

Temporal and spatial properties of ion solvation in simple liquids

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Abstract. A research of the diffusion of an ion in a liquid is carried out. Dependences of the diffusion coefficient on the ion-molecule potential, ion mass, liquid temperature and density are defined. The results are related to the ion solvation. The classical molecular dynamics method is applied. The effect of the ion solvation is discovered. Firstly, ion mass has no influence on the diffusion coefficient. This is because the total mass of the cluster formed by the ion and the ion solvation shell varies slightly while the mass of the ion changes significantly. In addition, the dependence on short-range interaction is found to be rather weak. The dependence of the diffusion coefficient on long-range interaction is found to be really stronger than on short-range. The ion velocity autocorrelation function calculated reveals a strong oscillatory character superimposed on the conventional functional liquid-type form. It reflects the oscillations of the ion inside the solvation shell. The relation between the ion mobility and temperature is found to be of the Arrhenius-type form.

1. Introduction

Transport properties of ions in weakly ionized plasma are very significant in nature and technical applications. They are important for describing processes in atmosphere [1] and plasma sources, that are used to etch semiconductors [2], in development of an electrical breakdown [3, 4]. The difference in mobility of ions in gas are used in ion mobility mass-spectroscopy [5, 6].

Transport properties of ions in gas can be calculated using Boltzmann kinetic equations when the pressure of gas and ion concentration are rather low. There are a lot of experimental data of ion mobility, especially for ions, from environment, that have big practical significance, for example SF₆ [7]. However, measuring of ion mobility is usually made only with small pressure of gas. It is difficult for dense environment [8, 9].

Classical molecular dynamics [10, 11] could be used to describe processes in dense environments. This method is widely used in simulation of liquids [11–13], including electrolytes and ion solvation [14, 15], formation of molecular and ion-molecular clusters [16] and nonideal plasma [17, 18]. This approach allows to take into consideration collective processes.

The fact of ion solvation is discussed in section four. Lifetime of molecules around the ion is calculated as function of ion-atom distance. This is done in order to locate the cluster. Oscillations of ion velocity autocorrelation function are studied in section five. It is shown, that they are caused by cluster oscillations. Dependences of the diffusion coefficient on the ion-molecule potential, ion mass, liquid temperature and density are defined in section six. Solvation effects are discussed.



2. Model

Information about interaction potentials is necessary to describe system. Quite simple potential [19–21] is enough to use for ions:

$$U(r) = \frac{n\epsilon}{3n-12} \left[\frac{12}{n} \left(\frac{\sigma-a}{r-a} \right)^n - 3 \left(\frac{\sigma-a}{r-a} \right)^4 \right]. \quad (1)$$

The most widespread and simple form of this potential with $a = 0$ and $n = 12$ is used in this work. It can describe huge variety of simple ions. This allows to get dependences of transport coefficients on system parameters. Molecular dynamics simulation could be applied to do it.

Let us consider ion immersed in liquid. Ion-liquid molecules interaction potential:

$$U(r) = (E_0/2) [(r_0/r)^{12} - 3(r_0/r)^4]. \quad (2)$$

It could be rewritten as:

$$U(r) = \beta/r^{12} - \alpha/r^4. \quad (3)$$

Representation (3) is used because it allows to make the analysis of obtained results. The potential for liquid is Lennard-Jones:

$$U(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (4)$$

r is a distance between particles in both cases.

System can be described using eight parameters: density, temperature, ion mass, liquid atoms mass, two parameters of liquid-liquid potential, two parameters of ion-liquid potential. Diffusion coefficient must be the function of this parameters

$$D = D(\sigma, \epsilon, m_{liquid}, \alpha, \beta, m_{ion}, T, n).$$

The liquid atoms mass and liquid-liquid potential parameters (ϵ, σ) are taken as units of mass, energy and distance respectively. Consequently, the system of units is changed to the Lennard-Jones system of units. Only five parameters define the system after this

$$D = D(1, 1, 1, \alpha, \beta, m_{ion}, T, n).$$

All the parameters but one are fixed and this one is changed. The value of the diffusion coefficient is gotten for the different values of it. Such dependences are studied in this work.

