

Third-order transport properties of ion-swarms from mobility and diffusion coefficients

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Abstract

A method is presented for the calculation of third order transport properties of ions drifting in gases under the action of an electrostatic field with the use of mobility and ion-diffusion coefficients. The approach is based on a three-temperature treatment of the Boltzmann equation for the ion transport and follows the development of generalized Einstein relations (GER), between diffusion coefficients and mobility. The whole procedure is tested by comparison with numerical and molecular dynamics simulation results for three available alkali ion-noble gas systems. Extension to systems involving internal degrees of freedom and inelastic collisions is shown to follow the development of molecular GER.

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1. Introduction

The flux of a swarm of ions in low-density gases under the action of a homogeneous electrostatic field is analyzed in various terms, each depending on density gradients of different order (and rank) [1]. A zeroth order homogeneous term represents steady drift and the rest of the terms diffusional and high order transport motion of the ions. The latter contribution is described by high rank transport coefficients of certain symmetry due to the action of the electric field and the density gradients. Traditional drift-tube experiments have been interpreted without the consideration of high order transport [2], though it has been suspected to influence the motion of the ions [3].

However, since third order transport coefficients, \mathbf{Q} , are most likely to be the next transport coefficients to be measured, it is important to develop methods for their calculation. Such information can help in the design of future experiments as well as in the interpretation

of their results. Except from the analytic solution of kinetic theories for the ion transport [4,5], it is useful to develop relations between the ion transport properties that would enable most easily the calculation of high order transport coefficients from lower order ones, in analogy to generalized Einstein relations (GER) [6–9].

Here, we present such a method, which relates \mathbf{Q} to ion diffusion coefficients and mobility, based on a previously developed analytic solution of Boltzmann equation. It, thus, becomes possible through simple relations to calculate the \mathbf{Q} components from experimental ion transport data as a function of the field strength with minimal reference to the specific atomic ion–neutral interactions. This approach provides an extension of the procedure produced for the calculation of diffusion coefficients from mobility through the use of GER in the past [8,9].

The determination of all three independent Q_{ijk} components requires the introduction of certain symmetry properties to the moment equations. This is so, because the use of scalar products in the continuity equation for the determination of \mathbf{Q} , as is described below, hides the symmetry properties of the transport coefficients. To

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obtain all three components of \mathbf{Q} , we employ the symmetry scheme introduced in a three-temperature moment solution of the Boltzmann equation [5].

We mention that in the past a relation between high order transport coefficients and field derivatives of mobility and reaction rate constants for charged particle swarms has been obtained through the use of a momentum transfer theory, MMT [10]. This procedure was applied and tested at first for the reproduction of Q_{ZZZ} components of electrons in gases. A straightforward generalization for ions of arbitrary mass could be based on the procedure employed for the development of GER from MMT [7], though additional evaluation of intermediate quantities related to high order moments of the velocity distribution (v -distribution) function would be required. Unfortunately, procedures for the calculation of such moments have not been developed so far even for use in the GER. The present approach, however, as based on the Boltzmann kinetic equation is free from such restrictions though it may appear less accurate in the case of electrons in the same way the relevant approach of Waldman and Mason [8] produced transverse diffusion components, D_{\perp} , not compatible to experimental data. Part of this deficiency has been alleviated through the development of GER based on model calculations [11].

In the following, we first develop a method for the calculation of high-order moments of the v -distribution function and relevant transport coefficients from a three-temperature solution of the Boltzmann kinetic equation for the ions. Further, the procedure for the calculation of intermediate quantities, such as effective temperatures, is presented in terms of low order transport properties. Finally, we test the whole method against Q_{ZZZ} components obtained independently from the numerical solution of Boltzmann equation for Li^+ in He and Ar, as well as against nonequilibrium molecular dynamics simulation results for all three Q components of K^+ in Ar.

2. Theory

The macroscopic motion of a small amount of ions moving in low density gases under the action of a homogeneous electric field is characterized by a flux, \mathbf{J} , that can be analyzed in terms of a drift term, a diffusion term and higher order transport terms [1,2],

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

where n is the ion-number density and \mathbf{v}_d , \mathbf{D} , \mathbf{Q} , etc. are drift velocity, diffusion coefficient, third order transport coefficient, etc., respectively. The mobility, K , is defined through $K = |\mathbf{v}_d|/E$, where the field, \mathbf{E} , and the drift velocity are collinear. The diffusion coefficient is a diagonal second order tensor with two independent components $D_{XX} = D_{YY} \equiv D_{\perp}$ and $D_{ZZ} \equiv D_{\parallel}$ with the field in

the z -direction. Similarly, the \mathbf{Q} coefficient is a third order tensor with seven non-vanishing components. Three of the components are independent, $Q_{XZX} = Q_{XXZ} = Q_{YZY} = Q_{YYZ} \equiv Q_{\perp}$, $Q_{ZXX} = Q_{ZYY} \equiv Q_X$ and $Q_{ZZZ} \equiv Q_{\parallel}$, due to the symmetry of the ion motion and the irrelevance of the position of the gradient terms in the above expansion of \mathbf{J} .

