Molecular dynamics simulations of the Ba$^+$ ion mobility in liquid xenon

Georgiy K. Ozerov$^1$, Dmitry S. Bezrukov$^{1,2}$, Alexei A. Buchachenko$^1$

$^1$ CEST, Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Nobel str. 3, Moscow 143026, Russia
$^2$ Department of Chemistry, M.V. Lomonosov Moscow State University, Moscow 119991, Russia
E-mail: g.ozerov@skoltech.ru

Abstract. Improved molecular dynamics approach is proposed to simulate the mobility of atomic ion in the non-polar solvents such as liquefied rare gases. The many-body solvent polarization is described in the dipole approximation as the Car-Parrinello degrees of freedom of the Nosé-Poincaré-Anderson extended Hamiltonian function for NPT ensemble. Separation of the dipole induction from other ion-neutral interaction terms retained in the force field is accomplished by reparameterizing the accurate \textit{ab initio} potential energies for di- and tri-atomic fragments. Effect of the external electric field is treated perturbatively, by reconstructing the trajectories at a finite external field from those propagated in the field-free case. Mobility definitions that use ensemble averages of ion velocity and field-induced dragging force are analyzed together with their Green-Kubo counterparts. The simulations of the Ba$^+$ mobility in liquid Xe are in good agreement with the experimental data [Jeng S-C \textit{et al.} 2020 \textit{J. Phys. D} 42 035302].

1. Introduction
Tagging of the Ba$^+$ ion in liquid xenon is of prime importance for improving the sensitivity of the double beta decay $^{136}$Xe measurements [1, 2] and the neutrino oscillation experiments [3, 4, 5, 6, 7, 8]. Manipulating the single ion with external fields requires the knowledge of transport coefficients, first of all, ion mobility. Laboratory ion mobility measurements in liquids suffer from poor reproducibility and are affected by unavoidable collective effects of ion-cloud and charge-induced liquid dynamics upon injection of ion swarm [9, 10]. Most of the existing theoretical approaches to ion mobility deal with the polar liquids or electrolytes, where the strong electrostatic ion-solvent interactions mask weaker many-body induction forces (see Refs. [11, 12, 13, 14, 15, 19] and references therein). The latter, however, dominate in the case of monoatomic solvents like liquefied rare gases. An ion induces global polarization of the media, which responds to ion motion. Together with slow ion thermalization towards the steady-state field-induced drift, dynamic polarization interactions severely complicate accurate transport simulations, which seldom go beyond empirical models that combine macroscopic mechanical concepts with simplified transport equations [10, 16, 17, 18].

In this communication we put forward the molecular dynamics (MD) framework for simulations of the single ion mobility in monoatomic solvents with improved accuracy. MD is a widely accepted method to treat microscopic effects of complex fluid dynamics, appropriated
in a vast majority of applications [20]. However, as noted above, accurate modeling of ion-mobility in non-polar liquids is challenging. The main challenge is the microscopic description of the many-body polarization and its dynamic coupling to the motion of the ion. We address it here by introducing effective polarization degrees of freedom in a way similar to Car-Parrinello concept [21] combined with accurate ab initio-based segregation of induction terms in the force field. The use of Nosé-Poincaré-Anderson [22, 23, 24] (NPA) extended Hamiltonian ensures the proper MD averaging for a chosen thermodynamic ensemble (NPT in the present context). The second challenge is exceedingly slow convergence of MD simulations caused by large and slowly decaying fluctuations towards the steady-state drift of an ion dragged by external field. In this work, we adopt the perturbation treatment of the dynamics, normally valid at low and moderate external field strengths [25, 26]. Finally, as MD approach cannot define ion mobility as a true coefficient of a certain transport equation, the way of extracting it from ensemble averages is not unique. The definitions based on drift velocity and dragging forces, as well as on their complementary expressions in the frame of Green-Kubo perturbation theory [27], are compared.

The case of Ba$^+$ ion drifting in liquid Xe studied experimentally by Jeng et al. [10] is used as a first test of this methodology. Despite impressive agreement is achieved, uncertainties in the measured data call for more extensive assessment of the proposed MD approach.

2. Methodology

The system under consideration consists of the single Ba$^+$ ion in the liquid bath of Xe atoms. Following the reference experimental study [10], we implement the NPT thermodynamic ensemble at the standard $P = P_0$ pressure and temperature $T$ within the supercell method using the subsets of the orbits for lattice translation group action on the original cubic cell. The cell is exposed to the static homogeneous electric field $E_0$ and has the dimension $a = \lambda a_0$, where the factor $\lambda$ determines the volume scaling for the NPT ensemble. The dynamics of spatial variables complies with the periodic boundary conditions, which emulate a free stochastic migration of the charged particle.

