

Molecular dynamics simulation of ion transport in moderately dense gases in an electrostatic field

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The motion of ions in moderately dense gases under the action of an electrostatic field is simulated through a nonequilibrium molecular dynamics method. The method is developed through consideration of multiple ion-neutral collisions in a previously established procedure for low-density gases. The first two moments of the ion velocity distribution function for the representative system of K^+ in Ar are calculated at various gas densities and field strengths and through them the mobility and two effective temperatures, parallel and perpendicular to the field. Additional tests for the accuracy of analytic expressions for the effective temperatures in terms of drift velocity and differential mobility derived from a three-temperature treatment of the Boltzmann kinetic equation were successful supporting the extension of use of generalized Einstein relations in this area. The procedure is easily extendable to the case of molecular ions with internal degrees of freedom. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622377]

I. INTRODUCTION

We extend the use of a molecular dynamics (MD) method¹ for the simulation of the motion of nonreacting ions in an electrostatic field to systems involving moderately dense gases. Originally, the method was designed for the study of the ion motion in low-density gases, as taking place in conventional drift-tube experiments² where the transport of the ions is controlled solely by binary ion-neutral collisions. By allowing monitoring of triple and higher order multiple interactions in the MD method we are able to simulate the motion of ions in moderately dense gases where the kinetic theory treatment of ion-transport is expected to extend in the future. In addition, the method will reproduce the motion of ions at atmospheric conditions, where plasma chromatography or ion mobility spectrometry^{2,3} operates and other mobility experiments are conducted.⁴

So far, experimental interest has mainly been concentrated either to low-density systems at arbitrary field strength or to liquid and gas systems at various densities and weak fields, for different purposes. In the former, the predominance of binary collisions simplifies the ion-neutral collisions and makes possible the interpretation of the experimental data through a kinetic theory description based on a two-body ion-atom interaction potential.² The field strength behaves as an operational parameter similar to temperature enabling the determination of ion-neutral potentials of atomic species over a wide range of internuclear separations through inversion of atomic ion-transport data.⁵ Other microscopic properties such as ratios of thermally averaged cross sections for elastic and inelastic scattering of molecular ions,⁶ cross sections for atomic species and reaction cross sections have also been probed.⁷ In this limit, details of the ion dynamics are reproduced through simulation methods based on Monte Carlo⁸ and nonequilibrium molecular dynamics methods.¹

In the case of dense gaseous systems where many-body collisions take place experiments are conducted at low fields for the determination of mobility and its dependence on macroscopic state properties of the buffer fluid.^{4,9,10} The kinetic theory treatment of the ion motion connects the transport properties to microscopic properties such as the ion-atom interaction potentials¹¹ or to mesoscopic properties such as the frictional forces and the ionic radii.^{12,13} In addition, the simulation of the ion motion through MD methods has been used for the reproduction of the transport data as well as for the study of their dependence on structure and dynamics.^{13,14}

The transition from low-density gas to high-density gas or liquid has also been studied experimentally¹⁵ and the region where the kinetic theory treatment of the ion motion has to be replaced by the hydrodynamic description has been determined.

The present MD method is expected to extend the above studies at nonvanishing fields where the repulsive part of the potential contributes in the interactions and the ion motion acquires a cylindrical symmetry with the transport differentiated in directions along and transverse to the field. In general, the study of the density dependence of mobility and ion-diffusion coefficients parallel and perpendicular to the field will provide information about multiple ion-neutral interactions. It will thus become possible to probe the mean microscopic density around the ion and dynamic properties, such as velocity-, force-, and other correlation functions, among others. Further, since kinetic theory can be extended in this area, as in the case of moderately dense gases,¹⁶ the results of the current method are expected to assist in the development of an analytic theory treatment of the ion motion at nonvanishing fields.