In order to relate \mathbf{Q} to \mathbf{D} and K , we consider the moment equations obtained from the Boltzmann equation for the ion v -distribution function [5], $f(\mathbf{v})$,

$$n\langle J\psi \rangle = (q\mathbf{E}/m)n\langle \nabla_v \psi \rangle - \nabla(n\langle \mathbf{v}\psi \rangle) - \langle \psi \rangle \nabla(n\langle \mathbf{v} \rangle), \quad (2)$$

where ψ is an arbitrary function of the ion velocity \mathbf{v} , q and m are the charge and the mass of the ions, respectively. The brackets represent averages over the v -distribution function,

$$n\langle \psi \rangle = \int f(\mathbf{v})\psi(\mathbf{v})d\mathbf{v}, \quad (3)$$

where n is the ion-number density. Finally, J is the Boltzmann collision operator with the gas v -distribution function described by a Gaussian of certain temperature, T . This applies because in traditional drift tube experiments the neutral gas is in excess and can be considered to remain always at equilibrium. The above moment equations are derived under the assumptions that the ions do not interact with one another and that all moments are stationary and homogeneous except for the density, which can vary weakly in space.

To obtain relations between ion-transport coefficients we follow the method of Waldman and Mason [8] and consider the response of a reference case of spatially homogeneous ion transport, as described by Eq. (2) without spatial gradient terms, to the introduction of a density perturbation and a field variation. The final relations emerge from combination of the expansion coefficients of the perturbed moments of the v -distribution function, which relate directly to the transport coefficients.

Accordingly, first, the v -distribution function is expanded through a series of orthogonal polynomials [5,8,12], $\psi_{pqr}(\mathbf{v})$,

$$f(\mathbf{v}) = f^0(\mathbf{v}) \sum_{pqr} \alpha_{pqr} \psi_{pqr}(\mathbf{v}), \quad (4)$$

with

$$f^{(0)}(\mathbf{v}) = Z \exp(-w_x^2 - w_y^2 - w_z^2), \quad (5)$$

where Z is normalization factor and

$$w_x^2 = mv_x^2/2kT_{\perp}, \quad w_y^2 = mv_y^2/2kT_{\perp}, \quad (6)$$

$$w_z^2 = m(v_z - v_d)^2/2kT_{\parallel}. \quad (7)$$

Here, v_x , v_y , and v_z are cartesian velocity components of the ions. The basis functions are chosen to be

$$\psi_{pqr}(\mathbf{v}) = H_p(w_x)H_q(w_y)H_r(w_z), \quad (8)$$

where H_n are Hermite polynomials of order n . In general, the expansion coefficients are related to the moments of $f(\mathbf{v})$, $\langle \psi_{pqr} \rangle$, through

$$\alpha_{pqr} = N_{pqr}^{-1} \langle \psi_{pqr} \rangle, \quad (9)$$

with $N_{pqr} = 2^{p+q+r} p!q!r!$.

As reference case we consider a spatially homogeneous system for which the gradient terms in Eq. (2) vanish. For this case the parameters of $f^{(0)}(\mathbf{v})$ are given by

$$v_d = \langle v_z \rangle^0, \quad (10)$$

$$\frac{1}{2} kT_{\perp} = \frac{1}{2} m \langle v_x^2 \rangle^0 = \frac{1}{2} m \langle v_y^2 \rangle^0 \quad \text{and} \quad (11)$$

$$\frac{1}{2} kT_{\parallel} = \frac{1}{2} m \langle (v_z - v_d)^2 \rangle^0, \quad (12)$$

where the brackets $\langle \rangle^0$ denote averaging over the \mathbf{v} -distribution function of the reference case (not $f^{(0)}(\mathbf{v})$ [13]). These requirements imply that the a_{pqr} coefficients should be restricted so that $\alpha_{001} = \alpha_{010} = \alpha_{100} = \alpha_{002} = \alpha_{020} = \alpha_{200} = 0$, at this level of approximation.

The density perturbation is introduced through a series of density gradients [5],

$$n \langle \psi_{pqr} \rangle = n \langle \psi_{pqr} \rangle^0 - \sum_i \langle \psi_{pqr} \rangle_D^i \frac{\partial n}{\partial r_i} + \sum_{i,j} \langle \psi_{pqr} \rangle_Q^{ij} \frac{\partial^2 n}{\partial r_i \partial r_j}, \quad (13)$$

with indexes i, j and k representing x, y and z components. The second order density expansion moments, $\langle \psi_{pqr} \rangle_Q^{ij}$, must be invariant with respect to interchange of i and j since the order of differentiation of the density is irrelevant. The application of this expansions for $\psi_{100} = (2m/kT_{\perp})^{1/2} v_x$, $\psi_{010} = (2m/kT_{\perp})^{1/2} v_y$ and $\psi_{001} = (2m/kT_{\parallel})^{1/2} (v_z - v_d)$ and comparison to Eq. (1) furnishes the transport coefficients in terms of the density expansion moments. Then, the diffusion coefficients are given by

$$D_{\parallel} \equiv D_{ZZ} = \frac{1}{2\beta_{\parallel}} \langle \psi_{001} \rangle_D^Z, \quad (14)$$

