Transport properties of diatomic ions in moderately dense gases in an electrostatic field*

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Abstract: The motion of diatomic ions in moderately dense fluids under the action of an electrostatic field is studied through a nonequilibrium molecular dynamics simulation method. The method simulates the motion of the ions and the fluid molecules that constitute their immediate environment. Thus, effectively, the dissipation of the excess energy of the ions is reproduced leading to steady drift motion. Results revealed the effect of the fluid density on mobility, ion-effective temperatures and diffusion coefficients parallel and perpendicular to the field at various field strengths for a model diatomic ion in Ar. Extension of the method to dense fluids and to polyatomic ions and neutral molecules is discussed.

INTRODUCTION

Ion transport properties under the action of an electrostatic field in fluids of various densities have been studied extensively in the past. In low-density gases, the simplification of ion-neutral molecule interactions allows the reproduction of experimental ion transport properties, such as mobility and diffusion coefficients parallel and perpendicular to the field, through kinetic theory treatment of the ion motion [1], as well as via Monte Carlo [2,3] and molecular dynamics (MD) [4,5] simulation methods. In this case, except from the macroscopic quantities determining the gas state and the external field, only the two-body, ion-neutral interaction potential is required as input, since the ion motion is governed by binary ion-neutral interactions. Such conditions are utilized in drift-tube swarm experiments [1] from where the ion transport properties can be measured and occasionally velocity distribution moments [6] and orientation alignment [7] can be probed.

At atmospheric conditions, the development of ion-mobility spectrometry [8,9] enabled the determination of effective interaction potentials and cross-sections between molecular ions and gas molecules [10,11], as well as the study of molecular structure of clusters and biomolecules [12].

However, the motion of the ions in dense gases and liquids is affected by many-body interactions and is interpreted through model ion-neutral interactions and mesoscopic properties such as the mean ionic radii or frictional forces [13–18]. Here, the study of the ion or electron motion provides information about the structure of the fluid developed around the charged species [19].

So far, the experimental study of the transition from intermediate-density gas to high-density liquid [20] has revealed the region where the kinetic theory few-body treatment of the ion motion has to be replaced by the hydrodynamic description. Such studies have been conducted along the coexistence curve or close to the critical point at vanishing field strengths. Correspondingly, the interactions become more complex as the fluid density changes from low to high values and the theoretical treatment of the

ion motion is based progressively on cruder assumptions about the nature of ion-neutral interactions [13,14].

Though ion mobility studies are pursued successfully for low-density gas and liquid systems not so much has been done in the case of intermediate- to high-density gases. In this case, the ion motion remains relatively sensitive to the structure and the interactions of the molecular ions, and therefore the study of the ion transport properties could provide valuable information about the few-body interactions involved. This analysis is greatly assisted through MD simulation of the ion motion, which requires as input only the ion and neutral interaction potentials. The only difficulty lies in the nonequilibrium character of the state of the system since the fluid continuously dissipates the electric potential energy of the ions at constant rate. Such steady states can be simulated through the introduction of an effective cooling procedure for the fluid, which acts as a thermal bath. Although effective isothermal methods have been presented in the literature for liquid systems, the sensitivity of the transport properties on the details of the ion-neutral interactions at gas density requires procedures which do not alter the trajectories of colliding particles as the value of temperature is maintained constant. Accordingly, we employ an appropriate method developed in the past [5] for low-density gases which is extended to high density through the introduction of multiple ion-gas collisions in the simulation procedure.

The method can calculate dynamical and transport properties for the ions and in addition, structure and thermodynamic properties for the gas molecules. Special attention is paid to the calculation of mobility and ion-diffusion coefficients as a function of the gas density at various field strengths.

We mention that the procedure is extendable to systems of ions moving in liquid buffers, which traditionally are studied at very weak fields [16,17,21,22]. The introduction of nonvanishing fields can reveal the field dependence of the dynamic and transport properties of the ions in liquids. In addition, the dependence of these properties on the state of the buffer fluid can produce information about the properties of the fluid itself.

