Third-order transport coefficients for charged particle swarms

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Momentum-transfer theory has been used to obtain a relationship between the *n*th order tensorial transport coefficients in a swarm experiment, the $(n-1)$th derivative of the mobility, and the *n*th derivative of the reaction rate coefficient. Elastic, inelastic, and reactive collisions for gas mixtures have been taken into consideration. Numerical comparisons show that the results obtained from this relationship are in good agreement with those obtained by solution of the Boltzmann equation. Finally, we have analyzed the structure of the third-order tensorial transport coefficient by applying momentum-transfer theory and group theory; both approaches show that in general there are three independent components of this rank-three tensor. *© 1999 American Institute of Physics.* [S0021-9606(99)50805-2]

I. INTRODUCTION

Higher order transport coefficients generally have been ignored in the analysis of electron and ion swarm data. For electrons, only one experimenter claims to have observed a small effect from a higher order than diffusion.[1] A separate experiment[2] was aimed at obtaining reliable data for drift velocities, diffusion coefficients, and skewness, but failed[3] because well-defined arrival time spectra of the electrons could not be obtained. The theory developed to analyze the data from that experiment and the corresponding Monte Carlo simulations[4] remain as the only published data on skewness of electron swarms. The primary reason for the lack of accurate experimental data for higher order transport coefficients is that most experiments are designed to obtain very accurate lower order coefficients and thus operate under conditions where the effects of higher order coefficients are negligible.[5]

A wealth of data now exists[6–9] about ion transport coefficients. These data can be accessed on the Internet[10] at newton.slu.edu once the username and password are obtained from viehland@ions.slu.edu The database also includes hundreds of sets of transport coefficients that have been calculated from accurate models of the ion–neutral interaction potentials using Monte Carlo simulations[11,12] and numerical solutions[13] to the Boltzmann equation. Nevertheless, little is known about ion transport coefficients of higher order than diffusion except for some speculations in a figure caption[14] about the small difference between the shapes of the experimental data and analytic forms of the arrival time spectra.

The transport coefficient that is one order higher than the diffusion coefficient is the one most likely to be measured in the near future. Numerical solutions of the Boltzmann equation will be necessary to compare such measurements with predictions based on information about the ion–neutral collision cross sections and interaction potentials. However, it is important to have analytical formulas available in order to get a better physical insight, to analyze the structure of the transport coefficient tensors on the basis of symmetry considerations, and to guide both the experimental developments and the analysis of the data. Providing such formulas and testing them numerically are two of the purposes of this paper. The third purpose is to understand the difference between the results of Koutselos, who found[15] that there are only two independent components in the transport coefficient tensor one order higher than the diffusion coefficient, and those of earlier analyses[16,17] that predicted three independent terms.

II. THEORETICAL EVALUATION OF HIGHER ORDER TRANSPORT COEFFICIENTS

A. Background

Momentum transfer theory (MTT) has been developed, mostly through the efforts of Robson and co-workers,[18,19] to provide a simple method for obtaining analytical formulas with reasonable numerical accuracy. The theory has been applied to study ion transport in pure gases and mixtures,[20,21] electron transport with conservative[22] and nonconservative collisions,[18,19,23] and even to describe muon transport.[24] One of the particular advantages of MTT is that it provides a way to develop generalized Einstein relations (GERs) that are analytic relations between diffusion coefficients and mobility.

Recently, two of the present authors have developed (in a paper[25] hereafter designated as I) an extended version of MTT that includes all of the elements required to describe the transport of electrons or ions in mixtures of gases with nonconservative processes. This MTT may be regarded as a technique to simplify the calculation of the particle energy distribution function and consequently of transport and rate coefficients. The analytic forms that are obtained are more general than the approximations involved in representing the collisional frequencies and may be used with more accu-

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rately calculated or measured collision rates and other transport data. Thus we claim that these forms, including the GERs, have a general meaning that extends beyond the MTT as a technique for calculation.

Paper I allows us to consider high-order gradients of the number density, and high-order transport coefficients. There is a degree of confusion in labeling the transport coefficient that is one order higher than the diffusion coefficient. It has been called the ''third-order diffusion'' coefficient in recent literature,[15] but this term is confusing because it implies that it is the coefficient two orders beyond diffusion. We shall use the term third-order transport coefficient because it is a tensor of rank three and because it is the coefficient of the third gradient of the number density in the extension of the diffusion equation to high orders. (The drift velocity is the coefficient of the first gradient and the diffusion tensor of rank two is the coefficient of the second gradient.)

Confusion also arises about the meaning of the term skewness. Here we shall use this term to refer exclusively to one of the components of the third-order transport coefficient. This meaning is completely different from that used in the ion transport literature[11,12] and the previously mentioned database,[10] where skewness describes the asymmetric distortion of the ion distribution function that occurs at high electric field strengths but in the absence of ion density gradients.

The analogues of the GERs derived in this paper should not be confused with some apparently similar relations[11,12,26–28] obtained by expanding the transport coefficients in powers of the square of the electric field strength. Our relations consider only Fickian higher-order transport coefficients, but the electrostatic field **E** may be arbitrarily large and the mobility K and all components of the higher-order transport tensors may depend strongly on **E**.

B. Basic equations

Consider a swarm of particles of charge e and mass m moving through a l-component gas mixture of number density n_0 under the influence of **E**. The collision processes of interest are limited to elastic, inelastic, and reactive (which include attachment and ionization) collisions of individual swarm particles with neutral gas molecules. As in I, it is assumed that the stage of evolution of the swarm is the hydrodynamic limit (HDL). In the HDL, the space ($\mathbf{r}$) and time (t) dependence of all properties is carried by the number density, $n(\mathbf{r},t)$, of the charged particles and the swarm can be characterized by time-independent transport coefficients.

