Velocity correlation functions, Fickian and higher order diffusion coefficients for ions in electrostatic fields via molecular dynamics simulation

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(Received 2 January 1996; accepted 22 February 1996)

The dynamic and transport properties of swarms of ions in a uniform electrostatic field are studied by using a molecular dynamics method. For a representative system, K^+ in Ar, using a universal interaction model potential, second and third order ion-velocity correlation functions are determined at various field strengths. From them, Fickian diffusion coefficients parallel and perpendicular to the field, as well as higher order diffusion coefficients, Q_{zzz}, are obtained within estimated overall accuracy 5% and 7%, respectively. Comparisons of the Fickian diffusion coefficients against results of the moment solution of Boltzmann kinetic equation and a Monte Carlo simulation method using the same interaction potential as well as against experimental data, reveal consistency among all calculation procedures and in addition agreement with drift tube measurements. These comparisons provide new tests for the accuracy of the employed interaction potential. The method has been applied for up to third order velocity correlations and diffusion coefficients but it is extendible to higher order dynamic and transport properties. [S0021-9606(96)51020-2]

I. INTRODUCTION

We probe the dynamic and transport properties of ions drifting in gases under the influence of an electrostatic field by using a molecular dynamics simulation method. Already, we have applied the method successfully, in the past, for the reproduction of experimental mobilities, effective temperatures parallel and perpendicular to the field and skewness parameters of the velocity distribution of the ions.[1] Here, we further determine second and third order ion-velocity correlation functions and from them Fickian and higher order diffusion coefficients.

Experimental data for ion-transport properties have been collected for many ion-molecule combinations from drift tube experiments and have been compiled in the past decades.[2–6] They consist primarily of mobilities and Fickian ion-diffusion coefficients parallel and perpendicular to the electric field. For selective systems third and fourth order moments of the ion-velocity distribution[7,8] have been measured as well as population distributions of rotational states and alignment of angular momentum of molecular ions with respect to the field have been probed.[9]

The transport data have been reproduced mainly through the moment solution of Boltzmann kinetic equation especially in the case of atomic systems.[2] Recent advances, however, in the incorporation of rotational motion into the kinetic theory description are promising for the interpretation of transport properties in the case of molecular ions.[10–12] An alternative procedure for the description of ion motion has been based on simulations through a Monte Carlo method[13,14] which has been developed in the past based on a prescribed distribution of free times between ion-neutral collisions. This method has been employed for the reproduction of mobilities and Fickian diffusion coefficients but has not been applied for the determination of dynamic properties so far.

The straightforward application of our MD method for the calculation of velocity correlation functions enables us to determine the dynamic properties of ions in steady drift motion. The present procedure consists of a usual equilibrium molecular dynamics technique with periodic boundary conditions supplemented by an effective dissipation mechanism of iconical interactions[1] which mimics realistically and efficiently the loss of electric energy of the ions through transfer to the buffer gas as thermal energy.

By using this procedure we have obtained in the past drift velocities and effective ion-temperatures parallel and perpendicular to the field, which enabled us to establish the accuracy of the method by comparison against experimental, theoretical and simulation results. Further, here, we calculate Fickian diffusion coefficients parallel and perpendicular to the field as well as a third order non-Fickian diffusion coefficient for the ions at various field strengths. The former coefficients are compared and tested against experimental data as well as against results from the moment solutions of the kinetic theory and Monte Carlo simulations using the same interaction potential.

A different situation arises for the third order diffusion coefficients, since they have not been measured so far, although they are suspected to interfere to the results of drift tube experiments.[15] However, a method has been developed for the calculation of such coefficients from the moment solution of Boltzmann equation,[16] though it has not been applied to real systems but only for model ion-atom potentials and in relation to the testing of generalized Nernst-Einstein relations between high order diffusion coefficients and nonlinear mobility.[16–18]

In the following section we obtain statistical expressions for diffusion coefficients from velocity autocorrelation functions by analyzing the stochastic evolution of a correlation function in analogy to equilibrium.[19] Although the derivation is similar, it differs in that the diffusion coefficients at moderate and higher field strengths become high rank tensorial quantities and a careful treatment for the emerging dimensions is required. In the third section we present the employed simulation method and the relevant operational parameters in its use. In the fourth section we calculate autocorrelation functions for a representative system, K^+ in Ar, and study the dynamic behavior of the ionic motion in the buffer gas as a function of the field strength. We then discuss the possibility of utilizing such information for explaining the form of the ion velocity distribution function. This analysis is expected to be more important in the case of molecular ions which acquire internal degrees of freedom.