Our general MD scheme is close to that described in Refs. [28, 24]. We start with the $N$-particle Hamiltonian function $H(\xi) = K(p) + U(q)$, where $K$ and $U$ are the kinetic and potential energy contributions, respectively. The $\xi = (q, p)$ is a representing phase-space point of the system, or the vector of particle coordinates in the space-fixed Cartesian frame $r$ with $q_k = r_k$ and momenta $p_k$ canonically conjugated to them. For the particles with masses $m_k$ the kinetic energy term has the standard form $K = \sum_k p_k^2 / 2m_k$ and $U$ is the many-body potential energy surface. Note that for the present problem it cannot be approximated by the sum of pairwise interactions as the dominating electrostatic induction interactions has inherently many-body nature and depend on the external electric field.

To handle the many-body polarization, we amend the phase space of the system by adding to $\xi$ the set of the Cartesian components of the polarization vector $P_k$ at each particle $k$ and their canonically-conjugated momenta $p_k^P$. The latter contribute to the kinetic energy function as $K^P = \sum_k (p_k^P)^2 / 2m_k^P$ with the fictitious mass constants $m_k^P$, which should be small and tuned on the case by case basis.

A variety of approaches has been suggested to incorporate the polarization in the force fields [29]. The present one is most close to the induced point dipoles or Drude-oscillator methods [30]. The potential energy surface is recast as $U = \tilde{U} + U^P$, where the last term accumulates the many-body electrostatics associated with ion- and field-induced polarization appearing in the second-order (dipole) approximation (see Ref. [31]). More precisely, it comes from the general expression of the electrostatic energy, which falls into Coulomb and polarization components. The latter one describes the interaction of the polarization with overall electric field including the Coulomb, polarization and external contributions. For the induced dipole moments are being considered as independent quantities, one extra term of the work to create a
polarization distribution should be accounted. The remaining potential term $\tilde{U}$ contains all the residual interactions of non-induction origin (for the present problem mostly electron exchange and dispersion interactions) and presumably small high-order induction contributions. Assuming that their many-body components are negligible, we approximate them by summing up the two-body atom-atom and ion-atom potentials. In brief, we use accurate ab initio potential energy surfaces for the di- and triatomic ionic moieties BaXe$^+$ and BaXe$_2^+$ to determine the pairwise interactions and the switching parameters $\gamma$ for asymptotically correct elimination of the dipole induction. The level of ab initio calculations matches that described in Ref. [32]. Further details will be presented elsewhere.

The NPA method provides the NPT sampling by letting the system evolve with the extended Hamiltonian, depending upon the set of dummy bath variables, volume and time scaling parameters included. Our working expression for the extended Hamiltonian function is

$$\mathcal{H} = s[H - H^0],$$

$$H = K/\lambda^2 s^2 + K^P/s^2 + \pi^2/2M_\lambda + \pi^2_0/2M_\lambda + U(\lambda q) + gT\ln s + \lambda^2 P_0 V_0,$$

where $H^0$ is arbitrary constant being chosen as a minimum of $H$ function, $s$ and $\lambda$ are the time- and volume-scaling variables with the conjugate momenta $\pi_s$ and $\pi_\lambda$, respectively, $\lambda q$ defines the scaling of the Cartesian coordinates $\lambda : \mathbf{r} \mapsto \lambda \mathbf{r}$ and $g = 6N + 1$ is the number of the degrees of freedom (components of position and polarization vectors per particle plus the $\lambda$ variable).

MD trajectory propagation with this extended Hamiltonian function is quite time-consuming. To reduce the computational cost, we first neglect the dependence on the time-scaling variable $s$ and minimize the $H$ energy in the extended phase space providing the $H^0$ value. Furthermore, we found it excessive to use additional Nosé chain-like thermostat [28] for instant polarization degrees of freedom. Instead, we keep their mean equilibrium values in a manner similar to the Car-Parrinello alternative to the self-consistent minimization of the $H(P)$ functional.