To make apparent the resulting density dependence of the ion transport properties we consider below density expansions valid at moderate gas density for both mobility and

diffusion coefficient for completeness though only the former will interest us here. Thus, at low buffer gas density where binary collisions prevail, the mobility, K , and the components of the ion-diffusion coefficient in longitudinal and transverse directions to the field, $D_{L,T}$, when multiplied by the gas number density, N , depend on the field strength, E , and the gas density only through the ratio E/N . In addition, the irrelevance of the direction of the field in the transport properties indicates that the ion transport coefficients can be expanded in even powers of E/N ,²

$$K_0(E/N) = K(0)[1 + \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \dots], \quad (1)$$

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

where K_0 is standard mobility, $K_0 = NK/N_0$, with $N_0 = 2.686763 \times 10^{19} \text{ cm}^{-3}$, the ideal gas density at standard state of $T = 273 \text{ K}$ and $P = 1 \text{ atm}$. Also, $K_0(0)$ and $D(0)$ are transport properties at zero field strength. The coefficients α and d are independent of E and N though they still depend on gas temperature, T . These expressions, however, converge well only up to fields of moderate strength.

At moderate- and high-density buffer fluids these expansions have to be extended so that the field and density dependencies appear separately. Here, we prefer to keep as independent variables E/N and N in order for the expansions to approach the ones of low density. Thus, we denote the mobility and diffusion coefficient at high density by μ and d , respectively, and consider

$$\mu_0(E, N) = K_0(E/N) + K_2(E/N)N^2 + K_3(E/N)N^3 \dots, \quad (3)$$

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

with $\mu_0 = \mu N/N_0$. The first terms in the expansions are the low-density limits of the transport coefficients presented above, Eqs. (1) and (2). Further, since in this limit μ_0 and $Nd_{L,T}$ are independent of N , the limiting values of the transport coefficients will constitute a local extremum with respect to the density dependence and therefore the corresponding linear terms have been excluded. The remaining expansion coefficients should depend on T and even powers of E/N . The series however is expected to converge well at low gas density.

In the following, we first present the MD method developed for the simulation of the motion of ions in dense gases. In Sec. III, the method is applied in the case of a representative ion-atom system, $\text{K}^+ - \text{Ar}$. It thus becomes possible to study the effect of density on the mobility and the mean kinetic energies parallel and perpendicular to the field. Since there are no other independent results for comparison in this area, the accuracy is established through statistical analysis. Further, using the simulation data we test the performance of analytic expressions for the effective temperatures obtained from kinetic theory treatment of the ion transport at low gas density. Finally, in the conclusion we summarize our results and present areas of potential application of the current MD method.

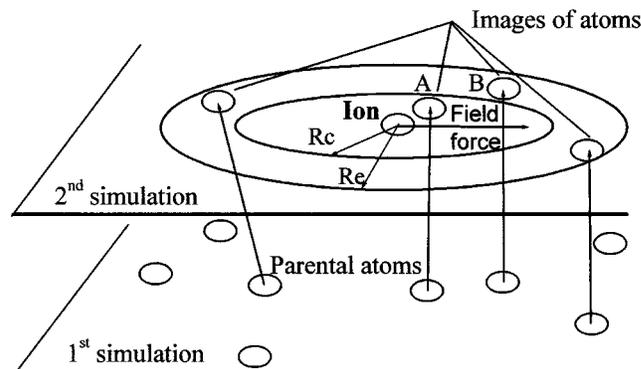


FIG. 1. Two-dimensional analog of the nonequilibrium MD procedure for the simulation of the ion motion in gases under the action of an electrostatic field. R_c is a cutoff interaction radius and R_e is a radius for the generation of images of atoms in dense gas systems specifically for each ion (in low densities $R_c = R_e$).

II. NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATION METHOD

The system consists of independent ions moving in a moderately dense gas under the action of an electrostatic field. The ions acquire a steady motion due to frequent multiple collisions with gas atoms which are assumed to be in excess so that the dissipated energy they acquire from the ions is extracted from the system efficiently without their macroscopic state being disturbed from equilibrium.

