On the Motion of Small Spheres in Gases

II. Thermo-phoresis, Diffusio-phoresis and Related Phenomena

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Using the general theory developed by the author in the previous paper, the problems of thermo-phoresis and diffusio-phoresis have been examined with a view to elucidating the effect of a general gas-surface scattering law on the associated forces. It is found that, in thermo-phoresis, there exists a close coupling between the first anisotropic moment of the gas-surface scattering law and the solution of the Chapman-Enskog conductivity equation. Explicit calculations indicate that for an arbitrary combination of any type of purely elastic scattering, e. g. specular, Lambert or backward, there is no change in the creep velocity of the particle. On the other hand, diffuse scattering with redistribution, leads to a marked decrease in the creep velocity. These conclusions are independent of the force law between gas atoms and depend only on the gas-surface interaction.

In diffusio-phoresis, using only the simplest Chapman-Enskog solution for a binary mixture, it is found that unless the gas-surface laws differ greatly for the two species, there is virtually no influence of gas-surface scattering on the particle motion: the effect is due almost entirely to the mass difference and concentration ratio.

We also investigate the way in which particles move in gas streams close to boundaries; slip flow is used as an example and it is shown that for diffuse reflection a particle at the wall travels with a speed which is about 60% of the gas speed at the wall.

1. Introduction

A small particle suspended in a non-uniform gas or gas-mixture will experience a force due to the associated temperature and concentration gradients. A definitive study of this problem has recently been made by Loyalka[1] who has considered the complete range of Knudsen numbers, i. e. mean free path of gas atoms divided by radius of particle. References to previous work in the field may be found in Loyalka's paper. Despite the generality of Loyalka's work, its application to problems with general boundary conditions is complicated and does not show explicitly how the properties of the gas and the gas-surface scattering law interact with each other. The purpose of this paper, therefore, is to clarify some of these points and, in particular, we shall consider only the limit of large Knudsen number. This restriction enables the general theory developed in paper I[2] to be employed and from it we shall see how the forces due to thermo-phoresis (i. e. motion in a temperature gradient) and diffusio-phoresis (i. e. motion in a concentration gradient) are governed by the nature of the gas, the nature of the gas-surface scattering and the interaction of these two processes.

The general formulation developed here leads to the results of previous workers in the field, but also to some new results for incomplete accommodation. It also clarifies one or two obscure points which have been discussed in the literature.

2. General Theory for Thermo-phoresis

2.1.

We consider the forces acting on a particle in a general gas flow defined by the velocity distribution function $f(\boldsymbol{v}, \boldsymbol{r}, t)$. Then from the Appendix the force $\boldsymbol{F}$ can be written

$$
\begin{aligned}
\boldsymbol{F} = m \int_0^\infty \mathrm{d}g\, g^3 \int_0^\infty \mathrm{d}g'\, g'^2 \int \mathrm{d}\boldsymbol{\Omega}'\, \boldsymbol{\Omega}'\, \sigma_1(g' \to g)& \\
\cdot f(g', \boldsymbol{n}\cdot\boldsymbol{\Omega}', \boldsymbol{r}, t)& \qquad (1)\\
- m\,\sigma \int_0^\infty \mathrm{d}g\, g^4 \int \mathrm{d}\boldsymbol{\Omega}\, \boldsymbol{\Omega}\, f(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t)&
\end{aligned}
$$

where $\boldsymbol{n}$ is a unit vector denoting the direction of motion of the particle and we have written the distribution function as $f(\boldsymbol{v}, \boldsymbol{r}, \mathrm{t}) = f(v, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, \mathrm{t})$, $\boldsymbol{\Omega}$ being a unit vector denoting direction of motion of a gas atom of speed v. The other quantities are defined in paper I.

If the particle is moving with velocity $\mathbf{V}$, and the temperature gradient is ∇T, then $f(\ldots)$ can be

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written

$$f(v, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}) \tag{2}$$
$$= f_0(v)\left\{1 - 2\,\mathbf{V}\cdot\boldsymbol{v}\left(\frac{m}{2\,k\,T}\right) - \frac{1}{T}\,F(v^2)\,\boldsymbol{v}\cdot\nabla T\right\}.$$

$F(v^2)$ is the solution of the Chapman-Enskog conductivity integral equation[3] and the validity of (2) is subject to the usual restrictions of the Chapman-Enskog expansion. A further limitation is that the presence of the particle (radius a) does not alter the distribution function, i. e. a is very much less than a mean free path. Finally, we note that $f_0(v)$ is the unperturbed Maxwellian

$$f_0(v) = n_0\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2}\exp\{-m\,v^2/2\,k\,T\}\,. \tag{3}$$

Inserting Eq. (2) into Eq. (1), we see that the net force is given by

$$\boldsymbol{F} = \boldsymbol{F}_V + \boldsymbol{F}_T \tag{4}$$

where $\boldsymbol{F}_V$ is the frictional force de to motion of the particle and $\boldsymbol{F}_T$ is an accelerating force caused by the non-uniform temperature. Explicitly, we may write

$$\boldsymbol{F}_V = \tfrac{4}{3}\,\sigma\,n_0\,m\,(8\,k\,T/\pi\,m)^{1/2}\,\mathbf{V}\,Q_1 \tag{5}$$

where (see Appendix):

$$Q_1 = 1 - \frac{1}{\sigma}\int_0^\infty \mathrm{d}t\,t^3\int_0^\infty \mathrm{d}t'\,t^3\,\tilde{\sigma}_1(t'\to t)\,e^{-t'^2}\,. \tag{6}$$