The starting point of the hydrodynamic description is the continuity equation,

$$\frac{\partial}{\partial t}n(\mathbf{r},t)+\frac{\partial}{\partial \mathbf{r}}\cdot[n(\mathbf{r},t)\langle \mathbf{v}\rangle^{\mathrm{mix}}]=-n(\mathbf{r},t)\tilde{\nu}^*, \tag{1}$$

which describes the change in $n(\mathbf{r},t)$ due to the nonreactive particle flux, $n(\mathbf{r},t)\langle \mathbf{v}\rangle^{\mathrm{mix}}$, and the reaction described by $-n(\mathbf{r},t)\tilde{\nu}^*$. The assumption is made that both of these quantities can be expressed as power series in the gradient operator $\partial/(\partial\mathbf{r})$ with coefficients that are constant, except for a possible dependence upon **E** that is left implicit for the moment. Equation (1) may then be expressed as[29]

$$\left[\frac{\partial}{\partial t}-\sum_{k=0}^{\infty}\hat{\boldsymbol{\omega}}^{(k)}\odot\left(-\frac{\partial}{\partial \mathbf{r}}\right)^k\right]n(\mathbf{r},t)=0. \tag{2}$$

The quantities $\hat{\boldsymbol{\omega}}^{(k)}$ are tensorial transport coefficients of order k, and $\odot$ indicates a k-fold scalar product. By truncating Eq. (2) at $k=3$, we obtain

$$\left[\frac{\partial}{\partial t}+\mathbf{W}^{\mathrm{mix}}\cdot\frac{\partial}{\partial \mathbf{r}}-\hat{\mathbf{D}}^{\mathrm{mix}}\cdot\frac{\partial}{\partial \mathbf{r}}\frac{\partial}{\partial \mathbf{r}}+\hat{\mathbf{Q}}^{\mathrm{mix}}\odot\frac{\partial}{\partial \mathbf{r}}\frac{\partial}{\partial \mathbf{r}}\frac{\partial}{\partial \mathbf{r}}\right]n(\mathbf{r},t)$$
$$=-\rho^*n(\mathbf{r},t), \tag{3}$$

where we identify $\rho^*=-\hat{\boldsymbol{\omega}}^{(0)}$ as the reaction rate, $\mathbf{W}^{\mathrm{mix}}=\hat{\boldsymbol{\omega}}^{(1)}$ as the drift velocity, $\hat{\mathbf{D}}^{\mathrm{mix}}=\hat{\boldsymbol{\omega}}^{(2)}$ as the diffusion tensor and $\hat{\mathbf{Q}}^{\mathrm{mix}}=\hat{\boldsymbol{\omega}}^{(3)}$ as the third-order transport coefficient tensor.

The momentum balance equation in HDL with a gas mixture is Eq. I-(43),

$$\langle \mathbf{v}\rangle^{\mathrm{mix}}=\boldsymbol{\omega}^{\mathrm{mix}}\left(\mathbf{E}-\frac{k_B}{e}\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}\right), \tag{4}$$

where the quantity in braces is the argument of the function $\boldsymbol{\omega}^{\mathrm{mix}}$. The energy balance equation for charged particles colliding with molecules of type α is Eq. I-(44),

$$\langle\langle \epsilon_\alpha\rangle\rangle_\alpha^{\mathrm{mix}}=\epsilon_\alpha^{\mathrm{mix}}\left(\mathbf{E}-\frac{k_B}{e}\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}\right),\quad \alpha=1,..,l, \tag{5}$$

where the quantity in braces is the argument of the function. In these equations k_B is Boltzmann constant and

$$\mathbf{G}(\mathbf{r},t)=\frac{1}{n(\mathbf{r},t)}\frac{\partial}{\partial \mathbf{r}}n(\mathbf{r},t), \tag{6}$$

is the (logarithmic) number density gradient. The temperature tensor $\hat{\mathbf{T}}^{\mathrm{mix}}$ appearing on the right side of Eqs. (4) and (5) is defined by

$$k_B\hat{\mathbf{T}}^{\mathrm{mix}}=m\langle(\mathbf{v}-\langle \mathbf{v}\rangle^{\mathrm{mix}})(\mathbf{v}-\langle \mathbf{v}\rangle^{\mathrm{mix}})\rangle^{\mathrm{mix}}. \tag{7}$$

One should note that the temperature tensor is assumed to be symmetric with components T_{ij}^{mix} in an arbitrary orthonormal basis $(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3)$ of a three-dimensional Euclidean space. Moreover, functions $\boldsymbol{\omega}^{\mathrm{mix}}$ and $\epsilon_\alpha^{\mathrm{mix}}$ are, respectively, the average velocity and energy (in the center-of-mass frame with respect to species α) under spatially uniform conditions; these quantities are found by solving the system of nonlinear equations, Eqs. I-(41) and I-(42), for a given value of the electric field. Since the reaction rate $\tilde{\nu}^*$ depends only upon the set of energies $\epsilon_\alpha^{\mathrm{mix}}$, $\alpha=1,..,l$, it also is a function of $\mathbf{E}-(k_B/e)\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}$; it is given by Eq. I-(45),

$$\tilde{\nu}^*=\alpha^*\left(\mathbf{E}-\frac{k_B}{e}\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}\right). \tag{8}$$

Further information about these basic equations is available in paper I.

