

Dynamic properties and third order diffusion coefficients of ions in electrostatic fields

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Velocity correlation functions and third order diffusion coefficients of ions moving in a buffer gas under the influence of an electrostatic field are determined via molecular dynamics simulation. For the closed shell system of K^+ in Ar using a universal interaction model potential, the general form of the third order correlation functions is found to be monotonically decaying in time except in the cases of $\langle \Delta v_z(0)\Delta v_x(t)^2 \rangle$, $\langle \Delta v_z(0)\Delta v_y(t)^2 \rangle$, and $\langle \Delta v_z(0)\Delta v_z(t)^2 \rangle$, with $\Delta v(t) = v(t) - \langle v(t) \rangle$ and the field in the z direction. These functions acquire positive slope at short times showing enhancement of correlations between instantaneous v_z components of the ions and their future kinetic energies or velocity measures. This feature is shown to quantify the dynamics of correlations between velocity components suggested in the past by Ong, Hogan, Lam and Viehland [Phys. Rev. A **45**, 3997 (1992)] in order to explain the form of an ion velocity distribution function calculated through a Monte Carlo simulation method. In addition, within a stochastic analysis which establishes a relation between velocity correlation functions and third order diffusion coefficients, only two independent components of the diffusion tensor, Q_{\parallel} and Q_{\perp} , are predicted. We thereby calculate the Q_{\perp} component, which has not been determined so far, over a wide field range. The magnitudes of the resulting third order diffusion coefficients indicate that their contribution to the ion transport in usual drift-tube measurements should be very small. © 1997 American Institute of Physics. [S0021-9606(97)52617-1]

I. INTRODUCTION

The transport of nonreactive ions in a gas under the influence of a homogeneous electrostatic field is characterized by a steady drift and a superposed diffusional motion.¹ The corresponding ion flux may then be expressed as

$$\mathbf{J} = n\mathbf{v}_d - \mathbf{D} \cdot \nabla n + \mathbf{Q} : \nabla \nabla n + \dots, \quad (1)$$

where n is the ion density, \mathbf{v}_d is the drift velocity, and \mathbf{D} , \mathbf{Q} etc. are diffusion tensors of second, third etc. rank. Terms of the form $(\nabla n)^2$ need not be included in cases where the density gradient is negligible, as we assume here.

Although the number of components of the diffusion tensor increases quadratically with the rank, many of them vanish or coincide, due to the cylindrical symmetry of the ion motion and the irrelevance of the order of differentiation of n in Eq. (1). Thus, \mathbf{D} has only two independent components, $D_{\parallel} \equiv D_{zz}$ and $D_{\perp} \equiv D_{xx} = D_{yy}$, with the field, E , in the z direction. Similarly, \mathbf{Q} has only seven nonvanishing components, three of which should be independent according to a suggestion based on symmetries of the ion motion.^{2,3} In the following, however, we will show that this number is reduced by one within a stochastic analysis of the ion-density fluctuations. Further, at low fields, due to the spherical symmetry of the ion motion close to equilibrium, the components of odd rank vanish and the remaining even order ones become scalars.

In the past, drift velocities or mobilities, $K = v_d/E$, and Fickian diffusion coefficients have been measured for many

ion-atom systems.⁴ Contrary to this, third order and higher diffusion coefficients have so far not been probed experimentally, due to the small effect they should induce on the time of flight spectra of drift-tube experiments. However, through molecular dynamics simulation of the ion motion we were able to calculate the Q_{zzz} component for K^+ in Ar using an accurate intermolecular potential.⁵

In order to complete the determination of all \mathbf{Q} components of K^+ in Ar we proceed by first establishing a method of calculation from third order velocity correlation functions. We, thus, employ here a stochastic procedure equivalent to the one used at equilibrium⁶ but extended so that tensorial diffusion coefficients are accommodated in the analysis.⁵ Based on a generalized Onsager hypothesis for the regression of ion-density fluctuations towards the steady drift motion, we relate \mathbf{Q} with correlation functions and find that only two independent components are predicted, $Q_{\parallel} = Q_{zzz}$ and Q_{\perp} . This result, depends on microscopic assumptions which must hold at least for small and intermediate field strengths.