Similarly,

$$\boldsymbol{F}_T = \tfrac{4}{3}\,\sigma\,n_0\,m\left(\frac{8\,k\,T}{\pi\,m}\right)^{1/2}\frac{1}{2}\left(\frac{2\,k\,T}{m}\right)^{1/2}\frac{1}{T}\,\nabla \boldsymbol{T}\,\boldsymbol{Q}_2$$

where

$$Q_2 = \int_0^\infty \mathrm{d}t\,t^5\,F_0(t^2)\,e^{-t^2}$$
$$-\frac{1}{\sigma}\int_0^\infty \mathrm{d}t\,t^3\int_0^\infty \mathrm{d}t'\,t'^3\,e^{-t'^2}\,\tilde{\sigma}_1(t'\to t)\,F_0(t'^2) \tag{7}$$

and
$$F_0(t'^2) = \left(\frac{2\,k\,T}{m}\right)^{1/2} F\left(\frac{2\,k\,T}{m}\,t^2\right). \tag{8}$$

If there is no applied force to maintain the particle at constant velocity, we can find the natural velocity $\mathbf{V}_\mathrm{p}$ assumed by the particle in the temperature field if we set $\boldsymbol{F}=0$. Then, clearly, $F_V = -\boldsymbol{F}_T$ or

$$\mathbf{V}_\mathrm{p} = -\tfrac{1}{2}\,(2\,k\,T/m)^{1/2}\,(1/T)\,\nabla T\,(Q_2/Q_1)\,. \tag{9}$$

The ratio $Q_2/Q_1 = \Lambda$ is always positive for the models to be discussed and therefore our result indicates that the particle will move to regions of lower temperature. This is to be expected since, in the converse problem of thermal creep, the gas moves to regions of higher temperature.

The magnitude of the "creep velocity" $\mathbf{V}_\mathrm{p}$ is sensitively dependent on the parameter Λ, which we write down in full below, viz.:

$$\Lambda = \frac{\int_0^\infty \mathrm{d}t\,t^5\,F_0(t^2)\,e^{-t^2} - (1/\sigma)\int_0^\infty \mathrm{d}t\,t^3\int_0^\infty \mathrm{d}t'\,t'^3\,e^{-t'^2}\,\tilde{\sigma}_1(t'\to t)\,F_0(t'^2)}{1 - (1/\sigma)\int_0^\infty \mathrm{d}t\,t^3\int_0^\infty \mathrm{d}t'\,t'^3\,\tilde{\sigma}_1(t'\to t)\,e^{-t'^2}}\,. \tag{10}$$

Whilst, as we have said above, $\Lambda > 0$ for the models considered, it has not been proved that this is so for all models. However, on physical grounds it seems likely and so we shall not pursue the matter further.

2.2. *Magnitude of the Creep Velocity for Various Models*

(a) Specular Reflection

For this model of the gas surface interaction we know from paper I[2] that $\sigma_1(v'\to v) = 0$, hence Λ is given by

$$\Lambda = \int_0^\infty \mathrm{d}t\,t^5\,F_0(t^2)\,e^{-t^2}\,. \tag{11}$$

For Maxwell molecules it is known that

$$F_0(t^2) = \frac{4\,\lambda_\mathrm{T}}{5\,n_0\,k}\left(\frac{m}{2\,k\,T}\right)^{1/2}(t^2 - \tfrac{5}{2}) \tag{12}$$

where λ_T is the thermal conductivity, viz.:

$$\lambda_\mathrm{T} = \frac{5\,k^2\,T}{(2\,m\,K)^{1/2}\,A_2} \tag{13}$$

with K the force constant and A_2 as defined by CHAPMAN and COWLING[3].

The corresponding value of $\mathbf{V}_\mathrm{p}$ is therefore

$$\mathbf{V}_\mathrm{p} = -\frac{\lambda_\mathrm{T}}{5\,p}\,\nabla T \tag{14}$$

with $p = n_0\,k\,T$.

(b) Backward Reflection

Here we know that $\sigma_1(v' \to v) = -\sigma\,\delta(v'-v)/v$, thus

$$\Lambda = \int_0^\infty \mathrm{d}t\, t^5\, F_0(t^2)\, e^{-t^2} \tag{15}$$

which is the same as the value for specular reflection. This is a quite remarkable result since for velocity drag the forces involved in backward reflection are double those of specular reflection; it appears, however, that in the calculation of creep velocity certain factors cancel out. It would therefore be impossible to distinguish specular from backward scattering by measuring $\boldsymbol{V}_{\mathrm{p}}$.

(c) Lambert's Law

This involves elastic scattering with a cosine surface re-emission law and leads to

$$\sigma_1(v' \to v) = -\tfrac{4}{9}\,\sigma\,\delta(v'-v)/v\,. \tag{16}$$

The corresponding value of Λ is given by

$$\Lambda = \int_0^\infty \mathrm{d}t\, t^5\, F_0(t^2)\, e^{-t^2}\,. \tag{17}$$

Thus, yet again, a change in the model of surface scattering has no effect on the creep velocity $\boldsymbol{V}_{\mathrm{p}}$.