MOLECULAR DYNAMICS METHOD

The reproduction of molecular motion through MD simulation methods has become counterpart in gaining scientific knowledge to the theoretical treatment and experimental analysis of molecular systems [23,24]. At the expense of computer time, simulation methods can most easily produce information for the mesoscopic level cross-sections as well as for the macroscopic-level thermodynamic and transport properties, provided molecular interactions are known. Conversely, by trial and error adjustment, the interactions can be probed by testing the reproduction of corresponding experimental data.

Various integration methods, such as the Verlet, leap-frog, predictor-corrector, etc. algorithms, can be employed for the advancement of the state of a system in time and the calculation of phase space trajectories according to Newton's law [23]. Such information, in turn, can be used for the calculation of classic observable quantities. Other quantum, semiclassical, or mixed quantum-classical methods, which have been developed in the past for the calculation of properties such as relaxation and reaction rates will not concern us here [25].

Molecular systems involve various degrees of freedom and their contribution to the transport depends on their excitation. At low and intermediate field strength experiments (E/N below 100 Td, with 1 Td = 10^{-21} Vm^2) and normal temperatures, the relative collision energy between ion and neutrals is sufficiently low as to allow the neglect of vibration excitation in molecular simulations. The description of the remaining translational and rotational degrees of freedom can then be implemented through consideration of rigid atomic frames for the molecular species. Then, the relevant motion of rigid bodies is simulated through the use of angular coordinates in a body fixed frame and the integration of Euler's equations of motion for them. Even better, the use of quaternion parameters as independent variables allows the derivation of singularity-free evolution equations, which can be integrated uninterruptedly [24].

In the case of open systems, various control procedures have been employed to maintain systems at steady states with constant intensive parameters, whenever such states are attained. Thus, temperature, pressure, and chemical potential constraints are utilized by effective control mechanisms that play the stabilizing role of thermal, mechanical, and chemical baths [23].

At moderately dense gases, the MD simulation of ion motion requires calculation of ion-neutral scattering as accurately as possible, and therefore one relays on methods appropriate to low-density gas simulations. Such an appropriate method has been developed before for the simulation of independent ions moving in low-density gases [4]. It consists of two simulation procedures, a first one for the gas and a second one for the ions together with the gas molecules that represent the immediate environment of the gas medium and generated through use of the first procedure. This is done at the edge of the interaction region of each ion, which is determined through a cutoff radius, and by allowing the ion of the second simulation procedure to interact with images of the gas molecules of the first procedure. The gas molecules of the first procedure, however, evolve independent of the ions, and their state remains unaltered in time. Conversely, the images of the gas molecules generated in the second procedure follow an exact scattering trajectory as they collide with an ion and disappear whenever they move out of the interaction region. These species take away the excess energy of the ions in a way that mimics closely the actual energy dissipation that takes place in a buffer fluid. Extension to dense systems is utilized through the introduction of multiple gas–gas interaction in the second simulation procedure and by taking care that newly generated gas atoms feel forces from the first simulations as they remain at the edge of the (ion-neutral) interaction region.

The method allows calculation of nonequilibrium structure around an ion (which acquires cylindrical symmetry at high-field strengths), correlation functions (which provide information about the persistence of the ion motion), orientation alignment, etc. Such properties provide transport properties through averaging over time coordinates. Extension to higher densities seems straightforward though at the expense of high amount of computer time.

ION TRANSPORT PROPERTIES IN MODERATELY DENSE GASES

The transport of diatomic ions in fluids under the action of an electrostatic field has been studied experimentally in low-density gases [1], at atmospheric conditions [8,9], along the coexistence gas–liquid curve, or at supercritical states of the fluid [20]. Such data are most easily reproduced by MD simulation methods with consideration of the ion and neutral interactions only. In addition, the results of the method can be useful for the design of future experiments and the development of theoretical treatments of ion motion in moderately dense gases.

