The thermophoretic force in the Knudsen regime near a wall

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(Received 12 November 1987; accepted 12 January 1988)

The thermophoretic forces acting on a small Knudsen particle in the neighborhood of a boundary have been investigated. The applied temperature gradient is constant, but it is not normal to the wall, thereby leading to thermophoretic forces both normal to and parallel with the wall. Using the velocity distribution of the gas atoms for this problem it has been possible to obtain the variation of the thermophoretic force as a function of distance from the boundary. It is noted that, for equal temperature gradients, the force is greater in the direction normal to the wall than along it. In addition, it is observed that the velocity dependence of the mean free path has a significant effect on the force in the neighborhood of the wall. In contrast to the normal force, which is in the direction of decreasing temperature, the mass flow induced by thermal creep along the wall leads to a parallel wall force that moves the particle in the direction of increasing temperature. When these two forces are compounded they indicate that particles can move in curved paths en route to the wall surface. As a by-product of the calculation, an exact expression for the thermal creep velocity as a function of distance from the wall for the case of constant collision cross section is presented.

I. INTRODUCTION

The phenomenon of thermophoresis arises when a small particle, situated in a fluid in which there exists a temperature gradient, moves in the direction opposite to the temperature gradient. An analogous situation exists when a gas is in contact with an unequally heated solid boundary. In this case a shear stress is exerted by the gas on the wall and a correspondingly equal and opposite shear stress is exerted by the wall upon the gas leading to a flow of gas adjacent to the wall. This is called thermal creep. In this case the gas moves in the direction of increasing temperature. The physical reasons for this behavior were explained by Maxwell and an excellent description is given by Kennard.[1] Basically, there is an unequal transfer of tangential momentum at the surface of the solid body with a greater contribution coming from the hotter side than the colder one.

As far as the motion of small particles in temperature gradients is concerned, there have been many attempts to explain the situation theoretically. The method of approach depends crucially on the relative size of the particle compared to a mean free path of a gas atom. For Knudsen numbers (Kn) that are small, hydrodynamic theory can be used with slip boundary conditions. Brock[2] has made extensive calculations in this respect for a single particle in an infinite medium and his results are considered to be valid for $\mathrm{Kn} \leqslant 0.1$. Other authors have extended the range of validity as described by Talbot *et al.*[3] in their review. For very small particles, where the Knudsen number is large, hydrodynamic theory even with slip boundary conditions fails. In principle, one should employ the Boltzmann equation with appropriate gas–particle boundary conditions for the particle but this is difficult to do. An alternative procedure, when the particle is very small, is to use free-molecular theory in which the gas atom velocity distribution is assumed to be unaffected by the presence of the particle. Waldmann and Schmitt[4] have reviewed this procedure in detail.

In many practical situations the particle is not in a gas of infinite extent, but near a boundary. Thus the additional complication of a gas–particle–solid boundary interaction arises. The work described above does not address this problem. The earliest work to account for the presence of a boundary was performed by Reed and Morrison[5] and later by Williams[6] who examined, in the slip regime, the effect of a boundary on particles moving normally toward a heated wall. Far away from the wall the standard results of Brock are obtained but as the wall is approached there is a marked change in the thermophoretic force. It would be very difficult to extend these results into the transition regime of larger Knudsen numbers but in the free-molecule limit some progress can be made. In this region, as we have stated above, the particle does not affect the gas and so the gas distribution function may be calculated by standard kinetic theory methods and used to compute the net force on the particle. Many kinetic theory problems can be solved exactly in linear transport theory, such as the temperature slip, thermal creep, and slip flow problems as well as sound wave and related drag problems. Thus in principle, once the velocity distributions of gas atoms for these problems are known, it is possible to calculate the force on the particle. Even some nonlinear problems are amenable to treatement such as, for example, the plane shock wave using the Mott-Smith approach.[7] In a previous publication, the author[8] has calculated the force on a small particle (i.e., $\mathrm{Kn} \to \infty$) in the case where a temperature gradient exists normal to a solid wall. At some distances from the wall, i.e., several mean free paths, the classical Waldmann–Schmitt results arise but near to the wall the thermophoretic force is modified and there is a small reduction. The effect is not large but nevertheless indicates that some care must be exercised in employing infinite medium results when boundaries are present.

In the present work we wish to extend our investigation of thermophoresis near a wall for small particles in the free-molecule limit by considering the more general case of a temperature gradient that is not normal to the wall. In fact,

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since we already have the result of the normal case, it will only be necessary to consider the problem of a temperature gradient parallel to the wall and obtain the net result by superposition. We will, however, clarify some of the points that arise in the normal case. When a temperature gradient exists parallel to a wall, we have what is essentially the thermal creep problem discussed above. This has been discussed in some detail by the author[9] for the generalized BGK model[10] of scattering and so many of the results are already available. The outcome will be an expression for the thermophoretic force on the particle as a function of distance from the boundary and as a function of the gas, wall, and particle scattering properties.