(d) Diffuse Reflection

In this case the physical assumptions lead to

$$\sigma_1(v' \to v) = -\frac{8}{9}\,\sigma\left(\frac{m}{2\,k\,T}\right)^2 v\,v' \exp\left\{-\frac{m\,v^2}{2\,k\,T}\right\} \tag{18}$$

where we take the particle and the the surrounding gas to have the same local temperature.

An interesting phenomenon occurs for this model since, in the numerator of Λ, see Eq. (10), we find a term

$$\int_0^\infty \mathrm{d}t\, t^4\, F_0(t^2)\, e^{-t^2}$$

which, by definition of F_0, is zero. Thus Λ becomes

$$\Lambda = \frac{1}{1+\frac{1}{8}\pi}\int_0^\infty \mathrm{d}t\, t^5\, F_0(t^2)\, e^{-t^2} \tag{19}$$

which is a factor of $(1+\frac{1}{8}\pi)$ smaller than the value of Λ predicted by the three other surface models, irrespective of the value of $F_0(t^2)$.

(e) Compound Model

We can combine the results of the previous four models by writing σ_1 as a linear combination, viz.:

$$\begin{aligned}\sigma_1(v' \to v) = {}& \alpha\,\sigma_1(\text{diffuse}) + \beta\,\sigma_1(\text{Lambert}) \\ &+ \gamma\,\sigma_1(\text{specular}) + \delta\,\sigma_1(\text{backward})\end{aligned} \tag{20}$$

with $\alpha+\beta+\gamma+\delta = 1$.

Now Λ is given by

$$\Lambda = \frac{(1+\delta+\frac{4}{9}\beta)}{(1+\frac{1}{8}\pi\,\alpha+\delta+\frac{4}{9}\beta)}\int_0^\infty \mathrm{d}t\, t^5\, F_0(t^2)\, e^{-t^2}\,. \tag{21}$$

Clearly, for $\alpha = 0$, the model dependence disappears, thereby indicating the sensitivity of the process to the amount of diffuse surface scattering. This result accounts for the difference noted by CHAPMAN and MASON[4] between their value of $\boldsymbol{V}_{\mathrm{p}}$ and that of WALDMANN[5]. In fact the model used by Chapman and Mason was actually Lambert's law, i. e. a redistribution in angle after scattering but not speed. Waldmann used the diffuse scattering model in which both angle and speed are redistributed. This difference in model is particularly important if the magnitude of the force $\boldsymbol{F}_T$ is required, since it is easily seen from Eq. (7) that

$$(\boldsymbol{F}_T)_{\text{Lambert}} = \tfrac{13}{9}\,(\boldsymbol{F}_T)_{\text{diffuse}}\,. \tag{22}$$

Chapman and Mason note this effect for a mixture of specular and Lambert scattering and find that

$$(\boldsymbol{F}_T)_{\text{spec.+Lamb.}} = (1+\tfrac{4}{9}\,\beta)\,(\boldsymbol{F}_T)_{\text{diffuse}}\,, \tag{23}$$

β being the fraction of Lambert scattering. The implication in their paper is one of an unresolved discrepancy, we can see quite clearly, however, that there is no problem since Waldmann and Chapman and Mason use entirely different models of surface scattering.

(f) The Kuščer-Cercignani Model

We have discussed this model in paper I and the relevant expression for $\sigma_1(v' \to v)$ can be found in Eq. (42) of that paper. Inserting it into Eq. (10) we find that

$$\Lambda = \frac{1-\frac{1}{2}\,\Delta_0+\frac{3\pi}{16}\,\Delta^2}{1+\frac{1}{8}\,\pi-\frac{1}{2}\,\Delta_0+\frac{\pi}{32}\,\Delta^2}\,. \tag{24}$$

To the same order in Δ_0 and Δ^2, Eq. (24) reduces to

$$\Lambda = \frac{1}{1+\frac{1}{8}\pi}\left\{1-\frac{\pi}{2(\pi+8)}\,\Delta_0+\frac{3\,\pi(20+3\,\pi)}{16(\pi+8)}\,\Delta^2\right\} \tag{25}$$

$$= \frac{1}{1+\frac{1}{8}\pi}\left\{1-0.14\,\Delta_0+0.51\,\Delta^2\right\}. \tag{26}$$

In terms of the accommodation coefficients we may write this as

$$\Lambda = \frac{1}{1+\frac{1}{8}\pi} \{1 - 0.14(1-\alpha_{\|}) + 1.02(1-\alpha_{\mathrm{E}})\} . \tag{27}$$

We note, therefore, that the creep velocity depends more on the energy accommodation coefficient than on the tangential momentum one. Moreover, these quantities act in different directions: greater energy accommodation increases the creep velocity whilst greater tangential momentum accommodation decreases it.

3. General Theory for Diffusio-phoresis

3.1.

We shall consider in this section the force acting on a particle situated in a binary gas mixture in which there exists a concentration gradient. As before, it is assumed that the presence of the particle does not alter the flow field that would exist in its absence.

