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Transport processes in dilute gases over the whole range of Knudsen numbers. Part 1. General theory

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The mean-free-path approach to kinetic theory, initiated by Maxwell, and largely abandoned after the Chapman–Enskog success with Boltzmann's equation, is revised and considerably extended in order to find expressions for the heat flux vector $\mathbf{q}$ and pressure tensor $\mathbf{p}$, valid (it is hoped) for all Knudsen numbers, K. These expressions (equations (2.24) and (2.26)) are integrals taken over the whole volume of the fluid plus surface integrals taken over the solid boundaries. The one phenomenological element is the mean free path λ, which takes different values according to whether it is mass, momentum or energy that is transported by the molecules. The need for such an approach is evidenced by the existence of critical values of K, above which the Chapman–Enskog expansion in powers of K, truncated after a finite number of terms, fails to yield a solution. For example with the Burnett equations, which are correct to $O(K^2)$, the critical K in a shock wave is only 0·2 based upon the upstream λ.

As a first check on our general theory, we have found the $O(K^2)$ expansions for $\mathbf{q}$ and $\mathbf{p}$ from integral equations and found, at least for a Maxwellian gas, almost exact agreement with all 19 coefficients (8 are identically zero) appearing in the second-order terms of Burnett's equations. In a later paper the theory will be tested at high K numbers by applying it to the propagation of very high frequency waves, for which experimental results and alternative theories are available.

1. Introduction

1.1. *Methods in kinetic theory*

Three distinct methods have been used in the kinetic theory of gases to determine laws for the transport of fluid momentum and heat. These are (i) the general analytical approach that starts from a kinetic equation for the velocity distribution function f, (ii) the use of Maxwell's equations of transfer with special molecules such that pairs interacting a distance r apart repel with a force $\propto r^{-\nu}$, $\nu = 5$, and (iii) the older free-path treatment of hard-sphere molecules ($\nu = \infty$) based directly on the actual physical mechanism of transport.

As Maxwell discovered, with the 'soft', $\nu = 5$ molecules, it is unnecessary to evaluate f in order to find values for the coefficients of viscosity μ and thermal conductivity κ, and, despite the inaccurate linear dependence of μ and κ on the temperature T given by this model, it does yield the relation $\kappa = \frac{5}{2}c_v\mu$, which the general theory of Chapman and Enskog reveals to be accurate to within 1% over the range $5 \leqslant \nu \leqslant \infty$. Mean-free-path theories also do not require a kinetic equation for f, and while they have the additional merit of being physically lucid, in their simplest form they give

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inaccurate values for μ and κ. Let $\bar{c}$ be the mean molecular speed, λ_0 the usual mean free path and ρ the fluid density, then mean-free-path arguments yield

$$\mu = a_1 \rho \bar{c} \lambda_0, \quad \kappa = a_2 c_v \mu,$$

with the constants a_1 and a_2 having the values $\frac{1}{3}$ and 1 in the simplest version. It is possible, however, to improve the theory and to obtain values of a_1 and a_2 close to their true values of $\sim \frac{1}{2}$ and $\sim \frac{5}{2}$.

Thus the position is that we have two special theories with certain defects, but which do not require us to solve Boltzmann's nonlinear equation for f, and a general theory that depends on our being able to solve this equation. No exact solutions of Boltzmann's equation suitable for the general theory have been found, so an expansion procedure is necessary, a point we shall return to shortly. While the general theory holds for any force law between molecules, it is unfortunately beyond the capacity of present day molecular physics to determine the force law for given molecules from first principles, so adjustable parameters like κ and ν in the power law $\kappa r^{-\nu}$ must be found from experimental values of μ and κ. And as κ and ν are found to depend weakly on the temperature, the theory is close to degenerating into mere curve fitting. From a practical viewpoint one may as well accept μ itself as being the empirical element, whereupon the only advance provided by kinetic energy over phenomenological fluid dynamics would reside in the relation $\kappa = \frac{5}{2} c_v \mu$.