II. FORCE ON A PARTICLE IN A GAS

As we have shown in Ref. 11, the force on a small particle in a gas can be written as

$$\mathbf{F} = -m\int d\mathbf{v}\,\mathbf{v}\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}, \tag{1}$$

where

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = -v\sigma f(\mathbf{v},\mathbf{r}) + \int d\mathbf{v}'\,\sigma(\mathbf{v}'\to\mathbf{v})f(\mathbf{v},\mathbf{r}), \tag{2}$$

$f(\mathbf{v},\mathbf{r})$ is the velocity distribution function of the gas atoms, and $\sigma(\mathbf{v}'\to\mathbf{v})$ is the global scattering kernel for the gas–particle interaction. Here, σ is the total cross section for interaction and is simply πa^2 where "a" is the radius of the particle. Values of $\sigma(\mathbf{v}'\to\mathbf{v})$ have been obtained for a variety of gas–surface interactions by the author.[12]

In terms of the angular moments of the global scattering kernel, we can write the force as

$$\mathbf{F} = m\sigma\int_0^\infty dv\,v^4\int d\boldsymbol{\Omega}\,\boldsymbol{\Omega} f(v,\mathbf{n}\cdot\boldsymbol{\Omega},r) - m\int_0^\infty dv\,v^3\int_0^\infty dv'\,v'^2\sigma_1(\mathbf{v}'\to v)\int d\boldsymbol{\Omega}' f(v',\mathbf{n}\cdot\boldsymbol{\Omega},r). \tag{3}$$

Here we have written the velocity as $\mathbf{v} = v\boldsymbol{\Omega}$ and $\mathbf{n}$ is a unit vector in the direction of particle motion. Therefore, the problem reduces to a calculation of f for the particular case of interest.

III. THE TRANSPORT EQUATION

The Boltzmann transport equation may be written in the form[10]

$$\mathbf{v}\cdot\nabla f(\mathbf{v},\mathbf{r}) = n\hat{J}(f,f_1), \tag{4}$$

where $J(f,f_1)$ is a nonlinear collision term. An implicit assumption in our work on rarefied gases is that any deviations from the local Maxwellian distribution must be small. Thus we write

$$f(\mathbf{v},\mathbf{r}) = f_0(v,\mathbf{r})[1 + h(\mathbf{v},\mathbf{r})], \tag{5}$$

where f_0 is the local Maxwellian and h is, in an average sense, small compared with unity.

In the present problem, we consider a plane surface lying in the plane $x = 0$ so that x is the coordinate normal to the wall. Here, z is the coordinate along the wall and since we are only concerned with two-dimensional variations at this moment, we shall not require a third coordinate. The local Maxwellian is therefore

$$f_0(v,\mathbf{r}) = n(x,z)[m/2\pi kT(x,z)]^{3/2} \times\exp\{-[mv^2/2kT(x,z)]\}, \tag{6}$$

where the total particle density

$$n(x,z) = n_0[1 + (n_x/n_0)x + (n_z/n_0)z] \tag{7}$$

and the temperature is

$$T(x,z) = T_0[1 + (T_x/T_0)x + (T_z/T_0)z]. \tag{8}$$

The subscript x or z indicates gradient with respect to that direction. Assuming the perfect gas law, $p = nkT$, where p is constant, we eventually find for small perturbations

$$f_0(\mathbf{v},\mathbf{r}) = n_0 f_0(v)\{1 + (mv^2/2kT_0 - \tfrac{5}{2})(K_x x + K_z z)\}, \tag{9}$$

where $K_x = T_x/T_0$, $K_z = T_z/T_0$, and

$$f_0(v) = (m/2\pi kT_0)^{3/2}\exp[-(mv^2/2kT_0)]. \tag{10}$$

Inserting Eqs. (9) and (5) into Eq. (4) and neglecting second-order terms, leads to

$$K_x c_x\left(c^2 - \frac{5}{2}\right) + K_z c_z\left(c^2 - \frac{5}{2}\right) + c_x\frac{\partial h(\mathbf{c},x)}{\partial x} + V(c)h(\mathbf{c},x) = \int d\mathbf{c}'\,K(\mathbf{c},\mathbf{c}')e^{-c'^2}h(\mathbf{c}',x). \tag{11}$$

In arriving at Eq. (10) we have set $c^2 = mv^2/2kT_0$ and noted that the perturbation varies only in the direction normal to the plane. Here, $V(c)$ is the collision frequency and $K(\mathbf{c},\mathbf{c}')$ the scattering kernel between gas atoms.[13]