The obtained expressions for the Q coefficients depend on third order correlation functions of the form $N_{ijk} = \langle \Delta v_i \Delta v_j \Delta v_k \rangle$, with $\Delta v = v - \langle v \rangle$ and the brackets referring to averages of a steady state ensemble. Assuming ergodicity to hold, the averages are determined from trajectories generated by nonequilibrium molecular dynamics (MD) simulation of the ion motion.^{5,7} The method involves maintenance of the buffer gas at constant temperature through the introduction of 'iconical' ion-neutral collisions in usual MD methods. As an interaction potential between K^+ and Ar atoms we employ a universal interaction model which has

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been found in the past to reproduce successfully the mobilities and ion diffusion coefficients.

The velocity-correlation functions contain information about the mean microscopic (mesoscopic) ion motion and they can be studied for their own merit. For example, it has been suggested in the past by Ong *et al.*,⁸ in order to explain the form of the velocity distribution of Na⁺ in Ne obtained from Monte Carlo (MC) simulations, essentially that ions of high v_z components should acquire with increased probability also high v_x and v_y components. Such correlations and their evolution in time, that is their dynamics, can be studied through specific correlation functions, like $\langle \Delta v_z(0) | \Delta v_x(t) | \rangle$, or the ones we employ here for the calculation of diffusion coefficients, such as $\langle \Delta v_z(0) \times \{ \Delta v_x(t) \}^2 \rangle$ and $\langle \Delta v_z(0) \{ \Delta v_y(t) \}^2 \rangle$. Indeed, the latter functions are found not to decay at short times as normally would be expected, but to increase, until a maximum is reached, before they start decaying exponentially at long time values. This feature is studied further by calculating correlation functions for rapidly moving ions in the z -direction alone. It is thus confirmed that the observed non-monotonicity of the correlation functions is related directly with the correlations suggested by Ong *et al.*⁸ Even more, the form of these functions reveal the dynamics of the mesoscopic ion motion.

In the next section we obtain a relation between third order diffusion coefficients and velocity correlation functions through a stochastic analysis and show that only two independent components are predicted for \mathbf{Q} . In Sec. III we calculate correlation functions and diffusion coefficients for K⁺ in Ar from an MD simulation of the motion of the ions. Finally, in the conclusions we summarize our results and comment on the magnitude of the effects of \mathbf{Q} on the ion transport in usual drift-tube spectrometers.

II. STOCHASTIC ANALYSIS

The transport of a trace amount of ions in a buffer gas under the influence of an external homogeneous electrostatic field has been studied in the past through a stochastic analysis in order for the diffusion coefficients to be expressed in terms of velocity correlation functions.⁵ In this way, the obtained third order diffusion coefficient has been expressed in terms of a third order tensorial product of spatial displacements of a tagged ion, $\Delta \mathbf{r} = \mathbf{r}_i(t) - \langle \mathbf{r}_i(t) \rangle$,

$$\mathbf{Q}t = (1/3!) \langle \Delta \mathbf{r} \Delta \mathbf{r} \Delta \mathbf{r} \rangle, \quad (2)$$

with t approaching infinity and where the brackets represent a steady state ensemble average. The introduction of velocity correlation functions into the analysis is utilized by expressing $\Delta \mathbf{r}$ in terms of the velocity of the ion, $\mathbf{v}(t)$,

$$\Delta \mathbf{r} = \int_0^t dt' \Delta \mathbf{v}(t'), \quad (3)$$

with $\Delta \mathbf{v}(t) = \mathbf{v}(t) - \mathbf{v}_d$, where $\mathbf{v}_d = \langle \mathbf{v}(t) \rangle$ is the drift velocity of the ion. Substituting this expression into Eq. (2) we obtain

$$\begin{aligned} \mathbf{Q} &= (1/3!) \lim_{t \rightarrow \infty} (1/t) \int_0^t dt_1 \int_0^t dt_2 \\ &\times \int_0^t dt_3 \langle \Delta \mathbf{v}(t_1) \Delta \mathbf{v}(t_2) \Delta \mathbf{v}(t_3) \rangle. \end{aligned} \quad (4)$$

We can then integrate one of the time variables, like t_1 , since the correlation function at steady state should depend only on two time intervals, such as $s_1 = t_2 - t_1$ and $s_2 = t_3 - t_1$. Therefore, we change variables to (t_1, s_1, s_2) and derive for the ijk component

$$\begin{aligned} Q_{ijk} &= (1/3!) \lim_{t \rightarrow \infty} (1/t) \int_0^t dt_1 \int_{-t_1}^{t-t_1} ds_1 \\ &\times \int_{-t_1}^{t-t_1} ds_2 \langle \Delta v_i(t_1) \Delta v_j(s_1) \Delta v_k(s_2) \rangle. \end{aligned} \quad (5)$$

In order to perform the integration over t_1 we follow the procedure presented in the Appendix. Specifically, we first separate the integral into six contributions. Then, in the limit of t approaching infinity, we obtain the \mathbf{Q} components in terms of six characteristic integrals, $I_{ijk}^{(m)}$ defined in the Appendix,

$$Q_{ijk} = (1/6) \sum_{m=1}^6 I_{ijk}^{(m)}(s_1, s_2), \quad (6)$$

with m taking values from 1 to 6 and where the time variables s_1 and s_2 refer to the j and k velocity components, respectively.