While these tricks make the MD trajectory propagation computationally efficient stepwise, slow convergence in time still presents a natural problem. Transport properties should be extracted from ensemble average at the steady-state regime depending on the external field strength. However, contribution of the external field to polarization potential is normally smaller that the ion-solvent contributions. As a result, very long propagation times are necessary to discern the former on the background of large and slowly decaying stochastic fluctuations of the latter. To avoid huge computational demands for long-time propagation and reduction of numerical noise, we follow here original perturbation-like approach starting from the Liouville equation formalism [16, 33]. It allows one to recover the observables for the distribution function numerically without the perturbation due to external field by means of the Liouville propagator while keeping the stochastic force component for the field-free system. To be described in the forthcoming publication, this perturbation approach was preliminary tested as trustworthy for the system investigated.

Macroscopically, the ion mobility $\mu$ is defined as the proportionality coefficient between the mean velocity of the steady-state ion drift induced by the external electric field and the strength of that field. Quite naturally, this tensor quantity emerges as the kinetic coefficient in various transport equations. Within the MD frame, same quantity can be defined through the ensemble averages or through the relevant correlation functions. By definition, the first approach gives

$$\mu_{\text{drift}} = \langle v \rangle_{\text{drift}} / E_0, \quad v^{\text{drift}} = \langle v \rangle - \langle v \rangle_0,$$

where the mean velocities $\langle v \rangle_0 = \langle v \rangle_{f_0}$ and $\langle v \rangle = \langle v \rangle_f$ are calculated with the zero-field trajectories $\xi_0(t)$ and perturbatively constructed trajectories $\xi(t)$, respectively.
The second approach exploits the equilibration of the dragging and the frictional forces in the steady-state regime. Linear velocity dependence of the latter, or Stokes’ law, implies $F_{\text{drag}} = \zeta v_{\text{drift}}$, if the contributions from other slow degrees of freedom to friction are omitted. Expression for the mobility is

$$
\mu_{\text{drag}} = \frac{v_{\text{drift}}}{F_{\text{drag}}}, \quad F_{\text{drag}} = \langle F \rangle - \langle F \rangle_0.
$$

The same mobility definitions can be given in terms of the Green-Kubo perturbation theory for zero-field dynamics. The corresponding relations are [27]

$$
\mu_{\text{GK}}^{\text{drift}} = \lim_{\epsilon \to 0} \frac{1}{3T} \int_0^\infty e^{-\epsilon t'} \langle v(0)v(t') \rangle_0 dt',
$$

and

$$
\mu_{\text{GK}}^{\text{drag}} = \frac{z}{\zeta_{\text{GK}}}, \quad \zeta_{\text{GK}} = \lim_{\epsilon \to 0} \frac{1}{3T} \int_0^\infty e^{-\epsilon t'} \langle F(0)F(t') \rangle_0 dt',
$$

where $F$ is the instantaneous force exerted on the ion with the charge $z$ and instantaneous velocity $v$. These Green-Kubo (GK) formula provide the zero-field mobility limit.

3. Computational details

Following the procedure described above, we computed the mobility of Ba\(^+\) ion in Xe at the temperatures 162, 170, 187, and 190 K and the static homogeneous electric field strengths from 0 to 35000 V/cm. Initial linear size of the cubic cell was set to $a_0 \approx 30-40$ Bohr, which corresponds to 64 – 128 Xe atoms at the triple point conditions. Minimization of the Hamiltonian function with respect to the $\lambda$ parameter makes the simulations almost insensitive to further increase of initial cell volume. According to the preliminary tests, the polarization masses $m_P^k$ were chosen as 0.01 of the real mass of the particle $k$.

Adaptive version of the forth-order Runge-Kutta method [28] was used for integration. The initial time step $h$ was set to 20 or 100 a.u. (ca. 4 or 20 fs), while the average running step varied from 100 to 300 a.u. depending on the conditions. Each trajectory were integrated for about $10^4 – 10^6$ adaptive Runge-Kutta iterations. While each of the calculations are limited to $10^7$ iterations, the major exit criteria were the standard deviation to mean ratios for the mobility value required to be less than $\sim 5\%$. Note that preoptimization of the unscaled system practically eliminates the need in the initial thermalization trajectory piece. Separation of the instant and mean forces in the perturbation approach was performed at the $100h$ timescale.

In average, one MD run consisted of 10 independent trajectories and 4-5 runs were made for each set of macroscopic conditions $T$, $E_0$. Mobilities defined above are computed simultaneously. The root-mean-square deviations between the runs are used to approximate statistical error of the simulations.