In addition, we study the reproduction of experimental ion diffusion coefficients from the second order velocity correlation functions and compare our results against results of analytic calculations and Monte Carlo simulations. Further, we determine the Q_{zzz} component of the third order ion diffusion coefficient as a function of the field strength. Its accuracy is expected to be within ±7%. Finally, in the conclusions we comment for the possibility of calculating higher order diffusion coefficients.

II. STOCHASTIC ANALYSIS

The flow of a small amount of ions in a low density gas under the influence of an electrostatic field is characterized by a current, **J**, which is composed of two parts; one describing ordered drift motion and the other diffusional motion,[2]

$$\mathbf{J}=n\boldsymbol{v}_d-\mathbf{D}\cdot\nabla n+\mathbf{Q}:\nabla\nabla n+\cdots, \tag{1}$$

where n is the ion number density, $\boldsymbol{v}_d$ is the drift velocity and **D**, **Q**, etc. are diffusion coefficients of second, third, etc. rank, respectively. The number of dots in the expression denotes the order of the rank contraction between diffusion coefficients and gradient terms. In this expression high order gradient terms of the ion density, such as $(\nabla n)^2$, are not included due to the presence of a trace amount of ions.

The tensorial character of the diffusion emerges from the cylindrical symmetry of the ion motion due to the effect of the homogeneous electrostatic field. However, many of the elements of these coefficients are zero and from the remaining ones many are equal to each other due to this symmetry. Specifically, for the Fickian diffusion coefficients there are only two independent components, $D_\parallel = D_{zz}$ and $D_\perp = D_{xx} = D_{yy}$, with the field in the z direction, and for third order diffusion coefficients it has been suggested that there are only three independent components.[16]

The low density of the system ensures the fast enough decay of ion velocity correlations and thus the existence of all diffusion coefficients in consistence with the above expansion. However, at low field strengths odd rank diffusion coefficients vanish and the remaining even order ones render scalars.

The temporal change of ion density can now be obtained from an equation of continuity and Eq. (1),

$$\frac{\partial n}{\partial t}=-\boldsymbol{v}_d\cdot\nabla n+\mathbf{D}:\nabla\nabla n-\mathbf{Q}\vdots\nabla\nabla\nabla n+\cdots. \tag{2}$$

To derive a statistical expression for the above diffusion coefficients, we consider the motion of a tagged ion in the buffer gas and assume that at time t it has position $\mathbf{r}_i(t)$ when initially it is at $\mathbf{r}_i(0)$. The relevant quantity for the study of the ion drift and diffusion is the conditional probability $P(\mathbf{r},t;\boldsymbol{\rho},0)$ of finding the particle at time t at position $\mathbf{r}+\boldsymbol{\rho}$ provided it was initially at **p**. This probability is obtained form a steady state ensemble average through

$$P(\mathbf{r},t;\boldsymbol{\rho},0)\equiv P(\mathbf{r},t)=V\langle\eta(\mathbf{p},0)\,\eta(\mathbf{r}+\boldsymbol{\rho},t)\rangle, \tag{3}$$

where $\eta(\mathbf{r},\mathrm{t})=\delta[\mathbf{r}-\mathbf{r}_i(t)]$ is the local microscopic density of the ion in volume V, such that $\langle\eta\rangle=V^{-1}$, and $\delta(\mathbf{r})$ is a ''delta'' function. The independence of the final result on the initial position allows us to average over $\boldsymbol{\rho}$ and obtain

$$P(\mathbf{r},t)=\langle\delta(\mathbf{r}-\Delta\mathbf{r}_i)\rangle, \tag{4}$$

where $\Delta\mathbf{r}_i=\mathbf{r}_i(t)-\mathbf{r}_i(0)$ is the displacement of the ion. In order now to expand this probability in cummulants we first Fourier transform it with respect to the spatial coordinates,

