Diffusion regime of ion recombination in liquid

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Abstract. Recombination in liquid in diffusion regime is considered using molecular dynamics. A method to take into account change in interaction potential due to recombination act is suggested. Different processes that affect recombination rate are considered. It is found that ion cluster pair formation is important in addition to diffusion motion of ions. Results of the computation suggest that no other factors affect recombination at least within accuracy of 10%. It is shown with help of variation of recombination threshold radius and ion radius.

1. Introduction
Recombination in plasma is very significant in nature and technical applications. This process is important for describing processes in atmosphere [1] in development of an electrical breakdown in in high-voltage equipment [2, 3]. Recombination in liquid is also important because of the liquid ionization chambers [4]. Liquid xenon is practically important media because it is used in time projection chamber particle detectors [5]. There is a big interest to such detectors because of the search of weakly interacting massive particles [6].

Here we consider the case of ion–ion recombination. Ion plasma in liquid is formed as a consequence of electron attachment to electronegative molecules of the liquid or to impurities. Recombination of ions in liquid is usually a diffusion controlled process. A classical formula that allows to estimate recombination rate at diffusion regime is Langevin equation

\[
K = \frac{4\pi e^2 (D_+ + D_-)}{(kT\varepsilon)},
\]

where \(D_+\) and \(D_-\) are the diffusion coefficients of positive and negative ions respectively, \(e\) is electron charge, \(T\) is temperature, \(k\) is Boltzmann constant, \(\varepsilon\) is permittivity of liquid. However it could overestimate recombination rate [7]. One of the mechanisms that could decrease recombination rate is a cluster pair formation [8].

Classical molecular dynamics [9] could be used to describe processes in dense environments. This method is widely used in simulation of liquids [10–12], including electrolytes [13] and ion solvation [14–16], formation of molecular and ion-molecular clusters [17,18] and nonideal plasma [19]. This approach allows to take into consideration collective processes. It is used in this work to take into account both diffusion of ions and dynamics of ion cluster pairs at one simulation.

The paper is structured as follows. Firstly, model of liquid xenon and ions is explained in the section Model. Protocol of recombination is discussed in detail in section calculation technique. Then analysis of the results is given in the section analysis of the recombination. Computation is compared with the results obtained from Langevin relation.
2. Model

Interaction of xenon atoms is Lennard-Jones

\[ U_1(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right], \tag{2} \]

where \( r \) is the distance between xenon atoms, \( \sigma \) is the distance at which the inter-particle potential is zero and \( \varepsilon \) is the depth of the potential well. Parameters are taken from [20] \( \varepsilon = 0.02 \) eV \( \sigma = 3.94 \) Å. They are better than some other parameter sets available in the literature because they reproduce gas–liquid coexistence curve of xenon near the triple point. Also, they reproduce the triple point. Ion liquid molecules interaction potential is taken in a form [21]

\[ U_2(r) = \left(\frac{E_0}{2}\right)\left[\left(\frac{R_{\text{ion}}}{r}\right)^{12} - 3\left(\frac{R_{\text{ion}}}{r}\right)^4\right] = \beta/r^{12} + \alpha/r^4, \tag{3} \]

where \( r \) is the distance between the ion and xenon atom, \( R_{\text{ion}} \) is an ion radius and \( E_0 \) is the depth of the potential well. Parameter \( \alpha \) is chosen to reflect the interaction of a point charge, placed on the ion, and a dipole. It is taken in a from \( \alpha = \alpha_p q^2/2 \), where \( \alpha_p \) is polarizability of liquid xenon and \( q \) is a charge of the ion. While \( \alpha \) is fixed \( \beta \) is varied to reflect change in the ion radius \( R_{\text{ion}} = \sqrt[3]{3\beta/\alpha} \). Temperature is chosen to be 163 K. Density is 3 g/cm\(^3\). Dielectric permittivity of liquid xenon is taken to be \( \varepsilon = 1.83 \).

Small amount of impurity is added to liquid. Such impurity atoms are then ionized. Their interaction with each other and with ions is chosen to be weak compared with xenon atoms. Buckingham potential without attraction part is chosen to represent interaction of them with each other

\[ U_{\text{impurity}}(r) = A \exp\left(-r/\rho\right), \tag{4} \]

where \( r \) is a distance between the impurity atoms and \( A = 10 \) eV and \( \rho = 5 \) Å are potential parameters. This allows to avoid precipitation of the impurity. Physically this means that impurity molecules have low polarizability and consequently very weak attraction. Exact choice of the potential for impurity atoms is not important as number of impurity atoms is rather small.

3. Calculation technique

Classical molecular dynamics calculations are carried out using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [22]. Integration is carried out via Verlet integration scheme. A time step is 1 fs. Periodical boundary conditions are used. There are 5324 xenon atoms 15 impurity atoms 15 positive ions and 15 negative ions in a simulation box. The potential cut off radius is \( r_{\text{cut}} = 12 \) Å for the potential (2) and \( r_{\text{cut}} = 24 \) Å for the potential (3).

Dependence of the number of recombination acts on time is computed. It is done for a trajectory of 250,000 steps. Then such results are averaged over different initial conditions. This dependence is then fitted by a linear function figure 1. A slope of this function is used to obtain recombination rate. Non-linear behaviour near zero time is a consequence of system relaxation.

Recombination is considered to occur when atoms are achieving a chosen distance \( R_{\text{recomb}} \). This distance is an unfixed parameter of the model. However the dependence of recombination rate on it has a limit at \( R_{\text{recomb}} \rightarrow R_{\text{ion}} \) figure 4. This limit is taken to be real recombination rate.

