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Second Order in the Gradients Effects in a Dilute Binary Mixture[1]

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A study is made to compute relevant transport properties for a dilute binary mixture of inert gases to second order in the gradients without explicitly solving the Boltzmann equation to that order. This is done with the Chapman–Enskog method, seeking to express such quantities in terms of the solution to first order. The pressure tensor and the velocity of diffusion are two quantities which allow for this computation. In the particular case when the sum of the particle densities of the mixture (n_A, n_B) is constant, one finds that in order to keep the Chapman–Enskog method mathematically consistent, it is necessary that the divergence of the mass velocity be position independent. Finally, we consider the case of swarms of charged particles and study the prediction of the method in the Navier–Stokes and Burnett regimes for diffusion phenomena. In the latter case, the results are restricted to electrons in a gas.

KEY WORDS: Boltzmann equation; Burnett regime; Chapman–Enskog method; diffusion; mobility; pressure tensor; swarms.

1. INTRODUCTION

In this work, we study diffusion phenomena in swarms of charged particles by using the Chapman–Enskog method to solve the Boltzmann equation for a binary mixture. We analyze the solution to first and second order in the Knusden parameter (Navier–Stokes and Burnett regimes).

Assuming that the experimental temperature and pressure can be identified with the theoretical expressions given for these quantities in the case

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of a binary mixture [1], we study the conservation equation for the number density of charged particles (n_A) when the pressure and temperature are held constant. This is a common restriction in experiments made on swarms of charged particles [2, 3], and as a consequence of the identification mentioned above, the total number density (n) turns out to be a constant.

In the second section, we consider the Boltzmann equation for a dilute binary mixture for swarms. We also discuss the conservation equation for the number density of charged particles with a constant total density.

The third section contains the main part of this work. It is shown how the relevant fluxes in a binary mixture to second order in the gradients can be expressed in terms of the first order in the gradient's term for the distribution function in the Chapman–Enskog method. The results are applied both to computing the pressure tensor and to the diffusion velocity. In the latter case we derive a nonlinear partial differential equation for n_A whose structure and properties are discussed for a one-dimensional flow of electrons using the Lorentz approximation [1]. This is an oversimplification of a realistic swarm but allows for some quantitative predictions. A more detailed discussion of these features will be published elsewhere [4].

In the fourth and final section, we obtain the mobility to first and second order, using the conventional identity for the drift velocity [5].

2. THE BOLTZMANN EQUATION FOR THE BINARY MIXTURE

If f^i denotes the one-body distribution function for the ith species ($i = \mathrm{A, B}$), the evolution equations for the f^i's in the case of elastic collisions are given by

$$\begin{aligned} \frac{\partial f^{\mathrm{A}}}{\partial t} + \vec{c}_{\mathrm{A}} \cdot \nabla_{\vec{r}} f^{\mathrm{A}} + \vec{F}_{\mathrm{A}} \cdot \nabla_{\vec{c}_{\mathrm{A}}} f^{\mathrm{A}} &= -J_{\mathrm{AA}} - J_{\mathrm{AB}} \\ \frac{\partial f^{\mathrm{B}}}{\partial t} + \vec{c}_{\mathrm{B}} \cdot \nabla_{\vec{r}} f^{\mathrm{B}} + \vec{F}_{\mathrm{B}} \cdot \nabla_{\vec{c}_{\mathrm{B}}} f^{\mathrm{B}} &= -J_{\mathrm{BB}} - J_{\mathrm{BA}} \end{aligned} \tag{1}$$

where $-J_{\mathrm{AA}}$ represents the collisions between the A species, $-J_{\mathrm{AB}}$ the collisions between the A and the B species, etc. The form of this term is given in the literature [6]. Here $\vec{c}_i$ represents the molecular velocity of the ith species, and $\vec{F}_i$ the external force.

In the case of swarms of charged particles in which the density of charged particles (A species) is extremely low compared with that of the neutral species (B), it is possible to justify neglecting the term J_{AA} compared with J_{AB} and also of J_{AB} compared with J_{BB}. Hence Eqs. (1) reduce to

$$\begin{aligned}\frac{\partial f^{A}}{\partial t}+\vec{c}_{A}\cdot\nabla_{\vec{r}}f^{A}+\vec{F}_{A}\cdot\nabla_{\vec{c}_{A}}f^{A}&=-J_{AB}\\ \frac{\partial f^{B}}{\partial t}+\vec{c}_{B}\cdot\nabla_{\vec{r}}f^{B}+\vec{F}_{B}\cdot\nabla_{\vec{c}_{B}}f^{B}&=-J_{BB}\end{aligned}\tag{2}$$

In this system the equation for f^{B} is uncoupled, and given f^{B}, the equation for f^{A} is linear in f^{A}. Usually f^{B} is taken as a global Maxwellian [7].

2.1. The Conservation Equation for the Number of Particles

As is well known, the existence of the collision invariants implies the existence of conservation equations. For the number of particles of the A and B species, these are [8]

$$\frac{\partial n_i}{\partial t}+\nabla\cdot(n_i\langle\vec{c}_i\rangle)=0,\qquad i=\mathrm{A},\mathrm{B}\tag{3}$$

where $\langle\psi(\vec{c}_i)\rangle=(1/n_i)\int\psi(\vec{c}_i)\,f^i\,d\vec{c}_i$.