C. Higher order transport coefficients

Our first aim is to derive *relationships* between experimentally measured quantities. In particular, the aim is to obtain semiquantitative relations between the third- and the lower-order transport coefficients in HDL, where **G** is small.

Therefore, we expand functions $\boldsymbol{\omega}^{\text{mix}}$ and α^* in a Taylor series and keep only the terms in second and third order in $\mathbf{G}$, respectively. Substituting these expansions into the equation of continuity, Eq. (1), leads, after some mathematics given in the Appendix, to the extended diffusion equation, Eq. (3), and to specific expressions for the drift velocity, diffusion tensor, and third-order transport coefficient tensor. The components of the drift velocity become

$$W_i^{\text{mix}}(\mathbf{E}) = \omega_i^{\text{mix}}(\mathbf{E}) - \frac{k_B}{e}\sum_{j=1}^{3} T_{ij}^{\text{mix}} \frac{\partial}{\partial E_j}\alpha^*(\mathbf{E}). \tag{9}$$

Similarly, the components of the diffusion tensor become

$$D_{ij}^{\text{mix}}(\mathbf{E}) = \frac{k_B}{e}\sum_{k=1}^{3} T_{ik}^{\text{mix}} \frac{\partial}{\partial E_k}\omega_j^{\text{mix}}(\mathbf{E}) - \frac{1}{2}\left(\frac{k_B}{e}\right)^2 \times \sum_{k=1}^{3} T_{ik}^{\text{mix}} \sum_{l=1}^{3} T_{jl}^{\text{mix}} \frac{\partial}{\partial E_l}\frac{\partial}{\partial E_k}\alpha^*(\mathbf{E}), \tag{10}$$

which may be expressed in terms of the drift velocity as

$$D_{ij}^{\text{mix}}(\mathbf{E}) = \frac{k_B}{e}\sum_{k=1}^{3} T_{ik}^{\text{mix}} \frac{\partial}{\partial E_k} W_j^{\text{mix}}(\mathbf{E}) + \frac{1}{2}\left(\frac{k_B}{e}\right)^2 \times \sum_{k=1}^{3} T_{ik}^{\text{mix}} \sum_{l=1}^{3}\left[2\frac{\partial}{\partial E_k}\left(T_{jl}^{\text{mix}}\frac{\partial}{\partial E_l}\alpha^*(\mathbf{E})\right) - T_{jl}^{\text{mix}}\frac{\partial}{\partial E_k}\frac{\partial}{\partial E_l}\alpha^*(\mathbf{E})\right]. \tag{11}$$

Finally, the components of the third-order transport coefficient tensor become

$$Q_{ijk}^{\text{mix}}(\mathbf{E}) = \frac{1}{2}\left(\frac{k_B}{e}\right)^2 \sum_{l=1}^{3} T_{il}^{\text{mix}} \sum_{m=1}^{3} T_{jm}^{\text{mix}} \frac{\partial}{\partial E_m}\frac{\partial}{\partial E_l}\omega_k^{\text{mix}}(\mathbf{E}) - \frac{1}{6}\left(\frac{k_B}{e}\right)^3 \sum_{l=1}^{3} T_{il}^{\text{mix}} \sum_{m=1}^{3} T_{jm}^{\text{mix}} \sum_{n=1}^{3} T_{kn}^{\text{mix}} \times \frac{\partial}{\partial E_n}\frac{\partial}{\partial E_m}\frac{\partial}{\partial E_l}\alpha^*(\mathbf{E}), \tag{12}$$

which may be expressed in terms of the drift velocity as

$$Q_{ijk}^{\text{mix}}(\mathbf{E}) = \frac{1}{2}\left(\frac{k_B}{e}\right)^2 \sum_{l=1}^{3} T_{il}^{\text{mix}} \sum_{m=1}^{3} T_{jm}^{\text{mix}} \frac{\partial}{\partial E_m}\frac{\partial}{\partial E_l} W_k^{\text{mix}}(\mathbf{E}) + \frac{1}{6}\left(\frac{k_B}{e}\right)^3 \sum_{l=1}^{3} T_{il}^{\text{mix}} \sum_{m=1}^{3} T_{jm}^{\text{mix}} \times \sum_{n=1}^{3}\left[3\frac{\partial}{\partial E_l}\frac{\partial}{\partial E_m}\left(T_{kn}^{\text{mix}}\frac{\partial}{\partial E_n}\alpha^*(\mathbf{E})\right) - T_{kn}^{\text{mix}}\frac{\partial}{\partial E_l}\frac{\partial}{\partial E_m}\frac{\partial}{\partial E_n}\alpha^*(\mathbf{E})\right]. \tag{13}$$

It should also be noted that the net average reaction rate is evaluated from

$$\rho^* = \alpha^*(\mathbf{E}) = \tilde{\nu}^*(\epsilon_1^{\text{mix}}(\mathbf{E}),..,\epsilon_l^{\text{mix}}(\mathbf{E})) = \tilde{\nu}^{(A)}(\epsilon_1^{\text{mix}}(\mathbf{E}),..,\epsilon_l^{\text{mix}}(\mathbf{E})) - \tilde{\nu}^{(I)}(\epsilon_1^{\text{mix}}(\mathbf{E}),..,\epsilon_l^{\text{mix}}(\mathbf{E})), \tag{14}$$

where $\tilde{\nu}^{(A)}$ and $\tilde{\nu}^{(I)}$ denote the total rates for attachment (A) and ionization (I) [see Eqs. I-(5) and I-(14)].