For a binary gas mixture with partial concentrations n_1, n_2 for particles of masses m_1 and m_2, respectively, it is know from CHAPMAN and COWLING [3] that the molecular distribution function for atoms of gas 1 is, in its crudest form (neglecting thermal diffusion), given by

$$f_1(\boldsymbol{v}_1) = f_0^{(1)}(\boldsymbol{v}_1) \left\{ 1 - D \frac{m_1}{k\,T} \frac{1}{\gamma_1} \boldsymbol{v}_1 \cdot \nabla \gamma_1 \right\} \tag{28}$$

where

$$\gamma_1 = n_1/(n_1+n_2) \tag{29}$$

and D is the binary diffusion coefficient [3]. $f_0^{(1)}(\boldsymbol{v}_1)$ is the Maxwellian function for gas atoms of type 1.

If we assume that the particle in the gas moves under the concentration gradient with a velocity $\boldsymbol{V}_{\mathrm{d}}$, then we can refer Eq. (28) to a local velocity coordinate $\boldsymbol{V}_{\mathrm{d}}$ such that the gas moves and the particle is stationary. In the case that $\boldsymbol{V}_{\mathrm{d}} \ll (2\,k\,T/m)^{1/2}$, $f_1(\boldsymbol{v}_1)$ now becomes

$$f_1(\boldsymbol{v}_1) = f_0^{(1)}(\boldsymbol{v}_1) \cdot \left\{ 1 - D \frac{m_1}{k\,T} \frac{1}{\gamma_1} \boldsymbol{v}_1 \cdot \nabla \gamma_1 - 2\,\boldsymbol{v}_1 \cdot \boldsymbol{V}_{\mathrm{d}} \left(\frac{m_1}{2\,k\,T} \right) \right\} \tag{30}$$

$$f_2(\boldsymbol{v}_2) = f_0^{(2)}(\boldsymbol{v}_2) \cdot \left\{ 1 - D \frac{m_2}{k\,T} \frac{1}{\gamma_2} \boldsymbol{v}_2 \cdot \nabla \gamma_1 - 2\,\boldsymbol{v}_2 \cdot \boldsymbol{V}_{\mathrm{d}} \left(\frac{m_2}{2\,k\,T} \right) \right\} . \tag{31}$$

Similarly, for gas atoms of type 2 where we have noted that $\gamma_1 = 1 - \gamma_2$.

Now the total force $\boldsymbol{F}_{\mathrm{d}}$ acting on the particle in the mixture is given by

$$\boldsymbol{F}_{\mathrm{d}} = \sum_{i=1}^{2} \left(\frac{\partial \boldsymbol{M}_i}{\partial t} \right)_{\mathrm{coll}} . \tag{32}$$

$\boldsymbol{M}_{\mathrm{i}}$ being the momentum of the gas atoms of type i hitting the particle.

If the distribution function $f(\boldsymbol{v})$ is rewritten, we see that both Eqs. (30) and (31) take the form

$$f_i(\boldsymbol{v}_i) = f_0^{(i)}(\boldsymbol{v}_i) \cdot \left\{ 1 - 2\,\boldsymbol{v}_i \cdot \left[\boldsymbol{V}_{\mathrm{d}} \pm \frac{D}{\gamma_i} \nabla \gamma_i \right] \left(\frac{m_i}{2\,k\,T} \right) \right\} . \tag{33}$$

Hence

$$\left(\frac{\partial \boldsymbol{M}_1}{\partial t} \right) = \tfrac{4}{3}\,\sigma\,n_1\,m_1 \left(\frac{8\,k\,T}{\pi\,m_1} \right)^{\frac{1}{2}} \left[\boldsymbol{V}_{\mathrm{d}} + \frac{D}{\gamma_1} \nabla \gamma_1 \right] Q_1^{(1)} \tag{34}$$

and

$$\left(\frac{\partial \boldsymbol{M}_2}{\partial t} \right) = \tfrac{4}{3}\,\sigma\,n_2\,m_2 \left(\frac{8\,k\,T}{\pi\,m_2} \right)^{\frac{1}{2}} \left[\boldsymbol{V}_{\mathrm{d}} - \frac{D}{\gamma_2} \nabla \gamma_1 \right] Q_1^{(2)} \tag{35}$$

where Q_1 is defined by Equation (6).

Considering the case where the particle reaches a terminal velocity, we can use (32) with $\boldsymbol{F}_{\mathrm{d}} = 0$ to find

$$\boldsymbol{V}_{\mathrm{d}} = - \frac{\{ m_1^{1/2}\,Q_1^{(1)} - m_2^{1/2}\,Q_1^{(2)} \}}{\{ \gamma_1\,m_1^{1/2}\,Q_1^{(1)} + \gamma_2\,m_2^{1/2}\,Q_1^{(2)} \}} D\,\nabla \gamma_1 . \tag{36}$$

The actual magnitude and direction of motion will depend upon the numerator. This result is in agreement with some less general ones of WALDMANN [5] and BAKANOV and DERJAGUIN [6].

The force necessary to prevent movement is given by Eq. (32) with $\boldsymbol{V}_{\mathrm{d}} = 0$. We then find that

$$\boldsymbol{F}_{\mathrm{d}} = \frac{4}{3}\,\sigma \left\{ n_1\,m_1 \left(\frac{8\,k\,T}{\pi\,m_1} \right)^{\frac{1}{2}} \frac{1}{\gamma_1} Q_1^{(1)} - n_2\,m_2 \cdot \left(\frac{8\,k\,T}{\pi\,m_2} \right)^{\frac{1}{2}} \frac{1}{\gamma_2} Q_1^{(2)} \right\} D\,\nabla \gamma_1 . \tag{37}$$

3.2. Magnitude of Particle Velocity due to Concentration Gradient

We can now evaluate $\boldsymbol{V}_{\mathrm{d}}$ for the various models discussed earlier.