The reproduction of the ion motion through an MD simulation method is based on the successive integration of Newton's law for all particle positions over a small time interval.¹⁷ However, since it is impractical to simulate with a computer the irreversible action of the buffer gas by considering many molecules (degrees of freedom), effective methods are invoked for that purpose.

Here, we employ a method that has been developed for low-density systems in the past¹ and allows the simulation of the scattering of the ions by the neutrals without interruptions from the temperature preserving procedure. This is necessary at low densities since transport properties depend on the details of the ion-atom interaction.

According to the low-density approach, as depicted in Fig. 1, the neutrals interact only with one another and are considered without the effect of forces exerted from the ions (first equilibrium MD simulation), though each of the ions interacts only with images of the neutrals (second simulation), and in addition feels the force exerted from the electrostatic field. The images are created, specifically for each ion, in the memory of the computer at the beginning of an ion-neutral encounter and last as long as this interaction takes place. We mention that the space coordinates and the volume match in the two procedures and that each ion can interact with any of the atoms of the first procedure. The range of the interaction region is defined through a cutoff radius, $R_c = 3.2\sigma$, where σ is a distance scaling factor for the

gas interaction potential. This radius covers a few times the internuclear distance at the minimum of the ion–atom interaction potential. With these requirements the approach is exact whenever binary uncorrelated ion–neutral collisions take place.

To extend the method to higher densities we have to consider the possibility of triple and higher multiplicity interactions taking place. At the gas density and field strength ranges considered here, N up to 1.0 nm^{-3} and E/N up to 300 Td ($1 \text{ Td} = 10^{-21} \text{ Vm}^2$), the collisions remain mostly binary except at the highest limit of the density where the ions encounter correlated pairs of atoms. Such species are treated as dimers in the kinetic theory treatment of moderately dense gases^{18,19} and their population has been studied in the past. Using the reduced equilibrium constants for the dimer formation for Ar and the interaction parameters of Kim and Ross,¹⁹ for example, we find the dimers to be less than about a few percent of the gas atoms at 300 K and 10 atm and to reach 10% at the highest densities considered here.

Expecting, thus, ions to encounter mostly such pairs of atoms and higher multiplicity interacting atoms with lower probability, we have introduced two modifications in the low-density method in order to simulate the motion of the ions in moderately dense gases. First, as presented in Fig. 1, the reproduction of the motion of an ion as it approaches an image of an atom, A, which interacts with other atoms, such as B, requires the monitoring of all secondary interacting atoms, B. For this reason the cutoff radius, which controls the generation of the images of neutrals, has been increased to 6σ . This value has been decided after studying results of simulations until calculated properties varied below a reasonable statistical error. However, the increase of the cutoff radius is not unlimited, since the volume of the simulation cell has to be increased appropriately and similarly the number of simulated species so that the density remains at a prescribed value.

Further, the generated images of atoms are allowed to interact with one another with the standard cutoff radius of 3.2σ . We also mention that many-body interactions of an ion with independent atoms are treated accurately as in the case of the low-density method.

Technically, in this approach, two independent MD simulation procedures are considered in parallel. In the first simulation procedure, the moderately dense gas is reproduced at equilibrium alone providing initial conditions for the atoms that interact with the ions of the second procedure. In the second procedure, however, the drifting of a number of independent ions is simulated together with the motion of images of gas particles generated specifically for each ion. Thus, around each ion an ion-specific microenvironment of images of neutral atoms is created. In general, new images of neutrals are created at the front of the ion as it moves in the direction of the field and old images are left behind, and eventually disappear, especially with the additional drag exerted on them by the rest of the (images of) gas atoms.

The above approach allows effectively the extraction of the thermal energy from the system with the use of equilibrium MD methods and periodic boundary conditions, even though the nonequilibrium motion of the ions acquire cylin-

drical symmetry, due to the action of the electrostatic field. For the integration of the equations of motion we employ here the Verlet algorithm¹⁷ which is fast and stable for atomic systems.