Following standard procedure, we change $\mathbf{c} = (c,\mu,\chi)$ to polar coordinates, where $\mu = \cos\theta$ and define

$$g(c,\mu,x) = \frac{1}{\pi}\int_0^{2\pi} d\chi\,\cos\chi\, h(\mathbf{c},x), \tag{12}$$

$$p(c,\mu,x) = \frac{1}{2\pi}\int_0^{2\pi} d\chi\, h(\mathbf{c},x), \tag{13}$$

where Eq. (11) decouples for p and g in the following way:

$$K_x c\left(c^2 - \frac{5}{2}\right)\mu + c\mu\frac{\partial p(c,\mu,x)}{\partial x} + V(c)p(c,\mu,x) = \sum_{L=0}^{\infty}\frac{2L+1}{2}P_L(\mu)\int_0^\infty dc'\,c'^2 e^{-c'^2}K_L(c,c') \times\int_{-1}^{1} d\mu'\,P_L(\mu')p(c',\mu',x) \tag{14}$$

and

$$K_z c\left(c^2 - \frac{5}{2}\right)(1-\mu^2)^{1/2} + c\mu\frac{\partial g(c,\mu,x)}{\partial x} + V(c)g(c,\mu,x) = \sum_{L=1}^{\infty}\frac{2L+1}{2L(L+1)}P_L^{(1)}(\mu)\int_0^\infty dc'\,c'^2 e^{-c'^2}K_L(c,c') \times\int_{-1}^{1} d\mu'\,P_L^{(1)}(\mu')g(c',\mu',x). \tag{15}$$

The angular moments $K_L(c,c')$ are defined in Ref. 13.

The gas–wall boundary condition is taken for simplicity to be perfectly accommodating with diffuse reemission. This leads to[13]

$$g(c,\mu,x) = 0, \quad \mu > 0, \tag{16}$$

$$p(c,\mu,0) = 4\int_0^1 d\mu'\,\mu' \int_0^\infty dc'\,c'^3 e^{-c'^2} p(c',-\mu',0), \quad \mu > 0. \tag{17}$$

Although it does not appear to be possible to solve these equations as they stand, it is useful to extract as much physical information as possible from them before introducing further approximations. Thus it is readily shown that the solutions can be written as

$$p(c,\mu,x) = B_0(c^2 - \tfrac{5}{2}) - K_x c a(c)\mu - \rho_p(c,\mu,x) \tag{18}$$

and

$$g(c,\mu,x) = c[A_0 - K_z a(c)](1-\mu^2)^{1/2} - \rho_g(c,\mu,x), \tag{19}$$

where ρ_p and ρ_g are functions that tend rapidly to zero as x increases. Here, B_0 and A_0 are constants to be found and $a(c)$ is the solution of the Chapman–Enskog thermal conductivity equations,[13] viz.,

$$-c\left(c^2 - \frac{5}{2}\right) + c\nu(c)a(c) = \int_0^\infty dc'\,c'^3 e^{-c'^2} K_1(c,c')a(c'), \tag{20}$$

where

$$\int_0^\infty dc\,c^4 e^{-c^2} a(c) = 0. \tag{21}$$

Therefore, at distances several mean free paths from the wall the asymptotic parts of Eqs. (18) and (19) will describe the distribution function.

We can also write the force on the particle in terms of g and p by means of Eq. (3). Thus the force arising from the component of temperature gradient perpendicular to the wall is

$$F_\perp(x) = \frac{4kn_0T_0}{\sqrt{\pi}}\left(\sigma\int_0^\infty dc\,c^4 e^{-c^2}\int_{-1}^1 c\mu\,\mu p(c,\mu,x) - \int_0^\infty dc\,c^3\int_0^\infty dc'c'^2 e^{-c'^2}\tilde{\sigma}_1(c'\to c) \times \int_{-1}^1 d\mu'\,\mu' p(c',\mu',x)\right), \tag{22}$$

where

$$\tilde{\sigma}_1(c'\to c) = (2kT_0/m)\sigma_1(v'\to v). \tag{23}$$

Similarly, the force resulting from the parallel gradient is

$$F_\parallel(x) = \frac{2kn_0T_0}{\sqrt{\pi}}\left(\sigma\int_0^\infty dc\,c^4 e^{-c^2} \times \int_{-1}^1 d\mu(1-\mu^2)^{1/2} g(c,\mu,x) - \int_0^\infty dc\,c^3\int_0^\infty dc'\,c'^2 e^{-c'^2}\tilde{\sigma}_1(c'\to c) \times \int_{-1}^1 d\mu'(1-\mu'^2)^{1/2} g(c',\mu',x)\right). \tag{24}$$

In the remaining sections we will solve the equations for p and g under various assumptions and hence obtain expressions for $F_\perp$ and $F_\parallel$.