Equations (3) immediately lead to

$$\frac{\partial n}{\partial t}+\nabla\cdot(n_A\langle\vec{c}_A\rangle+n_B\langle\vec{c}_B\rangle)=0$$

Thus, for n constant it follows that $\nabla\cdot\vec{\omega}=0$, where $\vec{\omega}=1/n\sum_{i=A}^{B}n_i\langle\vec{c}_i\rangle$ is the number velocity. Using this fact, Eq. (3) for n_A can be rewritten as [9]

$$\frac{\partial n_A}{\partial t}=-\nabla\cdot\left[\frac{n_An_B}{n}(\langle\vec{C}_A\rangle-\langle\vec{C}_B\rangle)\right]-\vec{\omega}\cdot\nabla n_A\tag{4}$$

where $\vec{C}_i=\vec{c}_i-\vec{c}_0$ is the peculiar velocity and $\vec{c}_0=(\sum_{i=A}^{B}\rho_i\langle\vec{c}_i\rangle/\rho)$ is the mass velocity. Here ρ_i is the mass density of the ith species and $\rho=\rho_A+\rho_B$.

3. SECOND ORDER IN THE GRADIENT EFFECTS

In the following we use the Chapman–Cowling [1] notation and do not express the solution in terms of the parametric Enskog expansion which is usually found in the literature [10]. The method is based on a series expansion for the distribution function of the form

$$f^i = f^{i(0)}[1 + \phi^{i(1)} + \phi^{i(2)} + \cdots], \qquad i = \mathrm{A, B}$$

where $f^{i(0)}$ is the local Maxwellian and $\phi^{i(1)}$, $\phi^{i(2)}$,..., etc., are corrections to $f^{i(0)}$. The expansion parameter is usually taken to be the Knusden parameter for the system under study [1, 9, 10].

3.1. The Navier–Stokes Regime

To first order in the expansion parameter, the distribution function is given by

$$f^{(i)} = f^{i(0)}[1 + \phi^{i(1)}]$$

where the correction $\phi^{i(1)}$ has the form [11]

$$\phi^{i(1)} = \vec{A}_i \cdot \nabla \ln T + \vec{D}_i \cdot \vec{d}_i + \tilde{B}_i{:}\nabla\vec{c}_0$$

Here, T is the temperature and $\vec{d}_i$ is given by

$$\vec{d}_i = (n_\mathrm{A}/n)\,\nabla n_\mathrm{A} + [n_\mathrm{A} n_\mathrm{B}(m_\mathrm{B} - m_\mathrm{A})/n\rho]\nabla \ln p - \frac{\rho_\mathrm{A}\rho_\mathrm{B}}{p\rho}(\vec{F}_\mathrm{A} - \vec{F}_\mathrm{B})$$

The equations satisfied by the tensors $\tilde{B}_i = B_i \vec{C}_i \vec{C}_i$ are

$$\begin{aligned} f^\mathrm{A} \vec{\mathscr{C}}^{\,o}_\mathrm{A} \vec{\mathscr{C}}_\mathrm{A} &= n_\mathrm{A}^2 I_\mathrm{A}(\tilde{B}_\mathrm{A}) + n_\mathrm{A} n_\mathrm{B} I_\mathrm{AB}(\tilde{B}_\mathrm{A} + \tilde{B}_\mathrm{B}) \\ f^\mathrm{B} \vec{\mathscr{C}}^{\,o}_\mathrm{B} \vec{\mathscr{C}}_\mathrm{B} &= n_\mathrm{B}^2 I_\mathrm{B}(\tilde{B}_\mathrm{B}) + n_\mathrm{A} n_\mathrm{B} I_\mathrm{BA}(\tilde{B}_\mathrm{A} + \tilde{B}_\mathrm{B}) \end{aligned} \tag{5}$$

Those for $\vec{A}_i$ and $\vec{D}_i$ are of no relevance for this paper and are given in Ref. 11. The form of the linear operators "I" has been considered elsewhere [12] and $\vec{\mathscr{C}}_i = (2kT/m_\mathrm{A})^{-1/2}\,\vec{C}_i$.

Taking $\vec{F}_\mathrm{A} = (e_\mathrm{A}/m_\mathrm{A})\vec{E}$, $\vec{F}_\mathrm{B} = 0$ with e_A the charge of the A species, it can be shown that [1] when the pressure and temperature are held constant, then

$$\langle \vec{C}_\mathrm{A} \rangle - \langle \vec{C}_\mathrm{B} \rangle = -(n^2/n_\mathrm{A} n_\mathrm{B}) D \left[\nabla\left(\frac{n_\mathrm{A}}{n}\right) - \frac{n_\mathrm{A} n_\mathrm{B} m_\mathrm{B} e_\mathrm{A} \vec{E}}{p\rho} \right] \tag{6}$$

where D is the diffusion coefficient. Substitution of Eq. (6) into Eq. (4) gives a nonlinear equation for n_A, which in the case of swarms ($n_\mathrm{A}/n \ll 1$) reduces to

$$\frac{\partial n_\mathrm{A}}{\partial t} = -\left(\vec{\omega} + \frac{n e_\mathrm{A} D}{P}\,\vec{E}\right) \cdot \nabla n_\mathrm{A} + D\,\nabla^2 n_\mathrm{A} \tag{7}$$

We discuss this equation in Section 4.

3.2. The Burnett Regime

To second order in the expansion parameter, f^i reads as $f^i = f^{i(0)}[1+\phi^{i(1)}+\phi^{i(2)}]$. It is possible to show that the equations for $\phi^{i(2)}$ satisfy the following identities [4]:

$$\begin{aligned} &\Gamma^{\mathrm{A}} + J_{\mathrm{AA}}[f^{\mathrm{A}(1)} f_1^{\mathrm{A}(1)}] + J_{\mathrm{AB}}[f^{\mathrm{A}(1)} f_1^{\mathrm{B}(1)}] \\ &\quad = -n_{\mathrm{A}}^2 I_{\mathrm{A}}[\phi^{\mathrm{A}(2)}] - n_{\mathrm{A}} n_{\mathrm{B}} I_{\mathrm{AB}}[\phi^{\mathrm{A}(2)} + \phi^{\mathrm{B}(2)}] \\ &\Gamma^{\mathrm{B}} + J_{\mathrm{BB}}[f^{\mathrm{B}(1)} f_1^{\mathrm{B}(1)}] + J_{\mathrm{BA}}[f^{\mathrm{B}(1)} f_1^{\mathrm{A}(1)}] \\ &\quad = -n_{\mathrm{B}}^2 I_{\mathrm{BB}}[\phi^{\mathrm{B}(2)}] - n_{\mathrm{A}} n_{\mathrm{B}} I_{\mathrm{BA}}[\phi^{\mathrm{A}(2)} + \phi^{\mathrm{B}(2)}] \end{aligned} \tag{8}$$