Further, symmetry considerations about the interchange of the velocity components and the time variables show that many of the I integrals are equal to one another and that at most four of them are independent, indicated by A , B , C , and D . We also mention in advance that the calculated C and D integrals appear to be equal to each other within the statistical error of the simulation method. This may be due to an additional underlying symmetry of the I integrals which we have not been able to identify so far. Irrespective of this, the observed identities of the I integrals bring the nonvanishing components, with indexes ZXX , ZYY , XXZ , YYZ , XZX , and YZY , into coincidence and equal to

$$Q_{\perp} = (B + C + D)/3. \quad (7)$$

The six integrals of the remaining Q_{\parallel} component are equal to one another and thus we set $Q_{\parallel} = A$.

The above prediction appears to be in variance with an analysis of third order diffusion coefficients in Cartesian tensors that are irreducible under the three dimensional group, from which three independent \mathbf{Q} components are predicted.^{2,9} However, this analysis is based on the symmetries of the macroscopic ion motion, though our result depends on mesoscopic considerations about the regression of ion-density fluctuations. Thus, whenever our assumptions are met in drift tube experimental conditions, as it is expected especially at weak and intermediate field strengths, our predictions should be in compliance with experiment.

We proceed now to the determination and study of velocity correlation functions, as well as to the calculation of Q_{\perp} .

III. RESULTS

In order to complete the calculation of the Q components for a representative system and study its dynamics at a mesoscopic level, we have chosen to simulate the motion of K^+ in Ar in usual drift tube experimental conditions at various field strengths via molecular dynamics. The method maintains constant gas temperature and steady drift for the ions through the use of iconical ion–atom interactions. That is, each ion interacts only with images of the neutrals which are created and stored in the computer during every ion–neutral encounter. Consistently, the ‘‘real’’ neutrals, which in a sense provide initial conditions for the exact scattering of the ions, are simulated with a conventional equilibrium MD method without allowing them to feel forces from the ions. With this mechanism eventually the electric energy of the ions is dissipated without the real neutrals being perturbed from equilibrium. This is in compliance with drift tube experiments where the neutral molecules being in excess provide a thermal bath for the ions. The additional neglect of ion–ion interactions and many body ion–neutral correlations is reasonable at the low density experimental conditions where uncorrelated binary ion–atom collisions prevail.

Since the method allows uninterrupted evolution of the trajectories of the ions and atoms, we implement periodic boundary conditions and collect data for statistical analysis continuously. Results are derived from simulations of 500 ions in 108 neutral atoms using Verlet algorithm¹⁰ for the integration of the equations of motion. During each run, which involves 7×10^5 steps of 10^{-14} s time interval each, about 10^6 ion–atom collisions take place. More details of the method have been presented in the past.^{5,7}

At the present ideal gas conditions we use an efficient Lennard–Jones potential, $V(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$, for the interactions of Ar atoms,¹¹ with $\sigma = 6.4345\alpha_0$ and $\epsilon = 3.791 \times 10^{-4}e^2/\alpha_0$. For K^+ –Ar we use an accurate universal interaction model¹² which consists of a short-range exchange part and a long-range Coulombic part

$$V(r) = v[A \exp(-aR/\rho) - B \exp(-bR/\rho)] - (C_4/R^4 + C_6/R^6 + C_8/R^8)h(R, R_m), \quad (8)$$

where

$$h(R, R_m) = \begin{cases} \exp[-(1.28R_m/R - 1)^2] & \text{for } R \leq 1.28R_m \\ 1 & \text{for } R \geq 1.28R_m \end{cases},$$

is a damping function and $A = 146.98$, $B = 70.198$, $a = 1.5024$, $b = 1.4041$. The remaining parameters in atomic units are: $v = 1.202$, $\rho = .9478$, $R_m = 5.87$, $C_4 = 5.540$, $C_6 = 66.04$, $C_8 = 1007.4$. This potential has been found through kinetic theory calculations¹² as well as through Monte Carlo^{13,14} and MD simulations^{5,7} to reproduce successfully the experimental mobilities and ion-diffusion coefficients.