Equation (11) is a generalized Einstein relation appropriate to reacting particle swarms, while Eq. (13) plays the same role for the third-order transport coefficient that the GERs play for diffusion. Equation (13) establishes the *form* of the relationship between $\hat{\mathbf{Q}}^{\text{mix}}$, $\mathbf{W}^{\text{mix}}$ and α^*; it is also possible to give a similar equation for the relationship of the third-order transport coefficient to the diffusion tensor and reaction rates. Relations (11) and (13) are most useful in an empirical context: From measurements of the drift velocity $\mathbf{W}^{\text{mix}}$ and the reaction rate α^* as a function of reduced electric field E/n_0, it is possible to predict the diffusion coefficients and skewness, as long as the temperature tensor $\hat{\mathbf{T}}^{\text{mix}}$ can be evaluated from higher order moment equations. The reactive term can be simplified further, both for $\hat{\mathbf{D}}^{\text{mix}}$ and $\hat{\mathbf{Q}}^{\text{mix}}$, if we assume that $\hat{\mathbf{T}}^{\text{mix}}$ is independent of $\mathbf{E}$; then Eq. (11) becomes identical to Eq. (5.24) of Robson.[18]

Using a similar procedure as above, the following relation for the tensorial transport coefficient of the order $k>1$ can be obtained:

$$\omega_{i_l\cdots i_k}^{(k)}(\mathbf{E}) = \frac{1}{(k-1)!}\left(\frac{k_B}{e}\right)^{k-1} \sum_{j_1=1}^{3} T_{i_1 j_1}^{\text{mix}}\cdots \times \sum_{j_{k-1}=1}^{3} T_{i_{k-1}j_{k-1}}^{\text{mix}} \frac{\partial}{\partial E_{j_1}}\cdots\frac{\partial}{\partial E_{j_{k-1}}} W_{i_k}^{\text{mix}}(\mathbf{E}) + \frac{1}{k!}\left(\frac{k_B}{e}\right)^{k} \sum_{j_1=1}^{3} T_{i_1 j_1}^{\text{mix}}\cdots\sum_{j_{k-1}=1}^{3} T_{i_{k-1}j_{k-1}}^{\text{mix}} \times \sum_{j_k=1}^{3}\left[k\frac{\partial}{\partial E_{j_1}}\cdots\frac{\partial}{\partial E_{j_{k-1}}}\left(T_{i_k j_k}^{\text{mix}}\frac{\partial}{\partial E_{j_k}}\alpha^*(\mathbf{E})\right) - T_{i_k j_k}^{\text{mix}}\frac{\partial}{\partial E_{j_1}}\cdots\frac{\partial}{\partial E_{j_k}}\alpha^*(\mathbf{E})\right], \quad i_1,\cdots,i_k=1,2,3. \tag{15}$$

This result leads to the general conclusion that kth order transport coefficient tensor ($k\geqslant 2$) depends upon the ($k-1$)th derivative of the drift velocity and the kth derivative of the reaction rate coefficient with respect to the electric field.

In the derivation of Eqs. (4) and (5) in paper I, it was assumed that the heat flux in the energy balance equation can be neglected. Since this assumption is decreasingly valid as the swarm particles have larger mass, one may expect that Eqs. (11), (13), and (15) are not correct in cases where the mass of the swarm particle is comparable with the mass of the gas atoms. Using MTT, Robson[30] has established that Eq. (11) is inadequate for an accurate description of the ion transport in such cases. He showed that an additional factor involving the heat flux must appear in the GER for diffusion. By similar arguments, a correction for Eq. (13) may be developed, but this will not be attempted here.

III. CALCULATIONS FOR ELECTRONS IN RARE GASES

The components of the third-order transport coefficient tensor $\hat{\mathbf{Q}}^{\mathrm{mix}}$ can be evaluated from knowledge of the drift velocity, diffusion coefficients, and reaction rate coefficients using Eq. (13). The only data for $\hat{\mathbf{Q}}^{\mathrm{mix}}$ available in the literature are the calculations for electrons in He, Ne, and Ar performed by Penetrante and Bardsley.[4] Therefore, in this section we will present calculation of the third-order transport coefficients for electrons in these pure gases in which reactions do not occur.

We consider values of E/n_0 for which the mean electron energies are well below the first inelastic threshold. In this case, the distribution of electron velocities is nearly isotropic. This observation allows us to greatly simplify Eq. (13) by dropping the references to mixtures and setting

$$T_{ij}=T\delta_{ij}\approx\frac{2\epsilon}{3k_B}\delta_{ij}, \tag{16}$$

where $\epsilon\approx(m/2)\langle\mathbf{v}^2\rangle$. This simplifies Eq. (13) to

$$Q_{ijk}=\frac{1}{2}\left(\frac{k_BT}{e}\right)^2\frac{\partial}{\partial E_j}\frac{\partial}{\partial E_i}W_k. \tag{17}$$

If the electric field $\mathbf{E}$ is aligned with the positive $\mathbf{e}_3$ axis, then the ion drift velocity is directed along the negative $\mathbf{e}_3$ axis and the longitudinal component of the third-order transport coefficient (the skewness) is obtained from Eq. (17) as

$$Q_L\equiv Q_{333}=-\frac{1}{2}\left(\frac{k_BT}{e}\right)^2\frac{\partial^2W}{\partial E^2}. \tag{18}$$