3. Simulation technique

Molecular dynamics method is applied for obtaining the results. Atoms are placed in the lattice sites in the beginning of the simulation. The position of the ion is random. The system is brought to the equilibrium. The diffusion coefficient and other properties of the system are calculated after that. It is anticipated that the system can be described by classical mechanics equations. The problem is solved in two ways: using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22] and using a self made program code. The Velocity Verlet integration scheme is applied in the first case. Newton method is applied in the second case. A time step is 2.1 fs in both cases. Periodical boundary conditions are used. System is brought to the chosen temperature using Berendsen and Langevin thermostats respectively. The number of particles is 512 and 5324. The potential cut off radius is $r_{cut} = 4.5\sigma$ for the potential (4) and $r_{cut} = 8\sigma$ for the potential (3) in the first case. For both potentials $r_{cut} = 4\sigma$ in the second case because the simulation box size is 8.5σ and it is useless to increase r_{cut} . Calculation of a diffusion coefficient is carried out after the temperature stabilization. Three methods are used for the determination of a diffusion coefficient.

(i) Trajectory with N steps is calculated and broken into parts with n steps in each part. Then the mean square deviation of a particle position on the step $nk + i$ from the position on the step nk ($k \in [0, (N/n) - 1]; i \in [0, n]$) is calculated. Values are averaged over the k . A dependence of $\langle r^2 \rangle$ on t is obtained. Then a value of the diffusion coefficient is gotten from the slope of this dependence, using formula $\langle r^2 \rangle = 6Dt$. This method is applied using LAMMPS.

(ii) The autocorrelation function $\langle \vec{v}(0)\vec{v}(t) \rangle$ for $t < p\Delta t$ is calculated. Values of ion velocity on the trajectory with N steps are calculated, to do it. Then $(\vec{v}(k \cdot \Delta t) \cdot \vec{v}([k+i] \cdot \Delta t))$ are calculated and averaged over all k ($k \in [0, N - p]; i \in [0, p]$). This gives the value of $\langle \vec{v}(0)\vec{v}(t) \rangle$. Then diffusion coefficient is calculated using the Green-Kubo formula:

$$D = (1/3) \int_0^\infty \langle \vec{v}(0)\vec{v}(t) \rangle dt. \quad (5)$$

The integral is calculated numerically. This method is applied using LAMMPS.

(iii) The ion mobility is calculated. Ion is affected with a constant force F . The average speed of this ion is calculated. Ion trajectory with N steps is calculated to do it. Then it is separated into n parts with length N/n . A new calculation is started from the end of each part. A constant force is applied to the ion in this new calculation. Then a projections of a speed to the force in the moment t are averaged over all parts of initial trajectory. The dependence $v(t)$ is averaged over time $\langle v(t) \rangle = \langle v \rangle (k \cdot \Delta t) = \sum_{i=0}^k v(i \cdot \Delta t)/k$ ($k \in [0, N/n]$). Speed value $\langle v(t) \rangle$ converges to a constant with time. This value is used as an average speed of the ion. A time of a MD run for all the calculations is quite small. Therefore a temperature remains constant during the calculation. This is also true for the system total impulse. The dependence $v(F)$ is obtained, using this algorithm. Ion mobility is gotten using $v = BF$. The diffusion coefficient could be determined from the ion mobility and vice versa because $D = kBT$. This method is applied using self made code.

Usage of this three methods allows to confirm the results.

4. Solvation

Firstly, the system with parameters values, that corresponds to the ion O_2^- in liquid argon with $T = 87$ K, $\rho = 1.4$ g/cm³, is studied. The radial distribution function is calculated (figure 1) to determine the ion cluster properties.

There are five peaks on it; those correspond to layers of the cluster. Dependences of ion-atom distance as a function of time is calculated for every layer of the cluster. No averaging is applied. Ion-atom distance oscillates near layer radius for all the layers. Atoms of the first layer do not leave it on times that are reached in computations. Atoms from the other layers jump from layer to layer.