where

$$\begin{aligned} \Gamma^i = {} & \frac{\partial_1 f^{\mathrm{A}(0)}}{\partial t} + \frac{D_0 f^{i(1)}}{Dt} + \left(\vec{F}_i - \frac{D_0 \vec{c}_0}{Dt}\right) \cdot \nabla_{\vec{r}} f^{i(1)} \\ & + \vec{C}_i \cdot \nabla f^{i(1)} - (\nabla_{\vec{C}_i} f^{i(1)} \vec{C}_i) : \nabla_{\vec{r}} \vec{c}_0, \qquad i = \mathrm{A, B} \end{aligned} \tag{9}$$

In Eq. (9) the operators $\partial_1/\partial t$ and D_0/Dt are defined in Ref. 1. However, at this stage it is important to point out that in order that the Chapman–Enskog expansion is mathematically consistent for the case $n = cte$, $\nabla(\nabla \cdot \vec{c}_0)$ has to be equal to zero. The proof of this is given in Appendix A. This condition will be used later.

Let us now consider the second-order contribution for the pressure tensor $\mathbb{P}^{(2)} = \sum_{i=\mathrm{A,B}} m_i \int f^{i(0)} \phi^{i(2)} \vec{C}_i \vec{C}_i \, d\vec{c}_i = \sum_{i=\mathrm{A,B}} m_i \int f^{i(0)} \phi^{i(2)} \vec{C}_i^{\circ} \vec{C}_i \, d\vec{c}_i$, which in terms of the adimensional velocities $\vec{\mathscr{C}}_i = (2kT/m_{\mathrm{A}})^{-1/2} \vec{C}_i$, takes the form

$$\mathbb{P}^{(2)} = 2kT \left\{ \sum_{i=\mathrm{A,B}} \left[\int f^{i(0)} \phi^{i(2)} \vec{\mathscr{C}}_i^{\circ} \vec{\mathscr{C}}_i \, d\vec{c}_i \right] \right\} \tag{10}$$

By substituting Eqs. (5) in Eq. (11), we obtain

$$\begin{aligned} \frac{\mathbb{P}^{(2)}}{2kT} = {} & \int \phi^{\mathrm{A}(2)} [n_{\mathrm{A}}^2 I_{\mathrm{A}}(\tilde{B}_{\mathrm{A}}) + n_{\mathrm{A}} n_{\mathrm{B}} I_{\mathrm{AB}}(\tilde{B}_{\mathrm{A}} + \tilde{B}_{\mathrm{B}})] \, d\vec{c}_{\mathrm{A}} \\ & + \int \phi^{\mathrm{B}(2)} [n_{\mathrm{B}}^2 I_{\mathrm{B}}(\tilde{B}_{\mathrm{B}}) + n_{\mathrm{A}} n_{\mathrm{B}} I_{\mathrm{BA}}(\tilde{B}_{\mathrm{A}} + \tilde{B}_{\mathrm{B}})] \, d\vec{c}_{\mathrm{B}} \\ = {} & n_{\mathrm{A}}^2 [\tilde{B}_{\mathrm{A}}, \phi^{\mathrm{A}(2)}] + n_{\mathrm{A}} n_{\mathrm{B}} [\tilde{B}_{\mathrm{A}} + \tilde{B}_{\mathrm{B}}, \phi^{\mathrm{A}(2)} + \phi^{\mathrm{B}(2)}] + n_{\mathrm{B}}^2 [\tilde{B}_{\mathrm{B}}, \phi^{\mathrm{B}(2)}] \end{aligned} \tag{11}$$

Using the symmetry properties of [,] and its definition, we have

$$\begin{aligned} \frac{\mathbb{P}^{(2)}}{2kT} = {} & n_{\mathrm{A}}^2 \int \tilde{B}_{\mathrm{A}} I_{\mathrm{A}}[\phi^{\mathrm{A}(2)}] \, d\vec{c}_{\mathrm{A}} + n_{\mathrm{A}} n_{\mathrm{B}} \int \tilde{B}_{\mathrm{A}} I_{\mathrm{AB}}[\phi^{\mathrm{A}(2)} + \phi^{\mathrm{B}(2)}] \, d\vec{c}_{\mathrm{A}} \\ & + n_{\mathrm{A}} n_{\mathrm{B}} \int \tilde{B}_{\mathrm{B}} I_{\mathrm{AB}}[\phi^{\mathrm{A}(2)} + \phi^{\mathrm{B}(2)}] \, d\vec{c}_{\mathrm{B}} + n_{\mathrm{B}}^2 \int \tilde{B}_{\mathrm{B}} I_{\mathrm{B}}[\phi^{\mathrm{B}(2)}] \, d\vec{c}_{\mathrm{B}} \end{aligned} \tag{12}$$

If we multiply the first equation in (8) by $\tilde{B}_A$ and integrate over $\vec{c}_A$, then multiply the second equation by $\tilde{B}_B$ and integrate over $\vec{c}_B$, we have, after summing the results and comparing with Eq. (11),

$$\frac{\mathbb{P}^{(2)}}{2kT} = -\sum_{i=A,B} \int [\Gamma^i + J_i^{(1)}]\, \tilde{B}_i \tag{13}$$

where

$$J_A^{(1)} = J_{AA}[f^{A(1)} f_1^{A(1)}] + J_{AB}[f^{A(1)} f_1^{B(1)}]$$
$$J_B^{(1)} = J_{BB}[f^{B(1)} f_1^{B(1)}] + J_{BA}[f^{B(1)} f_1^{A(1)}]$$