$$D_{\perp} \equiv D_{XX} = \frac{1}{2\beta_{\perp}} \langle \psi_{100} \rangle_D^X = D_{YY} = \frac{1}{2\beta_{\perp}} \langle \psi_{010} \rangle_D^Y, \quad (15)$$

where $\beta_{\parallel, \perp} = (m/2kT_{\parallel, \perp})^{1/2}$ and the third order transport coefficients through

$$Q_{\parallel} = \frac{1}{2\beta_{\parallel}} \langle \psi_{001} \rangle_Q^{ZZ}, \quad (16)$$

$$Q_X = \frac{1}{2\beta_{\parallel}} \langle \psi_{001} \rangle_Q^{XX} \quad \text{and} \quad (17)$$

$$Q_{\perp} = \frac{1}{2\beta_{\perp}} \langle \psi_{100} \rangle_Q^{XZ} = \frac{1}{2\beta_{\perp}} \langle \psi_{100} \rangle_Q^{ZX}. \quad (18)$$

In the above equations X can be replaced by Y when in addition $\langle \psi_{100} \rangle$ is replaced by $\langle \psi_{010} \rangle$.

When expansions (13) are substituted into Eq. (2) taking into account the continuity equation,

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n \langle \mathbf{v} \rangle) = -\mathbf{v}_d \cdot \nabla n + \mathbf{D} : \nabla \nabla n - \mathbf{Q} : \nabla \nabla \nabla n + \dots, \quad (19)$$

three sets of moment equations are obtained; one for each of the moments, $\langle \psi_{pqr} \rangle^0$, $\langle \psi_{pqr} \rangle_D^i$ and $\langle \psi_{pqr} \rangle_Q^{ij}$. Since the first two sets of equations have been presented many times in the past [2,8,12], we present here only the one for the second order density perturbed moments [5] which are related to the components of \mathbf{Q} ,

$$\sum_{stu} b(pqr; stu) \langle \psi_{stu} \rangle_Q^{ij} = 2r\varepsilon \langle \psi_{pq(r-1)} \rangle_Q^{ij} + h_{pqr}^{ij}, \quad (20)$$

where

$$h_{pqr}^{ZZ} = (1/2N\beta_{\parallel}) [\langle \psi_{pq(r+1)} \rangle_D^Z + 2r \langle \psi_{pq(r-1)} \rangle_D^Z] - D_{ZZ} \langle \psi_{pqr} \rangle^0, \quad (21)$$

$$h_{pqr}^{XX} = (1/2N\beta_{\perp}) [\langle \psi_{(p+1)qr} \rangle_D^X + 2p \langle \psi_{(p-1)qr} \rangle_D^X] - D_{XX} \langle \psi_{pqr} \rangle^0, \quad (22)$$

$$h_{pqr}^{XZ} = (1/2N\beta_{\perp}) [\langle \psi_{(p+1)qr} \rangle_D^Z + 2p \langle \psi_{(p-1)qr} \rangle_D^Z], \quad (23)$$

$$h_{pqr}^{ZX} = (1/2N\beta_{\parallel}) [\langle \psi_{pq(r+1)} \rangle_D^X + 2r \langle \psi_{pq(r-1)} \rangle_D^X], \quad (24)$$

and $\varepsilon = (qE/N)(2mkT_{\parallel})^{-1/2}$. The collision operator matrix elements $b(pqr; stu)$ are

$$b(pqr; stu) = \int d\mathbf{v} f^{(0)} \psi_{stu} \mathcal{J} \psi_{pqr} / \int f^{(0)}(\mathbf{v}) \psi_{stu}(\mathbf{v})^2 d\mathbf{v}. \quad (25)$$

The $\langle \psi \rangle_Q^{ij}$ moments have to be determined under the following restrictions,

$$\begin{aligned} \langle \psi_{000} \rangle_Q^{ij} &= 0; & \langle \psi_{pqr} \rangle_Q^{ZZ} &= \langle \psi_{qpr} \rangle_Q^{ZZ}, \\ \langle \psi_{pqr} \rangle_Q^{XZ, ZX} &= 0 & \text{for all odd } q; \\ \langle \psi_{qpr} \rangle_Q^{ZZ, XX} &= 0 & \text{for all odd } p \text{ or } q. \end{aligned} \quad (26)$$

In addition, the irrelevance of the order of gradient terms in Eq. (1), requires Q_{ijk} to be symmetric under exchange of j and k indexes, or $h_{pqr}^{XZ} = h_{pqr}^{ZX}$. To induce this symmetry to the last two of the above equations we combine them and obtain a new equation for symmetrized moments $\langle \psi_{pqr} \rangle_Q^{XZ-ZX}$,

$$\sum_{stu} b(pqr; stu) \langle \psi_{stu} \rangle_Q^{XZ-ZX} = 2r\varepsilon \langle \psi_{pq(r-1)} \rangle_Q^{XZ-ZX} + h_Q^{XZ-ZX}, \quad (27)$$

with $h_Q^{XZ-ZX} = (h_{pqr}^{XZ} + h_{pqr}^{ZX})/2$. The Q_{\perp} component will then be obtained from $Q_{\perp} = \frac{1}{2\beta_{\perp}} \langle \psi_{100} \rangle_Q^{XZ-ZX}$. Alternatively, one can employ Eqs. (23) and (24) to calculate unsymmetrized $\langle \psi_{100} \rangle_Q^{ij}$ moments and obtain the actual component through

$$Q_{\perp} = \frac{1}{4\beta_{\perp}} (\langle \psi_{100} \rangle_Q^{XZ} + \langle \psi_{100} \rangle_Q^{ZX}). \quad (28)$$