A. Correlation functions

The relative scarcity and uniformity of interactions lead to uncorrelated binary collisions between ions and buffer gas atoms at the usual drift tube experimental conditions. This simple picture leads one to expect that the ion velocity correlation functions have the form of an exponentially decaying function irrespective of the field strength. However, as has been inferred, for example, from an MC simulation of Na^+ in Ne at high fields the v distribution function acquires an egglike cylindrical form which is inseparable as a product of functions that depend on different v components.⁸ This inseparability has been attributed to correlations between v_Z and v_X or v_Y .

To investigate these correlations and their dynamic behavior, one can study the form of the correlation functions $\langle \Delta v_Z(0) | \Delta v_X(t) | \rangle$ and $\langle \Delta v_Z(0) | \Delta v_Y(t) | \rangle$ or the qualitatively similar functions $C_{ZXX} = \langle \Delta v_Z(0) \{ \Delta v_X(t) \}^2 \rangle$ and $C_{ZYY} = \langle \Delta v_Z(0) \{ \Delta v_Y(t) \}^2 \rangle$, since the squared velocity components differ from the measures only in magnitude. The latter functions constitute special cases of the correlation function needed for the calculation of third order diffusion coefficients, and therefore we examine these here, first.

The correlation functions are calculated from averages of 1900 such functions which are determined consecutively, each starting 300 time steps after the previous one. During the simulation, values for the correlations are collected every 200 steps. Their accuracy is best at intermediate field strengths, where, for example, at 150 Td, at time values 30, 75 and 210 ps, the standard deviation of C_{ZXX} is found to be 25%, 22%, and 28% of the mean, respectively. Similarly, the relevant errors for C_{ZZZ} are 20%, 20%, and 29%. At weaker and stronger fields the error increases gradually until it almost doubles at the limits of the employed field range. However, the corresponding diffusion coefficients acquire better accuracy due to the fact that they are calculated through time integration of these correlation functions.

In contrast to what one would anticipate at low densities, the calculated C_{ZXX} and C_{ZYY} acquire a positive slope at short times and reach a maximum, between 70 and 100 ps depending on the field strength, before they start decaying exponentially (Fig. 1). Also their extension is quite large since they attain again their initial value between 200 and 300 ps. To our surprise even $C_{ZZZ} = \langle \Delta v_Z(0) \{ \Delta v_Z(t) \}^2 \rangle$ had a similar shape, as depicted in Fig. 2, but only at intermediate and high field strengths. In order to elucidate further if this behavior stems primarily from ions with high V_Z components in conformity to the observation of Ong *et al.*,⁸ we have calculated the same correlation functions but with $\Delta v_Z(0) = v_Z - \langle v_Z \rangle$ lying in one of the four segments: I ($v_0, +\infty$), II ($0, v_0$), III ($-v_0, 0$), and IV ($-\infty, -v_0$), where V_0 is a convenient velocity limit.

Although the shapes of the obtained correlation functions vary from region to region, a general conclusion about the origin of the nonmonotonicity of these functions can be drawn beyond the uncertainty of the calculations. Specifically, in the case of C_{ZZZ} , (Fig. 3) we observe that all the ions contribute to the nonmonotonic behavior except those

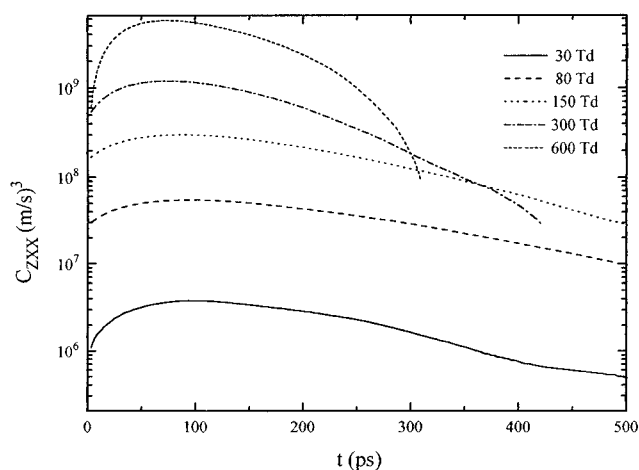


FIG. 1. Third order C_{ZZX} correlation functions for K^+ in Ar at various field strengths.

with high initial v_z component. This behavior should be due to the persistence of the instantaneous ion motion caused by the action of the electric field. This ordered motion lasts for a few collisions with the neutrals before randomization of the velocity sets in. The latter process, however, seems to be dominant in the case of energetic ions in the direction of the field, region I, where the correlation function decays monotonically.

