



Dynamics and drift motion of O_2^- in supercritical argon

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ABSTRACT

A method is presented for the study of the mean motion and the dynamics of ions under the action of an electrostatic field in supercritical fluids through a nonequilibrium molecular dynamics simulation technique. In the case of O_2^- in Ar, the ion–neutral interaction potential is determined through the reproduction of the experimental mobility data. This enabled the prediction of the radial distribution around the ion and the dynamics of the ion motion. In addition, the diffusion coefficient components, parallel and perpendicular to the electric field, have been calculated and found to be almost equal to one another and to depend weakly to the Ar density. The appearance of a shell around an ion is confirmed and found to be strengthened with density increase. The method has been applied at moderate Ar densities and low field strengths but can be extended to denser systems and stronger field strengths at the expense of high amounts of computer time.

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1. Introduction

The motion of ions in supercritical (SC) fluids moving under the action of an external electric field depends on the ion–neutral local interactions and the density fluctuations of the buffer media [1,2]. In the case of O_2^- in weakly polarizable noble gases, He and Ne, it has been suggested that the repulsive forces determine the radius of a bubble that is created around the ion [3]. The phenomenon is augmented at low temperatures due to delocalization of the oxygen electron around the ion. In the case of the polarizable Xe, however, a cluster of atoms has been found to accumulate around the ion instead [4]. The condition of the neutral medium affects also the ion motion, as seen from the appearance of a minimum in the mobility of O_2^- as a function of Ar density at temperatures close and above the critical gas temperature [5]. A similar behavior has not been observed with the Ne gas [6]. A proposed explanation has been based on the appearance of a bubble around the ion which acquires an acoustic dissipation mechanism that resonates with the density fluctuations of Ar [7].

The mobility dip of O_2^- in Ar has been reproduced through the use of an equilibrium molecular dynamics method [8]. Such methods produce the ion mobility indirectly, since first the diffusion coefficient, D , is produced and the mobility, μ , is calculated through the use of the Einstein relation, $ND/N\mu = kT$, where N and T are the number density and the temperature of the gas. This simplification is accurate at weak fields, as is the case at the traditional experimental conditions, however the use of this relation at SC conditions may be questioned due to density fluctuations that modify the ion transport [7]. At strong fields and low densities generalization of this relation has been presented [9].

In order to study directly the ion motion, we apply below a nonequilibrium molecular dynamics method [10] for the O_2^- –Ar system, and calculate the mean ion velocity, and from it directly the ion–mobility. The diffusion coefficient components, one parallel and one perpendicular to the field, are also obtained through the calculation of the velocity autocorrelation functions. The simulations extend from the low gas density region up to moderate densities, which have not been studied so far. We determine first an interaction potential model by requiring the ion mobility to be reproduced within the experimental accuracy and then use it to predict the mean properties and the dynamics of the ion. The fluid Ar properties are reproduced well with an accurate model potential.

2. Method

The system consists of ions moving independently from one another in a fluid that being in excess always remains at equilibrium. The ions are forced to accumulate excess energy as they move due to the action of an electrostatic field and collide with the neutral gas. This motion in moderately dense fluids can be reproduced through a simulation method that treats effectively the fluid buffer constrained at equilibrium [10, 11].

According to the employed technique, the temperature control is avoided through the use of two simulation procedures, one for the fluid and one for the ions, with all the particles placed in the same space. The motion of the fluid is reproduced independently from the ions through an equilibrium MD procedure. The ions are simulated through a second procedure that involves independent ions interacting with ionic neutral molecules that initially are created beyond an ion–neutral cutoff radius, R_c , as images of neutrals from the first simulation

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procedure. The ionic neutrals remain in the memory of the computer as long as ion-neutral encounters last.

Further, in the case of moderately dense fluids, a provision is required so that the initially created images of neutrals feel forces from the outer environment of the ion and do not collapse on the ion. This is avoided by allowing interactions of the neutral images with parental neutrals of the first procedure that lie between R_e and a second outer radius, R_s .

