makes reasonable to consider Coulomb and ion-neutral interactions in a different way.





**Figure 1.** Dependences of the recombination rate constant (a) on the choice of the inverse value of the recombination radius,  $\Gamma = 0.2$  and  $n_a\sigma = 5L^{-1}$ ,  $n_a$  is a number density of neutrals, and (b) on the background gas pressure at low values of the Coulomb non-ideality: approximation according to Natanson (1) and Langevin (2) models, open circles are MD calculation result.

### 2.1. Interparticle interactions of charges

The full MD approach is applied. Pure Coulomb potential is taken for charges of both the same and opposite sign. Dynamic taking into account recombination events permits to remove effects of the numerical scheme instability without the artificial cutoff of the Coulomb potential at small distances. The recombination takes place in real plasmas when two ions of the opposite sign approach each other at the critical distance  $r_0$  which is sufficient for the tunnel transfer of an electron. The same criterion is applied in the MD modeling. Two ions are removed from the system when recombination occurs. Two new ions of the opposite sign are added to the system in the random positions to maintain the stationary character of the process modeled. The velocities of new ions are chosen according to the Maxwell distribution at the temperature of the background gas.

The recombination rate calculated is found to be weakly dependent on the choice of the  $r_0$  value, at least at high densities of the background gas (figure 1a) where  $\Gamma = (4\pi n_-/3)^{1/3}(e^2/kT)$ ,  $n_- = n_+$  is number density of negative/positive ions.  $r_0 = 0.0625L$  is taken in our calculations in the range where there is no such a dependence.  $L = e^2/kT$  is Landau length.

### 2.2. Ion-neutral interactions

The direct simulation of the motion of the neutral component requires the description of systems with a cell volume of a few mean free paths of molecules. This would require the analysis of a few hundred billion of particles, which is impossible at the modern technological level.

However, ion-neutral interactions can be reduced to pair collisions if the media considered are enough dilute. On the other hand, the media are enough dense, Maxwell distribution to be established at times compared with times of the ion-neutral interactions collisions. These conditions are satisfied at pressures from dozens of torr till several atmospheres, the range being considered in this paper.

Therefore, to describe the interaction between ions and molecules, we use an indirect model that simulates this interaction as a series of collisions of ions with the particles of the background gas. In this case, the velocity distribution of background gas molecules is assumed to be Maxwellian, the correlations between neutral and charged particles are neglected, and the

scattering is assumed to be spherically symmetric in the center-of-mass system. Under these assumptions, the probability of collisions of particles per time unit can be calculated by the formula

$$p = 0.5\sigma n_a V_{\text{av}}[\exp(-x^2) + 0.5\pi^{1/2}\text{erf}(x)/x] + \sigma n_a V_0 \text{erf}(x), \quad (1)$$

where  $\sigma$  is a collision cross section of ions and molecules,  $n_a$  is a molecules number density,  $V_0$  is an ion velocity,  $M$  is a mass of the background gas molecule,  $x = (MV_0^2/2kT)^{1/2}$ ,  $T$  is temperature of the background gas,  $k$  is Boltzmann constant, and  $V_{\text{av}} = (8kT/\pi M)^{1/2}$  is the average velocity of the background gas molecule. Direct MD simulations are carried out with regard to ion–molecule collisions by formula (1) using Monte Carlo type approach. The approach is similar to the collisional dynamics [15].

The approach makes it possible to obtain dependencies of the recombination rate constant on background gas density, temperature and concentration of charged particles.

### 3. Dependence on background gas pressure

There are three ranges with different regimes of the recombination (figure 1b).

The recombination rate constant is linearly dependent on the background gas density at low densities. It agrees with the Natanson model at low ion Coulomb nonideality. It is a range of collisional recombination. Its border is defined by the condition  $n_a\sigma < L^{-1}$ , where  $n_a$  is a neutral molecules concentration,  $\sigma$  is a cross-section of ion-molecule collisions.

Langevin model is valid at high densities of the background gas. Ion recombination rate constant is inversely proportional to the background gas density. It is a range of diffusive recombination. Its border is defined by the condition  $n_a\sigma > 4L^{-1}$ .

A complex nonmonotonic dependence of the recombination rate on the background gas density takes place in the intermediate region  $L^{-1} < n_a\sigma < 4L^{-1}$ . A maximum occurs in the range about  $n_a\sigma = 3L^{-1}$ .