The production of relations between mobility, diffusion coefficients and third order transport properties requires, additionally, the consideration of second order field variations to the homogeneous ion transport reference case. This is utilized through consideration of a field expansion of the moments of the v -distribution function

$$\langle \psi_{pqr} \rangle = \langle \psi_{pqr} \rangle^0 - \sum_i \langle \psi_{pqr} \rangle_E^i \delta E_i + \sum_{i,j} \langle \psi_{pqr} \rangle_E^{ij} \delta E_i \delta E_j. \quad (29)$$

The introduction of this equation into the moment equation (2) produces a set of equations for the field perturbed moments which are identical to Eq. (29) of Ref. [8]. We only mention that it is through these moments that the differential mobilities K' and K'' , with $K' = d \ln K / d \ln(E/N)$, are introduced into the procedure.

Before the above sets of equations are combined in a prediction scheme they have to be truncated. Here, we define the n th approximation by setting matrix elements $b(pqr;stu)$ in the homogeneous moment equations equal to zero when $p+q+r \geq n+2$, or $s+t+u \geq p+q+r+n$. For the first order perturbed moment equations the first restriction is replaced by $p+q+r \geq n+1$ and, similarly, for the second-order perturbed moments we set $p+q+r \geq n$. These considerations are consistent with previous truncation schemes of the three-temperature theory based on results of the Maxwell model where matrix elements vanish when $s+t+u > p+q+r$. This scheme has been proven useful for the calculation of ion transport properties [5,12].

3. Method

To design a procedure for the calculation of third order transport properties we employ the second approximation which has been used for the development of GER in the past [8,9]. Higher approximations require the calculation of a formidable large number of matrix elements which makes the method difficult to apply. For a high order approximation it is more useful to seek the full moment solution of the Boltzmann kinetic equation [4,5].

In the following we present the homogeneous and density perturbed moment equations which are necessary for the determination of Q coefficients. The field variation moment equations which assist in the coupling of the differential mobility to diffusion are omitted because their role has been analyzed in detail elsewhere [8] and only the relevant final results will be presented here.

Within the second approximation the homogeneous moment equations become

$$b(001;000) = 2\varepsilon, \quad (30)$$

$$b(200;000) + b(200;003)\langle \psi_{003} \rangle^0 + [b(200;201) + b(200;021)]\langle \psi_{201} \rangle^0 = 0, \quad (31)$$

$$b(002;000) + b(002;003)\langle \psi_{003} \rangle^0 + 2b(002;201)\langle \psi_{201} \rangle^0 = 0, \quad (32)$$

$$b(003;000) + b(003;003)\langle \psi_{003} \rangle^0 + 2b(003;201)\langle \psi_{201} \rangle^0 = 0, \quad (33)$$

$$b(201;000) + b(201;003)\langle \psi_{003} \rangle^0 + [b(201;201) + b(201;021)]\langle \psi_{201} \rangle^0 = 0. \quad (34)$$

As in previous applications, the first of the equations (30), is used to relate the value of an elementary matrix element with the field strength [8,9]. The next two of the equations (31) and (32), determine implicitly the effective temperatures, T_{\parallel} and T_{\perp} . Finally, the last two equations (33) and (34), will be employed for the calculation of the homogeneous moments, $\langle \psi_{003} \rangle^0$ and $\langle \psi_{201} \rangle^0$, which are needed in the density perturbed moment equations.

The corresponding equations for the perturbed moments in the z direction acquire the form,

$$b(001;001)\langle \psi_{001} \rangle_D^Z + b(001;002)\langle \psi_{002} \rangle_D^Z + 2b(001;200)\langle \psi_{200} \rangle_D^Z = 2t_{\parallel}, \quad (35)$$

$$[b(002;001) - 4\varepsilon]\langle \psi_{001} \rangle_D^Z + b(002;002)\langle \psi_{002} \rangle_D^Z + 2b(002;200)\langle \psi_{200} \rangle_D^Z = t_{\parallel}\langle \psi_{003} \rangle^0, \quad (36)$$

$$b(200;001)\langle \psi_{001} \rangle_D^Z + b(200;002)\langle \psi_{002} \rangle_D^Z + [b(200;200) + b(200;020)]\langle \psi_{200} \rangle_D^Z = t_{\parallel}\langle \psi_{201} \rangle^0, \quad (37)$$

and similarly, for the moments perturbed in the x direction, we have

$$b(100;100)\langle \psi_{100} \rangle_D^X + b(100;101)\langle \psi_{101} \rangle_D^X = 2t_{\perp}, \quad (38)$$

$$[b(101;100)\langle \psi_{100} \rangle_D^X - 2\varepsilon] + b(101;101)\langle \psi_{101} \rangle_D^X = t_{\perp}\langle \psi_{201} \rangle^0, \quad (39)$$

where $t_{\parallel,\perp} = (2kT_{\parallel,\perp}/m)^{1/2}/2N$. Equations (35) and (36) will be used for the calculation of $\langle \psi_{002} \rangle_D^Z$ and $\langle \psi_{200} \rangle_D^Z$, and equation (39) for the calculation of $\langle \psi_{101} \rangle_D^X$. These moments are needed at the next order density perturbed moment equations.