In an analogous manner one can show that [13]

$$\langle \vec{C}_A \rangle^{(2)} - \langle \vec{C}_B \rangle^{(2)} = -\frac{1}{n} \left\{ \sum_{i=A,B} \int d\vec{c}_i \vec{D}_i [\Gamma^i + J_i^{(1)}] \right\} \tag{14}$$

and for the heat flux it happens that

$$\frac{\vec{q}^{(2)}}{kT} = \frac{5}{2} \left[\sum_{i=A,B} n_i \langle \vec{c}_i \rangle^{(2)} \right] + \sum_{i=A,B} \left\{ \int d\vec{c}_i \vec{A}_i [\Gamma^i + J_i^{(1)}] \right\} \tag{15}$$

Equations (13)–(15) contain the main results of this work, namely, the expression of the second-order contribution to the fluxes in terms of the first-order solutions. Since we are interested mainly in the diffusion properties of swarms, we focus our attention on Eq. (14).

Since $\vec{D}_i$ is odd in $\vec{C}_i$ it is necessary to consider only the odd parts of $[\Gamma^i + J_i^{(1)}]$ in Eq. (14). Also, for swarms we have that $\vec{D}_B = 0$ [see Eq. (2)], and therefore we need to evaluate only $[\Gamma^A + J_A^{(1)}]^{\text{odd}}$. At constant pressure and temperature, Γ^A is given by [13]

$$\begin{aligned}
\Gamma^A = &-\frac{2}{3} \nabla \cdot \vec{c}_0 \left(T \frac{\partial D'_A}{\partial T} + \vec{C}_A^2 \frac{\partial D'_A}{\partial \vec{C}_A^2} \right) \vec{C}_A \cdot \vec{d}_A \\
&+ D'_A \vec{C}_A \cdot \left[\frac{D_0 \vec{d}_A}{Dt} - \nabla \vec{c}_0 \cdot \vec{d}_A \right] + \left\{ \left[\vec{C}_A \cdot \nabla \left(\frac{n_A}{n} \right) \right] (\vec{C}_A \vec{C}_A : \nabla^0 \vec{c}_0) \right. \\
&+ \left. \left(\frac{n^2}{n_B} \frac{\partial B'_A}{\partial n_A} + \frac{2p}{\rho_A} \frac{\partial B'_A}{\partial \vec{C}_A^2} \right) + \frac{2p}{\rho_A} B'_A (\vec{d}_A \vec{C}_A : \bar{\bar{\nabla}}^0 \vec{c}_0) \right\} \\
&- \left[(\vec{C}_A \cdot \vec{C}_A)(\vec{C}_A \vec{C}_A : \nabla \vec{c}_0) \left(\frac{2p}{\rho_A} \frac{\partial B'_A}{\partial \vec{C}_A^2} + 2 \frac{\partial D'_A}{\partial \vec{C}_A^2} \right) \right. \\
&+ \left. \frac{2p}{\rho_A} B'_A (\vec{d}_A \vec{C}_A : \nabla \vec{c}_0) + B'_A \vec{C}_A \cdot \nabla_r (\vec{C}_A \vec{C}_A : \nabla \vec{c}_0) \right]
\end{aligned} \tag{16}$$

where $A'_A = -[f^{A(0)}/T]\, A_A$, $D'_A = -f^{A(0)} D_A$, and $B'_A = 2f^{A(0)} B_A$.

To evaluate $\Gamma^{\mathrm{A\,odd}}$ it is necessary to give the form of A_{A}, D_{A}, and B_{A}. For the Lorentz approximation these quantities are given by [14]

$$\begin{aligned} A_{\mathrm{A}} &= (\mathscr{C}_{\mathrm{A}}^2 - \tfrac{5}{2})/[n_{\mathrm{B}}\,|\vec{C}_{\mathrm{A}}|\,\phi_{12}^{(1)}] \equiv \gamma_1'/n_{\mathrm{B}} \\ D_{\mathrm{A}} &= -n/[n_{\mathrm{A}} n_{\mathrm{B}}\,|\vec{C}_{\mathrm{A}}|\,\phi_{12}^{(1)}] \equiv (n/n_{\mathrm{A}} n_{\mathrm{B}})\,\gamma_2' \\ B_{\mathrm{A}} &= m_{\mathrm{A}}/[3 n_{\mathrm{B}} kT\,|\vec{C}_{\mathrm{A}}|\,\phi_{12}^{(2)}] \equiv \gamma_3'/n_{\mathrm{B}} \end{aligned} \tag{17}$$

where $\phi_{12}^{(l)}$ are defined by Eq. (9.33,4) of Ref. 1, and the quantities γ_j' are functions of $|\vec{C}_{\mathrm{A}}|$ and T. When the result of the substitution of Eq. (17) into Eq. (16) is used, it turns out that Eq. (14) can be written as