$$P(\mathbf{k},t)=\int d\mathbf{r}\;\; e^{i\mathbf{kr}}P(\mathbf{r},t)=\langle e^{i\mathbf{k}\Delta\mathbf{r}_i}\rangle, \tag{5}$$

and then expand the exponential, in such a way that high rank tensorial quantities emerge in an exponent,

$$\begin{aligned}\langle e^{i\mathbf{k}\Delta\mathbf{r}_i}\rangle = {}&\exp\{\mathbf{i}\langle\Delta\mathbf{r}_i\rangle\cdot\mathbf{k}+(\mathbf{i}^2/2)\langle\Delta\mathbf{r}\Delta\mathbf{r}\rangle:\mathbf{kk}+(\mathbf{i}^3/3!)\\&\times\langle\Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r}\rangle\vdots\,\mathbf{kkk}+\cdots\},\end{aligned} \tag{6}$$

where $\Delta\mathbf{r}=\Delta\mathbf{r}_i-\langle\Delta\mathbf{r}_i\rangle$. In this expression the factors with the brackets in front of the products of **k** are identified as cummulants of the distribution by comparison with the general expansion

$$\begin{aligned}P(\mathbf{k},t)= {}&\exp\{\mathbf{i}\mathbf{C}^{(1)}\cdot\mathbf{k}+(\mathbf{i}^2/2)\mathbf{C}^{(2)}:\mathbf{kk}+(\mathbf{i}^3/3!)\mathbf{C}^{(3)}\vdots\,\mathbf{kkk}\\&+\cdots\},\end{aligned} \tag{7}$$

where, here, $\mathbf{C}^{(n)}$ is the nth rank cummulant which is contracted by the same rank product of **k** vectors.

Assuming now that the regression of fluctuations towards the drift state of the ions at long times is described by the hydrodynamic equations, we derive another expression for the probability density which involves explicitly the diffusion coefficients. Accordingly, we Fourier transform with respect to the spatial coordinates both sides of Eq. (2) after replacing n with $P(\mathbf{r},t)$ and derive

$$\frac{\partial P(\mathbf{k},t)}{\partial t}=\{\mathbf{i}\boldsymbol{v}_d\cdot\mathbf{k}+\mathbf{i}^2\mathbf{D}:\mathbf{kk}+\mathbf{i}^3\mathbf{Q}\vdots\,\mathbf{kkk}+\cdots\}P(\mathbf{k},t),\quad\text{or}$$

$$P(\mathbf{k},t)=\exp\{\mathbf{i}\boldsymbol{v}_d\cdot\mathbf{k}+\mathbf{i}^2\mathbf{D}:\mathbf{kk}+\mathbf{i}^3\mathbf{Q}\vdots\,\mathbf{kkk}+\cdots\}t. \tag{8}$$

Finally, by comparing expression (6) and (8) we find

$$\boldsymbol{v}_d t=\langle\Delta\mathbf{r}_i\rangle,$$

$$\mathbf{D}t=(1/2!)\langle\Delta\mathbf{r}\Delta\mathbf{r}\rangle,$$

$$\mathbf{Q}t=(1/3!)\langle\Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r}\rangle,\ \text{etc.},\tag{9}$$

with t approaching infinity.

We can now utilize these expressions for the determination of ion transport properties by calculating averages from molecular dynamics simulations. The first expression provides the drift velocity or the mobility, through $\mathbf{K}=\boldsymbol{v}_d/E$, and the second one provides Fickian diffusion coefficients. This formula can be transformed to another useful form by noting first that

$$\Delta\mathbf{r}=\mathbf{r}_\mathbf{i}(t)-\langle\mathbf{r}_\mathbf{i}(t)\rangle=\int_0^t\Delta\boldsymbol{v}(t)dt,\tag{10}$$

with $\Delta\boldsymbol{v}(t)=\boldsymbol{v}(t)-\boldsymbol{v}_d$, where $\boldsymbol{v}(t)$ is the velocity of the ion at time t and $\boldsymbol{v}_d=\langle\boldsymbol{v}(t)\rangle$. We can then express the displacement tensorial product for D as follows:

$$\langle\Delta\mathbf{r}\Delta\mathbf{r}\rangle=\int_0^t dt_1\int_0^t dt_2\langle\Delta\boldsymbol{v}(t_1)\Delta\boldsymbol{v}(t_2)\rangle.\tag{11}$$