The whole procedure enables the calculation of moments of the velocity distribution as follows. The first moment determines the mean ion velocity, $v_d = \langle v_z \rangle$ with the field in the z direction, and through this the mobility, $\mu = v_d/E$. In addition, the mean kinetic energies parallel and perpendicular to the field or relevant effective temperatures are determined through the second moments,

$$T_L = \frac{m}{k} \langle (v_z - v_d)^2 \rangle$$

and

$$T_T = \frac{m}{k} \langle v_x^2 \rangle = \frac{m}{k} \langle v_y^2 \rangle.$$

Higher order moments of the velocity distribution function, such as the skewness parameter, $\delta = \langle (v_z - \langle v_z \rangle)^3 \rangle^{1/3} / \langle (v_z - \langle v_z \rangle)^2 \rangle^{1/2}$, can also be calculated easily, though they will not concern us here. The brackets in the above expressions indicate statistical averaging generated by the MD simulation method.

Other transport properties such as ion diffusion coefficients, third order transport properties, etc., can also be determined through the calculation of velocity autocorrelation functions. The latter contain dynamic information about the ion motion and require large amounts of computer time.

We turn now to the calculation of the first few moments of the velocity distribution function of an actual ion–neutral system.

III. APPLICATION

As a representative system we consider K^+ moving in Ar gas, using an ion–atom universal interaction model potential²⁰ which has been tested in the past through comparisons of MD simulations results and kinetic theory calculations against experimental mobility and diffusion coefficients. For the Ar–Ar interaction we employ a Lennard-Jones potential²¹ with $\epsilon = 119.7 \text{ K}$ and $\sigma = 3.405 \text{ \AA}$. This effective potential is used here because it reproduces better state properties of Ar over a range of high densities. Specifically, we find experimental pressure data²² to be reproduced at 300 K and up to 40 atm within the experimental accuracy, which is about 2% . Other more complex accurate two-body potentials exist in the literature but reproduce well only low-density properties. In addition, the LJ potential is one order of magnitude faster in computation than the more elaborate latter model potentials.

In order to obtain accurate results, we are simulating 500 independent ions in runs of 10^6 time steps with time interval of $3 \times 10^{-15} \text{ s}$. The gas is relaxed at an equilibrium state at 300 K and at densities ranging from around 0.03 nm^{-3} to 1.0 nm^{-3} with the corresponding gas pressure varying from 1 atm to about 40 atm . The cutoff radius for the interaction of the gas atoms has been set equal to 3.2σ , where σ is the distance at which the gas interaction potential vanishes. The

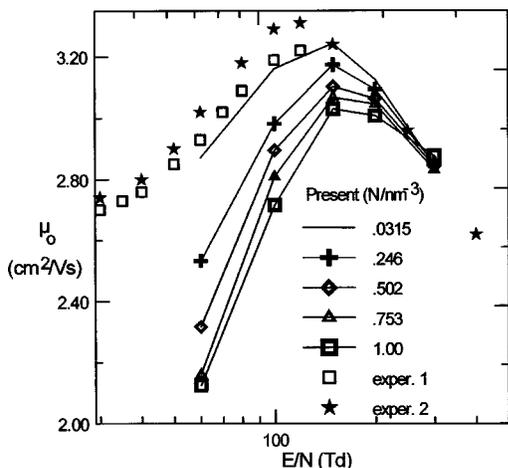


FIG. 2. Standard mobility, μ_0 , for K^+ in Ar at 300 K as function of E/N at various values of the gas density, N . The two sets of experimental data marked (1) and (2) are from Refs. 23 and 24 with 0.5% and 2.0% uncertainty, respectively.

cutoff radius for the generation of neutral images, however, has been set equal to 6σ , forcing us to consider a simulation box of large volume in order for the cutoff radius to remain within the box. We therefore choose to use 500 gas atoms though even 108 gas particles would have served all other purposes. The obtained simulation data are available upon request.

