Effect of sharp maximum in ion diffusivity for liquid xenon

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Abstract. Ion diffusion in a liquid usually could be treated as a movement of an ion cluster in a viscous media. For small ions this leads to a special feature: diffusion coefficient is either independent of the ion size or increases with it. We find a different behavior for small ions in liquid xenon. Calculation of the dependence of an ion diffusion coefficient in liquid xenon on the ion size is carried out. Classical molecular dynamics method is applied. Calculated dependence of the ion diffusion coefficient on its radius has sharp maximums at the ion radiuses 1.75 and 2 Å. Every maximum is placed between two regions with different stable ion cluster configurations. This leads to the instability of these configurations in a small region between them. Consequently ion with radius near 1.75 or 2 Å could jump from one configuration to another. This increases the speed of the diffusion. A simple qualitative model for this effect is suggested. The decomposition of the ion movement into continuous and jump diffusion shows that continuous part of the diffusion is the same as for the ion cluster in the stable region.

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 is used in ion mobility mass-spectroscopy [5].

Liquid xenon is practically important media because it is used in time projection chamber particle detectors [6]. There is a big interest to such detectors because of the search of WIMPs (weakly interacting massive particles) [7]. There are a lot of experimental data of ion mobility, especially for ions, from environment, that have big practical significance, for example SF$_6$ [8], Xe [9]. However, the experimental study of these systems is complicated by the difficulty in generating [10] and transporting ions of known identity while controlling for the effects of impurity ions [11]. This could lead to a huge discrepancy in experimental data [12].

Theoretical models usually rely on the so called solvent berg model. It states that molecules of the ion solvation shell attaches to the ion and moves together with it. Consequently, ion diffusion in a liquid could be treated as a movement of an ion cluster in a viscous media. Knowledge of the ion cluster radius $R$ is used to determine diffusion coefficient from Stokes–Einstein relation.
Cluster radius could be determined from Atkins snowball model [13] or based on HSK (Hilt–Schmidt–Khrapak) model [9].

HSK model states that ion diffusivity is independent of the ion radius. This result is confirmed with help of molecular dynamics for small ions in liquid argon [14]. However some deviations from it occur. Ion diffusivity could increase with ion radius [15, 16].

Classical molecular dynamics [17] could be used to describe processes in dense environments. This method is widely used in simulation of liquids [18], including electrolytes and ion solvation [19], formation of molecular and ion-molecular clusters [20] and nonideal plasma [21]. This approach allows taking into consideration collective processes.

Diffusivity of ions in water solutions was extensively studied via molecular dynamics [15,16,22,23]. Ion cluster properties were studied by the Monte Carlo method [24–26]. However, much less attention is paid to nonpolar liquids. On the other hand, study of simple nonpolar liquid could be used to determine mechanisms of ion diffusion in a liquid.

The paper is structured as follows. Firstly, model of liquid xenon and details of calculation is explained in the section Model and calculation technique. Then results of the calculation for diffusivity are given in the section ion diffusivity. Discussion of the diffusion in two observed regimes is separated into two subsections for the weak dependence and for the sharp maximum. Finally, comparison of calculated and experimental values of ions diffusivity is given in the section comparison with experiment.

2. Model and calculation technique

Interaction of xenon atoms is Lennard-Jones

\[ U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \]  

Parameters are taken from [27] \( \varepsilon = 0.02 \) 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 [28]

\[ U(r) = (E_0/2)[(R_i/r)^{12} - 3(R_i/r)^4] = \beta/r^{12} + \alpha/r^4, \]  

where \( R_i \) is an ion radius. 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 \( R_i = \sqrt[3]{3\beta/\alpha} \).

Classical molecular dynamics calculations was carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [29]. Integration was carried out via Verlet integration scheme. A time step is 3 fs. Periodical boundary conditions are used. System is brought to the chosen temperature using Langevin thermostat. The number of particles is 5324. The potential cut off radius is \( r_{cut} = 12 \) Å \( = 3\sigma \) for the potential (1) and \( r_{cut} = 24 \) Å for the potential (2). Calculation of a diffusion coefficient is carried out in the NVE ensemble after the temperature stabilization.

Trajectory with \( N = 2.8 \times 10^6 \) steps is calculated and broken into parts with \( n = 4000 \) 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 Einstein relation \( \langle r^2 \rangle = 6Dt \).
3. Ion diffusivity

Dependence of the ion diffusivity on its radius $R_i$ (2) is obtained figure 1. It is almost independent of it for $R_i < 1.7$ Å $< R_i < 1.9$ Å and $R_i > 2.1$ Å. For $R_i = 1.75$ Å and $R_i = 2$ Å there are sharp maximums in diffusivity. Theoretical analysis of these two regimes of diffusion (weak dependence and sharp maximum) is presented separately. The dependence of $\langle r^2 \rangle$ on $t$ is linear. No anomalous diffusion effects observed (figure 2).