Finally, within the second approximation the second order density perturbed moments equations involve only one term,

$$b(001;001)\langle \psi_{001} \rangle_Q^{ZZ} = t_{\parallel}\langle \psi_{002} \rangle_D^Z, \quad (40)$$

$$b(001;001)\langle \psi_{001} \rangle_Q^{XX} = t_{\perp}\langle \psi_{101} \rangle_D^X, \quad (41)$$

$$b(100;100)\langle \psi_{100} \rangle_Q^{XZ} = t_{\perp}\langle \psi_{200} \rangle_D^Z, \quad (42)$$

$$b(100;100)\langle \psi_{100} \rangle_Q^{ZX} = t_{\parallel}\langle \psi_{101} \rangle_D^X. \quad (43)$$

By combining the above equations with Eqs. (16), (17) and (28) we obtain the basic relations of the present

procedure, between the components of \mathbf{Q} and density expansion moments,

$$Q_{\parallel} = \lambda_{\parallel} \langle \psi_{002} \rangle_D^Z, \quad (44)$$

$$Q_X = \lambda_{\parallel} (T_{\perp}/T_{\parallel})^{1/2} \langle \psi_{101} \rangle_D^X \quad \text{and} \quad (45)$$

$$Q_{\perp} = \lambda_{\perp} (\langle \psi_{200} \rangle_D^Z + (T_{\parallel}/T_{\perp})^{1/2} \langle \psi_{101} \rangle_D^X), \quad (46)$$

where $\lambda_{\parallel} = kT_{\parallel}/2mNb(001;001)$ and $\lambda_{\perp} = kT_{\perp}/4mNb(100;100)$.

It remains now to present in detail the procedure that can produce the density perturbed moments and the effective temperatures from mobility and diffusion coefficients. In order to accomplish this we have first to consider an approach to calculate the matrix elements of the relevant moment equations and effective temperatures, T_{\parallel} and T_{\perp} . Following an analytic approximation [8,9], the matrix elements can all be calculated through expansion in terms of a few elementary matrix elements and the use of certain ratios of collision integrals,

$$\tilde{A} \equiv [0, 0]^2/[0, 0]^1 \approx [p, q]^2/[p, q]^1, \quad (47)$$

$$\tilde{F} \equiv [0, 0]^3/[0, 0]^1 \approx [p, q]^3/[p, q]^1. \quad (48)$$

In addition, it has been inferred that only two elementary matrix elements contribute significantly in the calculations [9], and these have been approximated through

$$b(1) \equiv b(001;001) \approx 1, \quad (49)$$

$$b(2) \equiv b(100;100) \approx 1/(1 + \beta_{\parallel}K'), \quad (50)$$

$$\text{with } \beta_{\parallel} = \frac{1 - e}{1 + \frac{1}{2}eK'} \frac{1 + (1 - e)K'}{1 + (1 + \frac{1}{2}e)K'}, \quad (51)$$

where M is the mass of the neutral gas, $e = M/(m + M)$ and $K' = d \ln K/d \ln(E/N)$. The required effective temperatures are obtained from exposure of the implicit temperature dependence of the matrix elements of Eqs. (31) and (32), through the relations of Appendix A, and use of the above elementary matrix elements. The final closed form expressions for the effective temperatures [9] are

$$kT_{\parallel} = kT + \zeta_{\parallel} M v_d^2 (1 + \beta_{\parallel}K'), \quad (52)$$

$$kT_{\perp} = kT + \zeta_{\perp} M v_d^2, \quad (53)$$

$$\text{with } \zeta_{\perp} = \frac{(m + M)\tilde{A}}{4m + 3MA} \quad \text{and} \quad \zeta_{\parallel} = 1 - 2\zeta_{\perp}. \quad (54)$$

Having a closed set of moment equations, we can obtain the Q components from low-order ion-transport properties. Though we can base the calculation only on elementary properties such as the gas temperature and the mobility as a function of the field strength over the gas density (E/N), we prefer to use as input quantities the diffusion coefficients. This could eliminate additional uncertainty that would be introduced at the level of accuracy of the GER. Thus, we first calculate the effective temperatures, T_{\parallel} and T_{\perp} , from Eqs. (52) and (53), and all the required matrix elements from the rela-

tions of Appendix A and the two elementary matrix elements approximated through Eqs. (49) and (50). We then obtain the homogeneous velocity moments, $\langle \psi_{003} \rangle^0$ and $\langle \psi_{201} \rangle^0$, from Eqs. (33) and (34), and subsequently the density perturbed moments, $\langle \psi_{002} \rangle_D^Z$, $\langle \psi_{200} \rangle_D^Z$, and $\langle \psi_{101} \rangle_D^X$, through equations (35), (36) and (39). In the latter equations, the required $\langle \psi_{001} \rangle_D^Z$ and $\langle \psi_{100} \rangle_D^X$ moments are determined from diffusion coefficients through Eqs. (14) and (15). Finally, third order transport properties can be obtained from Eqs. (44)–(46).