The present results at about 1 bar and 300 K coincide with the ones obtained in the past at drift tube experimental conditions.¹ In this case it has been found that the experimental mobility and diffusion coefficients were reproduced within the experimental accuracy and, in addition, comparisons against kinetic theory results obtained from a moment solution of the Boltzmann kinetic equation using the same ion-atom interaction potential were also successful within the uncertainties of both approaches.

At moderate gas densities, v_d and the mobility have converged below 1% and the effective temperatures around 1% at all field strengths presented here. As N and E/N increase together, the field becomes very strong causing high accelerations to the ions during their free flights between collisions. Although the time step still remains appropriate for the accurate integration of the equations of motion, the instantaneous velocity of certain ions occasionally becomes very large. Since beyond a velocity limiting value an ion may accelerate continuously (runaway phenomenon) or acquire long accelerating periods, we have set a velocity cutoff (30 km/s), beyond which the velocity of an ion is replaced by its local ensemble average value. This procedure protects the spoiling of the statistical averages of calculated physical properties, provided the total number of the observed “runaway” events remains small.

The results of the simulation for μ_0 are presented in Fig. 2 as a function of E/N at various densities together with two sets of drift tube experimental data at the same field range for comparison.^{23,24} At pressure below 1 atm the standard mobility reduces to K_0 , Eq. (3), and becomes solely a function of the combined variable E/N . At higher pressures, however, it depends additionally on the gas density as seen in Fig. 2.

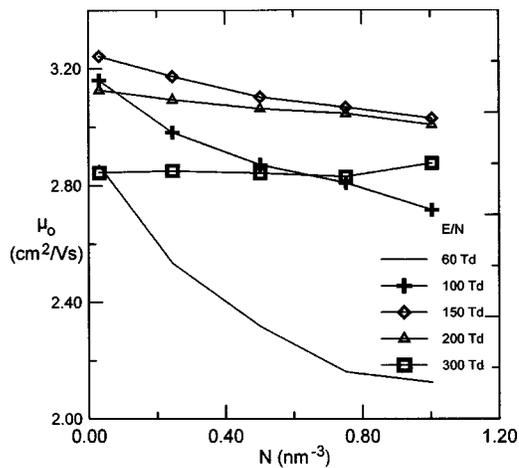


FIG. 3. Standard mobility for K^+ in Ar at 300 K as function of the gas density at various values of E/N .

To make apparent this density dependence of the calculated mobility, we present μ_0 as a function of the gas density at various field strengths in Fig. 3. We observe that the mobility decreases with the gas density and this effect diminishes at strong fields, though at 300 Td a small increase of μ_0 is observed around 1.00 nm^{-3} . In general, however, it appears that fast moving ions are less sensitive to the increase of the gas density at the density range considered here.

Similar density dependence is observed in the case of the effective temperatures, T_L and T_T , in Figs. 4 and 5. Such parameters generally remain unobservable but provide information for the form of the velocity distribution function and are useful intermediate quantities for the calculation of diffusion coefficients from mobility data through the use of generalized Einstein relations²⁵ (GER). In a low order approximation of the results of the kinetic theory for the ion transport²⁶ the effective temperatures are obtained through²⁷

$$kT_L = kT + \zeta_L m v_d^2 \{1 + \beta_L K'\}, \quad (5)$$

$$kT_T = kT + \zeta_T m v_d^2 \{1 + \beta_T K'\}, \quad (6)$$

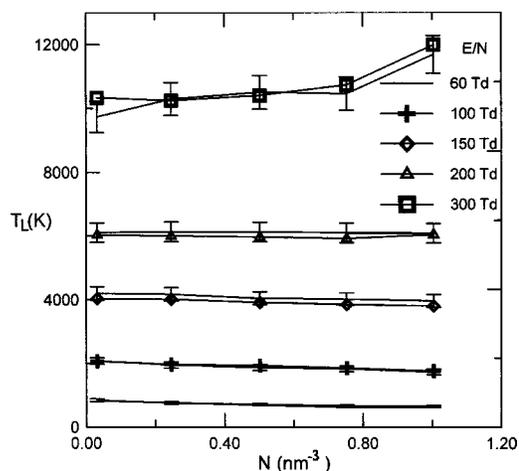


FIG. 4. Effective temperatures parallel to the field as a function of the gas density at various field strengths for the system in Fig. 1. Plane lines represent simulation results and lines with 5% bars are predictions from Eq. (5).