The ion motion in moderately dense gases can be examined analogously to the study of transport in low-density gases, with the difference that, here, the observation of nonequilibrium effects requires very strong fields that are at the edge of experimental reach. Thus, the ion transport properties in homogeneous electrostatic fields are defined through analysis of ion flux, $\boldsymbol{J}$, in various contributions as follows,

$$\boldsymbol{J} = n\,\boldsymbol{v_d} - \boldsymbol{d}\boldsymbol{\nabla}n - n\boldsymbol{D_T}\boldsymbol{\nabla}\ln T + \ldots, \tag{1}$$

where T is the gas temperature, n is the ion number density, and $\boldsymbol{v_d}$, $\boldsymbol{d}$, $\boldsymbol{D_T}$, etc. are drift velocity, diffusion coefficient, thermal diffusion coefficient, etc. of the ion, respectively. Other transport properties can be considered through introduction of higher-order density and/or temperature gradient terms. Here, $\boldsymbol{d}$ is a diagonal two-dimensional matrix with two independent components, $d_{XX} = d_{YY} = d_T$ and $d_{ZZ} = d_L$ with the field in z-direction. A similar structure is acquired for $\boldsymbol{D_T}$. At weak fields all transport properties become scalar quantities. In the following, we will be concerned only with the first two transport properties, which dominate the ion motion in the low-density and temperature gradient limit.

The mobility, $\mu = |v_d|/E$, expressed as standard mobility, $\mu_o = \mu N/N_o$, where N is the gas number density and $N_o = 2.686763 \times 10^{19}$ cm^{-3} is the ideal gas density at standard conditions, as well as, the density scaled components of the diffusion coefficient, $Nd_{T,L}$, should be functions of N and the field strength, E. However, since these properties at low densities depend only on the combined variable E/N, one can keep as independent variables N and E/N at high densities and consider the expansions [26] (around $N = 0$),

$$\mu_o(E, N) = K_o(E/N) + K_2(E/N)\, N^2 + K_3(E/N)\, N^3 \ldots, \tag{2}$$

$$Nd_{L,T}(E, N) = ND_{L,T}(E/N) + D_2^{L,T}(E/N)\, N^3 + D_3^{L,T}(E/N)\, N^4 \ldots, \tag{3}$$

where the first terms are the low-density limits of the transport coefficients. The standard mobility, K_o, is again defined from low-density mobility, K, through $K_o = KN/N_o$. These parameters, in turn, are expanded as follows [1]

$$K_o(E/N) = K_o(0)[1 + \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \ldots], \tag{4}$$

$$ND_{L,T}(E/N) = ND(0)[1 + d_2^{L,T}(E/N)^2 + d_4^{L,T}(E/N)^4 + \ldots], \tag{5}$$

with $K_o(0)$ and $ND(0)$ zero-field values of standard mobility and diffusion coefficients. These expansions contain even powers of E/N due to the irrelevance of the direction of the electric field on the ion transport. The α_n and d_n coefficients are independent of E or N and depend only on the gas temperature. Finally, in eqs. 2 and 3, the linear and second-order terms, respectively, are missing since the transport properties acquire extrema at the low-density limit and the remaining K_n and D_n parameters depend on T and are even functions of E/N.

The density dependence of these transport parameters is examined below through the study of a representative system of model X_2^+ diatomic ions in Ar gas with the mass of atom X set equal to that of Ar and fixed internuclear separation R = 1.10 Å. The ions are set to interact with the gas through a 12-6-4 site–site model potential of the form

$$V(r) = \varepsilon_o/2\ [(1 + \gamma)(r_m/r)^{12} - 4\gamma(r_m/r)^6 - 3(1 - \gamma)(r_m/r)^4], \tag{6}$$

where $r_m = 6.0\alpha_o$ and $\varepsilon_o = 2.0 \times 10^{-3}$ Hartree are the position and the depth, respectively, of a typical nonbonded interaction potential with polarization. The gamma parameter ($\gamma = .2876$), is determined by requiring the potential to acquire the exact polarization form at r_m, $e^2 a_d/2r_m^4 = (3\varepsilon_o/2)(1 - \gamma)$, where a_d is the dipole polarizability of Ar. For the interaction of the gas we use a LJ potential [27] with $\varepsilon = 119.8$ K and $\sigma = 3.41$ Å, which reproduces the gas state accurately even at high densities.