(a) Specular Reflection

We find that $Q_1 = 1$ and hence that

$$\boldsymbol{V}_{\mathrm{d}} = - \frac{\{ m_1^{1/2} - m_2^{1/2} \}}{\{ \gamma_1\,m_1^{1/2} + \gamma_2\,m_2^{1/2} \}} D\,\nabla \gamma_1 . \tag{38}$$

Thus the particle will move in the direction of the flow of the heavier component.

(b) Backward Reflection

For this model we know that $Q_1 = 2$ and obtain the same value of $\mathbf{V}_\mathrm{d}$ as for specular reflection.

(c) Lambert's Law

$Q_1 = \frac{13}{9}$ and again the specular result is obtained.

(d) Diffuse Reflection

$Q_1 = 1 + \frac{1}{8}\pi$ and Eq. (38) is predicted once more.

(e) Compound Model

Following Eq. (20), we find that

$$Q_1 = 1 + \tfrac{1}{8}\pi\,\alpha + \delta + \tfrac{4}{9}\beta\,. \tag{39}$$

Now it is possible that the values of α, β and δ will be different for the two atomic species. In such a case, the value of $\mathbf{V}_\mathrm{d}$ will become

$$\mathbf{V}_\mathrm{d} = -\frac{\{m_1^{1/2}(1+\frac{1}{8}\pi\,\alpha_1+\delta_1+\frac{4}{9}\beta_1) - m_2^{1/2}(1+\frac{1}{8}\pi\,\alpha_2+\delta_2+\frac{4}{9}\beta_2)\}}{\{\gamma_1\, m_1^{1/2}(1+\frac{1}{8}\pi\,\alpha_1+\delta_1+\frac{4}{9}\beta_1) + \gamma_2\, m_2^{1/2}(1+\frac{1}{8}\pi\,\alpha_2+\delta_2+\frac{4}{9}\beta_2)\}}\, D\,\nabla\gamma_1\,. \tag{40}$$

For $\alpha_1 = \alpha_2$, $\delta_1 = \delta_2$, and $\beta_1 = \beta_2$, we regain the Equation (38). Therefore certainly $\mathbf{V}_\mathrm{d}$ is not very sensitive to the gas-surface interaction parameters unless these are markedly different for the two species.

To regain the results of other workers in the field we can set $\delta = \beta = 0$, when we have Waldmann's result [5] for specular plus diffuse scattering. Conversely, setting $\alpha = \delta = 0$, we obtain the result of CHAPMAN and MASON [4]. Once again this highlights the reason for the aparent discrepancy between Waldmann's and Chapman and Mason's results, viz.: Waldmann uses a true diffuse scattering law whilst that of Chapman and Mason corresponds to Lambert's law.

Finally, we note that it is a trivial matter to include a more detailed velocity distribution function to account for the effects of thermal diffusion.

(f) The Kuščer-Cercignani Model

For this model the value of Q_1 is

$$Q_1 = 1 + \tfrac{1}{8}\pi - \tfrac{1}{2}\varDelta_0 + \tfrac{1}{32}\pi\,\varDelta^2$$

or (41)

$$Q_1 = 1 + \tfrac{1}{8}\pi - \tfrac{1}{2}(1-\alpha_{||}) + \tfrac{1}{16}\pi(1-\alpha_\mathrm{E})\,.$$

Unless $\alpha_{||}$ and α_E are different for the two gas species, the value of $\mathbf{V}_\mathrm{d}$ is unaffected by the gas-surface interaction.

4. Combined Effects of Thermo-phoresis and Diffusio-phoresis

For a particle in a binary mixture containing concentration and temperature gradients, we can obtain the net drift velocity by using the appropriate form of the Chapman-Enskog solution in Equation (32). In the simplest case where the thermal diffusion effect can be neglected (i. e. the production of a net heat flux due to the concentration difference) we can use quite simply Eqs. (4) and (37). For greater accuracy, particularly for isobaric mixtures, it is necessary to consider the Dufour effect; however, we shall not pursue this topic any further here.

5. Particle Motion in a General Gas Flow Field

The problems of diffusio-phoresis and thermophoresis are but special cases of forces acting on particles in general flow distributions. Thus we can also ask what the motion of a particle will be if it is situated in a sound-wave field, i. e. "sonar-phoresis", or in the velocity field set up by Couette flow, slip flow or Poiseuille flow or any other practical situation. The general formalism for such a calculation is available from Eq. (1) where $f(\ldots)$ is the appropriate velocity distribution function. We can use this to find the force on the particle or, more conveniently, the average velocity of the particle can be found by equating $\boldsymbol{F}$ to the drag force generated by a body moving with the particle velocity $\mathbf{V}_\mathrm{p}$.

As an example, of this procedure, consider the case of small perturbations such that the distribution function $f(\ldots)$ can be written

$$f(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t) = f_0(g)\,\{1 + h(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t)\} \tag{42}$$

where $f_0(g)$ is a local Maxwellian.