$$\begin{aligned} \langle \vec{C}_{\mathrm{A}} \rangle^{(2)} - \langle \vec{C}_{\mathrm{B}} \rangle^{(2)} = -\frac{1}{n} \Big\{ & -\frac{2}{3} \nabla \cdot \vec{c}_0 (n^2/n_{\mathrm{A}} n_{\mathrm{B}})\, \tilde{W}_1 \cdot \vec{d}_{\mathrm{A}} \\ & + (n^2/n_{\mathrm{A}} n_{\mathrm{B}})\, \tilde{W}_2 \cdot \left(\frac{D_0 \vec{d}_{\mathrm{A}}}{Dt} - \nabla \vec{c}_0 \cdot \vec{d}_{\mathrm{A}} \right) \\ & + (n^2/n_{\mathrm{A}} n_{\mathrm{B}}^3)\, \pi_1 \cdot (\nabla n_{\mathrm{A}} \nabla^0 \vec{c}_0) + \frac{2 m_{\mathrm{B}} e_{\mathrm{A}} n}{m_{\mathrm{A}} n_{\mathrm{B}}}\, \pi_2 \cdot (\nabla^0 \vec{c}_0 \vec{E}) \\ & + \frac{2 m_{\mathrm{B}} e_{\mathrm{A}} n}{m_{\mathrm{A}} n_{\mathrm{B}}}\, W_3 \cdot (\nabla \vec{c}_0 \cdot \vec{E}) \\ & - \frac{2n^2}{n_{\mathrm{A}} n_{\mathrm{B}}^2}\, \pi_3 \cdot (\vec{d}_{\mathrm{A}} \nabla^0 \vec{c}_0) + \frac{n}{n_{\mathrm{B}}^2}\, \pi_4 \cdot [\nabla(\nabla \vec{c}_0)] + \vec{J} \Big\} \end{aligned} \tag{18}$$

Here $\tilde{W}_j$, $j = 1, 2, 3$, are second-order tensors, and π_l, $l = 1, 2, 3, 4$, fourth-order tensors; the general form of them is given below. $\vec{J}$ represents the part corresponding to the collisions and its form is given in Appendix B.

For the tensors $\tilde{W}$ and π, we have

$$\begin{aligned} \tilde{W}_j &= \frac{2\pi}{3} w_j (\hat{\imath}\hat{\imath} + \hat{\jmath}\hat{\jmath} + \hat{k}\hat{k}), \qquad j = 1, 2, 3 \\ \pi_l &= \frac{4\pi}{15} \delta_l (3\hat{\imath}\hat{\imath}\hat{\imath}\hat{\imath} + \hat{\imath}\hat{\imath}\hat{\jmath}\hat{\jmath} + \hat{\imath}\hat{\imath}\hat{k}\hat{k} + \hat{\imath}\hat{\jmath}\hat{\jmath}\hat{\imath} + \hat{\imath}\hat{\jmath}\hat{\imath}\hat{\jmath} \\ &\quad + \hat{\imath}\hat{k}\hat{\imath}\hat{k} + \hat{\imath}\hat{k}\hat{k}\hat{\imath} + \hat{\jmath}\hat{\jmath}\hat{\imath}\hat{\imath} + 3\hat{\jmath}\hat{\jmath}\hat{\jmath}\hat{\jmath} + \hat{\jmath}\hat{\jmath}\hat{k}\hat{k} + \hat{\jmath}\hat{\imath}\hat{\imath}\hat{\jmath} \\ &\quad + \hat{\jmath}\hat{\imath}\hat{\jmath}\hat{\imath} + \hat{\jmath}\hat{k}\hat{\jmath}\hat{k} + \hat{\jmath}\hat{k}\hat{k}\hat{\jmath} + \hat{k}\hat{k}\hat{\imath}\hat{\imath} + \hat{k}\hat{k}\hat{\jmath}\hat{\jmath} \\ &\quad + 3\hat{k}\hat{k}\hat{k}\hat{k} + \hat{k}\hat{\imath}\hat{\imath}\hat{k} + \hat{k}\hat{\imath}\hat{k}\hat{\imath} + \hat{k}\hat{\jmath}\hat{\jmath}\hat{k} + \hat{k}\hat{\jmath}\hat{k}\hat{\jmath}) \end{aligned} \tag{19}$$

The integrals w_j and δ_l have been evaluated for a potential proportional to $r^{-(v-1)}$ ($v \geqslant 5$), and their values for the Maxwell model ($v = 5$) are given in Appendix B.

In order to simplify the calculations we take the one-dimensional case as defined by the relations $\nabla n_A = (\partial n_A/\partial z)(z, t)\hat{k}$, $\nabla \vec{c}_0 = (\partial c_0/\partial z)(z, t)\hat{k}$. Then Eq. (18) reduces to

$$[\langle \vec{C}_A \rangle^{(2)} - \langle \vec{C}_B \rangle^{(2)}] \cdot \hat{k} = -\frac{1}{n}\left[\left(\frac{n}{n_A n_B}\right) \Xi_1 \frac{\partial n_A}{\partial z} + \frac{n}{n_B n_A} \Xi_2 E\right] \tag{20}$$

To obtain Eq. (19) use was made of the relation $\nabla(\nabla \cdot \vec{c}_0) = 0$, and $\vec{E} = E\hat{k}$. Ξ_1 and Ξ_2 are given by

$$\begin{aligned}
\Xi_1 = \Bigg[& -\frac{16}{9}\pi w_1 - \frac{8}{3}\pi w_2 + \frac{16}{45}\pi\delta_1 \frac{n}{n_B} - \frac{32}{45}\pi\delta_3 \\
& - \frac{32}{27}\left(\frac{m_A}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2} \frac{\sigma}{kT}\gamma_1\gamma_2 \Bigg] K \\
\Xi_2 = \Bigg[& \frac{16}{9}\frac{\pi w_1 m_B}{p\rho} + \frac{8}{3}\frac{\pi w_2 m_B}{p\rho} + \frac{32}{45}\frac{m_B}{m_A}\frac{\delta_2}{n\rho} + \frac{16}{9}\frac{\pi w_3}{n\rho}\frac{m_B}{m_A} \\
& + \frac{32}{45}\frac{\pi\delta_3 m_B}{p\rho} + \frac{32}{27}\frac{\sigma}{kT}\left(\frac{m_A}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\frac{m_B}{\rho p}\gamma_1\gamma_2 \Bigg] n n_A e_A K
\end{aligned} \tag{21}$$

Here σ is the gas viscosity and $K = \nabla \cdot \vec{c}_0$. The collision integrals γ_1 and γ_2 are also given in Appendix B for the Maxwell model.