Contrary to this, the feature of C_{ZZX} , (or C_{ZYY}), function is found indeed to stem mainly from ions with high v_z component though ions from the other regions contribute also to the effect (see Fig. 4). It thus appears that the fast ions in the direction of the field in their near future acquire with increased probability high velocity components in transverse directions until their motion is randomized even more by the ion-atom collisions. This observation, further, elucidates the dynamic behavior of the correlations between v_z and v_x or v_y components. We turn now to the calculation of the third order diffusion component perpendicular to the field.

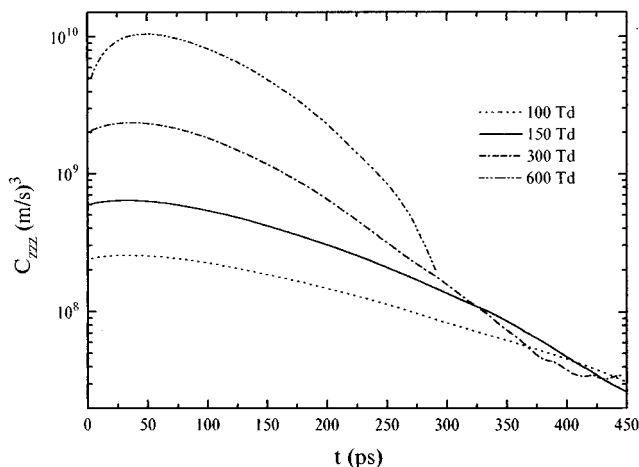


FIG. 2. Third order C_{ZZZ} correlation functions for K^+ in Ar at various field strengths.

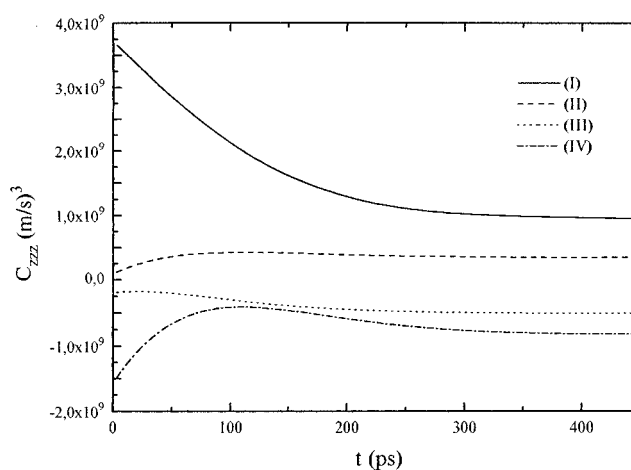


FIG. 3. C_{ZZZ} correlation functions of K^+ in Ar at 300 K at different velocity regions (I)–(IV) defined in with $v_0 = 2300$ m/s. During the simulation the mean number of the 500 ions in the regions were 93.14, 133.8, 172.7 and 100.3, respectively.

B. Third order diffusion coefficients

To obtain Q_{\perp} we have to integrate the corresponding correlation function of one of the nonvanishing Q_{ijk} , over six different regions of the time variables. Instead, since for example $Q_{\perp} = (1/3)(B+C+D)$ and by using the identities of the Appendix, we can as well obtain $Q_{\perp} = (1/6)\sum_n I_n^{(5)}$, where n represents all six ijk components. In this expression the space of integration is restricted to half of the first quadrant of the (s_1, s_2) plane, though the calculation of all six correlation functions is required. These functions, however, are easily determined simultaneously through the simulation procedure.

In order to extend the integration of the correlation functions to infinity we separate the integration into two parts. The first part, which includes the short-time region, is calculated arithmetically during the simulation and the second part analytically by first fitting the correlations below their inversion points with a two-time exponential function

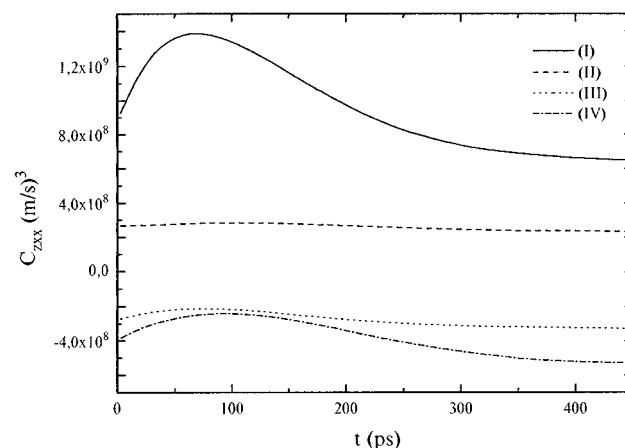


FIG. 4. Similar to Fig. 3 for C_{ZZX} .