Typical simulation runs are conducted with 130 independent diatomic ions in 108 gas atoms for 10^6 time steps with 10^{-15} s time interval. The gas number density ranges from .03 nm^{-3} to 3.0 nm^{-3} at 300 K, though higher densities are easily handled, and the value of the density-normalized field strength (E/N) varies from 50 to 400 Td. Depending on the gas density, the values of E vary from .006 to .6 V/nm.

Results are obtained through integration of translation coordinates and quaternion parameters via fifth- and fourth-order Gear's predictor-corrector integration procedure [23], respectively. The mobility is calculated from the mean ion velocity, $<v_z>$, in the direction of the field, (z), through $\mu = <v_z>/E$. The attained convergence for μ is better than 1 %. The results are presented in Fig. 1 as standard mobility μ_o with respect to E/N at two characteristic densities.

The mobility appears to be characterized by a low-field polarization limit, though not observed here, an intermediate-field region around the peak and a high-field region as in the case of low-density gases. However, as exemplified in Fig. 2, where μ_o is presented as a function of the density at certain E/N values, the mobility decreases with the density as the increase of ion-neutral encounters effectively diminish the persistence of the ion motion. This observation is in conformity to experimental results of the density dependence of the low-field mobility of O_2^- in near-critical Ar gas [21]. This trend, however, may not expected to be retained at higher densities.
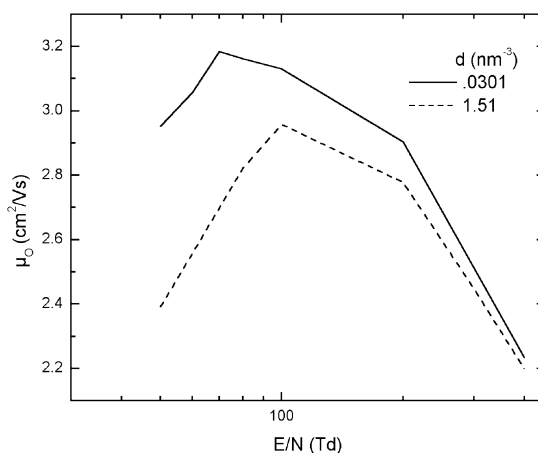
Fig. 1 Standard mobility for model system of X_2^+ in Ar as function of E/N at various gas densities.
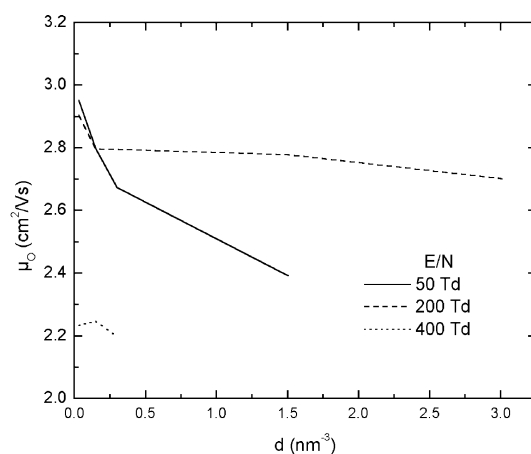

Fig. 2 Standard mobility for X_2^+ in Ar as function of the gas density at various values of E/N.