From Eq. (20) it follows that

$$\nabla \cdot \left\{\frac{n_A n_B}{n}[\langle \vec{C}_A \rangle^{(2)} - \langle \vec{C}_B \rangle^{(2)}]\right\} = -\frac{1}{n}\left\{\Xi_1 \frac{\partial^2 n_A}{\partial z^2} + \frac{\partial \Xi_1}{\partial z}\frac{\partial n_A}{\partial z} + E\frac{\partial n_A}{\partial z}\Xi_2^*\right\} \tag{22}$$

where $\Xi_2^* = \{1/n_A + [(m_B - m_A)/\rho]\}\,\Xi_2$. Since $(\partial\Xi_1/\partial z) = [\Xi_1/n_B + (16/45)(\pi K n \delta_1/n_B^3)](\partial n_A/\partial z)$, we notice that the second term in Eq. (22) is nonlinear in $\partial n_A/\partial z$. However, for the case of swarms, we can make an estimation of this term with respect to the first one. We take Ξ_1/n_B, the first coefficient of $(\partial n_A/\partial z)^2$, and compare it with Ξ_1/n, the coefficient of the first term in Eq. (22). Then, if L is a characteristic length of the density variations, so that $(\partial n_A/\partial z) \sim n_A/L$ and $(\partial^2 n_A/\partial z^2) \sim n_A/L^2$, we have $[\Xi_1 n_B^{-1}(\partial n_A/\partial z)^2]/[\Xi_1(\partial^2 n_A/\partial z^2)] \sim n_A/n$, and therefore the nonlinear term can be neglected. If we consider only the linear terms, then Eq. (21) can be written as

$$\nabla \cdot \left[\frac{n_A n_B}{n}(\langle \vec{C}_A \rangle^{(2)} - \langle \vec{C}_B \rangle^{(2)}\right] = -\frac{1}{n}\left\{\lambda_1 \frac{\partial^2 n_A}{\partial z^2} + E\lambda_2 \frac{\partial n_A}{\partial z}\right\} \tag{23}$$

where, in the case of swarms, λ_1 and λ_2 are given by

$$\begin{aligned}\lambda_1 &= \left[-\frac{16}{9}\pi w_1 - \frac{4}{3}\pi w_2 + \frac{16}{45}\pi\delta_1 - \frac{32}{45}\pi\delta_3 \right.\\ &\quad \left. - \frac{32}{27}\left(\frac{m_A}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\frac{\sigma}{kT}\gamma_1\gamma_2\right]K \\ \lambda_2 &= \frac{Ke_A}{p}\left[\frac{16}{9}\pi w_1 + \frac{8}{3}\pi w_2 + \frac{32}{45}\pi\frac{\delta_2 kT}{m_A} + \frac{16}{45}\pi\frac{w_3 kT}{m_A}\right.\\ &\quad \left. + \frac{16}{45}\pi\delta_3 + \frac{32}{27}\frac{\sigma}{kT}\left(\frac{m_A}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\gamma_1\gamma_2\right]\end{aligned} \tag{24}$$

Taking $f^{(i)}$ in the Burnett approximation in Eq. (4) and using the results obtained to first order [Eq. (7)], we come to the conclusion that when Eq. (23) is taken into account, then

$$\frac{\partial n_A}{\partial t} = -\left(\vec{w} + \frac{nDe_A E}{p} - \frac{\lambda_2 E}{n}\right)\frac{\partial n_A}{\partial z} + \left(D - \frac{\lambda_1}{n}\right)\frac{\partial^2 n_A}{\partial z^2} \tag{25}$$

is the equation satisfied by n_A in the Burnett regime. Noting that, for the Maxwell model, (kT/K_{12}) has dimensions of length^{-4} (see Appendix B) and using the expressions for the integrals given in Appendix B to evaluate λ_1 and λ_2, one can check that Eq. (25) is dimensionally correct.

4. THE MOBILITY

In the experiments on swarms of charged particles a very important quantity is the drift velocity (v_d), which is usually considered constant [2, 3]. The mobility y is defined by the relation $\vec{V}_d = y\vec{E}$ and it is important to give a theoretical evaluation of y. In order to do this, it is necessary to find the theoretical velocity that can be identified with the drift velocity. We use the usual identification (see below) and assume that the neutral species is at rest with respect to the laboratory reference frame so that $\langle \vec{c}_B \rangle = 0$.

With density gradients present besides an electric field, one would expect for the mean velocity of charged particles ($\langle \vec{c}_A \rangle$), a relation of the type

$$\langle \vec{c}_A \rangle = \sigma_1 \nabla n_A + \sigma_2 \vec{E} \tag{26}$$

From $\langle \vec{c}_A \rangle = \langle \vec{C}_A \rangle - \langle \vec{C}_B \rangle$ and Eq. (6), we see that this actually happens in the Navier–Stokes regime. From Eq. (25) we note that the mean velocity has a diffusion velocity ($\sigma_1 \nabla n_A$) and a part proportional to the electric field ($\sigma_2 \vec{E}$). The latter velocity is usually identified with the drift velocity, so that the transport coefficient σ_2 is the mobility. In the Navier–Stokes regime we obtain for the mobility [see Eq. (6)]

$$y = (e_A D)/(kT)$$

which is the well-known Einstein–Townsend relation [15].