This expression can further be simplified by noting that at steady ion motion the ensemble average should depend only on $t=t_2-t_1$. Accordingly, by changing coordinates to (t_1,t) and integrating over t_1, in the limit of t approaching infinity, we derive

$$\langle\Delta\mathbf{r}\Delta\mathbf{r}\rangle=2t\int_0^\infty dt\langle\Delta\boldsymbol{v}(0)\Delta\boldsymbol{v}(t)\rangle.\tag{12}$$

Finally, by introducing this expression into Eq. (9) we obtain an alternative expression for D in terms of the second order-second rank velocity correlation function, $\mathbf{M}=\langle\Delta\boldsymbol{v}(0)\Delta\boldsymbol{v}(t)\rangle$,

$$\mathbf{D}=\int_0^\infty\mathbf{M}dt.\tag{13}$$

This expression has been employed in the past in Monte Carlo simulations[13] and here we will employ the same formula for the calculation of $D_\parallel=D_{zz}$ and $D_\perp=(D_{xx}+D_{yy})/2$.

Similarly, the third of Eqs. (9) provides third order diffusion coefficients. For the calculation of Q_{zzz} coefficients, however, we will use the equivalent expression which is based on a correlation function,

$$Q_{zzz}=\int_0^\infty dt_1\int_0^{t_1}N_{zzz}dt_2,\tag{14}$$

where $N_{zzz}=\langle\Delta v_z(0)\Delta v_z(t_1)\Delta v_z(t_2)\rangle$ is a component of the third order-third rank velocity correlation function.

III. SIMULATION METHOD

The generation of ion configurations which are needed for the statistical analysis relays on standard equilibrium molecular dynamics techniques, such as the Verlet algorithm with periodic boundary conditions, supplemented by an effective dissipation mechanism for the ion electric energy.[1] In short, we permit the gas molecules to evolve without being disturbed from equilibrium by not allowing them to feel the forces of the ions. However, we permit the ions to interact, but only through iconical interactions, that is, with images of the neutral molecules created in the memory of the computer at the beginning of each ion-atom encounter and for as long as collisions last. Thus, the simulation of the gas motion provides initial conditions for the exact scattering of independent ions which move along continuous trajectories during the whole procedure. This approach mimics realistically and efficiently the ion energy dissipation which takes place in drift tube experiments.

The operational parameters of the simulation such as the number of ions, N_i, and neutrals, N_n, as well as the total time steps of the simulation, T, can be selected by examining their effect on the total cpu time which is required in order to attain certain accuracy in the results. For a given N_n, since the ions do not interact with each other, this time is proportional to $T(cN_iN_n+N_n^2)$, where c is a constant which is greater than unity whenever the functional form of the ion-atom interaction potential is more complex than the atom–atom potential. We see now that we can shorten lengthy simulations for the calculation of ion properties by decreasing the number of steps, though we have to increase N_i in order to maintain the same accuracy. The net effect is favorable due to the quadratic dependence of time on N_n, which emerges from the atom–atom interactions. Workable conditions have been achieved with 500 ions in 108 neutral atoms for runs up to 7×10^5 time steps of 10^{-14} s each. In addition, we increase the collision frequency by one order of magnitude by using two to three orders of magnitude denser but still ideal gases and likewise scaled field. This becomes possible because at low density conditions, where binary collisions prevail, the ion-transport properties depend on the ratio of the field strength over the gas density, E/N.

Initially, the gas atoms are left to relax to equilibrium after 7×10^4 time steps, starting from an fcc configuration, and subsequently the ions are introduced at random positions with Gaussian velocity distribution. The ions are then left to relax to a steady state for 1×10^5 time steps, before data start being collected for statistical analysis.

We have also to mention that a cutoff for the velocity has been set, in order to avoid accidental occurrence of single runaway ions due to velocity fluctuations at high field strengths. Such ions can not loose easily their energy and therefore endanger the accuracy of the statistical results. By experimentation we have found that the limit of 20 000 m/s is appropriate since it is crossed only by a few ions at very high field strengths.