3.1. Weak dependence region

Ion diffusion in a liquid usually could be treated as a movement of an ion cluster in a viscous media. Ion cluster radius is inserted into the Stokes–Einstein relation to determine diffusion coefficient

$$D = \frac{kT}{C \eta R_{\text{cluster}}} \quad (3)$$

Figure 1. Blue squares—dependence of the ion diffusivity on its radius; violet line—estimation of the HSK model (4)(3) (free parameter $C$ takes values from $4\pi$ to $6\pi$); black square—experimental value of $O^-$ ion diffusivity $[9]$. 

Figure 2. Dependence of mean square deviation on time for $R_i = 1.98$ Å: green line—linear approximation.
Figure 3. Ion cluster configuration (first and second layers) for \( R_i \leq 1.75 \text{ Å} \).

where \( \eta \) is viscosity of the liquid, \( C \) is a constant, that depends on the boundary condition on the boundary of the cluster \( (C \in [4\pi, 6\pi]) \).

Results for the region of weak dependence could be explained by the fact that solvation shell is big enough to neglect the changes of the ion inside it. As a result salvation, shell radius and other properties do not change significantly. This result is in a good agreement with molecular dynamics calculation of ions in liquid argon \([14]\). Moreover there is a model HSK \([9]\) that supports weak dependence.

HSK model is based on Atkins \([13]\) idea that interaction of liquid with ion causes crystallization of the liquid around the ion. Ion cluster radius could be determined assuming that cluster around the ion has a density of solid xenon and area around the cluster has a density of liquid xenon. Radius is determined taking into account chosen potential (2)

\[
R_{\text{cluster}} = \sqrt[n_l]{\frac{\alpha}{\Delta P}},
\]

where \( n_l \)—is number density of liquid, \( \alpha \)—parameter from (2), \( \Delta P \) is difference between crystallization pressure and current pressure. For ion radius \( R_i < 1.7 \text{ Å} \) \( R_i \in [1.8; 1.9] \text{ Å} \) and \( R_i > 2.1 \text{ Å} \) results of the calculation is in a good agreement with this model (figure 1). The agreement is especially good for \( C = 4\pi \).

3.2. Sharp maximum

Configuration of the ion cluster first layer is linear (figure 3) for \( R_i \leq 1.75 \text{ Å} \) triangle (figure 4) for \( R_i \in [1.75; 2] \text{ Å} \) and tetrahedral (figure 5) for \( R_i \geq 2 \text{ Å} \). They are stable in the region of weak dependence of diffusivity on \( R_i \). However, between the regions of stability there is a region where two of the configurations exists but they are unstable. Minimization of the potential energy for the system with \( R_i = 1.98 \text{ Å} \) from different starting configurations leads to formation of triangle and tetrahedral structures. They have almost the same energy. System could jump from one configuration to another figure 3 to figure 4 and figure 4 to figure 5. As a consequence, ion jumps inside the cluster. Diffusivity of the ion is increased by it.
This effect could be described by a random movement, that is a mixture of a continuous diffusion of the ion cluster and ion random jumps inside it. In this approximation displacement of the ion could be calculated as

\[ X = W(t) + \sum_{i=1}^{N(t)} h_i, \]  

where \( W(t) \) is a Wiener random process with \( W(t_2) - W(t_1) \in N(0, 2\Delta tD_0) \), \( N(t) \) is a Poisson process and \( h_i \) has a probability of 0.5 to be \( +h \) and 0.5 to be \( -h \). All the variables are independent. Probability density that corresponds to \( X(t_2) - X(t_1) \) is

\[ f(x) = \sum_{k=0}^{\infty} \frac{e^{-\lambda \Delta t} (\lambda \Delta t)^k}{k!} \left( N(hk, 2\Delta tD_0) + N(-hk, 2\Delta tD_0) \right) / 2, \]  

\[ N(a, \sigma^2) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-(x-a)^2/2\sigma^2}. \]

We could exclude high order terms, that correspond to 4 or more jumps, assuming that \( \Delta t \) is small.

Histograms of the ion displacement is calculated figure 6,7 to determine this model parameters and compare it with movement in regime of small diffusivity. Histogram of the ion with \( R = 1.98 \) Å (diffusivity maximum) could not be described by a normal distribution with zero mean and determined diffusivity. Diffusion in small diffusivity region (figure 7) is in a good agreement with simple normal distribution.