In the Burnett regime and for swarms, we obtain for the mean velocity the following expression (see Eq. (20)]:

$$\langle \vec{c}_A \rangle \cdot \hat{k} = -\left(\frac{D}{n_A} - \frac{\lambda_1}{n_A}\frac{1}{n}\right)\frac{\partial n_A}{\partial z} + \left(\frac{e_A D}{kT} - \frac{\lambda_2}{n}\right) E \tag{27}$$

Thus we have from Eq. (26) that the mobility in the Burnett regime is given by

$$y = \frac{e_A D}{kT} - \frac{\lambda_2}{n}$$

If $K \neq 0$ we see that the mobility is not given by the Einstein–Townsend relation.

To find out what can be said about the diffusion coefficient, we turn our attention to Eqs. (7) and (25). Since the gas is considered at rest, we have $|\vec{w}|/|\langle \vec{c}_A \rangle| = n_A | n$, thus allowing us to neglect the term $\vec{w} \cdot \nabla n_A$, which is very small in comparison to the terms proportional to $\vec{E} \cdot \nabla n_A$. Then the expressions for $\partial n_A/\partial t$ are

$$\frac{\partial n_A}{\partial t} = -\frac{n e_A D}{p} \vec{E} \cdot \nabla n_A + D \nabla^2 n_A \tag{28}$$

in the Navier–Stokes regime and

$$\frac{\partial n_A}{\partial t} = \left(-\frac{n e_A D}{p} + \frac{\lambda_2}{n}\right) E \frac{\partial n_A}{\partial z} + \left(D - \frac{\lambda_1}{n}\right)\frac{\partial^2 n_A}{\partial z^2} \tag{29}$$

in the Burnett regime for the one-dimensional case. The latter equation can be written as

$$\frac{\partial n_A}{\partial t} = -y^* E \frac{\partial n_A}{\partial z} + D^* \frac{\partial^2 n_A}{\partial z^2} \tag{30}$$

which is a diffusion-type equation, but with y^* and D^* no longer satisfying the Einstein–Townsend relation.

5. DISCUSSION

Since up to first order in the CE expansion we have obtained the Einstein–Townsend relation and the continuity equation used in the experiments (for low fields), the identification made between the experimental quantities (pressure and temperature) and their theoretical counterparts for low fields gains support.

In the Burnett regime and for the one-dimensional case, one can obtain the diffusion-type Eq. (25) with new transport coefficients y^* and D^*. They are expressed in terms of some integrals but are also proportional to the divergence of the mass velocity, which is a measure of the compressibility of the binary mixture. In order to evaluate them, one must know $\nabla \cdot \vec{c}_0$. In principle $\nabla \cdot \vec{c}_0$ can be determined from the conservation equations by imposing certain boundary or initial conditions to $\vec{c}_0$. The diffusion-type equation for n_A [Eq. (30)] has been solved using certain boundary conditions for n_A, casting some light on the above problem [2].

The above conclusions are a direct consequence of the relation $\nabla(\nabla \cdot \vec{c}_0) = 0$. Since the relation is obtained by a purely mathematical argument, one may ask if this is a physically acceptable condition. If not, then either it is not possible to interchange the order of derivation in $(D_0/Dt)\nabla$ or D_0/Dt does not satisfy the rules of differential calculus. In either case, the conclusion will be that the method is incomplete, since in this situation there is no way to evaluate quantities such as $(D_0/Dt)[\nabla(n_A/n)]$.

If $\nabla \cdot \vec{c}_0 = 0$, then the mobility and the diffusion coefficient are the same in the Burnett and Navier–Stokes regimes. However, from the conservation equation for the total mass $(D\rho/Dt) + \rho\nabla \cdot \vec{c}_0 = 0$, when the total density is a constant, one is led to

$$(m_A - m_B)\frac{\partial n_A}{\partial t} + (m_A - m_B)\,\vec{c}_0 \cdot \nabla n_A = 0$$

which shows that there are no diffusion terms in the equation for n_A, even if one takes the first-order expressions for $\vec{c}_0$, since the terms proportional to D are nonlinear in n_A.

The integrals mentioned in Section 3 can be divided into drift $(w_1, w_2, w_3, \delta_1, \delta_2, \delta_3)$ and collision (γ_1, γ_2) integrals, all susceptible to evaluation for a potential proportional to $r^{-(v-1)}$. For the Maxwell model the contribution to the mobility arising from the collisions (γ_1, γ_2) is proportinal to $(m_B/m_A)^{1/2}$ so that it may dominate over the drift terms. Note, however, that if the distribution function of the gas molecules is taken as a Maxwellian $[f^{B(1)} = 0]$, then their contribution is zero.

For the Navier–Stokes regime the results are valid no matter what the mass ratios are. However, since in the Burnett regime we have used the Lorentz approximation, the results are valid for light ions in a heavy gas. Furthermore, since we have considered elastic collisions, the results can also be applied to ions in monoatomic gases. In this way the Burnett predictions of the Chapman–Enskog method may be compared with measurements obtained from electrons in a monoatomic gas.

APPENDIX A

Let us now show that the condition $\nabla(\nabla\cdot\vec{c}_0)=0$, when n is a constant, is a necessary condition for the Chapman–Enskog method to be mathematically consistent. The action of D_0/Dt on the densities is given by [1]

$$\frac{D_0 n_i}{Dt}=\frac{\partial_0 n_i}{\partial t}+\vec{c}_0\cdot\nabla n_i=-n_i\nabla\cdot\vec{c}_0 \tag{31}$$

From Eq. (30) we obtain, after adding the equations for each species,

$$\frac{D_0}{Dt}n=-n\nabla\cdot\vec{c}_0 \tag{32}$$

If we assume that we can interchange the order of derivation to evaluate $(\partial_0/\partial t)[\nabla(n_A/n)]$ and noting that $(D_0/Dt)(n_A/n)=0$, we get

$$\frac{D_0}{Dt}[\nabla(n_A/n)]=\nabla\left[\frac{D_0}{Dt}(n_A/n)\right]-\nabla\vec{c}_0\cdot\nabla(n_A/n) \tag{33}$$

On the other hand, when n is held constant we have $\nabla(n_A/n)=(1/n)\nabla n_A$. Hence

$$\begin{aligned}\frac{D_0}{Dt}[\nabla(n_A/n)]&=\frac{D_0}{Dt}\left(\frac{1}{n}\nabla n_A\right)=(\nabla n_A/n)\nabla\cdot\vec{c}_0+\frac{1}{n}\nabla\left(\frac{D_0}{Dt}n_A\right)-\nabla\vec{c}_0\cdot\nabla(n_A/n)\\&=-\frac{n_A}{n}\nabla(\nabla\cdot\vec{c}_0)-\nabla\vec{c}_0\cdot\nabla(n_A/n)\end{aligned} \tag{34}$$

By comparing Eq. (33) and Eq. (34) we conclude that $\nabla(\nabla\cdot\vec{c}_0)=0$ when n is a constant.