Finally, in order to avoid multiple scattering between an ion and a neutral which may occur due to the introduction of iconical interactions, another conditional test has been applied in the technique. Specifically, after the end of an iconical interaction the initially interacting neutral atom may remain inside the sphere of influence of the ion thus initiating a second scattering event. This is avoided by not allowing an ion-atom pair to interact, unless a time interval has elapsed from its previous collision. This interval has been set equal to the mean duration of ion-atom encounters which is about 200 time steps.

We proceed now by applying these results for the calcu-

TABLE I. Potential parameters for the K^+ Ar system (a_0=0.529 177 25 Å).

System	$v(e^2/a_0)$	$\sigma(a_0)$	ϵ(K)	$R_m(a_0)$	$C_4(e^2a_0^3)$	$C_6(e^2a_0^5)$	$C_8(e^2a_0^7)$
K^+Ar[a]	1.202	0.9478		5.87	5.540	66.04	1007.4
ArAr[b]		6.4345	119.7				

[a] The parameters are from Ref. 21.

[b] From Ref. 20.

lation of velocity correlation functions and diffusion coefficients.

IV. RESULTS

As a representative system for the application of the procedure we have chosen K^+ in Ar because it has been extensively studied experimentally as well as through the analytic solution of the Boltzmann kinetic equation and by Monte Carlo simulations in the past. The interaction potential between Ar atoms is a Lennard-Jones potential[20] which is more efficient in the simulation and equally accurate to more complex model potentials at such low pressure conditions. For K^+–Ar, we employ the Koutselos *et al.* potential[21] which has been used in the past in analytic calculations and simulations and has been found to reproduce well the ion-transport properties. This potential consists of two parts, one describing short range exchange interactions and the other long range Coulombic interactions. The latter is expressed by a damped multiple expansion series and the former by a double exponential function with two empirical parameters,

$$V(R)=v(A^{-aR/\sigma}-Be^{-bR/\sigma}) \\ -(C_4/R^4+C_6/R^6+C_8/R^8)h(R), \qquad (15)$$

where

$$h(R)=\begin{cases}\exp-(1.28R_m/R-1)^2, & R_m\leqslant 1.28\\ 1, \quad R_m\geqslant 1.28,\end{cases}$$

is a damping function and $A=146.98$, $B=70.198$, $a=1.5024$, $b=1.4041$. All the remaining parameters as well as those of the Ar–Ar interaction potential are presented in Table I.

A. Second order correlation functions and Fickian diffusion coefficients

The ion-velocity correlation functions, $\mathbf{M}=\langle\Delta\boldsymbol{v}(0)\Delta\boldsymbol{v}(t)\rangle$, are calculated from averages of 1700 such functions which are determined consecutively one 200 steps after the other. Their length extends beyond the one required for the calculation of diffusion coefficients to within 1%. The obtained correlation functions are presented in Figs. 1 and 2. In general, at short times the correlation functions have a Gaussian form which characterizes almost free motion and at long times they acquire the form of an exponential due to loss of correlation through random ion-atom collisions. The long extent of the correlations, up to about 200 ps, is characteristic of the low density conditions of the system and depends on the field strength. At higher fields the correlation functions shrink due to the increase of ion-atom collision frequency.

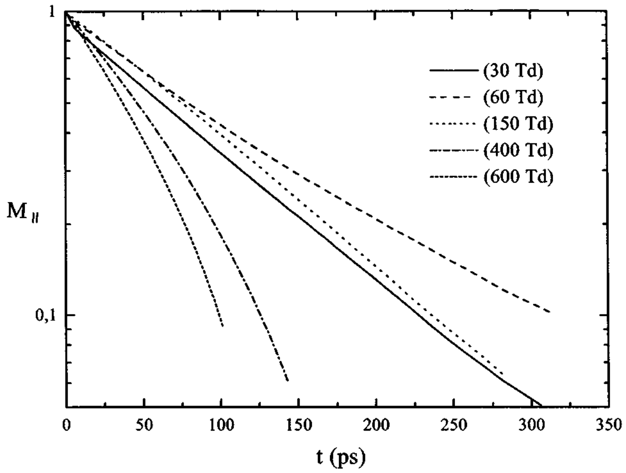

FIG. 1. Second order velocity correlation function, $M_{\parallel}$, of K^+ in Ar at various field strengths.