The force on a particle moving in the direction $\boldsymbol{n}$ and situated in this flow field is

$$\begin{aligned} F_n = m \int_0^\infty \mathrm{d}g\, g^3 \int_0^\infty \mathrm{d}g'\, g'^2 \int \mathrm{d}\boldsymbol{\Omega}'(\boldsymbol{n}\cdot\boldsymbol{\Omega}') \\ \cdot\, \sigma_1(g'\to g)\, f_0(g')\; h(g', \boldsymbol{n}\cdot\boldsymbol{\Omega}', \boldsymbol{r}, t) \qquad (43) \\ - m\,\sigma \int_0^\infty \mathrm{d}g\, g^4 \int \mathrm{d}\boldsymbol{\Omega}\,(\boldsymbol{n}\cdot\boldsymbol{\Omega})\, f_0(g)\, h(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t)\,. \end{aligned}$$

For particle speeds very much less than $(2\,kT/m)^{1/2}$ the corresponding drag force on a particle whose speed is $V_{pn}(\boldsymbol{r}, t)$ is given by

$$F_{\mathrm{d}} = \frac{m}{2\,k\,T}\,2\,m\,V_{pn}(\boldsymbol{r}, t)\;\Big\{\int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^3 \int \mathrm{d}\boldsymbol{\Omega}'\,(\boldsymbol{n}\cdot\boldsymbol{\Omega}')^2 \cdot \sigma_1(g'\to g)\,f_0(g') - \sigma \int_0^\infty \mathrm{d}g\,g^5 \int \mathrm{d}\boldsymbol{\Omega}\,(\boldsymbol{n}\cdot\boldsymbol{\Omega})^2 f_0(g)\Big\}\,. \tag{44}$$

If these two forces are equal, the particle will move with an average macroscopic velocity V_{pn} given by

$$\frac{m}{2\,k\,T}\,V_{pn}(\boldsymbol{r}, t) = \frac{\int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^2 \int \mathrm{d}\boldsymbol{\Omega}'\,\boldsymbol{n}\cdot\boldsymbol{\Omega}'\,\sigma_1(g'\to g)\,f_0(g')\,h(g', \boldsymbol{n}\cdot\boldsymbol{\Omega}', \boldsymbol{r}, t) - \sigma \int_0^\infty \mathrm{d}g\,g^4 \int \mathrm{d}\boldsymbol{\Omega}\,\boldsymbol{n}\cdot\boldsymbol{\Omega}\,f_0(g)\,h(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t)}{2\int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^3 \int \mathrm{d}\boldsymbol{\Omega}'\,(\boldsymbol{n}\cdot\boldsymbol{\Omega}')^2\,\sigma_1(g'\to g)\,f_0(g') - 2\,\sigma \int_0^\infty \mathrm{d}g\,g^5 \int \mathrm{d}\boldsymbol{\Omega}\,(\boldsymbol{n}\cdot\boldsymbol{\Omega})^2 f_0(g)} \tag{45}$$

The corresponding value of the macroscopic gas velocity $\mathbf{V}_g$ will be

$$\mathbf{V}_g(\boldsymbol{r}, t) = \frac{\int \mathrm{d}\boldsymbol{g}\,f_0(g)\,g\,\boldsymbol{\Omega}\,h(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t)}{\int \mathrm{d}\boldsymbol{g}\,f_0(g)}\,. \tag{46}$$

If we use the spherical harmonic expansion of $h(\ldots)$, i. e.

$$h(g, \boldsymbol{n}\cdot\boldsymbol{\Omega}, \boldsymbol{r}, t) = \sum_{l=0}^{\infty} \frac{2\,l+1}{4\,\pi}\,P_l(\boldsymbol{n}\cdot\boldsymbol{\Omega})\,h_l(g, \boldsymbol{r}, t) \tag{47}$$

then V_{pn} can be written

$$\frac{m}{2\,k\,T}\,V_{pn}(\boldsymbol{r}, t) = \frac{\int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^2 f_0(g')\,\sigma_1(g'\to g)\,h_1(g', \boldsymbol{r}, t) - \sigma \int_0^\infty \mathrm{d}g\,g^4 f_0(g)\,h_1(g, \boldsymbol{r}, t)}{\frac{4}{3} \int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^3 f_0(g')\,\sigma_1(g'\to g) - \frac{4}{3}\,\sigma \int_0^\infty \mathrm{d}g\,g^5 f_0(g)}\,. \tag{48}$$

This particular form is useful for studying the motion of spheres in one-dimensional sound wave fields with the appropriate form for $h_1(g, x, t)$. The details will not be given here, but it may be shown that the particles suffer no net flow away from the sound source but rather oscillate about a fixed position with an amplitude and speed whose magnitude is determined by the maximum velocity of the sound generator, the values of the wave number and attenuation length of waves in the gas and also on the nature of the gas-surface interaction. It may be possible by observing the motion of the spheres to obtain useful information on the above-mentioned parameters.

Another interesting calculation is the way in which spheres behave when placed in a flow field such as that arising from slip flow. The calculation is now rather more complicated since $h(\ldots)$ depends upon the azimuthal angle ψ as well as the polar one ϑ. Thus if we consider the motion of a gas in the z-direction parallel to a flat plane at $x = 0$, where x is the coordinate perpendicular to the plane, we find that

$$h(\ldots) = h(g, \mu, \psi, x)$$

where the angular coordinates define $\boldsymbol{\Omega}\ (\mu, \psi)$ in the usual way[7].