TABLE I. Drift velocities, elementary velocity-correlation integrals and third order transverse diffusion coefficients of K^+ in Ar at 300 K.

$E/N(\text{Td})^a$	$v_d(\text{m/s})$	N^2B^b	N^2C^b	N^2D^b	$N^2Q_{\perp}^b$
30	213.6	0.1604	0.04508	0.1039	0.1031
60	462.8	1.327	0.3209	0.3728	0.6736
80	645.3	2.721	0.7269	0.8096	1.419
100	849.3	5.579	1.368	1.724	2.890
150	1314	10.113	2.516	2.474	5.034
200	1680	12.220	3.782	3.768	6.590
300	2314	18.205	4.525	4.371	9.034
400	2832	32.634	4.717	4.184	13.84
600	3617	65.830	6.956	6.366	26.38

^a1 Td = 10^{-21} V m².

^bIn units of 10^{33} cm⁻³ s⁻¹.

$$C_{ijk}(s_1, s_2) = (e^{-a_1s_1 - b_1} - e^{-a_2s_1 - b_2})s_2/s_1 + e^{-a_2s_1 - b_2}. \quad (9)$$

The fitting is found to be quite accurate and leads to final errors less than 1%–2%.

The resulting diffusion coefficients for different field strengths are presented in Table I as N^2Q_{\perp} in order for an expected inverse quadratic dependence on the gas density to be removed. We also present drift velocities as well as the three elementary integrals which contribute to the diffusion coefficient. The dependence of N^2Q_{\perp} on the field is shown in Fig. 5 together with N^2Q_{\parallel} , which has been calculated earlier via our procedure using the same interaction potential,⁵ for comparison.

The dominant contribution to the third order diffusion coefficients comes from the B integral as can be inferred by inspection of the magnitude of the relevant correlation functions that determine the integrals. Thus, B , C , and D are calculated from $I^{(5)}$ integrals involving $\langle \Delta v_z(0)\Delta v_x(t_1)\Delta v_x(t_2) \rangle$, $\langle \Delta v_x(0)\Delta v_z(t_1)\Delta v_x(t_2) \rangle$ and $\langle \Delta v_x(0)\Delta v_x(t_1)\Delta v_z(t_2) \rangle$, respectively. The first of these functions at specific time values is larger than the other two, because it involves a product of similar velocity components

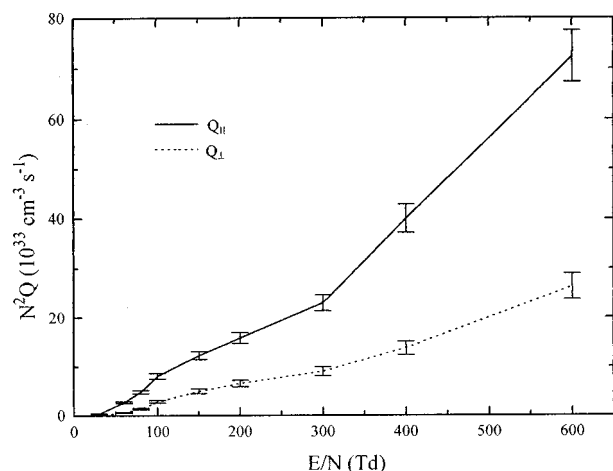


FIG. 5. Third order N^2Q_{\parallel} and N^2Q_{\perp} diffusion coefficients of K^+ in Ar at various field strengths with 7% and 10% error bars, respectively.

as functions of time which are more strongly correlated than $\Delta v_z(t_1)\Delta v_x(t_2)$ or $\Delta v_x(t_1)\Delta v_z(t_2)$, especially around $t_1 = t_2$.