Though the application of the second order approximation has been employed successfully for the calculation of diffusion coefficients through the GER, its accuracy for the calculation of third order transport properties requires independent testing especially since the moment equations for the Q components are of low order of approximation.

Before we turn to the testing of the procedure, we note that extension to molecular gases is straight forward following the development of molecular GER. These relations are based on the moment solution of the Wang Chang-Uhlenbeck-de Boer equation that is a generalization of the Boltzmann equation for internal degrees of freedom [9]. The relevant moment equations acquire the same structure with the present ones, though one more factor is needed in the basis functions of the expansion of the v -distribution function, Eq. (8), for the description of the contribution of the internal degrees of freedom. Finally, the calculation of complex matrix elements from elementary ones requires two additional ratios of collision integrals which have been found in the past to depend on the details of the inelastic interactions [9].

4. Applications

Instead of producing closed form expressions for the calculation of Q components, analogous to the GER for the diffusion coefficients, we prefer to determine them through the solution of two sets of 2×2 moment equations (33), (34) and (35), (36), for the homogeneous and density perturbed moments, respectively, ($\langle \psi_{pqr} \rangle^0$ and $\langle \psi_{pqr} \rangle_D^i$), in order to avoid further approximations.

Input parameters consist of mobility, its logarithmic field-derivative, diffusion components and two ratios of collision integrals, \tilde{A} and \tilde{F} . For the latter ratios, we use the values 0.85 and 1.2 recommended by Waldman and Mason [8]. At the level of approximation employed here, it is not necessary to employ a more elaborate parameterization scheme developed by these authors.

4.1. Li^+ in He and Ar

As input in our procedure for the calculation of Q components, we use experimental mobilities for Li^+ in

He [14–17], at 296 K, and in Ar [15,18], at 295 K, known within 1% and a few percent, respectively, and longitudinal diffusion coefficients, at 296 and 295 K, known within 5% in both cases [14,17,18]. The additionally required transverse diffusion coefficients are obtained from ratios to mobility, D_{\perp}/K [14,18,19] at 295 K, known within 2% and the employed mobility data. The resulting Q_{ZZZ} component is plotted in Figs. 1 and 2, as a function of E/N , together with accurate data obtained by Larsen et al. [4] for Li^+ in He and Ar, at 295 K, through solution of Boltzmann kinetic equation using a Kramers–Moyal expansion of the collision integral. The comparisons indicate reasonable agreement, especially for the low order of approximation employed

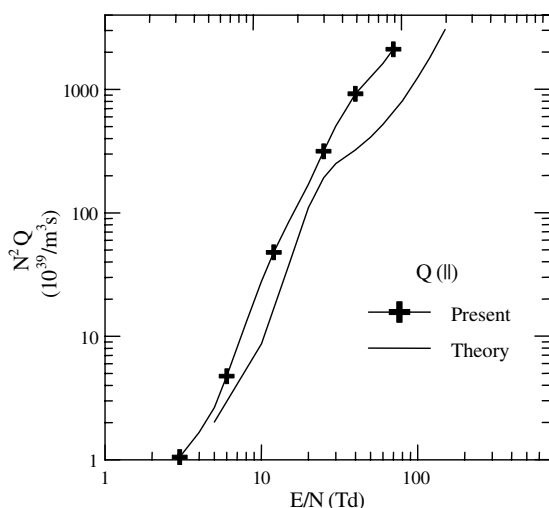


Fig. 1. Third order Q_{\parallel} component for Li^+ in He at 295 K as function of E/N ($1 \text{ Td} \equiv 10^{-17} \text{ V cm}^2$). Simple line represents Kramers–Moyal calculations and the symbols present results.

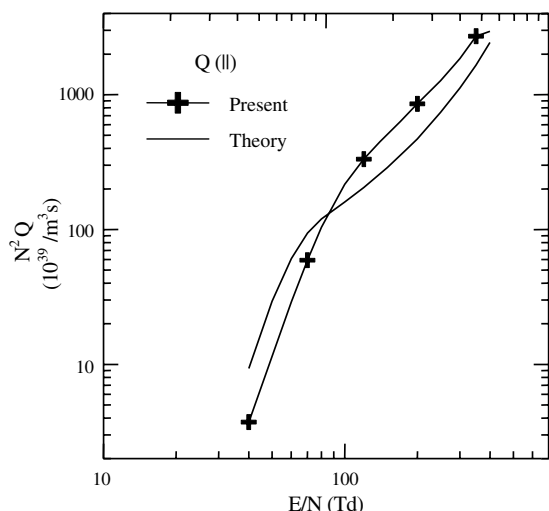


Fig. 2. Same as Fig. 1 for Li^+ in Ar at 295 K.

for the third order moment equation, Eq. (40). The overall accuracy depends partially on the uncertainty of the experimental diffusion coefficients and the ratios of collision integrals, \tilde{A} and \tilde{F} .