The ion flux, \mathbf{J} , is analyzed in two components one for the drift motion, $\mathbf{J}_{\text{drift}}$, and one for the diffusion [12], \mathbf{J}_{diff} , according to the relation

$$\mathbf{J} = \mathbf{J}_{\text{drift}} + \mathbf{J}_{\text{diff}} = n\mathbf{v}_d - \mathbf{D}\nabla n, \quad (1)$$

where n is the ion density. Bold letters indicate vectors and \mathbf{D} is a two dimensional diffusion matrix with only diagonal components, $D_{xx} = D_{yy} = D_{\perp}$ and $D_{zz} = D_{\parallel}$. The ion mobility is obtained through $K = v_d/E$, where v_d is the mean ion velocity, $v_d = \langle v_z \rangle$ with the field, E , in the z -direction. Further mean kinetic energies are presented as effective temperatures through

$$\frac{1}{2}kT_x = \frac{1}{2}m\langle(v_x - \langle v_x \rangle)^2\rangle, \quad (2)$$

$$\frac{1}{2}kT_y = \frac{1}{2}m\langle(v_y - \langle v_y \rangle)^2\rangle, \quad (3)$$

$$\frac{1}{2}kT_z = \frac{1}{2}m\langle(v_z - \langle v_z \rangle)^2\rangle, \quad (4)$$

where brackets indicate simulation averages and m is the mass of the ion. Due to the effect of the electric field on the ion motion $T_x = T_y = T_{\perp}$ and $T_z = T_{\parallel}$.

Diffusion coefficients are obtained through integration of the velocity correlation function which is defined relative to the ion mean motion [13],

$$D_{ii} = \int_0^{\infty} C_{ii}(t)dt, \quad (5)$$

where $C_{ii} = \langle(v_i(0) - \langle v_i(0) \rangle)(v_i(t) - \langle v_i(t) \rangle)\rangle$, and i representing $\{x, y, z\}$ directions. Since $C_{xx} = C_{yy}$ we set $D_{\perp} = (D_{xx} + D_{yy})/2$ and $D_{\parallel} = D_{zz}$.

3. Calculations

The ion mobility has been found to depend strongly on the gas density along a SC isotherm in the case of O_2^- in Ar. We therefore choose this system in order to study the transport and dynamics of ions up to moderate densities.

Table 1
Parameters of O_2^- -Ar interaction potential minima.

Source of interaction potential	ϵ (eV)	R_m (Å)
Dense fluids ^a	0.0311	4.07
MD simulation ^b	0.098	3.26
Ab initio ^c , X^2A''	0.212	3.147
Ab initio, A^2A'	0.173	3.128
Present 12-6-4, Ar- O_1	0.123	3.870
Present 12-6-4, Ar- O_2	0.070	3.870

^a LJ interaction potential parameters of O_2^- in dense Ar, Ref. [14].

^b Parameters of model potential used in MD simulations, Ref. [15]. The position is approximated by the expression of a LJ potential with $\sigma = 2.9$ Å.

^c Ab initio calculated potential parameters of global minima, Ref. [16].

3.1. Interaction potential

So far in the literature the proposed empirical ion-neutral potential models vary considerably in their characteristics, Table 1. An early attempt for the calculation of the mobility of (rigid) O_2^- in (dense) liquid Ar by Davis et al. [14] through the use of kinetic theory results was based on a model potential that involved a LJ model potential with hard-core plus a polarization term. The depth of the potential minimum was approximated by $\epsilon = 0.0311$ eV and the ion-neutral diameter by $\sigma = 3.63$ Å, which corresponds to the position of the minimum for LJ potential at $R_m = 4.07$ Å. A smaller hard-core diameter, $\sigma = 2.9$ Å, of a 12-6-4 model potential was used in MD calculations for the density profile around the ions at SC conditions [15]. This value corresponds to $R_m = 3.26$ Å and the depth was set at $\epsilon = 0.0980$ eV.

Here, we choose to base the construction of a model potential on the results of an ab initio RCCSD(T) calculation [16] in analogy to a previous study for O_2^+ in Kr [17]. The O–O distance is found to be close to the distance of the free O_2^- molecule, $R_{OO} = 1.35$ Å. For the O_2Ar^- system the two lower potential energy surfaces emerge as X^2A'' and A^2A' states. These two surfaces approach the same limit as Ar is moved to infinity, which is characterized by the $X^2\Pi_g$ state of O_2^- and 1S state of Ar, and therefore should be expected that both contribute equally to the ion-atom interaction. This can be utilized most easily through the use of a mean potential energy surface calculated from the X and A states of O_2Ar^- , as found in a previous MD calculation [18]. The ground state with the aug-cc-pV5z basis set, acquires a T-shaped global minimum of $\epsilon_X = 0.212$ eV at $R_{m,X} = 3.147$ Å measured from the center of O_2^- . Similarly, the A state acquires a symmetric minimum of $\epsilon_A = 0.173$ eV at $R_{m,A} = 3.128$ Å. From these surfaces the mean potential is expected to have a minimum of $\epsilon = 0.1925$ eV at $R_m = 3.138$ Å. In addition, the mean potential energy surface has a local minimum in the linear arrangement with about 20% smaller depth that appears at about 0.5 Å further out from the center of the ion. These main features of the mean potential can be reproduced through the use of two site-site 12-6-4 potential models additively,