Lifetimes of cluster atoms on the layer are calculated. Dependences of ion-atom distance is averaged for last 8.4 ps. This is done to exclude oscillations. Histograms for time from appearing of atom on a layer until leaving are found using such dependences. This histograms are on the figure 2 in semi-log scale. It is seen that they are linear. So the time, that atom spend on a layer, is exponential random quantity. Average values of this times are calculated (table 1). This times are much bigger than the time of atom oscillation on the layer (~ 0.1 ps as shown further) and time at that the dependence $r_{ion}^2(t)$ is found to be linear (8.4 ps). This means that these atoms are moving together with the ion as an organic whole during diffusion.

5. Autocorrelation function

The ion velocity autocorrelation function is shown for the same set of the system parameters in the figure 3. It has oscillations. The increase of the accuracy doesn't remove them. Consequently, they appears not because of the small accuracy of averaging. They are caused by natural oscillations of the cluster.

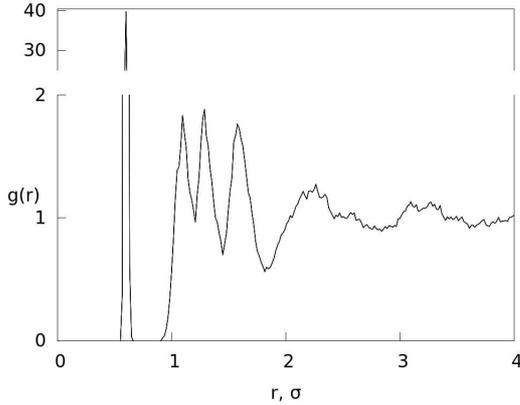


Figure 1. Ion-liquid molecules radial distribution function.

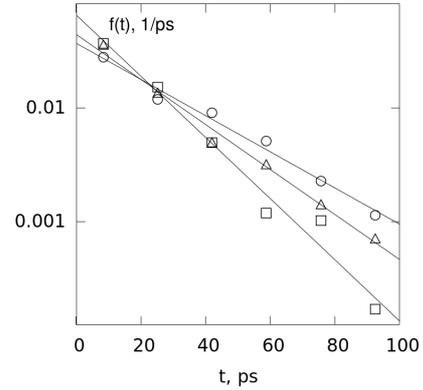


Figure 2. Atom from solvation shell lifetime probability density function $f(t)$: \circ is the second layer, \triangle is the third layer, \square is the fourth layer.

Table 1. Average time that liquid atoms spend on cluster layers.

layer number	1	2	3	4	5
lifetime, ps	> 1000	26.6	17.7	17.6	17.05

The first stable layer of the cluster has a form of a tetrahedron. This is understood from the visualization of the system. The small oscillations, near the equilibrium state, of the tetrahedron with ion in its center is considered. The geometry of the system is defined but the scale is undefined. The system of axes is chosen to be rectangular. Center of it is in the center of the tetrahedron. Let the length of the tetrahedron side be L . Then coordinates of the particles could be expressed through the L . The potential energy of the system is found $U = \sum_{i,j} \varphi_{i,j}$. The necessary condition for equilibrium ($\partial U / \partial x_i = 0$) is used to obtain $L = 0.97\sigma$. The new coordinates are introduced $q_i = x_i / \sqrt{m_j}$, where j is the index of an atom. Expansion of the potential energy in a Taylor series is given by:

$$U = U_0 + \sum_i \frac{\partial U}{\partial q_i} q_i + \frac{1}{2} \sum_i \sum_j \frac{\partial^2 U}{\partial q_i \partial q_j} q_i q_j + \dots \quad (6)$$

Using Newton's second law

$$\ddot{q}_i + \frac{\partial U}{\partial q_i} = 0.$$

Substituting U from (6) and using $\partial U / \partial q_i = 0$ (because we are considering an equilibrium position)

$$\ddot{q}_i + \sum_j \frac{\partial^2 U}{\partial q_i \partial q_j} \cdot q_j = 0.$$

In a matrix form:

$$\ddot{\vec{q}} + A \cdot \vec{q} = 0, \quad A = \left\| \frac{\partial^2 U}{\partial q_i \partial q_j} \right\|. \quad (7)$$