The relative error of the calculations appears to be almost independent of the field and the direction of the diffusional motion. For the employed operational parameters it is found that the standard deviation of the correlations from single runs at 30 and 75 ps, for example, are less than 10% and 15% of the mean value, respectively. However, the corresponding diffusion coefficients acquire better accuracy due to the fact that they are calculated through the time integration of these correlation functions.

Specifically, diffusion coefficients parallel and perpendicular to the field are obtained from the correlation functions M_{zz} and $(M_{xx}+M_{yy})/2$, respectively. To achieve better accuracy by extending the integration up to infinity, we have split the integration in two parts. The first part, which corresponds to short time correlations, is integrated numerically and the second one, which includes the tail of the correlation function, is first fitted by an exponential and then integrated analytically up to infinity. The resulting ion-diffusion coefficients are reported in Table II ND as for the removal of an

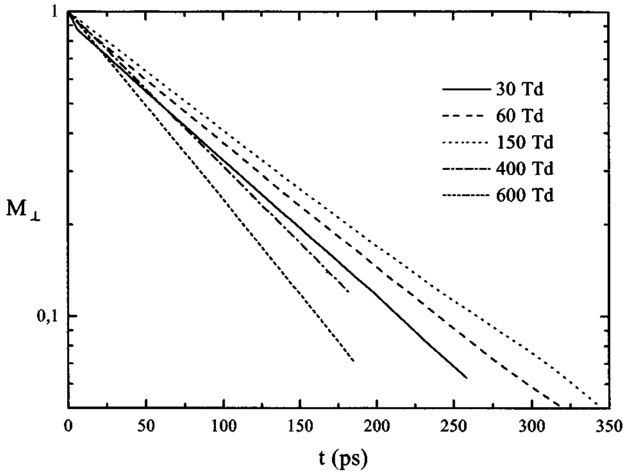

FIG. 2. Second order velocity correlation function, $M_{\perp}$, of K^+ in Ar at various field strengths.

TABLE II. Transport properties of the K^+Ar at 300 K using the KMV interaction potential.[a]

$E/N(Td)$[b]	v_d(m/s)	$T_\parallel$(K)	$T_\perp$(K)	δ	$ND_\parallel$[c]	$ND_\perp$[c]	NNQ_{zzz}[c]
30	213.6	408.5	358.4	0.5053	2.703	2.175	0.4081
60	462.8	830.8	589.7	0.8540	7.241	4.085	2.735
80	645.3	1 356	860.8	0.9413	11.83	6.145	4.836
100	849.3	2 068	1 264	0.9390	17.48	9.593	8.058
150	1 307	4 037	2 482	0.9043	28.80	18.87	12.30
200	1 680	6 039	3 826	0.8888	33.61	27.32	15.87
300	2 293	10 340	6 829	0.8564	46.51	45.22	23.07
400	2 832	15 600	10 390	0.8392	59.89	58.95	40.02
600	3 621	28 900	19 190	0.6848	78.78	91.51	72.43

[a] From Ref. 21.

[b] 1 Td=10^{-21} V m^2.

[c] The units of ND and NNQ are 10^{18} 1/cm s and 10^{33} 1/cm^3 s, respectively.

inverse density dependence at intermediate and higher field strengths. In the same table we present the ion drift velocity, effective temperatures parallel and perpendicular to the field, $T_i = (m/k_B)\langle(v_i - \langle v_i\rangle)^2\rangle$, and the skewness parameter of the velocity distribution which is defined through $\delta=\langle(v_z - \langle v_z\rangle)^3\rangle^{1/3}/\langle(v_z - \langle v_z\rangle^2\rangle^{1/2}$. In the past the first of these quantities has been found to agree very well with experimental data and the second one has been compared successfully to results of the kinetic theory and simulations. Their over all accuracy is found to be better than 2% and 5%, respectively, except at very low fields where the drifting motion appears vanishing and the relative error can be twice as much. The error here and in the subsequent calculations was estimated by performing simulations using different initial conditions. Better accuracies, however, can in principle be achieved by extending the number of the ions and the length of the simulation.