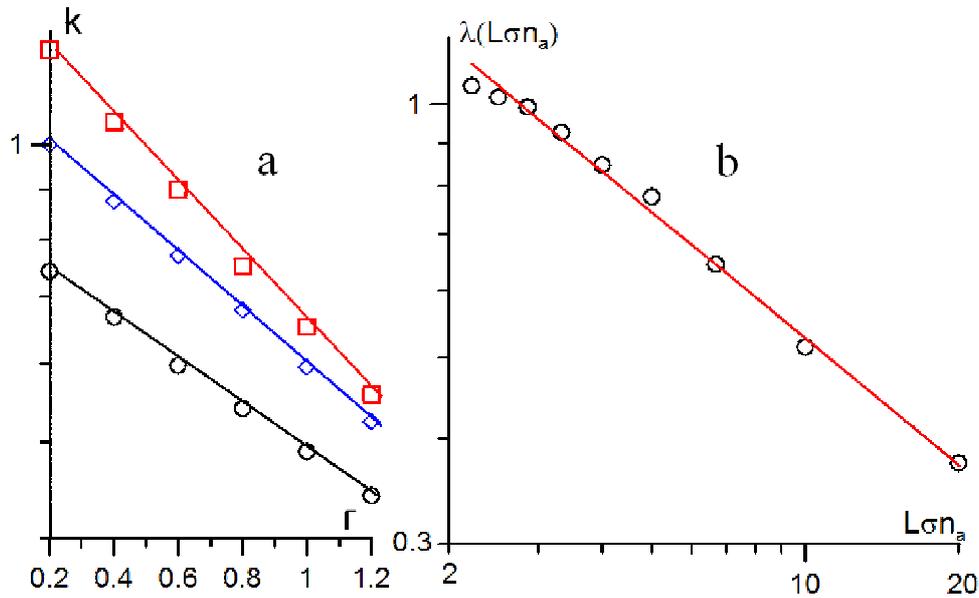
### 4. Dependence on the ion Coulomb nonideality in diffusion regime

The recombination rate constant becomes to be strongly  $\Gamma$ -dependent in both electron-ion plasmas [12,13] and ion plasma at moderate pressure of background gas [16] in collisional regime at transition from ideal to non-ideal plasmas. On the other hand, there is a statement [17] that such dependence does not exist for gases of high density. However, an abrupt break between two branches of the  $\Gamma$ -dependence looks hardly probable. A wide transient region should exist where the dependence changes smoothly from strong one at low pressure to the very weak at high pressure.

The problem is treated here using MD approach described in section 2. The results are presented in figure 2a for three values of the ion mean free path. The  $\Gamma$ -dependence remains evident at all values of  $\sigma n$ , in contrast to [17]. It can be described by the exponential function. Taking into account classical Langevine model, which is valid at small value of  $\Gamma$ , one is able to obtain

$$k(\Gamma, n_a) = 4\pi e(K_0^+ + K_0^-) \frac{n_0}{n_a} \exp(-\lambda(L\sigma n_a)\Gamma), \quad (2)$$

where  $K_0^+$  and  $K_0^-$  are positive and negative ion mobility at  $\Gamma = 0$  and neutrals number density  $n_0$ .  $\lambda(L\sigma n_a)$  is a certain universal function of the ratio of Landau length to mean free path of ion with respect to collision with neutrals. It decreases with increase of the background gas number density. One is able to expect that  $\lambda(L\sigma n_a)$  tends to zero at liquid density and  $\Gamma$ -dependence vanishes. However, the value of  $\lambda(L\sigma n_a)$  is sufficiently large for gases at pressure about several atmospheres and  $\Gamma$ -dependence of the ion recombination rate constant remains to be considerable.



**Figure 2.** (a) Dependence of the ion recombination rate constant on the Coulomb nonideality parameter  $\Gamma$  at different values of the mean free path of ions with respect to collision with neutrals:  $\sigma n_a = 5$  ( $\square$ ),  $6.7$  ( $\diamond$ ) and  $10$  ( $\circ$ ). (b) Dependence of the function  $\lambda(L\sigma n_a)$  on the background gas number density: points are MD modeling results, line is formula (3).

The function  $\lambda(L\sigma n_a)$  is shown in figure 2b. It can be approximated as

$$\lambda(L\sigma n_a) = \frac{A}{\sqrt{L\sigma n_a}}, \quad (3)$$

where  $A = 1.67$ . After substitution of (3) in (2) a formula is obtained for the recombination rate constant  $\Gamma$ -dependence which is valid for high pressures of background gas at  $n_a\sigma > 4L^{-1}$

$$k(\Gamma, n_a) = 4\pi e(K_0^+ + K_0^-) \frac{n_0}{n_a} \exp\left(-A\sqrt{\frac{kT}{e^2\sigma n_a}}\Gamma\right). \quad (4)$$

Note that a relatively fast decrease of  $\lambda(L\sigma n_a)$  with the increase of the background gas number density can result in an increase of the recombination rate constant at high ion concentration unlikely the case of the low ion concentration limit.

## 5. Conclusions

A dependence of the ion recombination rate constant on the background gas number density is considered in the whole range from low to high ion concentrations. The numerical molecular dynamics results are presented in the form of analytic expressions.

- (1) A quantitative formula is suggested which describes the ion recombination rate constant in the diffusion regime at different values of ions and background neutrals concentrations.
- (2) A remarkable dependence of the ion recombination rate constant on ions concentrations is shown for the diffusion regime.
- (3) Borders are specified of the diffusion, collisional and intermediate ion recombination regimes.

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