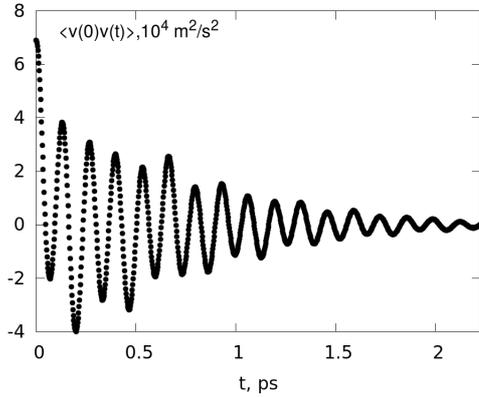


Figure 3. Ion's velocity autocorrelation function.

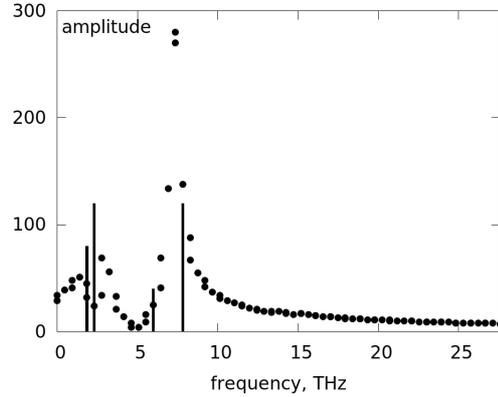


Figure 4. ● is Fourier transformation of the velocity autocorrelation function. Vertical lines are the frequencies, which are found analytically.

If we go to a basis of eigenvectors of A , then the system of equations (7) goes into the system:

$$\ddot{f}_i + \lambda_i f_i = 0, \quad (8)$$

where λ_i are the eigenvalues of A , f_i are new variables. Solutions of the system (8)

$$f_i = C_{i,1} \cdot \sin(\sqrt{\lambda_i}t) + C_{i,2} \cdot \cos(\sqrt{\lambda_i}t).$$

f_i are connected with q_i by the relationship:

$$\vec{q} = \sum_i \vec{a}_i \cdot f_i,$$

where \vec{a}_i is the eigenvectors of the matrix A . Thus we finally obtain:

$$\vec{q} = \sum_i \vec{a}_i \cdot [C_{i,1} \cdot \sin(\sqrt{\lambda_i}t) + C_{i,2} \cdot \cos(\sqrt{\lambda_i}t)]. \quad (9)$$

Small initial deviations from the equilibrium state cause cluster's oscillations with frequencies λ_i . It could be understood from the formula (9).

The discrete Fourier transform of the velocity autocorrelation function ($F_n = \sum_{j=1}^{n-1} x_j \cdot \exp(-2\pi i n j / N)$), allows to present it in the form $f(x_n) = 1/N \sum_{j=1}^{n-1} \exp(-2\pi i n j / N)$. Figure 4 shows this transformation. The frequencies of the natural oscillations are also shown. Computer algebra system maxima is used to find them, according to the method described above. Vertical lines length are chosen related to the multiplicity of the corresponding frequencies. Multiplicity of frequencies in ascending order of frequency is 2,3,1,3. Also, six zero frequencies are obtained. They correspond to rotations and translations of the cluster.

Match of analytically and numerically found frequencies is quite good (figure 4). Each of the three peaks on the Fourier transform corresponds to the frequency, that is found analytically. One of the natural frequencies does not hit the peak. But it is close to the largest peak and can probably be attributed to it. The shift can be explained by the influence of the outer layers of the cluster. This frequency can also be suppressed due to the impact of the external layers.