The attained accuracy of the Fickian diffusion coefficients is within 5% and as can be seen in Figs. 3 and 4 compare well with the experimental data,[22,23] as well as with previously calculated coefficients from the moment solution of Boltzmann kinetic equation[21] and Monte Carlo simulations[23] using the same interaction potential. In the figures, in order to make vivid the comparison tests, we have plotted reduced coefficients defined through

$$\tilde{D}_{\perp,\parallel}=qD_{\perp,\parallel}/K(0)kT_{\text{eff}}(0),$$
$$kT_{\text{eff}}(0)=kT+(1/3)M[K(0)E]^2, \tag{16}$$

where $K(0)$ is the zero field mobility at the gas temperature T. This reduction removes an approximately quadratic dependence of the diffusion coefficients on E/N.

B. Third-order correlation functions and non-Fickian diffusion coefficients

In a similar way, we proceed for the calculation of three-time velocity correlation functions. By way of an example, we determine the $N_{zzz} = \langle\Delta v_z(0)\Delta v_z(t_1)\Delta v_z(t_2)\rangle$ correlation functions. These correlations last longer than the second order ones and a time range up to 600 ps is required in order to determine them in their whole extent until they become

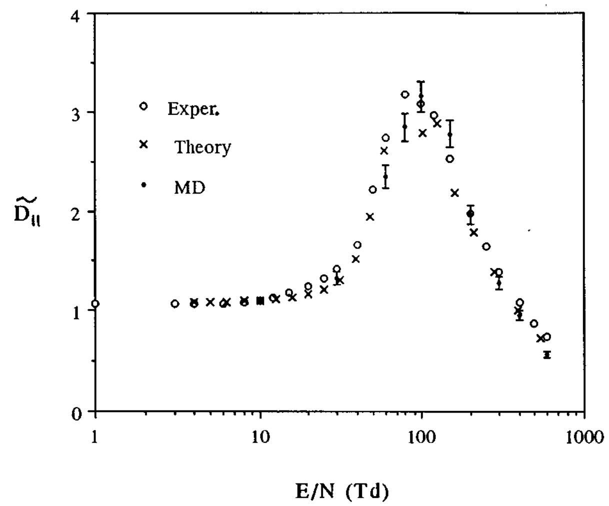

FIG. 3. Reduced diffusion coefficients parallel to the field for K^+ in Ar at 300 K. Circles are experimental data of roughly 10% accuracy from Ref. 22, crosses have been determined through kinetic theory within 5%, Ref. 21, and points with 5% error bars are present MD results.

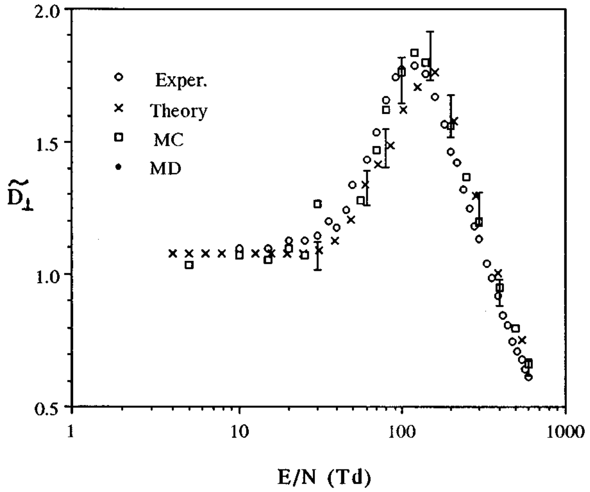

FIG. 4. Reduced diffusion coefficients perpendicular to the field for K^+ in Ar at 300 K. Circles are experimental data of about 3% accuracy from Ref. 23, crosses have been determined through kinetic theory within 5%, Ref. 21, squares have been calculated by MC simulation within 3%, Ref. 23, and points with 5% error bars are present MD results.