IV. SPECIAL SOLUTIONS

Equations (14) and (15), with their associated boundary conditions (16) and (17), have been studied extensively in the context of rarefied gas dynamics.[10,13] For example, Eq. (14) describes the temperature slip problem that leads to a knowledge of gas behavior in the neighborhood of a heated wall. Equation (16) is also well known; it describes the phenomenon of thermal creep, i.e., the movement of a gas along a wall because of local stresses in the gas at the wall surface. In the present problem we are making use of these solutions to calculate the force on a small particle. For purposes of illustration, therefore, it will only be necessary to obtain simple solutions to find general trends. More accurate solutions would require extensive numerical studies that we wish to avoid here. Also, in order to avoid the use of complex gas–particle scattering laws, we will assume a mixture of specular and diffuse reflection. Then, the form of $\sigma_1(c'\to c)$ becomes[12]

$$\sigma_1(c'\to c) = -(8\sigma/9)\alpha cc' e^{-c^2}, \tag{25}$$

where α is the thermal accommodation coefficient. With this assumption, we may write

$$F_\perp(x) = \frac{4kn_0T_0\sigma}{\sqrt{\pi}}\int_0^\infty dc\,c^4 e^{-c^2}\int_{-1}^1 d\mu\,\mu p(c,\mu,x), \tag{26}$$

where we have made use of the relation

$$\int_0^\infty dc\,c^3 e^{-c^2}\int_{-1}^1 d\mu\,\mu p(c,\mu,x) = 0, \tag{27}$$

which can be derived from Eq. (14).[13]

Also we have

$$F_\parallel(x) = \frac{2kn_0T_0\sigma}{\sqrt{\pi}}\int_0^\infty dc\,c^3\left(c + \frac{\alpha\sqrt{\pi}}{3}\right) \times e^{-c^2}\int_{-1}^1 d\mu(1-\mu^2)^{1/2} g(c,\mu,x). \tag{28}$$

Knowledge of p and g will enable the forces on the particle to be obtained.

A. The force normal to the surface

The problem involving $F_\perp$ has been solved by the author in an earlier publication[8] using a simple BGK model with a constant cross-section. Thus we assumed that $K_l(c,c') = 0$ for $l > 1$ and

$$K_l(c,c') = \gamma cc' V(c)V(c'), \tag{29}$$

where

$$\gamma^{-1} = \int_0^\infty dc\,c^4 e^{-c^2} V(c).$$

For the constant cross-section model we further assume that $V(c) = c\Sigma$ where Σ is a constant and is related to the thermal conductivity of the gas by the relation

$$\frac{1}{\Sigma} = \frac{2\sqrt{\pi}}{3}\frac{\lambda_T}{n_0k}\left(\frac{m}{2kT_0}\right)^{1/2}. \tag{30}$$

The resulting transport equation may be solved exactly and the force given by

$$F_\perp(x) = -\frac{4n_0\sigma kT_0}{\sqrt{\pi}}\left(\frac{9\sqrt{\pi}}{64}\frac{K_T}{\Sigma} - \frac{\beta}{3}p_{11}(x)\right), \quad (31)$$

where $\beta = 3(1 - 81\pi/256)$ and $p_{11}(x)$ arises from the nature of the solution of the equation, which we have been able to write as

$$p(c,\mu,x) = p_0(\mu,x) + cp_1(\mu,x) + c^2p_2(\mu,x) \quad (32)$$

and

$$p_{11}(x) = \int_{-1}^{1} d\mu\, \mu p_1(\mu,x)\,. \quad (33)$$

An exact expression for $p_{11}(x)$ can be obtained by the Wiener–Hopf technique[14] but we have found that the following simpler expression is accurate to better than 0.5%, viz.,

$$p_{11}(x) = -\frac{K_x}{\Sigma}\left(\frac{4}{9\sqrt{\pi}} - \frac{3}{8}E_4(\Sigma x)\right), \quad (34)$$

where $E_4(x)$ is an exponential integral.[15]

Inserting this into Eq. (31) and using (30) leads to

$$F_\perp(x) = -\frac{32}{27\sqrt{\pi}}\sigma\lambda_T\left(\frac{m}{2kT_0}\right)^{1/2}\frac{dT}{dx} \times\left(1 - \frac{9\beta\sqrt{\pi}}{32}E_4(\Sigma x)\right). \quad (35)$$

We observe that as $x\Sigma \to \infty$, $F_\perp$ becomes equal to the classical infinite medium value of Schmidt and Waldmann for a constant mean free path. It is interesting to note that the ratio of the force at infinity to that at the surface is 1.003. Thus there is a very small variation indeed in the force as the surface is approached. How much this depends on the assumption of a constant mean free path can only be decided by solving for $p(c,\mu,x)$ with other scattering laws. Unfortunately, only the constant cross-section case of the temperature jump problem has been solved completely although numerical results do exist for other cases. Thus in order to obtain an estimate of the effect of a velocity-dependent collision cross section we shall adopt an approximate method suggested by Kladnik and Kuscer[16] for a problem in neutron transport theory. This method enables an approximate value of the force at the surface to be obtained.