Recombination is a process of charged atom with potential (3) becoming neutral atom with potential (4). This could not be done instantly. Otherwise it will lead to discontinuous change of system potential. Such change causes numerical problems. We are trying to avoid this by making such transition smoother. This is done by introducing intermediate potential

\[ U_{\text{intermediate}} = U_2 \exp\left(-t/\tau\right), \tag{5} \]
Figure 1. Number of recombination acts as a function of time for $R_{\text{ion}} = 2.6$ Å. Green line is a linear fit.

Figure 2. Dependence of recombination rate on thermostat parameter. Horizontal line is a value from Langevin relation. Radius of the ion is $R_{\text{ion}} = 2.6$ Å.

where $U_2$ is the potential (3). Multiplier is chosen to be exponential because it reflects physical nature of electron transfer during the recombination. Such transfer occurs as electron tunnelling through barrier. Waiting time before tunnelling is exponential. Thus average potential could
Figure 3. Dependence of temperature on thermostat parameter. Radius of the ion is $R_{\text{ion}} = 2.6$ Å.

be represented as

$$E[U] = E(\alpha_p q(t^2)/r^4) = (\alpha_p e^2/r^4)P(q = e)$$

$$= (\alpha_p e^2/r^4) \exp(-t/\tau) = U_1 \exp(-t/\tau) = U_{\text{intermediate}}.$$ Exponential decay time $\tau$ should have a time scale of 10 fs [23] to meet average tunnelling time. On the other hand, numerical experiment showed that it should be from ten to hundreds of time steps to make numerical scheme stable. Physical and numerical timescales of $\tau$ are comparable as a typical time step is a femtosecond. At the present work $\tau = 250$ fs. Thus we can avoid computational problems and make recombination act more physically accurate at the same time.

Recombination constant could depend on system temperature. Thermostat usage is necessary as a recombination is exothermic process. Langevin thermostat was used. Let $\gamma$ be a Langevin thermostat parameter. At the limit of $\gamma \to \infty$ thermostat influence becomes negligible. However, at a finite value of $\gamma$ it affects recombination. One of the possible ways is a decrease of the ion diffusivity. This happens as Langevin thermostat adds external friction to system. Such friction is inversely proportional to thermostat parameter $\gamma$. Friction becomes zero at a big values of the $\gamma$ and diffusion coefficient approaches correct values. Computation of the dependence of recombination rate on $\gamma$ was made figure 2. It was checked that results are independent of the thermostat constant above some value. It is also important that temperature does not change significantly at this range of $\gamma$ values figure 3. Graphics in figure 2 and figure 3 looks similar. This is due to the fact that temperature rises with rise of recombination rate as it defines system heating.

Ion recombination threshold is chosen to be 12 Å for dependence on $\gamma$. This is bigger than cluster pair size. As a consequence recombination rate should be close to Langevin relation result. This is achieved for values of $\gamma$ bigger than 3 with discrepancy about 10%. Following computations are made with $\gamma = 3.5$. Thus possible influence of the thermostat is neglected.

Recombination rate was also calculated using (1) and diffusivity data from [24]. Diffusion coefficients were computed for wide range of ion radii (figure 4).
4. Analysis of the recombination

This section is based on the analysis of the dependences of recombination rate on two radii: ion radius and recombination threshold radius. Ion radius is $R_{\text{ion}}$ from potential (3). Recombination threshold radius is a distance at which recombination is assumed to appear at given computation.
Recombination rate for different recombination radii is compared with Langevin result (figure 5). At a big recombination radius they are rather close. This radius is bigger than the size of cluster pair. Thus formation of cluster pairs is not possible and they do not affect recombination. Satisfactory agreement between Langevin relation and direct computations at this recombination radius means that possible breakdown of Langevin relation is probably only related to processes at small ion separation distance. On the other hand, recombination rate is much smaller for small values of recombination radius. This means that ion cluster pair formation indeed slows down recombination in liquid.

Increase in the dependence of diffusivity on ion radius is attributed to the structural diffusion that involves jumps of ion inside the solvation shell [24, 25]. On the other hand at small ion radius ion does not move inside solvation shell. Ion moves together with solvation shell [15, 24]. This is observed at ion radius range between 2.3 and 3 Å (figure 5). Consequently at a small ion radius ion cluster is rather stable [15, 24] while with increase of ion size it becomes less stable. This decreases lifetime of it. Consequently lifetime of cluster pair is decreased. As a result Langevin relation is in a better agreement with direct computation at higher ion radius (figure 5). Discrepancy is about 10% for big ions and about 50% for small ions.

Addition of ions and impurity atoms could change recombination rate due to change of system viscosity. This will lead to change in ion diffusivity and then in Langevin recombination rate. This could be a possible explanation of 10% discrepancy between Langevin result and direct computation with big recombination threshold radius or big ion radius.

5. Conclusion

Molecular dynamics is applied to study ion–ion recombination in liquid. Major factors that affect computation and kinetics of the recombination are determined and studied.

Classical potential changes during the act of recombinations. Direct change of the potential between ion and neutral could lead to crash of the computation or non physical heating of the system. A smooth change of the potential allows to make computational scheme more stable and satisfy physical nature of the electron tunnelling at the same time.

Deviation from Langevin relation for recombination rate are observed. They are attributed to the influence of cluster pairs. Langevin relation is rather good approximation for recombination rate in case of recombination at ion separation bigger than cluster pair size. This is correct even for small ions that could form stable cluster pairs.

Formation of cluster pairs only affects recombination when such pairs could be stable. Unstable cluster leads to formation of unstable cluster pair. Thus recombinion of ions that have low stability of ion cluster could be described by Langevin relation with error about 10%. Such ions usually have big diffusivity due to structural diffusion.

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