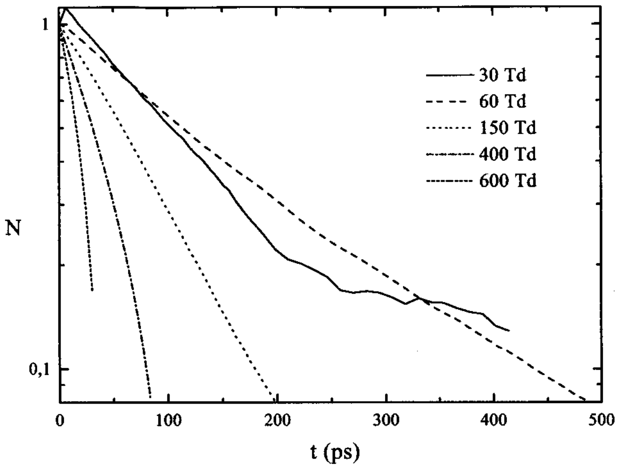

FIG. 5. Third order velocity correlation function, N, of K^+ in Ar at various field strengths.

negligible. The relative standard deviation of the calculation appears to be relatively independent of the field and is about 20% at 30 and 75 ps, except at very low fields where the error can double. The form of selective functions which are defined through $N(t) = \langle \Delta v_z(0) \Delta v_z(0) \Delta v_z(t) \rangle$, is depicted in Fig. 5. In general, these functions acquire Gaussian form at short times and they decay exponentially at longer times in resemblance to the second order correlation functions. At very low fields, however, a small peak, within the error uncertainty, is observed below 6 ps. If it is not an artifact of the statistics, it could be attributed to the persistence of the ion motion when weak interactions prevail during ion-neutral collisions. Further study in this direction is under way.

The long extent of the third order correlation functions, in comparison to the second order ones, may be related to the inseparability of velocity distributions along the three velocity directions observed in Monte Carlo simulation for Na^+ in Ne.[24] The long survival of such correlations may indicate characteristic motion in velocity space, which results in the specific deformation of the velocity distribution. To justify this assertion, however, special test are required.

These correlation functions can now be used for the calculation of non-Fickian ion-diffusion coefficients. We, thus, calculate the Q_{zzz} component of the third order diffusion coefficient and present it in Table II scaled with the gas number density as NNQ_{zzz} in order for an inverse quadratic density dependence at low and intermediate field strengths to be removed. In addition, we report the skewness parameter because it provides a measure of the initial unreduced triple velocity correlations, since $N_{zzz}(0,0) = \delta^3 (k_B T_\parallel / m)^{3/2}$.

The accurate extension of the integration of the correlation function to infinity requires fitting of its tail by a two-dimensional exponential function

$$C(t_1,t_2)=(e^{-a_1 t_1 - b_1} - e^{-a_2 t_1 - b_2}) t_2 / t_1 + e^{-a_2 t_1 - b_2}. \tag{17}$$

Obviously, for $t_2 = 0$ or $t_1 = t_2$ this function reduces to a single exponential and for certain t_1, $C(t_1,t_2)$ is a linear function in t_2. The resulting fitting is quite accurate leading to 1%–2% errors in the final diffusion coefficient.

As in the case of second order correlation function, the integration is performed numerically at short times and analytically using the above function at the tail of the correlation. The overall error in the calculation of Q_{zzz}, including the error of the statistical calculation, is found to be within about 7%, except at very weak fields where it can become twice as much.

V. CONCLUSIONS

For the first time we probe the dynamic properties of ions moving in neutral gases under the influence of an electrostatic field using a molecular dynamics method. Specifically, for a representative system, K^+ in Ar, two and three time velocity correlation functions for the ions have been determined and their shape and extent characterized. From these functions Fickian and third order diffusion coefficients have been calculated. The former compare well with experimental data and results from the moment solution of Boltzmann kinetic theory and Monte Carlo simulations using the same ion-atom interaction potential. The latter coefficients are expected to be accurate within about 7%. Higher order diffusion coefficients of comparable accuracy can also be determined from the present method but at the cost of higher amount of computer time.

ACKNOWLEDGMENT

The author acknowledges gratefully the computer time provided in a CONVEX C3820 computer by the Department of Computer Science of the National University of Athens.

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