$$V(R_i) = (\epsilon_i/2) \times \left[(1 + \gamma_i) \left(R_{m,i}/R_i \right)^{12} - 4\gamma_i \left(R_{m,i}/R_i \right)^6 - 3(1 - \gamma_i) \left(R_{m,i}/R_i \right)^4 \right], \quad (6)$$

where $R_{m,i}$ and ϵ_i are the positions and the depths of the site-site potentials. We use $\epsilon_1 = 0.123$ eV for the O_1 -Ar interaction and $\epsilon_2 = 0.070$ eV for the O_2 -Ar interaction when $R_1 < R_2$. When $R_1 > R_2$ the values of the parameters for the two sites are interchanged. The positions of the global minima are set equal to each other $R_{m,1} = R_{m,2}$. This consideration reproduces as closely as possible the features of both the linear and T-arrangements. However, in order to reproduce the mobility data at high densities we increase the value of R_m to 3.87 Å, Table 1. The gamma parameter, γ_i , is determined by requiring the potential to acquire the exact polarization form at large ion-atom separations, $e^2a_d/2r^4$, where $a_d = 11.08 \alpha_0^3$ is the dipole polarizability of Ar.

Though the ion-neutral interaction potential has been based on ab initio results for the O_2Ar^- system, the final R_m values have been increased so that the experimental ion mobility is reproduced within the combined experimental and calculation accuracy. This modification is in the direction of Davis et al. model potential [14] and the appearance of enhanced local density of He and Ne around O_2^- suggested in the past through a self-consistent method by Volykhin et al. [3]. However, the increase of the depth of the interaction potential produces a similar effect on the mobility, that is, it decreases its value and therefore one could look for such a modification in order to reproduce the experimental data. Since the sensitivity of the mobility on the depth is lower than that on the position of the minimum, we preferred not to apply it here, even though future studies may show that the actual potential is even deeper than the present ab initio one. In the case of Ar we have

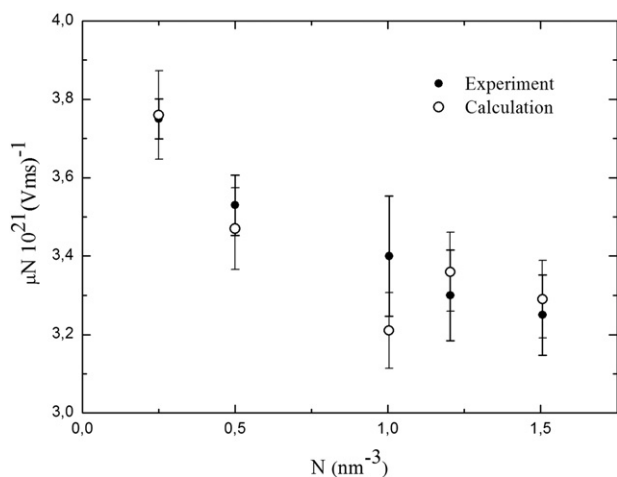


Fig. 1. Experimental and calculated density scaled mobility of O_2^- with respect to Ar density at $T = 152$ K.

employed an accurate Lennard-Jones (LJ) model potential that has been inferred from the second Virial coefficient data and has been found to reproduce quite well the pressure equation of state around the critical point, with depth of minimum $\epsilon = 0.01323$ eV and diameter $\sigma = 3.405$ Å [19].

3.2. Results

We have followed the trajectories of 500 independent ions in 864 Ar atoms, for about 10^7 time step of 10^{-16} s each. Statistical results have been obtained after the nonequilibrium MD simulation has relaxed numerically at steady operation. With this procedure the remaining mean properties, distributions and correlations are predicted along a SC isotherm of Ar at $T = 152$ K. This value of the temperature has been chosen because it is controlled with an uncertainty of 0.5 K and thus remains close to the experimental one of 151.5 K without endangering crossing the critical point of Ar, $T_c = 150.7$ K. Since the transport properties at weak electric fields do not depend on the field strength, E , and the gas number density, N , independently but only through the ratio E/N , we have set the value of this ratio equal to 10 Td, ($1 \text{ Td} = 10^{-21} \text{ Vm}^2$). This actually dictates that the field will increase linearly with the density though always remaining small.