Finally, combining Eqs. (16) and (18) yields

$$Q_L=-\frac{2\epsilon^2}{9e^2}\frac{\partial^2W}{\partial E^2}. \tag{19}$$

In the first, most straightforward, application of the results in this section we consider light swarm particles in a cold gas, neglect inelastic and reactive processes, and assume (the hard-sphere model) a constant elastic cross section, $\sigma^{(\mathrm{el})}=\sigma^0/4\pi$. Following the procedure in Sec. II of paper I for finding transport coefficients, the drift velocity can be written in the analytical form:

$$W=e^{1/2}\left(\frac{m+m_0}{mm_0^2}\right)^{1/4}\left(\frac{E}{n_0\sigma^0}\right)^{1/2}. \tag{20}$$

Differentiating Eq. (20) with respect to the electric field E and inserting the result in Eq. (19) gives

$$n_0^2Q_L=\frac{e^{1/2}m_0^2}{72}\left(\frac{m+m_0}{mm_0^2(\sigma^0)^2}\right)^{5/4}\left(\frac{E}{n_0}\right)^{1/2}. \tag{21}$$

This formula, obtained by a different technique, is explicitly given in Ref. 5. Thus we may conclude that the GER for skewness under the standard assumptions produces the well-established formula for the constant collision cross section.

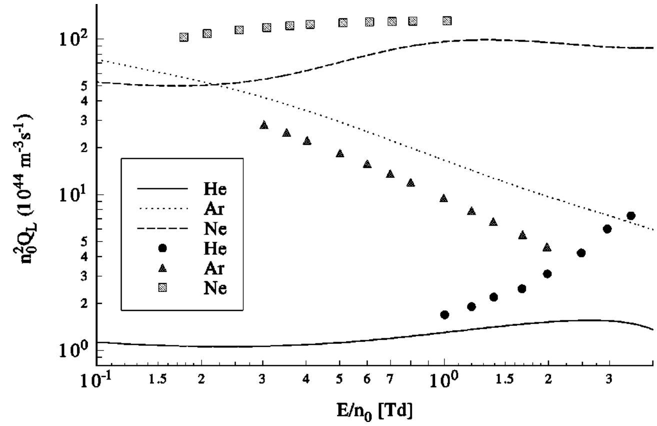

FIG. 1. Comparison of the skewness coefficients calculated by solving the Boltzmann equation (points) and by using Eq. (19) (lines).

As the second example we calculate the skewness Q_L as a function of E/n_0 for electrons in He, Ne, and Ar, using the cross sections for rare gases from the recommendations of the JILA (Joint Institute for Laboratory Astrophysics of the University of Colorado, Boulder) Data Center.[31] Results based on Eq. (19) are compared with those obtained[4] from solutions of the Boltzmann equation in Fig. 1. In general, the agreement is good, especially since the present results are obtained by numerically differentiating two times the drift velocities. The general shape of the E/n_0 dependence is preserved but one may conclude that the accuracy of the MTT-derived relationship for skewness is lower than the accuracy of the GERs for the diffusion coefficients, mostly due to the double differentiation problem. In addition, we were not able to get the exact tabulation of the cross sections used by Penetrante and Bardsley, but have attempted to select the closest match; better agreement is obtained when we digitize the data in the figures for the drift velocities in their paper.[4] In the case of argon the agreement becomes almost exact, but in the case of neon a visible discontinuity in the graph for the drift velocity produces a large difference in skewness.

It is interesting to note that the best agreement is achieved for argon, which has a cross section that varies significantly with energy. In the case of neon, the cross section has some variation with energy and the skewness is still significant and in good agreement with the MTT. The poorest agreement is achieved for helium where the skewness is very small and the results are strongly dependent on the numerical procedures employed. In any event, these results indicate that the skewness is especially dependent on the structure in the cross sections and may be a valuable addition to the list of transport coefficients used to obtain cross sections by comparison of calculated and measured values. In particular, the effect of inelastic cross sections close to their thresholds may help resolve some of the ongoing controversies[32] and may prove a sufficient incentive for the development of the experimental apparatus needed to measure the skewness for electron swarms.

As a final note about these calculations, experimental data and theoretical data obtained by Monte Carlo calculations or by solution of the Boltzmann equation are, in principle, more accurate than the MTT-based drift velocities we have used. Therefore, if they are used as an input into Eq. (19), much better results should be obtained.

IV. THE STRUCTURE OF THE TENSOR FOR THE THIRD-ORDER TRANSPORT COEFFICIENT

A. MTT theory of the tensorial transport coefficients of order $k=3$

Earlier studies[16] found that the 27-component tensor $\hat{\mathbf{Q}}^{\mathrm{mix}}$ has only three independent components. The procedure followed by Koutselos,[15] on the other hand, leads to only two independent components. In this section we investigate this situation by applying Eq. (13) to obtain the components of the third-order transport coefficient. The procedure that we use is similar to the procedure used by Robson[18,19] to analyze the diffusion tensor. The analysis is made assuming that there is no magnetic field and that the reaction rate is zero. Inclusion of these effects would increase the complexity of the skewness tensor, not reduce it.