We note that the boundary condition (17) relates the values of $p(\pm\mu)$ at the wall for $\mu > 0$. Kladnik and Kuscer assume that for $\mu < 0$ the value of p takes on its asymptotic value, viz.,

$$p(c,\mu,x) = B_0(c^2 - \tfrac{5}{2}) - K_x ca(c)\mu, \quad \mu < 0\,. \quad (36)$$

Now using Eq. (27) we may show that

$$p(c,\mu,0) = -\tfrac{1}{2}B_0, \quad \mu > 0\,. \quad (37)$$

Also using another relationship derivable from Eq. (14), viz.,

$$\int_{-1}^{1} d\mu\, \mu \int_0^\infty dc\, c^5 e^{-c^2} p(c,\mu,x) = -\frac{2}{3}K_x\int_0^\infty dc\, c^6 a(c)e^{-c^2} \quad (38)$$

we obtain

$$B_0 = \frac{2}{3}K_x\int_0^\infty dc\, c^6 a(c)e^{-c^2}\,. \quad (39)$$

From its definition, therefore, we find

$$F_\perp(0) = -\frac{4kn_0T_0\sigma}{3\sqrt{\pi}}K_x\int_0^\infty dc\, c^5\left(1 + \frac{3\sqrt{\pi}}{16}c\right)a(c)e^{-c^2}. \quad (40)$$

The corresponding expression for $F_\perp(\infty)$, which uses no approximation to p, is

$$F_\perp(\infty) = -\frac{8n_0T_0\sigma}{3\sqrt{\pi}}K_x\int_0^\infty dc\, ca(c)e^{-c^2}\,. \quad (41)$$

Since $F_\perp(0)$ is an approximation, it is useful to estimate its accuracy by comparison with the exact result that we have for constant cross section, viz.,

$$F_\perp(0) = -(n_0T_0\sigma/\sqrt{\pi})(K_x/\Sigma)\,. \quad (42)$$

For this case, the approximate value of $F_\perp(0)$ is given by

$$F_\perp(0) = -\frac{n_0T_0\sigma}{\sqrt{\pi}}\frac{K_x}{\Sigma}\left(\frac{8}{9\sqrt{\pi}} + \frac{9\sqrt{\pi}}{32}\right). \quad (43)$$

The value of the quantity in round brackets in Eq. (43) is equal to 1.000 005 and so our approximation is extremely good. It can be expected that the results for other scattering models will be of high accuracy. Thus if we now assume that the collision frequency is constant, viz., $V(c) = \lambda$, then we find that

$$F_\perp(\infty) = -(4n_0T_0\sigma/3\sqrt{\pi})(K_x/\lambda) \quad (44)$$

and

$$F_\perp(0) = -(2n_0kT_0\sigma/3\sqrt{\pi})(1 + 90\pi/256)(K_x/\lambda)\,. \quad (45)$$

The quantity $F_\perp(\infty)/F_\perp(0) = 0.950\,36$ is of interest because it indicates that the ratio of the force at the surface to that at infinity is sensitive to the scattering law. For constant cross section there is a very small reduction in the force at the surface of 0.3%. On the other hand, for constant collision frequency, which is a more realistic variation, the surface force is some 5% greater than the value at infinity. Using the correct form for $V(c)$, viz.,[13]

$$V(c) = (e^{-c^2}/\sqrt{\pi}) + (c + 1/2c)\,\mathrm{erf}(c) \quad (46)$$

it may be shown that $F_\perp(\infty)/F_\perp(0) = 0.977\,23$. Thus it does seem, on the basis of the BGK model at least, that the force increases as the particle approaches the surface but only by about 3%. The constant cross-section model is therefore somewhat misleading in this respect. However, definitive conclusions cannot be drawn until a more realistic energy exchange model is employed for the gas. Experience shows, however, that the velocity dependence of the mean free path is far more important in determining the transport behavior near a wall than the detailed energy exchange process.