Likewise, the accuracy of N^2Q_{\perp} depends mostly on the accuracy of B which consists of two parts each calculated with different accuracy. The first part, which involves the short time correlations, is calculated numerically with standard deviations equal to a few percent of the mean values and the second part which includes long time correlations is calculated through an interpolation with higher errors. Repeated calculations using variable length simulations and different initial conditions indicate that the overall relative error of the diffusion coefficient is about 10% at intermediate field strengths, which almost doubles at very small and large fields. This is because, at weak fields the mean values of the correlations vanish but the magnitudes of their fluctuations remain high. At strong fields, however, fluctuations become high due to frequent exchange of large amounts of energy during ion–neutral collisions. In general, the accuracy of the procedure can be improved with the use of longer runs and smaller time step in the simulation, though with the cost of high amount of computer time.

IV. CONCLUSIONS

We have shown that within our stochastic analysis only two independent components can be established for the third order diffusion coefficient of ions drifting in gases under the influence of a homogeneous electrostatic field. To complete the determination of Q components for the representative system of K^+ in Ar, we determined the Q_{\perp} from third order velocity correlation functions. The other third order component, Q_{\parallel} , has been determined similarly in the past using the same interaction potential.

The order of magnitude of our results and the fact that these coefficients contribute to the ion transport only at the very early relaxing stages, where high ion density gradients prevail, indicate that Q should interfere negligibly with drift tube experimental results in the case of K^+ in Ar.

The correlation functions were determined first from a nonequilibrium MD simulation of the motion of the ions. In general, the form of the derived correlation functions appears exponentially decaying except in the cases of $\langle \Delta v_z(0) \times \{\Delta v_x(t)\}^2 \rangle$, $\langle \Delta v_z(0)\{\Delta v_y(t)\}^2 \rangle$, and $\langle \Delta v_z(0) \times \{\Delta v_z(t)\}^2 \rangle$, where a nonmonotonic behavior at short times has been observed. This behavior is in compliance with the observed correlations between velocity components of Na^+ in Ne through analysis of the results of a Monte Carlo simulation in the past.⁸ In this sense, the present correlation functions quantify the dynamic behavior of the previously suggested correlations.

Although the systems studied so far involve ions and atoms of comparable mass, the observed effects should be general and thus present in other systems as well.

ACKNOWLEDGMENTS

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irreducible tensors. In addition, the computer time provided in a CONVEX C3820 computer by the Institute of Computer Science of the National University of Athens is gratefully acknowledged. This work was partially supported by grants from the National University of Athens, No. 70/4/2505, and from the Ministry of Industry and Development of Greece, No. 95EΔ/364.

APPENDIX

In order to integrate the t_1 variable of the integral of Eq. (5), we first split the integration of $(t_1, s_1=t_2 - t_1, s_2=t_3 - t_1)$ in six contributions so that $Q_{ijk} = \sum_{n=1}^6 J_{ijk}^{(n)}$, with

$$J_{ijk}^{(1)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_{-t}^0 ds_1 \int_0^{t+s_1} ds_2 \int_{-s_1}^{t-s_2} dt_1 N_{ijk}, \quad (\text{A1})$$

$$J_{ijk}^{(2)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_{-t}^0 ds_1 \int_{s_1}^0 ds_2 \int_{-s_1}^t dt_1 N_{ijk}, \quad (\text{A2})$$

$$J_{ijk}^{(3)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_{-t}^0 ds_1 \int_{-t}^{s_1} ds_2 \int_{-s_2}^t dt_1 N_{ijk}, \quad (\text{A3})$$

$$J_{ijk}^{(4)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t ds_1 \int_{s_1}^t ds_2 \int_0^{t-s_2} dt_1 N_{ijk}, \quad (\text{A4})$$

$$J_{ijk}^{(5)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t ds_1 \int_0^{s_1} ds_2 \int_0^{t-s_1} dt_1 N_{ijk}, \quad (\text{A5})$$

$$J_{ijk}^{(6)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t ds_1 \int_{-t+s_1}^0 ds_2 \int_{-s_2}^{t-s_1} dt_1 N_{ijk}, \quad (\text{A6})$$

with $N_{ijk} = \langle \Delta v_i(t_1) \Delta v_j(s_1) \Delta v_k(s_2) \rangle$ and $\Delta v(t) = v(t) - \langle v(t) \rangle$. The integrations over t_1 can now be performed in the limit of t going to infinity leading to six elementary integrals

$$I_{ijk}^{(1)} = \lim_{t \rightarrow \infty} \int_{-t}^0 ds_1 \int_0^{t+s_1} ds_2 N_{ijk}, \quad (\text{A7})$$

$$I_{ijk}^{(2)} = \lim_{t \rightarrow \infty} \int_{-t}^0 ds_1 \int_{s_1}^0 ds_2 N_{ijk}, \quad (\text{A8})$$