If $\mathbf{E}$ is aligned with the $\mathbf{e}_3$ axis of the coordinate system, the temperature tensor has the diagonal structure[33]

$$T_{ij}^{\mathrm{mix}}=[T_{\mathrm{perp}}^{\mathrm{mix}}(\delta_{i1}+\delta_{i2})+T_{\mathrm{para}}^{\mathrm{mix}}\delta_{i3}]\delta_{ij}. \tag{22}$$

If we write $\mathbf{W}^{\mathrm{mix}}=K^{\mathrm{mix}}\mathbf{E}$, where the mobility, K^{mix}, is implicitly a function of the magnitude of the field, then

$$\frac{\partial}{\partial E_k}W_j^{\mathrm{mix}}(\mathbf{E})=\delta_{kj}K^{\mathrm{mix}}+(K^{\mathrm{mix}})'\frac{E_kE_j}{E} \tag{23}$$

and

$$\frac{\partial}{\partial E_l}\frac{\partial}{\partial E_k}W_j^{\mathrm{mix}}(\mathbf{E})=\delta_{kj}(K^{\mathrm{mix}})'\frac{E_l}{E}+(K^{\mathrm{mix}})''\frac{E_lE_kE_j}{E^2}+(K^{\mathrm{mix}})'\frac{(\delta_{kl}E_j+\delta_{lj}E_k)E^2-E_kE_jE_l}{E^3}. \tag{24}$$

Assuming the diagonal form of Eq. (22) for the temperature tensor, we find that Eqs. (13), (23), and (24) lead to the following form for the components of the third-order transport tensor:

$$Q_{ijk}^{\mathrm{mix}}=\frac{1}{2}\left(\frac{k_B}{e}\right)^2\begin{bmatrix}0&0&T_{\mathrm{perp}}T_{\mathrm{para}}K'\\0&0&0\\T_{\mathrm{perp}}T_{\mathrm{para}}K'&0&0\end{bmatrix}\quad(k=1), \tag{25}$$

$$Q_{ijk}^{\mathrm{mix}}=\frac{1}{2}\left(\frac{k_B}{e}\right)^2\begin{bmatrix}0&0&0\\0&0&T_{\mathrm{perp}}T_{\mathrm{para}}K'\\0&T_{\mathrm{perp}}T_{\mathrm{para}}K'&0\end{bmatrix}\quad(k=2), \tag{26}$$

$$Q_{ijk}^{\mathrm{mix}}=\frac{1}{2}\left(\frac{k_B}{e}\right)^2\begin{bmatrix}T_{\mathrm{perp}}^2K'&0&0\\0&T_{\mathrm{perp}}^2K'&0\\0&0&T_{\mathrm{para}}^2(2K'+EK'')\end{bmatrix}\quad(k=3). \tag{27}$$

Here the superscript ''mix'' has been omitted for brevity.

These equations show that $\hat{\mathbf{Q}}^{\mathrm{mix}}$ has at most three independent components. Fewer components are possible, depending upon the transverse and/or longitudinal components of the temperature tensor and on the first and/or second derivatives of the mobility. Equations (25)–(27) can be reduced to the equations of Koutselos provided that we assume that the temperature tensor is effectively isotropic, i.e., $T_{ij}^{\mathrm{mix}}=T\delta_{ij}$.

B. Symmetry considerations

The analysis in this section is more general than the previous analysis and makes no assumptions that depend on the mass ratio of the swarm particles. The transport of trace amounts of charged particles moving through a dilute neutral gas under the influence of a homogeneous electrostatic field is characterized by a steady drift velocity, $\mathbf{W}$, and a superposed diffusional motion. The ion flux, $\mathbf{J}$, may then be written as

$$\mathbf{J}=n(\mathbf{r},t)\mathbf{W}(\mathbf{E})-\hat{\mathbf{D}}(\mathbf{E})\cdot\frac{\partial}{\partial\mathbf{r}}n(\mathbf{r},t)+\hat{\mathbf{Q}}(\mathbf{E}):\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}}n(\mathbf{r},t)+\cdots, \tag{28}$$

and the transport coefficients extracted from a comparison of the experimental ion flux with Eq. (28). Whealton and Mason[16] found that $\hat{\mathbf{Q}}$ should have three independent components, whereas Koutselos[15] found that there are only two. Koutselos based his calculations and theoretical arguments on the following definition:[34]

$$\hat{\mathbf{Q}}_K=\frac{1}{3!}\frac{1}{t}\langle\delta_n\mathbf{r}\delta_n\mathbf{r}\delta_n\mathbf{r}\rangle_n,\quad t\to\infty. \tag{29}$$

Here the the brackets represent an average defined as

$$\langle\psi(\mathbf{r})\rangle_n=\frac{1}{N}\int d\mathbf{r}\psi(\mathbf{r})n(\mathbf{r},t), \tag{30}$$

with

$$N=\int d\mathbf{r}n(\mathbf{r},t), \tag{31}$$

and

$$\delta_n\mathbf{r}=\mathbf{r}-\langle\mathbf{r}\rangle_n. \tag{32}$$

This microscopic definition is certainly appealing, based on its close analogy to a similar definition of $\hat{\mathbf{D}}$. However, the following analysis shows that $\hat{\mathbf{Q}}_K$ does not have the same symmetry properties as $\hat{\mathbf{Q}}$ and hence that the two cannot be equated, even though the microscopic and macroscopic definition of $\mathbf{D}$ are equivalent.

Since $\hat{\mathbf{Q}}$ and $\hat{\mathbf{Q}}_K$ are tensors of rank three in a three-dimensional space, they have 27 components labeled by three indices. From the work of Coope, Snider, and McCourt,[35] this means that each of them can be represented in terms of seven independent, irreducible tensors constructed from its components; one must be of weight 0, three of weight 1, two of weight 2, and one of weight 3. Thus, there are at most seven independent components for $\hat{\mathbf{Q}}$ and $\hat{\mathbf{Q}}_K$.