B. The force parallel to the surface

Before dealing in detail with this case, it is useful to look at the value of $F_\parallel(\infty)$ using the asymptotic solution of Eq. (15), viz.,

$$g_{\rm asy}(c,\mu,x) = c[A_0 - K_z a(c)](1 - \mu^2)^{1/2}\,. \quad (47)$$

From Eq. (28) we observe that

$$F_{\parallel}(\infty)=\frac{8kT_0n_0\sigma}{3\sqrt{\pi}}\Big[A_0\Big(1+\frac{\alpha\pi}{8}\Big)$$
$$-K_z\int_0^\infty dc\, c^5e^{-c^2}a(c)\Big], \tag{48}$$

where, as yet, A_0 is unknown. To obtain an estimate of the surface force $F_{\parallel}(0)$ we can use the same approximate device as before, viz.,

$$g(c,\mu,x)=0,\quad \mu>0, \tag{49}$$
$$=[A_0-K_za(c)]c(1-\mu^2)^{1/2},\quad \mu<0. \tag{50}$$

From this we obtain

$$F_{\parallel}(0)=\tfrac{1}{2}F_{\parallel}(\infty). \tag{51}$$

Thus the force decreases towards the surface quite markedly in contrast to $F_{\perp}(x)$, which changes by only a small amount.

To make further progress it will be necessary to obtain a solution of the equation for $g(c,\mu,x)$. Advances in this direction have been made by Williams[9] where an exact solution has been obtained for the velocity-dependent BGK model as defined by Eq. (29). In that work, the primary goal was the calculation of the thermal creep velocity of the gas along the wall, viz.,

$$q(x)=\frac{1}{\sqrt{\pi}}\int_0^\infty dc\, c^3e^{-c^2}\int_{-1}^1 d\mu(1-\mu^2)^{1/2}g(c,\mu,x). \tag{52}$$

Using the representation of Eq. (19), we can write Eq. (52) as

$$q(x)=\frac{1}{2}A_0-\frac{1}{\sqrt{\pi}}\int_0^\infty dc\, c^3e^{-c^2}$$
$$\times\int_{-1}^1 d\mu(1-\mu^2)^{1/2}\rho_g(c,\mu,x), \tag{53}$$

where ρ_g tends rapidly to zero as $x\to\infty$. Thus the asymptotic creep velocity of the gas past the wall is

$$q_{\rm asy}=\tfrac{1}{2}A_0. \tag{54}$$

Therefore, the gas moves in the direction of *increasing* temperature. Now we have shown in Ref. 9 that for the constant cross-section model

$$A_0=2K_z/3\Sigma\sqrt{\pi}, \tag{55}$$

and for constant collision frequency

$$A_0=\frac{K_z}{\lambda}\Big(\frac{\sigma_0^2}{2}+\frac{1}{4}\Big), \tag{56}$$

where $\sigma_0=0.7662,\ldots$. Using these values we can write the forces as follows from Eq. (48). For constant cross section

$$F_{\parallel}(\infty)=\tfrac{2}{9}n_0kT_0\sigma\alpha(K_z/\Sigma) \tag{57}$$
$$=\frac{4\sqrt{\pi}}{27}\sigma\alpha\lambda_T\Big(\frac{m}{2kT_0}\Big)^{1/2}\frac{dT}{dz} \tag{58}$$

and for constant collision frequency

$$F_{\parallel}(\infty)=\frac{8kn_0T_0\sigma}{3\sqrt{\pi}}\frac{K_z}{\lambda}\Big[\Big(\frac{\sigma_0^2}{2}+\frac{1}{4}\Big)\Big(1+\frac{\alpha\pi}{8}\Big)-\frac{1}{2}\Big] \tag{59}$$
$$=\frac{32}{15\sqrt{\pi}}\sigma\lambda_T\Big(\frac{m}{2kT_0}\Big)^{1/2}\frac{dT}{dz}$$
$$\times\Big[\Big(\frac{\sigma_0^2}{2}+\frac{1}{4}\Big)\Big(1+\frac{\alpha\pi}{8}\Big)-\frac{1}{2}\Big], \tag{60}$$

where λ_T is the thermal conductivity of the gas. The ratio of the two values of $F_{\parallel}(\infty)$ for constant cross section and constant collision frequency is 0.848 98 for $\alpha=1$.

While the general form of $g(c,\mu,x)$ can be obtained by means of the Wiener–Hopf technique[9] the result is complex and no simple expression is available for $F_{\parallel}(x)$, except in the case of constant cross section. Then it may be shown that the exact solution is

$$g(c,\mu,x)=-(K_z/\Sigma)(1-\mu^2)^{1/2}(c^2-\tfrac{5}{2})$$
$$\times[1-e^{-\Sigma x/\mu}H(\mu)], \tag{61}$$

where $H(\mu)$ is the Heaviside unit function.