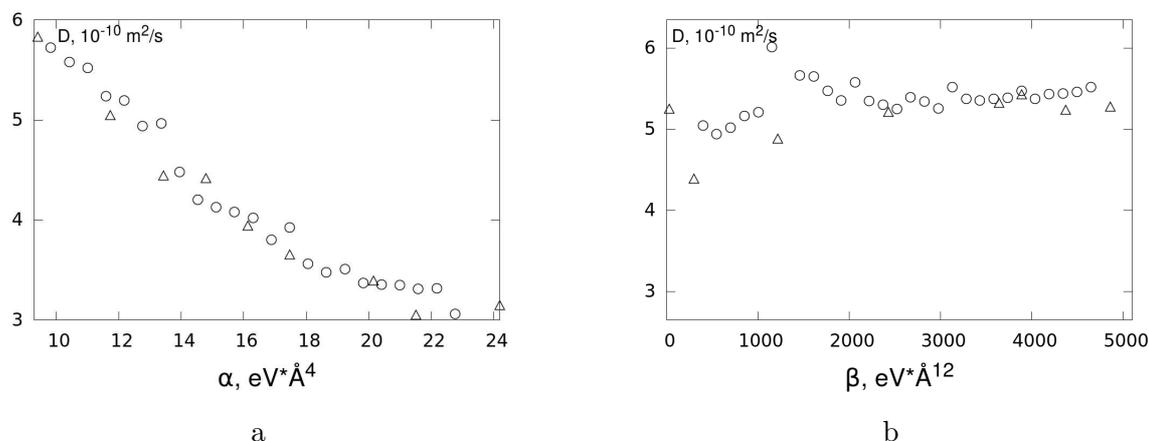


Figure 5. Relation between the ion diffusion coefficient and α (a), β (b). Here α , β are the parameters of the potential (3); Δ is for the method of calculation from the ion mobility, \circ is for the method of calculation from the Einstein's relation.

Vibrational nature of the autocorrelation function is due to fluctuations of the cluster in any case.

The dependence of the mean square deviation of the particle on time is found. It is linear in accordance with the law of Einstein relationship. The slope of the line gives the diffusion coefficient $D = 0.048 * 10^{-8} m^2/s$.

Value of the integral $(1/3) \int_0^t \langle \vec{v}(0)\vec{v}(\tau) \rangle d\tau$ is found. It converges to the value of the diffusion coefficient, that is defined from the Einstein relation. This convergence follows from the formula (5) and confirms the validity of the results.

6. Dependences on parameters

The calculation of the relations between the diffusion coefficient and parameters of the system is carried out. The method of obtaining the diffusion coefficient from the Einstein relation is used. Also, the diffusion coefficient is calculated using the value of mobility.

The graphs (figure 5,6) shows the dependences on the system parameters, obtained from the mobility and diffusion calculations. This graphs are the same within a small error. The calculations for this graph are carried out by different programs with different number of particles and thermostats. This confirms the obtained results.

Dependence on mass is in the figure 6. The diffusion coefficient is independent of the ion mass. The effect on the diffusion has not the ion mass, but the mass of the entire cluster as it moves as a whole. It is shown that cluster contains all the atoms up to five layers in the section four. The average number of atoms in the five layers is 56. Their total mass is 2240 u. Ion mass is much smaller than the mass of the cluster, in a chosen range. Therefore, the total mass of the cluster varies slightly when we change the mass of the ion.

Figure 5,b shows the relation between the diffusion coefficient and the ion potential (3) parameter β . The dependence is virtually absent. Figure 5,a shows the relation between the diffusion coefficient and the ion potential parameter α . The dependence is much stronger than on the coefficient discussed earlier and it is decreasing. Thus, the diffusion coefficient is determined by the value of α and it is only slightly dependent on the value of β .

The parameters in the interaction potential of the ion with atoms (3) admit the following interpretation: β describes the short-range interaction, α describes long-range. This is because at long distances $1/r^{12}$ is much smaller than $1/r^4$. Thus the fact that there is no dependence

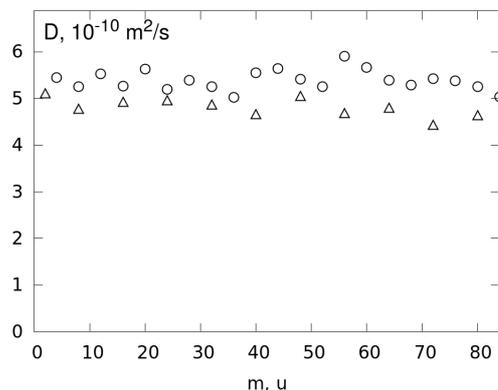


Figure 6. Relation between the ion diffusion coefficient and the ion mass. Δ is for the method of calculation from the ion mobility, \circ is for the method of calculation from the Einstein's relation.