APPENDIX B

To show how we obtained Eq. (19) we sketch the evaluation of the collision term which appears in this equation. From Eqs. (18) and (19) it turns out that the ith component of $\vec{J}$ is given by

$$\vec{J}_i = \sum_{j,\lambda,y} \int D_A \frac{n}{n_B} \gamma_2' \vec{C}_{A_i} \phi_{12}^{(1)} \vec{C}_{A_j} \left(\int d\vec{c}_0 \, \mathscr{C}_B^o \mathscr{C}_B \right) d\vec{c}_A \, \vec{d}_{A_j} (\nabla \vec{c}_0)_{y\lambda} \times \left[-\frac{2\sigma}{kT} \left(\frac{m_B}{2\pi kT} \right)^{3/2} \right]$$

where σ is the viscosity of the gas. To obtain this equation we took the first Enskog approximation for $f^{B(1)}$ and used the relations $\int (\vec{C}_A' - \vec{C}_A) b \, db \, de = \vec{C}_A \phi_{12}^{(1)}$, $g = |\vec{C}_A|$, and $\vec{C}_B' = \vec{C}_B$.

J may be written as

$$J = \left[-\frac{2\sigma}{kT} \left(\frac{m_A}{2\pi kT} \right)^{3/2} \left(\frac{m_B}{2\pi kT} \right)^{3/2} \frac{n}{n_B} \right] \times \left[\int D_A \vec{C}_A \vec{C}_A \exp(-\vec{e}_A^2) \tilde{W} \, d\vec{c}_A \right] \cdot (\vec{d}_A \nabla^0 \vec{c}_0)$$

where $\tilde{w} = \int d\vec{c}_B \, \vec{\mathscr{C}}_B \vec{\mathscr{C}}_B$ and the dot product is defined as $(T \cdot T_1)_i = T_{ij} \hat{\lambda}_y T_j \hat{\lambda}_y$ when T is a fourth-order tensor and T_1 a third-order tensor. Using the fact that if $w = \int d\vec{c}_A \, f(\vec{C}_A^2) \, \vec{C}_A \vec{C}_A$, then $w = (2\pi/3)[\int_0^\infty d\,|\vec{C}_A| \, \vec{C}_A^4 \, f(\vec{C}_A^2)](\hat{\imath}\hat{\imath} + \hat{\jmath}\hat{\jmath} + 2\hat{k}\hat{k})$, we conclude that

$$J = -\frac{2\sigma}{kT} \left(\frac{m_A}{2\pi kT} \right)^{3/2} \left(\frac{m_B}{2\pi kT} \right)^{3/2} \frac{\gamma_1 \gamma_2 n^2}{n_A n_B^2} (W^+ W^+) \cdot (\vec{d}_A \nabla^0 \vec{c}_0) \left(\frac{4}{9} n^2 \right)$$

where $W^+ = (\hat{\imath}\hat{\imath} + \hat{\jmath}\hat{\jmath} + 2\hat{k}\hat{k})$ and γ_1 and γ_2 are given by

$$\gamma_1 = \int_0^\infty \vec{\mathscr{C}}_B^2 \vec{C}_B^2 \exp(-\vec{\mathscr{C}}_B^2) d\,|\vec{C}_B| = \frac{3}{8} \sqrt{\pi} \left(\frac{m_B}{2kT} \right)^{-3/2}$$

$$\gamma_2 = \int_0^\infty \vec{C}_A^4 \gamma_2' \exp(-\vec{\mathscr{C}}_A^2) d\,|\vec{C}_A| = -\frac{3}{16} \frac{1}{\sqrt{\pi}} \left(\frac{2kT}{K_{12}} \right)^{1/2} \left(\frac{2kT}{m_A} \right)^{3/2} \frac{1}{A_1(5)}$$

The last value of γ_2 is for the Maxwell model. The other integrals which appear in the paper are given, for the Maxwell model, by

$$w_1 = \frac{9}{32} \frac{kT}{K_{12}} \frac{1}{\pi^3 A_1^2(5)}, \qquad w_2 = -\frac{3}{16} \frac{kT}{K_{12}} \frac{1}{\pi^3 A_1^2(5)}$$

$$w_3 = \frac{1}{8}\frac{m_A}{K_{12}}\frac{1}{\pi^3 A_1(5)\,A_2(5)}, \qquad \delta_1 = \delta_4 = 5\frac{kT}{K_{12}}\frac{1}{A_1(5)\,A_2(5)}$$

$$\delta_2 = -\frac{1}{8}\frac{m_A}{K_{12}}\frac{1}{\pi^3 A_1(5)\,A_2(5)}, \qquad \delta_3 = \frac{3}{16}\frac{kT}{K_{12}}\frac{1}{\pi^3 A_1^2(5)}$$

where $A_1(5) = 0.422$ and $A_2(5) = 0.436$. The interaction potential for the ions and the gas is given for the Maxwell model by $\phi_{AB}(\vec{r}) = K_{12}/4r^4$.

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