The weight 0 irreducible tensors must be proportional to $\hat{\epsilon}$, the completely antisymmetric third-rank unit tensor. However, $\hat{\mathbf{Q}}_K$ is completely symmetric, so the proportionality constant between it and $\hat{\epsilon}$ must be 0. Moreover, $\mathbf{J}$ is related to $\hat{\mathbf{Q}}$ by Eq. (28), where the order of differentiation of n is irrelevant. This means that $Q_{ijk}=Q_{ikj}$. However, ϵ_{ijk} is equal to the negative of ϵ_{ikj}. Since $\hat{\mathbf{Q}}$ and $\hat{\epsilon}$ have different symmetries, the proportionality constant between them must be 0. We have thus shown that neither $\hat{\mathbf{Q}}$ nor $\hat{\mathbf{Q}}_K$ is proportional to a weight 0 irreducible tensor, and hence that there are at most six independent components for these tensors.

The same type of reasoning as in the previous paragraph shows, after considerably more mathematical argument, that neither $\hat{\mathbf{Q}}$ nor $\hat{\mathbf{Q}}_K$ can be proportional to any weight 2 irreducible tensor. This reduces the maximum number of independent components to four for each tensor.

The weight 3 irreducible tensor is formed from a rank three tensor in a three-dimensional space by symmetrizing and making the result traceless. It is given for an arbitrary tensor by Eq. (39) of Ref. 35. Since none of the symmetry properties of $\hat{\mathbf{Q}}$ or $\hat{\mathbf{Q}}_K$ contradicts the properties of such a weight 3 irreducible tensor, we have accounted for one independent component of each tensor.

One weight 1 irreducible tensor is given by Eq. (28) of Ref. 35, and the other two follow by replacing the subscript 1 by 2 and 3. Since $\hat{\mathbf{Q}}_K$ is completely symmetric, the coefficients relating this tensor to the three weight 1 irreducible tensors must be exactly the same, leaving us with only two independent components, one relating $\hat{\mathbf{Q}}_K$ to the weight 3 irreducible tensor and the other relating it to these weight 1 irreducible tensors.

To analyze $\hat{\mathbf{Q}}$ further, we can again make use of the independence of the order of differentiation in Eq. (28). The weight 1 irreducible tensors that involve the second and third indices in $\hat{\mathbf{Q}}$ must be identical, but there is no necessary relationship between these two and the weight 1 irreducible tensor involving the first index. Consequently, we have accounted for three independent components of $\hat{\mathbf{Q}}$, one relating it to the weight 3 irreducible tensor, a second relating it to the weight 1 irreducible tensor along the field direction and a third relating it to the weight 1 irreducible tensor perpendicular to the field.

In this section we have given a more abstract proof of the arguments used by Whealton and Mason[16] to claim that there are three independent components of $\hat{\mathbf{Q}}$. The same arguments show that $\hat{\mathbf{Q}}_K$ has only two independent components, since it is more symmetric than $\hat{\mathbf{Q}}$. Hence, the microscopic third-order diffusion coefficient analyzed by Koutselos[15] is not identical with the macroscopic third-order diffusion coefficient analyzed by Whealton and Mason[16] and used in the other parts of this article.

The equations used in paper I in formulating the MTT and used as the foundation for the analysis in this section are consistent with the following definition of the third-order transport coefficient [see Eq. (9d) of Ref. 29];

$$\hat{\mathbf{Q}}=\frac{1}{3!}\frac{d}{dt}\langle\delta_n\mathbf{r}\delta_n\mathbf{r}\delta_n\mathbf{r}\rangle_n. \tag{33}$$

Although this equation appears at first glance to become identical to Eq. (29) at long times, the symmetries of the two equations are different. There is no difference between dividing by time in direction of the field and perpendicular to it but the first derivatives may differ in the two directions. Such a difference in the theoretical expression for the third-order transport coefficient is generally necessary, since different transport coefficients in the two directions ordinarily will be exploited in matching Eq. (28) to arrival time spectrum. Note that in the absence of an anisotropic temperature (which was covered in the preceding section) or an anisotropic derivative (as in Ref. 29), our symmetry argument would lead to the two weight-1 irreducible tensors being identical and, therefore, (as found by Koutselos) there would be only two independent components of third-order transport coefficient.

V. CONCLUSION

Application of the momentum transfer theory (MTT) in a quite general case of elastic, inelastic, and reactive collisions (including mixtures of gases as well) allowed us to derive a generalized form of the relationship between the components of the third-order diffusion tensor and the components of the temperature tensor and mobility. A general conclusion is that the GER for the kth order transport coefficient will depend on the $(k-1)$th derivative of the mobility and the kth derivative of the reaction rate coefficient. The formulas were, for simplicity, derived for the case of light swarm particles but may be generalized to an arbitrary mass ratio by using the same procedure as that developed by Robson[18,19] for the diffusion tensor.

Application of the theory to electron skewness in rare gases reveals that the skewness is very sensitive to the shape of the cross section. The best results were obtained for argon. For helium the value of the skewness is very small and, therefore, it is strongly affected by the inadequacies in the data used for differentiation.

Comparison with the values calculated by Penetrante and Bardsley[4] indicates a reasonable qualitative agreement with the predictions of the MTT-derived formulas. The comparison is not direct since we could not make sure that the identical cross sections were used (in this case details of tabulation and interpolation become important) and it is hard to define such comparisons for tabulated cross-section sets. The best direct comparison would involve application of the theory to analytic sets of cross sections; then each technique could define a best suited numerical procedure that would give the required accuracy.

In any case, MTT-derived formulas can be used with either calculated or experimental data to give qualitative and semiquantitative information about the skewness and other components of the third-order transport coefficient. Such analysis may be useful in the development of experimental techniques for accurately measuring the higher-order transport coefficients.