The obtained ion mobility multiplied by the number density is presented with respect to the gas density in Fig. 1. In overall, we observe

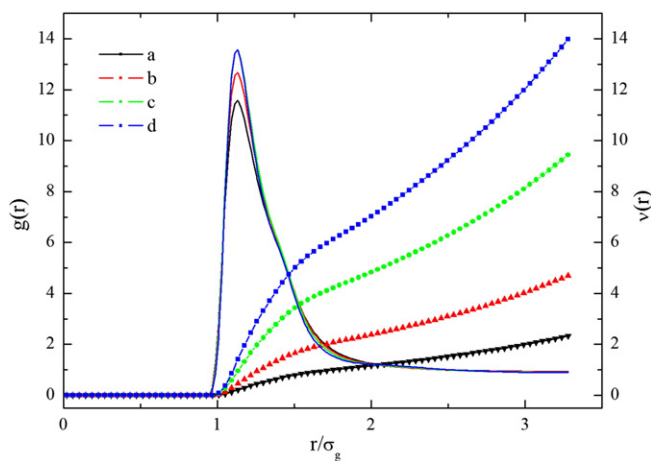


Fig. 2. O–Ar radial distribution functions at various Ar densities; a) 0.25 nm^{-3} , b) 0.50 nm^{-3} , c) 1.00 nm^{-3} and d) 1.51 nm^{-3} . Coordination numbers, $\nu(r)$, at the right side scale.

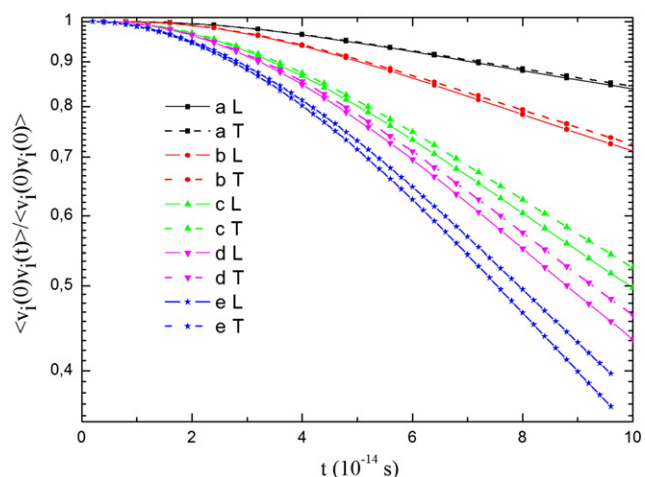


Fig. 3. Normalized velocity autocorrelation functions for parallel, (L), and perpendicular, (T), to the field velocity components, (with i being z or x and y), at various densities; a) 0.25 nm^{-3} , b) 0.50 nm^{-3} , c) 1.00 nm^{-3} , d) 1.20 nm^{-3} and e) 1.51 nm^{-3} .

that the employed interaction potential reproduces the experimental data within the combined uncertainty of the simulation and the measured mobility.

The decrease of the mobility with Ar density can be traced at the density distribution around the ion. As seen in Fig. 2, the calculated radial distribution function, $g(r)$, of O–Ar pair is peaked at the ion-neutral minimum of the linear configuration. The shoulder that appears next to the peak is due to the second minimum of the interaction potential of the T-shaped configuration. The integrated $g(r)$ around $r = 2\sigma_g$, $\nu(r)$, shows that up to six Ar atoms are located within the first, and only, coordination shell around the ion. The coordination number of Ar at the same conditions is quite smaller indicating the emergence of a shell around the ion with mean radius of about 4.0 Å which is close to the value obtained from the equilibrium MD procedure [8], though at higher density. However, we do not observe a second shell at the densities we have employed, it is possible that at higher density a second shell would appear.

As the Ar density increases the height of the peak increases, Fig. 2, without shifting at higher radii indicating increase of the local density around the ion. This effect may cause increase of the drag of the ion and thus decrease of the mean velocity and mobility. This is in accord with the observed dynamics, which become faster with the density, since the velocity autocorrelation functions get dampened faster at

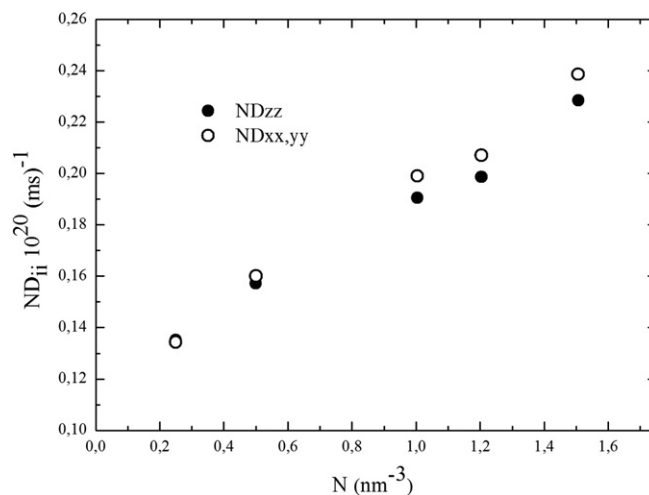


Fig. 4. Density normalized diffusion components, D_{\perp} and D_{\parallel} , of O_2^- at various Ar densities, $T = 152$ K.