1.2. *The Chapman–Enskog expansion*

The Chapman–Enskog method (Chapman & Cowling 1970) of solving Boltzmann's equation starts by expanding the velocity distribution function in the power series

$$f = f_0(1 + K\phi_1 + K^2\phi_2 + \ldots), \tag{1.1}$$

where f_0 is the equilibrium (Maxwellian) distribution function and $K = \lambda_0/L$ is the Knudsen number, L being the scale-length for changes in macroscopic variables. The Newtonian formula for the pressure tensor $\mathbf{p}$ and the Fourier law for the heat flux vector $\mathbf{q}$ are obtained by ignoring terms $O(K^2)$ in (1.1) (i.e. by assuming $K \ll 1$, and hoping that $\phi_2, \phi_3, \ldots$ remain bounded), while Burnett's (1935) nonlinear transport equations, and similar formulae due to Grad (1949), include terms $O(K^2)$ but ignore higher-order terms. The theory is not as instructive about the underlying physics as are free-path arguments, especially when terms $O(K^2)$ and higher are pursued, for the analysis becomes quite complicated. In fact according to Ferziger & Kaper (1972) one reason that Burnett's equations have not enjoyed much popularity is that there exists no heuristic, physically transparent derivation for them.

But there is a more serious objection to the Burnett equations, namely their failure in strong shock waves or in very high frequency sound waves, at apparently quite modest values for K. For example, at Mach numbers over 1·65 no solution to the equations can be found; with K based on the upstream value of λ_0, this failure occurs for $K > 0{\cdot}2$. While extension of the series (1.1) to higher powers in K improves the situation by increasing the critical Mach number (Elliot & Baganoff 1974), the improvement is small compared with the labour involved. As remarked by Chapman & Cowling (1970, p. 292), when K is not small, a new method of approximating to f becomes necessary, but short of resorting to numerical procedures for approximating solutions to Boltzmann's equation (Bird 1976), none has been found.

The only avenue open to the domain $K > 1$ appears to be via a somewhat generalized mean-free-path approach, which is to admit the possibility of some errors in numerical coefficients in exchange for a fluid theory covering the whole of the K range. Even a mean-free-path derivation of Burnett's equation would be instructive, and perhaps also provide an explanation of why they appear to be subject to much the same constraint ($K \ll 1$) as the Navier–Stokes equations. The object of this paper is the development of such a theory. We shall test its accuracy by deriving Burnett's equations on the one hand, and (in a later paper) deducing known results for $K \gg 1$ on the other hand.

1.3. *Generalized free-path theory*

The classical mean-free-path calculations of μ and κ for the linear transport equations, associated with the names Maxwell, Clausius, Boltzmann, Meyer and Jeans, are in error by numerical factors between 1 and $\frac{5}{2}$. However, the reasons for these errors are understood, being explained by the 'persistence of (molecular) velocities' after collisions and by the higher rate of convection of the molecular kinetic energy by the faster molecules. We shall incorporate these effects into our theory by adopting different mean free paths for the transport of momentum (λ_1) and energy (λ_2), relating these lengths to the usual or 'particle' mean free path λ_0 by $\lambda_1 = a_1 \lambda_0$, $\lambda_2 = a_2 \lambda_0$, where a_1, a_2 are numbers that we could assign either with the help of the accepted values of μ and κ, or by quite separate arguments independent of the solution of Boltzmann's equation.

Even with the errors in μ and κ removed in the manner described, their initial appearance suggests that any effort to extend mean-free-path theory to a range of K values could be beset by even more serious discrepancies. Certainly with the generalized mean-free-path theory developed below, we had no expectation of getting agreement with all the additional nineteen numerical coefficients appearing in the Burnett equations – six terms in $\mathbf{p}$, eight vanishing terms in the trace of $\mathbf{p}$ and five terms in $\mathbf{q}$. It was merely our hope to get values for these second-order terms sufficiently close to the Burnett values to give credibility to our general expressions for $\mathbf{p}$ and $\mathbf{q}$. In fact we find that, at least for Maxwellian molecules, the theory gives exact values for all but three of the Burnett terms, with errors of less than 1 % in two coefficients and about 7 % in the third term. We take this to be strong support for our model. We have thus filled the gap mentioned by Ferziger and Kaper of providing a heuristic treatment of Burnett's equations, although we hope the reader can agree that it is better than merely 'heuristic', even where it is not entirely deductive.

Burnett's theory holds for K values rather less than unity. In a later paper we shall test our model over a wide range of K values by studying the propagation of sound waves of wavelength λ_w such that $\kappa = \lambda_0/\lambda_w$ varies from near zero to 10^2 or more. The results so far obtained for these high frequency waves reveal good agreement with experiment, encouraging us to believe that our generalized fluid dynamics is accurate over the whole Knudsen number range.