Nonlinear least-squares regression of histograms on figures 6,7 with function (6) gives values of parameters table 1. Diffusion coefficient of \( R_i = 1.98 \) Å ion, that corresponds to continuous
Table 1. Estimated parameters of model (5) and (6) as well as molecular dynamics results $D_E$ obtained from the Einstein relation are given for comparison.

| $R_i$ (Å) | $h$, Å | $1/\lambda$, ps | $D_0$, $10^{-10}$ m²/s | $D_m = D_0 + \lambda h^2$, $10^{-10}$ m²/s | $D_E$, $10^{-10}$ m²/s |
|-----------|--------|-----------------|---------------------------|---------------------------------|------------------|
| 1.98      | 0.14   | 0.3             | 4.6                       | 11                             | 10.2             |
| 2.1       | 0.008  | 59              | 4.86                      | 4.86                           | 4.5              |

Figure 6. Red points—density probability function for displacement along the x axis during 0.15 ps for $R_i = 1.98$ Å. Blue dashed line—normal distribution density with measured $D$. Green line—estimation of density in form (6) with parameters from table 1.

diffusion ($D_0$), is the same as diffusivity of ions in the weak dependence region. This means that ion cluster moves through the liquid in the same way but there is an additional movement of the ion inside the cluster. A distance between ions in different cluster configurations is about 0.5 Å. It is smaller than determined jump amplitude $h$. This is because $h$ corresponds to movement of the ion along the x axis that is a random projection of the distance between the configurations. Application of this model to pure continuous movement of $R_i = 2.1$ Å ion gives negligibly small values of jumps intensity and amplitude. This confirms applicability of this method.

4. Comparison with experiment

Experimental data of different ions mobility $B$ is available in the literature. Diffusivity could be determined from it $D = kBT$.

A positive charge carrier in xenon is not an ion but a hole [6,9]. If we assume that results [30] referred as a measurement of $Xe e^2_+$ ion mobility are actually measurement of impurities mobility, as suggested in [9], then good agreement between experimental value [30] of $5.8 \times 10^{-10}$ m²/s and calculated value of diffusivity in weak dependence region $\approx 5 \times 10^{-10}$ m²/s is found. Some data of positive Ti, Ba, Th ions mobility is available [11] but there is a problem with determination of ions charges.

We have also compared our results with experimental value of $O_2^-$ diffusivity [9]. Ion radius should be determined in order to compare calculated values with the experiment. Determination
of it is done with help of a simple model from the article [31]. The wave function of an excess electron is approximated by a function

\[ \psi(r) \sim \frac{r - R_{hc}}{r^2} \exp(-\gamma r), \]

where \( R_{hc} = 0.5 \) Å for \( \text{O}_2^- \) and \( \gamma \) is determined from ion solvation energy. Ion radius is determined as an expectation value of electron radius with this wave function. This method gives \( R_{\text{O}_2^-} = 1.75 \) Å. However this approximation is quite crude and could be used only for qualitative determination of the ion radius. This result is also supported by the fact that xenon could form chemical compounds with oxygen \( \text{XeO}_4, \text{XeO}_3 \). They all have \( \text{O–Xe} \) bound length near 1.8 Å [32]. On the other hand, it is non trivial to determine possible mistake in calculation of anion ion radius without complicated quantum calculation.

Using this radius \( \text{O}_2^- \) ion diffusivity is compared with its experimental value on figure 1. The sharp maximum could explain big mobility of oxygen ions in liquid xenon.

### 5. Conclusion

Dependence of ion diffusivity on its radius in liquid xenon is calculated for single charged ions. Results of the calculation are explained in terms of existing solvation models and suggested model of continuous movement with jumps.

Comparison of calculated ion diffusivity with HSK model predictions shows good agreement for ions with \( R_i < 1.7 \) Å \( R_i \in [1.8; 1.99] \) Å and \( R_i > 2.1 \) Å. There are almost no dependence of ion diffusivity on ion radius for them.

In the region of \( R_i \in [1.9 \) Å; 2.1 Å] and \( R_i \in [1.7 \) Å; 1.8 Å] there are sharp maximums in diffusivity. They reflect instability of the ion cluster in these regions. This leads to jumps from one cluster configuration to another and forces ion jumps. They increase ion diffusivity. Quantitative model of ion movement in this regime is presented and its parameters are determined. The continuous diffusion parameter \( D_0 \) is the same as for the weak dependence region.

Results are compared with experimental value of \( \text{O}_2^- \) ion diffusion coefficient. High diffusivity of this ion could probably be explained by the sharp maximum found in this work. Also, mobility
of the charged impurities is in agreement with obtained results for ion diffusivity in the region $R_i < 1.7 \, \text{Å}$ $R_i \in [1.8; 1.9] \, \text{Å}$ and $R_i > 2.1 \, \text{Å}$.

Acknowledgments
The calculations are performed on the MVS-100K cluster of the Joint Supercomputer Center RAS (the center of collective use). The work is supported by the Russian Science Foundation (grant No. 14-50-00124).

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