If we wish to calculate the particle velocity in the z-direction we note that $\boldsymbol{n}\cdot\boldsymbol{\Omega} = \Omega_z = (1-\mu)^{1/2}\cos\psi$, moreover we define

$$G(g, \mu, x) = \frac{1}{\pi} \int_0^{2\pi} \mathrm{d}\psi\,\cos\psi\,h(g, \mu, \psi, x) \tag{49}$$

and find that $V_{pz}(x)$ is given by

$$\frac{m}{2\,k\,T}\,V_{pz}(x) = \frac{\int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^2 f_0(g')\,\sigma_1(g'\to g) \int \mathrm{d}\mu'\,(1-\mu'^2)^{1/2}\,G(g', \mu', x) - \sigma \int_0^\infty \mathrm{d}g\,g^4 f_0(g) \int \mathrm{d}\mu\,(1-\mu^2)^{1/2}\,G(g, \mu, x)}{\frac{8}{3} \int_0^\infty \mathrm{d}g\,g^3 \int_0^\infty \mathrm{d}g'\,g'^3 f_0(g')\,\sigma_1(g'\to g) - \frac{8}{3}\,\sigma \int_0^\infty \mathrm{d}g\,g^5 f_0(g)}\,. \tag{50}$$

Now in slip flow the complete expression for $G(g, \mu, x)$ is rather lengthy and is only known for special models. However, we can write down the form of $G(g, \mu, x)$ for x several mean free paths from the boundary, i. e. the asymptotic value. This is [7]:

$$G_{\text{asy}}(g, \mu, x) = 2\, K_0\, t (1-\mu^2)^{1/2} \{x - \zeta_{\text{v}} - \mu\, t\, b(t)\} \tag{51}$$

where $t^2 = m\, g^2/2\, k\, T$ and K_0 is the asymptotic gradient of velocity in the x-direction multiplied by $(m/2\, k\, T)^{1/2}$.

ζ_{v} is the slip coefficient and $b(t)$ the Chapman-Enskog viscosity function. Inserting (51) into (50) and (46) shows that, asymptotically, the gas and particle velocities are equal. On the other hand, at the surface of the gas where it meets the wall, the value of $G(g, \mu, x)$ in the B.G.K. approximation, subject to perfect accommodation of the gas and wall, is [7]:

$$G(g, \mu, 0) = \frac{2\, K_0\, t\, l(t)\, (1-\mu^2)^{1/2}\, \Psi(t, \mu)}{\Sigma_{\min}\, \tau_-(0)} \,. \tag{52}$$

In Eq. (52), $l(t)$ is the mean free path, $\Sigma_{\min}$ is the reciprocal of $\max[l(t)]$ and $\tau_-(0)$ and $\Psi(t, \mu)$ are universal functions characterized by the velocity dependence of the mean free path. The function Ψ satisfies certain relations which may be found in Reference [7].

Using (52) in (50) we can find the velocity of particles at the wall. For simplicity we will assume that the particle-gas interaction is a mixture of specular and diffuse scattering so that $\sigma_1(v' \to v) = f \times$ Equation (18). A simple calculation then shows that the relationship between the particle velocity and the gas velocity is

$$S_{\text{p}z}(0) = \frac{\pi f}{8+\pi f}\, S_{\text{g}}(0) + \frac{8}{5}\, \frac{K_0}{8+\pi f} \int_0^\infty \mathrm{d}t\, t^5\, l(t)\, e^{-t^2} \tag{53}$$

where $S(0)$ is $V(0)$ divided by $(2\, k\, T/m)^{1/2}$.

For a collision frequency which is independent of velocity we can show that

$$\frac{S_{\text{p}z}(0)}{S_{\text{g}}(0)} = \frac{3\sqrt{2}\, \pi + 2\, \pi\, f}{2\,(8+\pi\, f)} \,. \tag{54}$$

For $f = 0$, the ratio is equal to 0.47 whilst for $f = 1$ it is 0.62.

If we consider a mixture of Lambert, specular and backward scattering it is found that the result becomes independent of the gas-particle scattering model and equal to

$$S_{\text{p}z}(0) = \frac{K_0}{5} \int_0^\infty \mathrm{d}t\, t^5\, l(t)\, e^{-t^2} \,. \tag{55}$$

For constant collision frequency we get the ratio $S_{\text{p}z}(0)/S_{\text{g}}(0)$ equal to that of Eq. (54) with $f = 0$, i. e. 0.47.

We see from this exercise that the non-equilibrium nature of the flow near a boundary causes a differential speed, or slip, between the particle and gas flow. This is of no significance in the main stream but can become of importance near boundaries. Similar effects are to be expected in other flow patterns.

6. Summary and Discussion

Using the general theory of global scattering developed in paper I and the expression for the net force on a particle derived in the Appendix, we have studied the general nature of the forces induced by temperature and concentration gradients on aerosol particles. The force induced by the temperature gradient is seen to depend mainly on the first angular moment $\sigma_1(v' \to v)$ of the gas-surface kernel, but also on the way in which this interacts with the solution of the corresponding Chapman-Enskog conductivity equation. There is a sensitive interaction here and the net force is markedly model dependent. This is in contrast to the resulting creep velocity of the particle in which the model dependence cancels out unless there is a substantial proportion of diffuse reflection. We have been able here to distinguish clearly between the results of Waldmann and of Mason and Chapman for the creep velocity and the net force.