It may be objected that our theory can apply only to the hard-sphere molecules for which the concept of free path is unambiguous. But we shall not accept this constraint, following instead the usual device of using the hard-sphere relation between μ and λ_1 to define an effective λ_1 for 'soft' molecules. The mean free path that appears in our theory may be interpreted as being a phenomenological parameter that assumes the usual precise free-path meaning only for hard-sphere molecules, although in setting up the model we find it convenient to use the free-path interpretation to illustrate the steps. The real justification of the model lies not so much with its mechanistic description (which we hope is convincing) but with the agreement of its consequences with known results, especially at high K numbers.

1.4. *Generalized fluid dynamics*

The principal contributions of the paper are expressions for $\mathbf{p}$ and $\mathbf{q}$ as integrals over the whole of the fluid volume. Apart from the phenomenological parameters $\lambda_i = \lambda_i(\rho, T)$, $i = 1, 2$, these integrals involve the velocity field $\mathbf{v}(\mathbf{r}, t)$ of the fluid, the density $\rho(\mathbf{r}, t)$ and the temperature $T(\mathbf{r}, t)$ at all points in the flow, and hence, taken with the three conservation equations of fluid dynamics, they generalize the Navier–Stokes equations into a set of integro-differential equations for $\mathbf{v}$, ρ and T. Thus we have developed a non-local theory of fluid dynamics which should find application in rarefied gas dynamics, astrophysical gas dynamics and plasma physics. Contributions to the integrals for $\mathbf{p}$ and $\mathbf{q}$ from solid boundaries will depend on whether one supposes molecular reflexion to be diffuse or specular, so this *bête noire* of standard kinetic energy remains with us.

The theory is developed initially for a single molecular speed and then generalized by averaging over a Maxwellian distribution of speeds. Our equations are thus non-local in real space and averaged over the equilibrium distribution in velocity space, in contrast to ordinary kinetic theory, which is local in real space and non-local in velocity space.

Finally the underlying motivation for our work should be mentioned. With ordinary gases, unless boundary conditions force extremely sudden changes to occur within the flow, e.g. as in sound waves forced at very high frequencies or in strong shock waves, the usual linear laws for $\mathbf{p}$ and $\mathbf{q}$ are adequate. However the situation is different in plasma physics. Transition regions are often dominated by electric fields and currents and can thus be much shorter than mean free paths, giving $K \gg 1$. If a fluid description is to be attempted for such a plasma, then non-local expressions for $\mathbf{p}$ and $\mathbf{q}$ are certainly required. Of course kinetic equations for f could be used, but these are much more complicated to solve than the fluid equations and, where plasma turbulence exists, their correct form remains a topic for conjecture. The mean-free-path approach, depending as it does directly on a physical mechanism, rather than on an uncertain mathematical equation for f, has much in its favour, despite its requiring a phenomenological element in the mean free path.

For an entirely different form of generalized fluid dynamics the reader is referred to a paper by Bixon, Dorfman & Mo (1971). Their work is based on the linearized Boltzmann equation and leads to linear hydrodynamic equations, but is nevertheless somewhat complicated analytically. Linearization is a severe constraint, cutting out for example as many as seven of the eleven Burnett terms and disqualifying the theory for shock wave studies.

2. The model

2.1. *Molecular velocities*

We shall be considering the motion of a typical molecule S that experiences a collision in a volume element dv' at the point $P'(\mathbf{r}', t')$ and subsequently passes through a unit surface $\Sigma\mathbf{n}$ at $Q(\mathbf{r}, t)$, which we shall call the 'target'. Let $\mathbf{v}' = \mathbf{v}(\mathbf{r}', t')$ and $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ denote the fluid velocities at P' and Q, then, imposing the velocity $-\mathbf{v}$ on the origin of co-ordinates O, we have a frame in which Q is stationary. In this frame a fluid particle† P will have a velocity $(\mathbf{v}'-\mathbf{v})$ when it passes through P'. Let $S(\mathbf{r}_s, t_s)$ be the position of S after it has moved a distance s along its path relative to P and let $s = R$ when S arrives at the target Q. If P has reached $\bar{P}$ at the instant S reaches Q, the vector $\overrightarrow{\bar{P}Q}$ can be written as $R\hat{\boldsymbol{\alpha}}$, where $\hat{\boldsymbol{\alpha}}$ is unit vector. Thus $\bar{P}$ is the point $(\bar{\mathbf{r}}, t)$ $\bar{\mathbf{r}} = \mathbf{r} - R\hat{\boldsymbol{\alpha}}$, as shown in figure 1, and, if $\mathbf{v}_p$ is the velocity of P in the defined frame,