4. Results and discussion

The unique measurements of the alkaline-earth ion mobilities in Xe were reported by Jeng et al. [10] in the temperature and field ranges 162-182 K and 250-3500 V/cm. Data analysis assumed that all deviations of the ion velocity field dependence from linearity emerge due to the motion of a liquid induced by ion-cloud charge. Correction to this collective effect, as well as various sources of uncertainty, were taken into account to derive the global-fit mobility value, which, for Ba\(^+\) ion, amounts to $2.11^{+0.20}_{-0.12} \times 10^{-4}$ cm\(^2\)/Vs at 170 K.

The mobility dependence on the electric field strength is illustrated in the Figure 1a. Note that plotting global experimental result, we took the covered field range as a horizontal
Figure 1. (a) The field-dependence of the Ba\(^+\) mobility in Xe at 170 K. Experiment is represented by the global fit value [10]. MD mobilities are presented with their statistical uncertainties. Green-Kubo mobilities representing zero-field limit are shown as horizontal lines. (b) Temperatures dependence of the Ba\(^+\) mobility in Xe. See text for explanation of experimental data retrieved from Ref. [10].

error bar (vertical bar is shown as reported [10]). Mobility extracted from MD simulations shows remarkable field-dependence increasing by ca. 5\% in experimentally covered range. Mobility definition through the drift velocity, Eq.(3), provide much better agreement with the measurements than the definition based on the dragging force (4) (see e. g. [18, 34, 35] for a discussion of some additional contributions in the drag force expression). The latter fact can be attributed to initial assumption that the only dissipation mechanism is reduced to the friction for the stationary liquid flow. Underestimation of the friction constant \(\zeta\) leads overestimated mobility value. The GK theory also gives quite reasonable description in the zero-field mobility limit. Note that “drift” and “drag” GK definitions agree with each other better than their MD counterparts and show an opposite order owing to bypassing the direct restriction of the explicit form for the dissipation forces. Referring to MD \(\mu_{\text{drift}}\) as to our best result, we estimate the Ba\(^+\) mobility in Xe at 170 K as \((2.18 \pm 0.05) \times 10^{-4} \text{ cm}^2/\text{Vs}\), the value that exceeds the experimental result by 3\% only.

Figure 1b demonstrates the temperature dependence of the Ba\(^+\) mobility. It can be viewed as an illustration of the difficulties of accurate experimental liquid mobility determination. In addition to the global fit value derived from hundreds of runs, the raw data for runs at \(E_0 = 1466 \text{ V/cm}\) are shown scaled to the global fit (see Fig. 10 in Ref. [10]). Unscaled results of a single run (Fig. 9 in Ref. [10]) are also presented to better emphasize slow linear temperature dependence. Partial single-temperature fits exhibit much stronger variation, though the huge overlapping error bars effectively diminish it. Our MD results shown in Fig. 1b for two \(E_0\) values approximate the trends in experimental data very reasonable. GK theory predicts weaker temperature dependence that notably deviates from the MD simulations nearby the triple point.

The famous Atkins mobility model [36] assumes that an ion drifts as a ‘snowball’ or ‘bubble’ carrying its closest solvation shells and the simplest Stoke’s law can be resorted to relate the mobility and the radius for this new phase. Jeng et al. [10] estimated the latter as 8.6 Å. MD simulations offer another means of recovering this quantity, e.g., analysis of the average radial distribution functions. We found that, depending on \(E_0\) and \(T\), the Ba\(^+\)@Xe ‘snowball’ consists of 20-22 Xe atoms and has effective radius about 8.2-8.4 Å.

While the agreement between our MD simulations and measurements for Ba\(^+\) in Xe can be considered as impressive, uncertainties of the latter prevents one from making a quantitative assessment. With existing data, it is only possible by studying a series of related systems that differ by ion or solvent. We plan to consider them in future.

5. Conclusions
The MD approach for simulation of the ion mobility in non-polar liquids is proposed. Its essential feature is the treatment of the many-body polarization of the liquid as the system variables of
the Nosé-Poincaré-Anderson extended Hamiltonian function accompanied by careful segregation of the dipole induction interactions between the polarization potential and the pairwise force field. The use of Car-Parrinello dynamics for polarization degrees of freedom and perturbative treatment of the external field reduce the computational cost of the simulations. The results obtained for the Ba\(^{+}\) ion in liquid Xe slightly above the triple point temperature are in good agreement with the experimental data by Jeng \textit{et al}. [10]. Further validation of the approach will be presented in the forthcoming publications.

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