From this we can obtain a very simple expression for the creep velocity, viz.,

$$q(x)=\frac{K_z}{3\sqrt{\pi}\Sigma}\Big(1-\frac{3}{4}[E_2(\Sigma x)-E_4(\Sigma x)]\Big), \tag{62}$$
$$=\frac{2}{9}\frac{\lambda_T}{p}\frac{dT}{dz}\Big(1-\frac{3}{4}[E_2(\Sigma x)-E_4(\Sigma x)]\Big). \tag{63}$$

Thus

$$q_{\rm asy}=\frac{2}{9}\frac{\lambda_T}{p}\frac{dT}{dz}, \tag{64}$$

where p is the gas pressure, and

$$q(0)=\tfrac{1}{2}q_{\rm asy}. \tag{65}$$

While the limiting cases $q_{\rm asy}$ and $q(0)$ have been given before,[9] we present for the first time the complete solution for $q(x)$ over the whole range of x. From this expression we may conclude that the asymptotic velocity is reached very rapidly, i.e., within about two mean free paths from the surface.

For a constant collision frequency two simple results emerge, viz.,

$$q_{\rm asy}=\Big(\frac{\sigma_0^2}{2}+\frac{1}{4}\Big)\frac{2}{5}\frac{\lambda^T}{P}\frac{dt}{dz} \tag{66}$$

and

$$q(0)=\Big(\frac{\sigma_0}{\sqrt{2}}-\frac{1}{2}\Big)\frac{2}{5}\frac{\lambda_T}{p}\frac{dT}{dz}. \tag{67}$$

In this case $q_{\rm asy}=3.5q(0)$.

Using Eq. (61), we can now calculate the force and find

$$F_{\parallel}(x)=\frac{4\sqrt{\pi}}{27}\sigma\alpha\lambda_T\Big(\frac{m}{2kT_0}\Big)^{1/2}\frac{dT}{dz}$$
$$\times\{1-\tfrac{3}{4}[E_2(\Sigma x)-E_4(\Sigma x)]\}, \tag{68}$$

which has the same functional dependence on x as does the creep velocity. Clearly, $F_{\parallel}(\infty)=2F_{\parallel}(0)$ confirming the accuracy of the approximate method. We also note, in contrast to the normal force $F_{\perp}$, that $F_{\parallel}$ is in the same direction as the temperature increase. At first sight this is curious because we expect particles to move in the direction of decreasing temperature. However, in this case there is a mass motion of the gas with velocity $q(x)$ that carries the particle along. A more realistic measure of the thermophoretic force would be to refer the particle to a system in which the particle is at rest with respect to the mass motion caused by thermal creep. This can be done by calculating the drag force on the particle caused by the creep velocity $q(x)$.

As we have shown in Ref. 8, the drag on a small particle moving with velocity U is

$$F_U = -\frac{8mn_0}{3\sqrt{\pi}}\left(\frac{2kT_0}{m}\right)^{1/2} U \times\left(\sigma - \int_0^\infty dc\, c^3 \int_0^\infty dc'\, c'^3 \tilde{\sigma}_1(c' \to c) e^{-c'^2}\right). \quad (69)$$

In terms of the specular-diffuse model, this becomes

$$F_U = -\frac{8mn_0}{3\sqrt{\pi}}\sigma\left(1 + \frac{\alpha\pi}{8}\right)\left(\frac{2kT_0}{m}\right)^{1/2} U. \quad (70)$$

Thus the net force on the particle when $U = q(x)$ will be

$$F = F_U + F_\parallel , \quad (71)$$

which, from Eqs. (62) and (68), leads to

$$F = \frac{2\sqrt{\pi}}{27}\lambda_T \sigma \left(\frac{m}{2kT_0}\right)^{1/2} \frac{dT}{dz}\left(\alpha - \frac{8}{\pi}\right) \times\{1 - \tfrac{3}{4}[E_2(\Sigma x) - E_4(\Sigma x)]\}. \quad (72)$$

This force is always negative and is consistent with conventional thinking about thermophoresis.

In practice, if the particle is allowed to move, it will acquire a constant velocity $U_\parallel$ given by setting $F = 0$, viz.,

$$U_\parallel(x) = \frac{3\pi}{108}\frac{\alpha}{1 + \alpha(\pi/8)}\frac{\lambda_T}{P}\frac{dT}{dz} \times\{1 - \tfrac{3}{4}[E_2(\Sigma x) - E_4(\Sigma x)]\}. \quad (73)$$

Thus there is net motion in the direction of increasing temperature. We might also enquire about the velocity of the particle normal to the wall arising from $F_\perp(x)$. Since the particle is moving in the x direction, it will experience acceleration and thus it will be necessary to solve the equation

$$m\frac{dU}{dt} = F_\perp(x) - F_U(x), \quad (74)$$

where $U_\perp = dx/dt$. However, since $F_\perp(x)$ varies so slowly over the range $x = 0$ to ∞, it seems not unreasonable to neglect the acceleration term and obtain

$$U_\perp(x) = -\frac{2}{9}\frac{\lambda_T}{p}\frac{1}{1 + \alpha\pi/8}\frac{dT}{dx} \times[1 - (9\beta\sqrt{\pi}/32)E_4(\Sigma x)]. \quad (75)$$