$$\bar{\mathbf{r}} = \mathbf{r}' + \int_{t'}^{t} \mathbf{v}_p \, dt \quad (\mathbf{v}_p = \mathbf{v}' - \mathbf{v} \quad \text{at} \quad t = t'). \tag{2.1}$$

During the collision in dv' S will acquire a thermal velocity component, say $c\hat{\mathbf{R}}$, along the unit vector $\hat{\mathbf{R}}$. Later the speed c will be averaged over a Maxwellian distribution. In order to separate macroscopic effects in c from the entirely random effects, we shall find it convenient to introduce the ratio ω, and speeds C_0, C_1 and C_2 defined by

$$\left.\begin{array}{c} c = \omega(2kT/m)^{\frac{1}{2}} = \omega\delta_0 C_0 = \omega\delta_1 C_1 = \omega\delta_2 C_2, \\ C_0 = \bar{c} = (8kT/\pi m)^{\frac{1}{2}}, \quad \delta_0 = \tfrac{1}{2}\sqrt{\pi}; \quad C_1 = (\overline{c^2})^{\frac{1}{2}} = (3kT/m)^{\frac{1}{2}}, \quad \delta_1 = (\tfrac{2}{3})^{\frac{1}{2}}; \\ C_2 = (\overline{c^4})^{\frac{1}{4}} = (\tfrac{5}{3})^{\frac{1}{4}} C_1, \quad \delta_2 = (\tfrac{4}{15})^{\frac{1}{4}}, \end{array}\right\} \tag{2.2}$$

where m is the molecular mass, k is Boltzmann's constant and T is the temperature. The averages C_i, $i = 0, 1, 2$, which, as we shall see later, arise naturally in the linear transport theory, depend on $(\mathbf{r}, t)$ via the temperature, whereas ω is a random variable independent of $(\mathbf{r}, t)$ distributed as a Maxwellian:

$$f(\omega)\, d\omega = (4/\sqrt{\pi})\, \omega^2 \exp(-\omega^2)\, d\omega, \quad 0 \leqslant \omega < \infty. \tag{2.3}$$

The factors δ_i in (2.2) result from the averages

$$\bar{\omega} = 2/\sqrt{\pi}, \quad \overline{\omega^3} = 4/\sqrt{\pi}, \quad \overline{\omega^2} = \tfrac{3}{2}, \quad \overline{\omega^4} = \tfrac{15}{4}. \tag{2.4}$$

Let $\mathbf{F}$ be the body force on the fluid per unit mass, $\mathscr{F}$ be the fluid stress density and $\mathbf{a}$ the fluid acceleration, then

$$\mathscr{F} = -\frac{1}{\rho}\nabla \cdot \mathsf{p}, \quad \frac{d\mathbf{v}}{dt} \equiv \mathbf{a} = \mathscr{F} + \mathbf{F}. \tag{2.5}$$

The force $\mathbf{F}$ acts continuously on the individual molecules, whereas the fluid stress density $\mathscr{F}$, although continuous in the fluid, must act impulsively on individual molecules at each collision. Thus the molecule S has the equation of motion $\ddot{\mathbf{r}}_s = \mathbf{F}_s$, the

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† By a 'fluid particle' P here and below we mean a region infinitesimal on a macroscopic scale, whose boundary moves with the local fluid velocity, and whose mass is therefore constant. In classical fluid dynamics such regions are taken to be much larger across than a mean free path, but here we merely require P to be sufficiently large for the various macroscopic averages to be smooth functions of $\mathbf{r}$ and t.