The second-order moment of the combined linear-angular velocity distribution, which are obtained through the present MD method, are plotted as effective temperatures, $kT_L = m<(v_Z - <v_Z>)^2>$, $kT_T = m<(v_X - <v_X>)^2> = m<(v_Y - <v_Y>)^2>$, and $kT_R = m<(w_X - <w_X>)^2> = m<(w_Y - <w_Y>)^2>$, at various gas densities in Fig. 3. Here w_i are angular velocity components defined in directions (x and y) perpendicular to the axis of the diatomic molecular ion. The convergence for $T_{L,T}$ and T_R are within 1 % and a few percent, respectively.

As expected from low-density results the translational temperatures parallel and perpendicular to the field differentiate from one other even at intermediate-field strengths. In addition, at moderate densities, the effective temperature parallel to the field and the rotational temperature decrease with increasing buffer gas density. This behavior correlates to the drop of μ_o with density. It thus seems that the lowering of μ_o or equivalently of v_d at certain value of E/N diminishes the feeding of translation energy parallel to the field as well as the rotational energy with amounts of thermal energy generated by the ion-neutral collisions. However, the corresponding T_T appears to be rather insensitive to the gas density increase.

Likewise, similar observations can be done for the density dependence of the density-scaled diffusion coefficients presented in Fig. 4. The attained accuracy for Nd_L and Nd_T is within a few percent
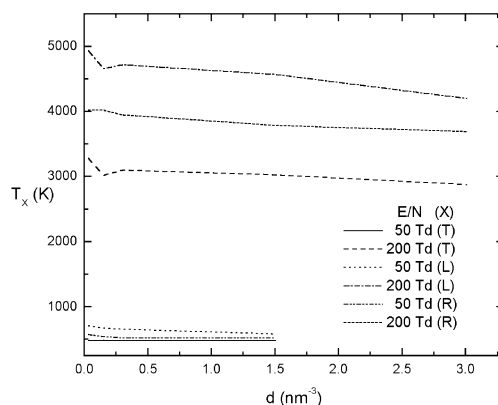
Fig. 3 Effective translation temperatures longitudinal (L) and transverse (T) to the field; as well as rotation temperatures (R), as functions of the gas density at various field strengths for the system in Fig. 1.
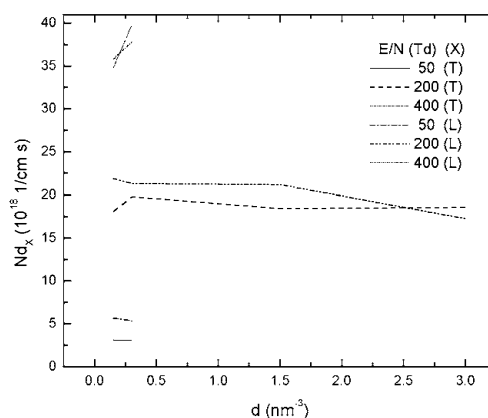

Fig. 4 Components of diffusion coefficients longitudinal (L) and transverse (T) to the field as functions of the gas density at various field strengths for the system in Fig. 1.

and 5 %, respectively. The coefficients perpendicular to the field seem to be less sensitive to gas density especially at low-field strengths.

CONCLUSIONS

The simulation of ion-motion in intermediate- and high-density fluids under the action of electrostatic fields allows the reproduction of mobility and ion diffusion coefficients from ion-neutral and neutral–neutral interaction potentials. In addition, moments of the combined linear and angular velocity distribution function as well as corresponding correlation functions of the linear and angular velocities can be determined probing the form of the distribution function and the dynamics of its fluctuations.

For diatomic ions in Ar with a model interaction potential we find the mobility to decrease with density at certain field strength. A similar behavior is observed for the second moments of the velocity distribution, or effective temperatures, and the components of the diffusion coefficient, though they vary at a smaller pace with the density. This behavior, however, may not continue at even higher densities.

Extension to polyatomic ions can provide information about microscopic information such as structural information and cross-sections already probed experimentally by ion mobility spectrometry [8–12]. Further, the study of ion transport in liquids at nonvanishing fields can provide information

about ion-neutral structure and dynamics as well as probe properties of the liquid around the coexistence curve and supercritical states [20–21].

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