The effect of incomplete accommodation has been studied via the Kuščer-Cercignani model and it is concluded that the creep velocity is much more dependent on energy accommodation than on tangential momentum accommodation.

The work on diffusio-phoresis is general in principle but specific results have been obtained only by using the simplest form of the non-equilibrium distribution function for a binary gas mixture. On this basis, we find that the velocity of the aerosol particle under a concentration gradient is extremely insensitive to the gas-surface scattering law unless these are very different for the two gases. The velocity depends mainly on the mass differences and concentration ratios of the gas species. As predicted by other workers, the particle generally moves in the direction of flow of the heavier component.

Finally, we have examined the motion of a particle in a general velocity distribution and obtained an expression for its average velocity. Applying the theory to the special case of slip flow, we see that in the main stream the particle velocity and macroscopic gas velocity are equal. However, near the wall. the particle suffers substantial slip and, depending on the nature of the gas-particle and gas-wall interaction, can be as much as 40% of the local gas flow velocity. These conclusions are probably typical of other gas flows.

Appendix

The force on a particle in a gas may be calculated, by definition, from the net rate of change of momentum due to collision with the gas atoms. Thus the net force $\boldsymbol{F}$ is given by

$$\boldsymbol{F} = (\partial \boldsymbol{M}/\partial t)_{\text{coll}} \, ; \tag{A.1}$$

$\boldsymbol{M}$ being the momentum of the gas atoms.

In terms of the gas atom distribution function f we can rewrite Eq. (A.1) as

$$\boldsymbol{F} = m \int \mathrm{d}\boldsymbol{v} \, (\boldsymbol{v} - \mathbf{V}) \, (\partial f/\partial t)_{\text{coll}} \tag{A.2}$$

where $\mathbf{V}$ is the velocity of the particle.

In paper I, we derived an expression for $(\partial f/\partial t)_{\text{coll}}$, which for a moving particle can be written

$$(\partial f/\partial t)_{\text{coll}} = \int \mathrm{d}\boldsymbol{v}' \, \sigma(\boldsymbol{v}' - \mathbf{V} \to \boldsymbol{v} - \mathbf{V}) \, f(\boldsymbol{v}', \boldsymbol{r}) \; - |\boldsymbol{v} - \mathbf{V}| \, \sigma \, f(\boldsymbol{v}, \boldsymbol{r}) \, . \tag{A.3}$$

Inserting (A.3) into (A.2) and changing variables leads to

$$\boldsymbol{F} = m \int \mathrm{d}\boldsymbol{g} \, \boldsymbol{g} \int \mathrm{d}\boldsymbol{g}' \, \sigma(\boldsymbol{g}' \to \boldsymbol{g}) \, f(\boldsymbol{g}' + \mathbf{V}, \boldsymbol{r}) \; - m \, \sigma \int \mathrm{d}\boldsymbol{g} \, \boldsymbol{g} \, g \, f(\boldsymbol{g} + \mathbf{V}, \boldsymbol{r}) \, . \tag{A.4}$$

Assuming $\boldsymbol{n}$ to be a unit vector in the direction of particle motion and expanding $\sigma(\boldsymbol{g}' \to \boldsymbol{g})$ in spherical harmonics as follows:

$$\sigma(\boldsymbol{g}' \to \boldsymbol{g}) = \sum_{l=0}^{\infty} \frac{2\,l+1}{4\,\pi} \, \sigma_l(g' \to g) \, P_l(\boldsymbol{\Omega}' \cdot \boldsymbol{\Omega}) \tag{A.5}$$

we find that

$$\boldsymbol{F} = m \int_0^\infty \mathrm{d}g \, g^3 \int_0^\infty \mathrm{d}g' \, g'^2 \int \mathrm{d}\boldsymbol{\Omega}' \, \boldsymbol{\Omega}' \, \sigma_1(g' \to g) \, f(g', \boldsymbol{n} \cdot \boldsymbol{\Omega}', \boldsymbol{r}) \; - m \, \sigma \int_0^\infty \mathrm{d}g \, g^4 \int \mathrm{d}\boldsymbol{\Omega} \, \boldsymbol{\Omega} \, f(g, \boldsymbol{n} \cdot \boldsymbol{\Omega}, \boldsymbol{r}) \tag{A.6}$$

where we have set $f(\boldsymbol{g} + \mathbf{V}, \boldsymbol{r}) \equiv f(g, \boldsymbol{n} \cdot \boldsymbol{\Omega}, \boldsymbol{r})$.

Finally we can write the force in terms of the unit vectors $(\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k})$ as

$$\boldsymbol{F} = (\boldsymbol{i} \, a_x + \boldsymbol{j} \, a_y + \boldsymbol{k} \, a_z) \, |\boldsymbol{F}| \tag{A.7}$$

where $a_i = V_i / (V_x^2 + V_y^2 + V_z^2)^{1/2} = V_i / V \, ;$

V_x, V_y, V_z beinig the components of $\mathbf{V}$.

We note that the force depends only on the $l = 1$ component of the scattering kernel (A.5) and we shall comment upon this fact in the text.

We have also found it convenient to define a new variable t, such that $t^2 = m \, g^2 / 2 \, k \, T$ and from this

$$\sigma_1(t' \to t) = \left(\frac{2\,k\,T}{m} \right) \sigma_1(g' \to g) \, . \tag{A.8}$$

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