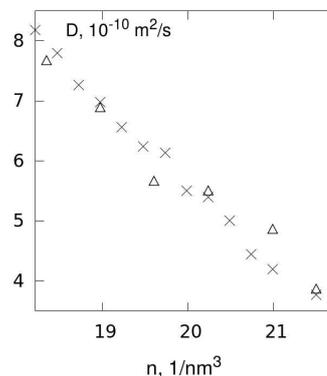


Figure 7. Dependence of the diffusion coefficient on concentration: \times is for molecules of liquid (the value of diffusion coefficient is divided by 5), Δ is for ion.

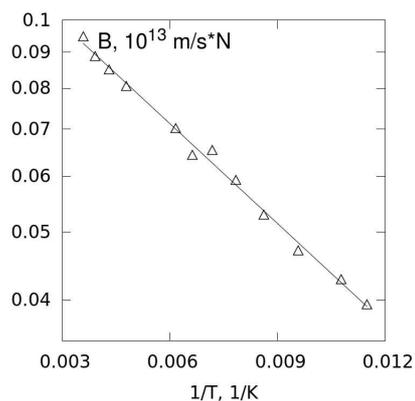


Figure 8. Dependence of the ion mobility on temperature in semi-log scale.

on the parameter β can be explained. It appears because β only influences the structure of the ion cluster and it does not change significantly, when β changes. Also, this parameter has practically no effect on interaction with atoms outside the cluster. On the other hand, the parameter α is responsible for interaction with atoms outside the cluster and it affects the diffusion of the cluster.

The diffusion coefficient of pure liquid is calculated as function of concentration. The Einstein relation is used to do it. This gives better understanding of the relation between the ion diffusion coefficient and concentration. The method of determining it is similar to the definition of the diffusion coefficient of the ion from the Einstein's relation. But in this case mean square deviation is averaged over all atoms. 13500 particles are used in this computation and due to this the number of steps is reduced. Figure 7 shows the dependence of the diffusion coefficient (divided by 5) of liquid on the concentration. Also it shows the dependence of the ion diffusion coefficient on the concentration. They are equal and linear with good accuracy. Thus, the diffusion coefficient of the ion is five times less than the diffusion coefficient of liquid atoms. Further reduction of the concentration leads to a break in both graphs. This gap is due to the transition to the

two-phase region.

In liquids the temperature dependence of the mobility is determined by the formula:

$$B = B_0 * \exp(-E/kT), \quad (10)$$

where E is an activation energy. The relation between the ion mobility and temperature is determined in Arrhenius plot figure 8. This graph is found to be linear. It confirms the feasibility of the formula (10). Another sign of the calculations correctness is the fact, that the dependence obeys this equation. Such graphs are plotted for different values of the potential parameter α . The activation energy is determined from this family of dependences. It is done to get the relation between E and α . This dependence is rather weak. However, even a slight change in E has a considerable effect on the value of mobility since E is in the exponent.

7. Conclusions

Dependences of the diffusion coefficient on the ion-molecule potential, ion mass, liquid temperature and density are defined. Strong influence of the solvation is found. It is proved by the following facts:

(i) The relation between the diffusion coefficient and ion mass is very weak. This is because the total mass of the cluster formed by the ion and the ion solvation shell varies slightly while the mass of the ion changes significantly.

(ii) The dependence on the potential (3) parameter β is found to be rather weak. This is because β defines mostly the geometry of the cluster, whereas the polarization part of the ion-molecule potential influences the interaction of the cluster with the ion environment. The dependence of the diffusion coefficient on α is found to be really stronger than on β .

(iii) Velocity autocorrelation function oscillates. These oscillations are the result of natural oscillations of the cluster. Their frequencies are found to be equal.

The relation between the mobility of the ion and temperature is found to be of the Arrhenius-type form. Dependence of the diffusion coefficient of the ion on liquid concentration is linear. In addition, it is five times less than diffusion coefficient of the liquid.

Time that atoms spend on the layers of the cluster is an exponential random variable.

Acknowledgments

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