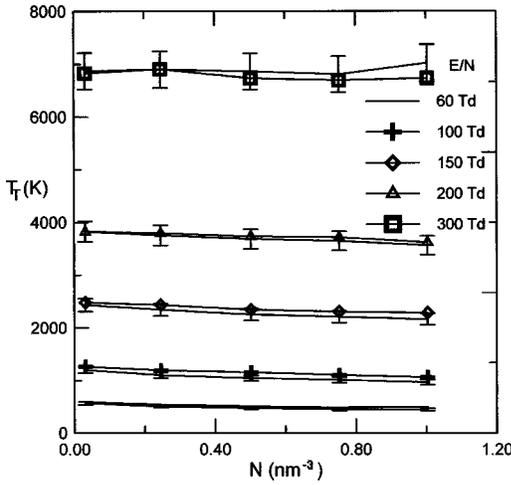


FIG. 5. Effective temperatures perpendicular to the field as a function of the gas density at various field strengths for the system in Fig. 1. Plane lines represent simulation results and lines with 3% bars are predictions from Eq. (6).

with $\zeta_L + 2\zeta_T = 1$, $\zeta_T = (m + M)\tilde{A}/(4m + 3M\tilde{A})$, $\beta_T = 0$,

$$\beta_L = \frac{1 - e}{1 + \frac{1}{2}eK'} \frac{1 + (1 - e)K'}{1 + (1 + \frac{1}{2}e)K'},$$

with $e = M/(m + M)$, where m and M are the masses of ion and gas atoms, respectively. The parameter \tilde{A} is a dimensionless ratio of two collision integrals with approximate value of 0.85 for ion-noble gas systems. Though these expressions have been obtained for low-density buffer gases, they do not depend explicitly on the density and therefore they may be extendable to higher densities. To assess their predictive ability at moderately dense gases we calculate the effective temperatures from the above expressions using as input data the drift velocity and logarithmic differential mobility, $K' = d \ln K / d \ln(E/N)$, obtained from the present results. Comparisons against simulation results are presented in Figs. 4 and 5. We observe that the simulation data for T_{\parallel} and T_{\perp} are reproduced within 5% and 3%, respectively, in the whole range of field strengths and densities employed here. This result is promising for the development of GER at moderate gas densities and high fields, though general production of such relations is required and relevant tests have to be conducted for their establishment.

Since there is no kinetic theory treatment of the motion of ions in dense gases at nonvanishing fields, in order to interpret the present results we have to resort to the low field kinetic theory results of Davis *et al.*¹¹ for model interactions as well as to mobility expressions obtained from a two-temperature moment solution of the Boltzmann kinetic equation for ions in low density gases and arbitrary field strength.^{2,28} The former treatment separates the ion-atom interaction in two parts; one due to an effective hard core of radius σ and a second part representing the attraction, $V(R)$. These contributions emerge in the resulting expression for the mobility,

$$\mu = \frac{e}{(8/3)N\sigma^2 g(\sigma) [2\pi\mu kT]^{1/2} + \zeta}, \quad (7)$$

where $g(\sigma)$ is the ion-neutral pair-correlation function at contact and μ is the relative mass. The first part of the denominator includes the effect of the hard core of the potential and the second one the friction exerted on the ion by the attraction of the medium. The latter can be approximated by²⁹

$$\zeta^2 = \frac{1}{3}\rho \int \nabla^2 V(R) g(R) d\mathbf{R} \quad (R \geq \sigma), \quad (8)$$

where ρ is the mass density of the fluid. The expression for μ is in conformity to the kinetic theory analytic results at low gas density and arbitrary field strength, provided the macroscopic variables determining the gas state and the ion drift, as well as the ion-atom interactions, are set alike in the two approaches. Specifically, in the former approach the low-density limit has to be taken with ξ set to zero and $g(\sigma) \approx 1$. Similarly, in the latter approach the low field limit has to be considered with hard-sphere ion-atom interaction.