Though it seems that an improvement on these results can be obtained through consideration of the next (third) approximation of the kinetic theory, the increase of the complexity would render the method obsolete. This is so because 55 new complex matrix elements would have to be calculated from elementary matrix elements through analytic relations like the ones presented in Appendix A.

It should be noted that the magnitude of the observed deviations at this approximation was such as to permit the use of diffusion coefficients obtained through the GER [8,9]. Then the scheme would depend only on the mobility, its field derivative and the values of collision integral ratios \tilde{A} and \tilde{F} .

4.2. K^+ in Ar

Third order Q components for K^+ in Ar have been calculated through a nonequilibrium MD simulation of the ion motion using a universal interaction model potential [20–22]. The Q_{ZZZ} component has been obtained within 7% accuracy at intermediate field strengths and with double as much uncertainty at low and high field regions. In addition, another quantity that has been identified as the mean of the remaining components [22],

$$\bar{Q} = (Q_{ZZX} + Q_{XZZ} + Q_{XXZ})/3, \quad (55)$$

has been calculated with 10% accuracy at intermediate field strengths with increasing uncertainty at both sides of the known field region.

To test the reproduction of these Q components, Q_{ZZZ} and \bar{Q} , we use as input in our procedure diffusion coefficients parallel and perpendicular to the field, which are known within about 5–20% and 3%, respectively, [14,23–25] and two sets of experimental mobilities which are known within 0.5% and 2% accuracy [14,26–29]. The corresponding sets of data depending on the mobilities are denoted set I and set II.

Comparisons between calculations and molecular dynamics simulation data over a wide field range appear in Fig. 3. The present results are in good agreement with the simulation results for both sets of input data, with the deviations being smaller than those in the case of Li^+ . The increase of deviations at high field strengths should be due to the increase of the uncertainty of the input diffusion coefficients and the reference Q components.

The performance of the procedure allows us to proceed and test the reproduction of individual $Q_{\perp} = Q_{XZX} = Q_{XXZ}$ and $Q_X = Q_{ZXX}$ components, obtained through an interpretation of the MD simulation results according to which

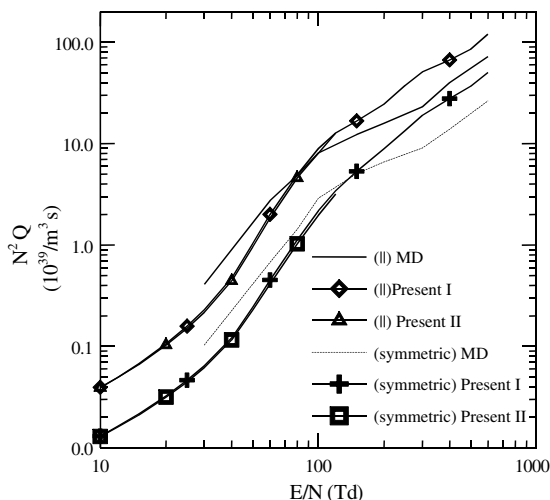


Fig. 3. Third order $Q_{||}$ and \bar{Q} components for K^+ in Ar, at 300 K, as function of E/N . Simple lines represent MD results, diamonds and crosses denote present results based on experimental data for K and K' of set I (Present I), and triangles and squares results based on data of set II (Present II).

$$\begin{aligned} Q_{\perp} &= (B + D)/2, \\ Q_x &= C, \end{aligned} \quad (56)$$

where B , C and D are integrals of two-time velocity correlation functions [5]. The Q_{\perp} component acquires the same accuracy with \bar{Q} , though Q_x , as being one order of magnitude smaller, is known less accurately.

Comparisons in Figs. 4 and 5 show agreement as in the previous case. This conformity is in line with the conjecture set forth for the symmetrization of MD simulation results [5].

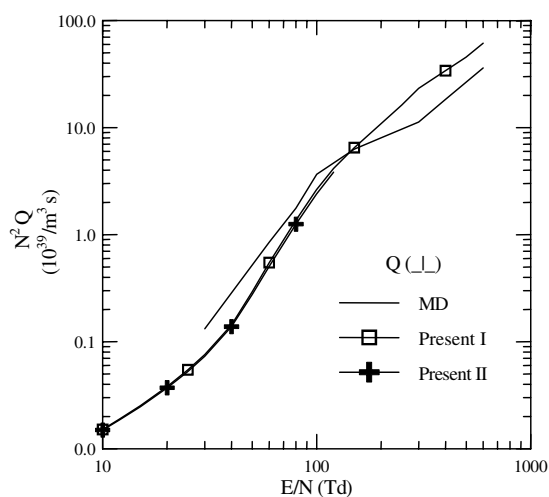


Fig. 4. Same as Fig. 3 for Q_{\perp} component, with simple lines representing MD results, squares results based on set I (Present I), and crosses results based on set II (Present II).