Thus in terms of absolute magnitude, we find that

$$|U_\parallel(\infty)/U_\perp(\infty)| = \alpha(\pi/8)|T_z/T_x| \quad (76)$$

and

$$|U_\parallel(0)/U_\perp(0)| = \alpha(\sqrt{\pi}/9)|T_z/T_x|, \quad (77)$$

where we have used the exact value of $F_\perp(0)$ to calculate $U_\perp(0)$, viz.,

$$F_\perp(0) = \frac{2}{3}\sigma\lambda_T\left(\frac{m}{2kT_0}\right)^{1/2}\frac{dT}{dx} \quad (78)$$

and we have written $dT/dx = T_x$ and $dT/dz = T_z$.

We observe that the relative magnitudes of $U_\perp$ and $U_\parallel$ depend on the respective temperature gradients, but if these are equal then $|U_\perp| > |U_\parallel|$. The general shape of the trajectory of the particle as it moves towards the wall can be obtained by integrating the equations of motion. In general the particles will not move normally to the wall but rather in a curve tending to positive z.

V. SUMMARY AND CONCLUSIONS

The forces acting on a small particle situated in a gas with a constant temperature gradient have been investigated. The gas is bounded by a plane wall and therefore it has been necessary to account for the simultaneous action of wall–gas and particle–gas interaction. It is found that the presence of the wall affects the conventional value of the thermophoretic force within a few mean free paths of the wall. It is also found that the gas atom scattering law has a non-negligible influence. Thus for a temperature gradient normal to the wall, a velocity-independent collision cross section predicts that the force at the wall will be less than that at infinity, whereas a velocity-independent collision frequency predicts the reverse situation. The change in the latter case is around 5%.

If the temperature gradient is parallel to the wall, then, owing to the existence of thermal creep, the particle will move in the direction of increasing temperature. Although this is at first glance inconsistent with our understanding of thermophoresis, it is in fact a result of the mass motion of the gas. If the latter is accounted for by working in a system of coordinates moving with the creep velocity then a net force in the direction of decreasing temperature is found. Nevertheless, in practice, the direction of motion of the particle will be governed by compounding the normal and transverse forces and will lead to curved paths as the particles approach the wall. The precise form of these paths will depend upon the relative magnitudes of the normal and transverse temperature gradients.

While the phenomenon of thermophoresis has been studied for many years, it is only recently that the influence of a wall has been included in the calculation of the force. In fact, the motion of a particle parallel to a wall has hitherto received no attention and it is of some interest to note its particular behavior especially in view of its possible effect on deposition onto surfaces. In most calculations of thermophoretic deposition it is tacitly assumed that the temperature gradient acts normally to the surface, whereas in many engineering situations this may not be the case. While this effect is a relatively small one in the Knudsen regime, it could be more influential for smaller Knudsen numbers and a study of this effect in the hydrodynamic regime, analogous to the work of Reed and Morrison[5] and Williams,[6] would be profitable.

Finally, we comment on the effect of diffusion on the motion of the particle. It is clear that a particle of such small dimensions is likely to be strongly influenced by Brownian motion unless it is exceptionally massive. Thus the actual concentration of particles in the neighborhood of a boundary has to be determined by a diffusion equation as discussed by Chandrasekhar.[17] Therefore, if $C(\mathbf{r})$ is the steady-state concentration of aerosol particles, we have the following balance equation:

$$D\nabla^2 C(\mathbf{r}) - \nabla\cdot[\mathbf{V}C(\mathbf{r})] = 0\,. \tag{79}$$

In plane geometry, with the velocity directed in the negative x direction, we can write

$$D\frac{d^2C(x)}{dx^2} - \frac{d}{dx}[V(x)C(x)] = 0\,, \tag{80}$$

where $C(0) = 0$. If C_∞ is the current of particles at infinity and $V(\infty) = V_\infty$, the solution of the above equation becomes

$$C(x) = \frac{C_\infty V_\infty}{D}\int_0^x dx' \exp\left(\frac{1}{D}\int_x^{x'} V(x'')dx''\right). \tag{81}$$

The particle current to the wall is readily seen to be equal to $C_\infty V_\infty$ and therefore does not depend on the variation of $V(x)$ with position. On the other hand, for spherical and cylindrical bodies, there is a dependence on $V(\mathbf{r})$ but, unless the radius of curvature of the body is comparable to a mean free path, the effect of variations in the thermophoretic velocity resulting from surface perturbations will be negligible as far as the value of the particle current to the surface is concerned.

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