higher Ar densities, Fig. 3. One would expect the increase of the number of neutrals around the ion to result in a higher collision frequency which, except for decreasing the ordered mean velocity, it also increases the randomization of the ion local motion.

The diffusion components parallel and perpendicular to the field are calculated through integration of the velocity correlation functions up to infinity. This is done through exponential fitting of these functions around their most accurate part close to the middle of their extent. The calculated components, Fig. 4, are found to depend weakly on the Ar density and increase linearly. This should be due to the fact that the value of the field does not remain constant as the density varies, (E/N is constant). The two components appear to be equal to one another within the calculation error, which is about 10%, as expected in the low field region. At higher fields, however, the diffusion components are expected to differ.

We mention that a small discrepancy is observed between the calculated quantities, K and D , in fulfilling the Einstein–Nernst–Townsend relation [9] beyond the estimated overall accuracy of the calculated transport properties. Though we do not expect a problematic application of the relation as in the case of O_2^- in Ne [20], since the gas densities used here are not approaching critical values, the effect could emerge from microscopic reasons and we intend to study it further in the future.

4. Conclusions

The reproduction of the mobility of O_2^- in SC Ar is used for the estimation of the ion–atom interaction potential. This is further used for the prediction of the mean motion and the dynamics of the ions in a weak electric field at moderate Ar density. The velocity correlations appear to relax faster at higher densities, though the integrated correlations produce diffusion coefficients that depend weakly on the Ar density. The observed local density around the ion indicates the

emergence of a single shell around the ion of radius as much as twice the ion–neutral radius. The extent of this loose cage is found to be insensitive to the density variation though the height of the peak is increasing indicating the increase of the local density around the ion as the Ar density increases.

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References

- [1] I. Skarmoutsos, D. Dellis, J. Samios, *J. Chem. Phys.* 126 (2007) 224503.
- [2] I. Skarmoutsos, D. Dellis, J. Samios, *J. Phys. Chem. B* 113 (2009) 2783.
- [3] K.F. Volykhin, A.G. Khrapak, V.F. Schmidt, *Sov. Phys. JETP* 81 (1995) 901.
- [4] O. Hilt, W.F. Schmidt, A.G. Khrapak, *IEEE Trans. Dielectr. Electr. Insul.* 1 (1994) 648.
- [5] A.F. Borghesani, D. Neri, A. Barbarotto, *Chem. Phys. Lett.* 267 (1997) 116.
- [6] A.F. Borghesani, D. Neri, M. Santini, *Phys. Rev. E* 48 (1993) 1379.
- [7] A.F. Borghesani, F. Tamburini, *Phys. Rev. Lett.* 83 (1999) 4546.
- [8] A.F. Borghesani, *Int. J. Mass Spectrom.* 277 (2008) 220.
- [9] A.D. Koutselos, E.A. Mason, *Chem. Phys.* 153 (1991) 351.
- [10] G. Balla, A.D. Koutselos, *J. Chem. Phys.* 119 (2003) 11374.
- [11] A.D. Koutselos, J. Samios, *Pure Appl. Chem.* 76 (2004) 223.
- [12] E.A. Mason, E.W. McDaniel, *Transport Properties of Ions in Gases*, Wiley, New York, 1988.
- [13] A.D. Koutselos, *J. Chem. Phys.* 104 (1996) 8442.
- [14] H.T. Davis, S.A. Rice, L. Meyer, *J. Chem. Phys.* 37 (1962) 2470.
- [15] A. Barbarotto, Thesis (University of Padua, 1996), unpublished.
- [16] A. Papakondylis, (private communication, 2010), unpublished results.
- [17] A. Papakondylis, *Chem. Phys. Lett.* 484 (2009) 165.
- [18] A.D. Koutselos, *J. Chem. Phys.* 134 (2011) 194301.
- [19] H.L. Johnston, E.R. Grilly, *J. Chem. Phys.* 46 (1942) 948.
- [20] A.F. Borghesani, D. Neri, A. Barbarotto, *Chem. Phys. Lett.* 267 (1997) 116.