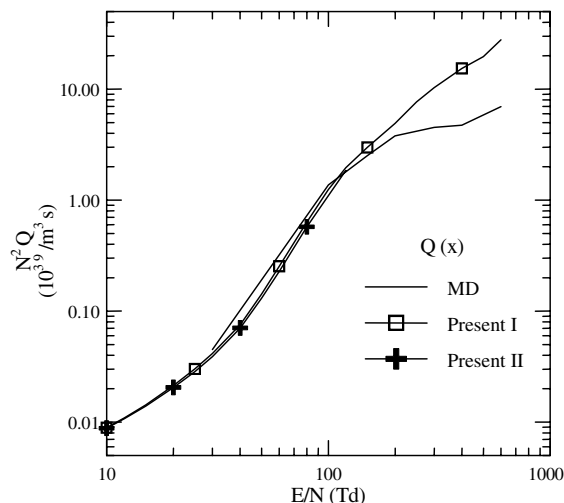


Fig. 5. Same as Fig. 4 for Q_x component.

5. Conclusions

A general procedure has been developed for the calculation of third order transport coefficients of ions in electrostatic fields based on the three-temperature treatment Boltzmann kinetic equation. The Q components are calculated through presently derived equations (44)–(46) in terms of density expansion moments. Eventually, the latter are determined through the use of mobility and diffusion coefficients as well as values of two ratios of collision integrals. Intermediate quantities required in the calculations, such as effective temperatures and velocity moments of the distribution function, are obtained through procedures developed in the past for the calculation of diffusion coefficients from GER. The testing was limited to only three available systems due to lack of knowledge of third order transport coefficients. The agreement was satisfactory for the order of approximation employed for the calculation of Q coefficient. The procedure is straightforwardly extendable to ions with internal degrees of freedom and inelastic collisions, though calculation of additional ratios of inelastic collision integrals is required. Such integrals appear in the GER for molecular systems and have been found to depend on the details of inelastic interactions.

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Appendix A

Here, we present the collision matrix elements required in the calculations in terms of one elementary collision integral, $b(2)$ approximated in Eq. (50), two collision integral ratios, \tilde{A} and \tilde{F} , and a few dimensionless parameters given below:

$$e \equiv M/(m+M), \quad \hat{v}_d \equiv (mv_d^2/2kT_{\parallel})^{1/2}, \\ R \equiv T_{\perp}/T_{\parallel}, d_{\perp,\parallel} \equiv MT_{\perp,\parallel}/(mT + MT_{\perp,\parallel}). \quad (\text{A.1})$$

The simplified expressions of the matrix elements are based on previous compilations except from the first two which are new:

$$b(101;100) = 2\hat{v}_d(1 - 2e + 3e\tilde{A}/2), \quad (\text{A.2})$$

$$b(101;101) = (1 - 2e + 3e\tilde{A}/2 + d_{\perp}) + (1 - d_{\perp})b(2), \quad (\text{A.3})$$

$$b(002;001) = 2\hat{v}_d(2 - 2e + e\tilde{A}) + 2e\hat{v}_d(\tilde{A} - 2)b(2), \quad (\text{A.4})$$

$$b(002;002) = (2 - 2e + e\tilde{A})b(2), \quad (\text{A.5})$$

$$b(002;200) = -e\tilde{A}R/2, \quad (\text{A.6})$$

$$b(200;001) = -(e\tilde{A}/R)\hat{v}_d[b(2) + 1], \quad (\text{A.7})$$

$$b(200;002) = -(e\tilde{A}/2R)b(2), \quad (\text{A.8})$$

$$b(200;200) + b(200;020) = 2 - 2e + e\tilde{A}/2, \quad (\text{A.9})$$

$$b(003;000) = 12e\hat{v}_d[\tilde{A} - 2 + e(1 - \tilde{A} + \tilde{F}/3)(d_{\parallel}^{-1} + 2\hat{v}_d^2) \\ + eRd_{\perp}^{-1}(1 + \tilde{A} - \tilde{F})] + 12e\hat{v}_d[\tilde{A} - 2 + 2ed_{\parallel}^{-1} \\ \times (1 - \tilde{A} + \tilde{F}/3)]b(2), \quad (\text{A.10})$$

$$b(003;003) = 3[1 + e(\tilde{A} - 2) + e^2(1 - \tilde{A} + \tilde{F}/3)]b(2), \quad (\text{A.11})$$

$$b(003;201) = 3e^2R(1 - \tilde{F})b(2)/2 - 3e(1 - e)\tilde{A}R/2, \quad (\text{A.12})$$

$$b(201;000) = 2e\hat{v}_d[-8 + 6\tilde{A} - \tilde{A}/R + e(1 + \tilde{A} - \tilde{F}) \\ \times (d_{\parallel}^{-1} + 2\hat{v}_d^2)/R + ed_{\perp}^{-1}(5 - 7\tilde{A} + 3\tilde{F})] \\ + 2e\hat{v}_d[-\tilde{A} + 2ed_{\parallel}^{-1}(1 + \tilde{A} - \tilde{F})]b(2)/R, \quad (\text{A.13})$$

$$b(201;003) = (e/2R)[e(1 + \tilde{A} - \tilde{F}) - \tilde{A}]b(2), \quad (\text{A.14})$$

$$b(201;201) + b(201;021) = (1 - e)^2b(2) + 2 + e(7\tilde{A}/2 - 4) \\ + e^2(3 - 7\tilde{A} + 3\tilde{F})/2. \quad (\text{A.15})$$

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