Our analysis of the components of the third-order transport coefficient gives explicit analytic results and indicates that in general there are three independent and seven nonzero components. The conclusion[15] that there are only two independent components was based on the use of a third-order transport coefficient that was defined microscopically[34] in terms of the mean displacement of the swarm particles. Such tensorial transport coefficient cannot be the same as the third-order transport coefficients defined macroscopically in terms of the extended diffusion equation or the equation for the ion flux. Our analysis, therefore, confirms the necessity for the three independent components of the third-order transport coefficient unless, for a limited range of low E/n_0 values, the temperature tensor reduces to a scalar.

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APPENDIX

When we expand the functions $\boldsymbol{\omega}^{\mathrm{mix}}$, Eq. (4), and α^*, Eq. (5), in a Taylor series in the vicinity of $\mathbf{E}$ to second and third order in $\mathbf{G}$, respectively, we obtain the following equations:

$$\langle \mathbf{v}\rangle^{\mathrm{mix}} = \boldsymbol{\omega}^{\mathrm{mix}}\left(\mathbf{E}-\frac{k_B}{e}\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}\right) = \boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E}) - \frac{k_B}{e}\sum_{i=1}^{3}(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_i\frac{\partial}{\partial E_i}\boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E}) + \frac{1}{2}\left(\frac{k_B}{e}\right)^2 \times\sum_{i=1}^{3}\sum_{j=1}^{3}(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_i(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_j\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E}) \tag{A1}$$

and

$$\tilde{\nu}^* = \alpha^*\left(\mathbf{E}-\frac{k_B}{e}\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G}\right) = \alpha^*(\mathbf{E}) - \frac{k_B}{e}\sum_{i=1}^{3}(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_i\frac{\partial}{\partial E_i}\alpha^*(\mathbf{E}) + \frac{1}{2}\left(\frac{k_B}{e}\right)^2\sum_{i=1}^{3}\sum_{j=1}^{3}(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_i(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_j\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\alpha^*(\mathbf{E}) - \frac{1}{6}\left(\frac{k_B}{e}\right)^3\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_i(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_j(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\mathbf{G})_k\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\frac{\partial}{\partial E_k}\alpha^*(\mathbf{E}). \tag{A2}$$

Substituting these expansions into equation of continuity, Eq. (1), we obtain

$$\frac{\partial}{\partial t}n(\mathbf{r},t) + k_1 - k_2 + k_3 = -n(\mathbf{r},t)\alpha^*(\mathbf{E}), \tag{A3}$$

where

$$k_1 = \boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E})\cdot\frac{\partial n}{\partial \mathbf{r}} - \frac{k_B}{e}\sum_{i=1}^{3}\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_i\frac{\partial}{\partial E_i}\alpha^*(\mathbf{E}), \tag{A4}$$

$$k_2 = \frac{k_B}{e}\frac{\partial}{\partial \mathbf{r}}\cdot\sum_{i=1}^{3}\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_i\frac{\partial}{\partial E_i}\boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E}) - \frac{1}{2n(\mathbf{r},t)}\left(\frac{k_B}{e}\right)^2\sum_{i=1}^{3}\sum_{j=1}^{3}\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_i \times\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_j\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\alpha^*(\mathbf{E}), \tag{A5}$$

$$k_3 = \frac{\partial}{\partial \mathbf{r}}\cdot\left[\frac{1}{2n(\mathbf{r},t)}\left(\frac{k_B}{e}\right)^2\sum_{i=1}^{3}\sum_{j=1}^{3}\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_i \times\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_j\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\boldsymbol{\omega}^{\mathrm{mix}}(\mathbf{E})\right] - \frac{1}{6n^2(\mathbf{r},t)}\left(\frac{k_B}{e}\right)^3 \times\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_i\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_j\left(\hat{\mathbf{T}}^{\mathrm{mix}}\cdot\frac{\partial n}{\partial \mathbf{r}}\right)_k \times\frac{\partial}{\partial E_i}\frac{\partial}{\partial E_j}\frac{\partial}{\partial E_k}\alpha^*(\mathbf{E}). \tag{A6}$$

Equation (A4) can be rearranged to give

$$k_1 = \mathbf{W}^{\mathrm{mix}}(\mathbf{E})\cdot\frac{\partial}{\partial \mathbf{r}}n(\mathbf{r},t), \tag{A7}$$

where the drift velocity is given by Eq. (9).

In order to simplify Eq. (A5), we assume that the temperature tensor is spatially homogeneous and that

$$\frac{1}{n(\mathbf{r},t)}\frac{\partial n}{\partial r_i}\frac{\partial n}{\partial r_j} \approx \frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j}n(\mathbf{r},t). \tag{A8}$$

Using these assumptions, we can rearrange Eq. (9) to give

$$k_2 = \sum_{i=1}^{3}\sum_{j=1}^{3}D_{ij}^{\mathrm{mix}}(\mathbf{E})\frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j}n(\mathbf{r},t), \tag{A9}$$

where the diffusion tensor is given by Eq. (10).

Similar to Eq. (A8) is the approximation

$$\frac{1}{n^2(\mathbf{r},t)}\frac{\partial n}{\partial r_i}\frac{\partial n}{\partial r_j}\frac{\partial n}{\partial r_k}\approx\frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j}\frac{\partial}{\partial r_k}n(\mathbf{r},t). \tag{A10}$$

With this approximation, Eq. (10) becomes

$$k_3=\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}Q_{ijk}^{\mathrm{mix}}(\mathbf{E})\frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j}\frac{\partial}{\partial r_k}n(\mathbf{r},t), \tag{A11}$$

where the third-order transport coefficient is given by Eq. (12).

It is obvious from Eqs. (3) and (A2) that the net average reaction rate ρ^* is given by Eq. (14).

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