$$I_{ijk}^{(3)} = \lim_{t \rightarrow \infty} \int_{-t}^0 ds_1 \int_{-t}^{s_1} ds_2 N_{ijk}, \quad (\text{A9})$$

$$I_{ijk}^{(4)} = \lim_{t \rightarrow \infty} \int_0^t ds_1 \int_{s_1}^t ds_2 N_{ijk}, \quad (\text{A10})$$

$$I_{ijk}^{(5)} = \lim_{t \rightarrow \infty} \int_0^t ds_1 \int_0^{s_1} ds_2 N_{ijk}, \quad (\text{A11})$$

$$I_{ijk}^{(6)} = \lim_{t \rightarrow \infty} \int_0^t ds_1 \int_{-t+s_1}^0 ds_2 N_{ijk}, \quad (\text{A12})$$

where here we can set $N_{ijk} = \langle \Delta v_i(0) \Delta v_j(s_1) \Delta v_k(s_2) \rangle$, with s_1 and s_2 defined relative to the time origin of $\Delta v_i(0)$.

We can now utilize symmetries of the correlation functions and the (s_1, s_2) coordinates to prove that all nonvan-

ishing components of diffusion coefficients, except the Q_{ZZZ} component, are equal to one another. First, the simultaneous interchange of s_1 with s_2 and j with k in the above equations leads to identical I 's,

$$I_{XXZ}^{(k)} = I_{XXZ}^{(k')}, I_{ZZX}^{(k)} = I_{ZZX}^{(k')} \quad \text{and} \quad I_{ZZZ}^{(k)} = I_{ZZZ}^{(k')}, \quad (\text{A13})$$

when the pair (k, k') takes values from $\{(1, 6), (2, 3), (4, 5)\}$ and vice versa for interchanged k and k' . These identities hold also with Y in the position of X .

With the use of the above identities we can obtain three independent components for Q in compliance with a previous suggestion.² However, one more set of relations between elementary integrals can be identified reducing the number of independent Q components to two. Specifically, the interchange of the origin of time, t_1 , with s_1 and i with j leads to analogous identities,

$$I_{XXZ}^{(k)} = I_{XXZ}^{(k')}, I_{XXZ}^{(k)} = I_{XXZ}^{(k')} \quad \text{and} \quad I_{ZZZ}^{(k)} = I_{ZZZ}^{(k')}, \quad (\text{A14})$$

with (k, k') taking values from $\{(1, 4), (2, 5), (3, 6)\}$ and vice versa for interchanged k and k' . Similarly, these relations hold also with Y in the position of X . The proof of these identities is not as obvious as is in the previous case, Eq. (A13), and we present it in detail.

Without loss of generality we present the proof of one of the above identities,

$$I_{ZZX}^{(2)} = I_{ZZX}^{(5)},$$

or

$$\begin{aligned} & \int_{-t}^0 ds_1 \int_{s_1}^0 ds_2 \langle \Delta v_z(r) \Delta v_x(r+s_1) \Delta v_x(r+s_2) \rangle \\ &= \int_0^t ds'_1 \int_0^{s'_1} ds'_2 \langle \Delta v_x(r') \Delta v_z(r'+s'_1) \Delta v_x(r'+s'_2) \rangle, \end{aligned} \quad (\text{A15})$$

with t approaching infinity and where r and r' are arbitrary time variables since the correlations do not depend on the time origin. It is now possible through a linear transformation of the time variables,

$$r = r' + s'_1, s_1 = -s'_1 \quad \text{and} \quad s_2 = s'_2 - s'_1, \quad (\text{A16})$$

to transform $I^{(2)}$ to $I^{(5)}$. The first of the above equation relates the reference times over which the s -time variables are defined and the remaining two constitute a linear transformation rule. The same rule can be used also for the proof of the remaining identities of Eqs. (A14).

As a result, both sets of the above identities, Eqs. (A13) and (A14), render all the components of Q , other than Q_{ZZZ} , equal to one another and in addition equal to

$$Q_{\perp} \equiv \frac{1}{3}(B + C + D), \quad (\text{A17})$$

where for example $B = I_{ZZX}^{(4)}$, $C = I_{ZZX}^{(1)}$, and $D = I_{ZZX}^{(2)}$. For the Q_{ZZZ} component all six I integrals are equal to one another and thus we set $Q_{\parallel} = Q_{ZZZ} = A$, with for example $A = I_{ZZZ}^{(5)}$.

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