Since, however, the Boltzmann kinetic theory results apply also at high fields we expect Eq. (7) to be extendable to nonvanishing fields by arguing as follows. Within the first order approximation of the two-temperature solution of the kinetic equation, extension to weak fields is obtained through replacement of T by an effective field-dependent ion temperature,

$$T_{\text{eff}} = (mT_i + MT)/(m + M), \quad (9)$$

with

$$\frac{3}{2}kT_i = \frac{1}{2}m\langle v^2 \rangle,$$

where \mathbf{v} is ion velocity. The same replacement of T by T_{eff} in Eq. (7) should extend its application at least to weak fields. In addition, application to actual interaction can be utilized through replacement of σ^2 by the collision integral $\Omega^{(1,1)}(T_{\text{eff}})/\pi$ of the two temperature theory. The Ω integral should be calculated through the use of the repulsive part of the interaction potential only.

With the above considerations we can then deduce that the observed density dependence of the mobility, μ_0 , at low approximation has to come from the dependence of the collision integral on T_{eff} and the dependence of $g(R)$ on the density. In the first case, Ω is a decreasing function of T_{eff} and the latter has been found here to vary appropriately with density at certain E/N ratio by approximating $T_{\text{eff}} = (T_L + 2T_T)/3$ (Figs. 4 and 5). Further, the density dependence of ion-atom $g(R)$ is more difficult to analyze since it has not been probed at nonequilibrium steady state conditions. However, as the density increases at normal temperature one expects the development of a weak structure around the ions, which in turn causes their slowing down. Similar but more pronounced effects have been observed in the case of dense gases where associative collisions and clustering have been suggested for the explanation of the density dependence of the mobility.¹⁵

Thus, except from the modification of the thermally averaged ion-atom cross sections, we find the resulting transport properties to be sensitive to the state of the buffer medium. The ion-dimer atom interactions have been found not to deteriorate the accuracy of the present results as simula-

tion tests with double duration indicate. However, for calculations beyond the present density limit, in order for triple and higher multiplicity gas interactions to be accurately reproduced the cutoff radius for the generation of images of neutrals has to be increased. Finally, we note that the present high field results are out of experimental reach since field up to thousands of kV/cm would be needed to attain E/N values at 300 Td.

IV. CONCLUSIONS

We have presented a molecular dynamics method for the simulation of the ion transport in moderately dense gases and arbitrary field strength. As an example, for a representative system we have calculated the density dependence of mobility and mean kinetic energies or effective temperatures parallel and perpendicular to the field at intermediate and strong electric fields. Similar calculations can be implemented for diffusion coefficients longitudinal and transverse to the field.

Extension to ions in high-density buffer gases and liquids at nonvanishing fields requires a change in the operational parameters or modification of the present procedure for the generation of new gas images of atoms around an ion. Specifically, triple and higher multiplicity interactions have to be adequately followed in the procedure well before an encounter with an ion takes place. We are working in this direction at present.

Since the method depends only on the ion and neutral interaction potentials, it can assist the development of kinetic theory treatment of ion motion in this area by providing valuable information about the importance of any analytic theory approximation. In a similar way, the method can assist in the design of future experiments by predicting in advance accessible properties. Such results enable the estimation of the accuracy of an experimental procedure and its sensitivity to relevant operational parameters.

Finally, extension to polyatomic ions can provide information about microscopic information such as the structural information,³⁰ interaction potentials,³¹ and cross sections³² already probed experimentally by ion mobility spectrometry. In addition, the method can be implemented for the simulation of the drift motion of the ions along the coexistence curve,¹⁵ as well as, close to critical states where the so-called parametric resonance is observed.³³

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