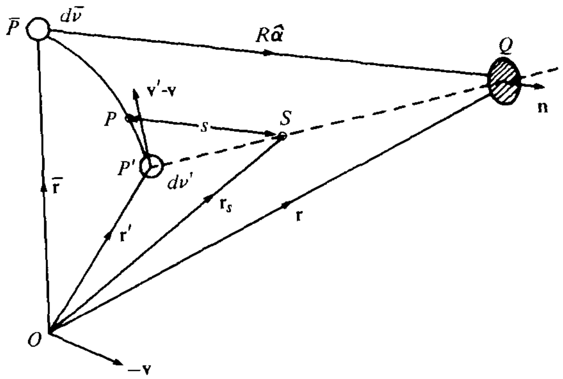

FIGURE 1. Particle trajectories: P, fluid particle molecular source; Q, molecular target; S, typical molecule.

subscript s denoting values on the trajectory at the point $(\mathbf{r}_s, t_s)$, and $\mathscr{F}$ contributes only to the initial velocity of S.

However not all components of $\mathbf{p}$ are transmitted in a collision between molecules unless, as we shall shortly explain, one of them is stationary in the frame in which $\mathbf{p}$ is measured. It is convenient to split $\mathbf{p}$ thus:

$$\mathbf{p} = p\mathbf{1} + \boldsymbol{\pi}, \tag{2.6}$$

where $\mathbf{1}$ is the unit tensor, p is the thermodynamic pressure and $\boldsymbol{\pi}$ is the viscous stress tensor, i.e. the stress due to differential fluid motions. At a collision sending S along $\hat{\mathbf{R}}$, the non-random component of force between the molecules will lie along $\hat{\mathbf{R}}$. Now if the colliding molecules, S and S', approach the collision point P' with stationary centre of mass and identical speeds C_1, the appropriate average speed for the transmission of momentum, as will be established later, then S and S', coming from previous collisions symmetrically disposed about P', will transport cancelling effects from $\boldsymbol{\pi}$, whereas if S' is initially stationary (or S is finally stationary) such cancellation will not occur. Let $\mathbf{p}_*$ be that part of the pressure tensor effective in a collision, then the point just made is satisfied if

$$\mathbf{p}_* = (p - \omega\delta_1 \hat{\mathbf{R}}\hat{\mathbf{R}} : \boldsymbol{\pi})\mathbf{1} + \boldsymbol{\pi},$$

for, when S has the speed C_1, $\mathbf{p}_* : \hat{\mathbf{R}}\hat{\mathbf{R}} = p$, and, when S is stationary, $\mathbf{p}_* : \hat{\mathbf{R}}\hat{\mathbf{R}} = \mathbf{p} : \hat{\mathbf{R}}\hat{\mathbf{R}}$. Accordingly it is our hypothesis that the force acting on S due to fluid stress is not $\mathscr{F}$, but $-\nabla . \mathbf{p}_*/\rho$, i.e.

$$\mathscr{F}_* = \mathscr{F} + \omega\delta_1 \frac{1}{\rho} \nabla\boldsymbol{\pi} : \hat{\mathbf{R}}\hat{\mathbf{R}}. \tag{2.7}$$

The initial velocity imparted to S will depend on what property it is assumed S is transporting. In (2.2) the subscripts i on C_i will be shown below to describe average speeds for particle ($i = 0$), momentum ($i = 1$) and energy ($i = 2$) transport. With the same convention, we shall write $\mathscr{T}_i$ ($i = 0, 1, 2$) for the three time-intervals associated with $\mathscr{F}_*$. In § 2.4 it will be shown that $\mathscr{T}_i$ is almost the same as the corresponding mean free time between collisions. Of course the impulsive velocity $\mathscr{T}_i \mathscr{F}_*$ is really due to a much larger force acting over a smaller time, our expression representing the integrated effect.

At P', in a frame in which Q is stationary, S starts off towards Q with the initial velocity

$$\mathbf{u}'_i = \omega\delta_i C'_i \hat{\mathbf{R}} + \mathscr{T}'_i \mathscr{F}'_* + \mathbf{v}' - \mathbf{v}, \quad i = 0,\ 1,\ 2, \tag{2.8}$$

where the dash denotes values at $(\mathbf{r}', t')$. At $(\mathbf{r}_s, t_s)$ on its trajectory S will have the velocity

$$\dot{\mathbf{r}}_{si} = \omega\delta_i C'_i \hat{\mathbf{R}} + \mathscr{T}'_i \mathscr{F}'_* + \mathbf{v}' - \mathbf{v} + \int_{t'}^{t_s} \mathbf{F}\, dt, \tag{2.9}$$

and in particular the velocity of S as it passes through the target at $Q(\mathbf{r}, t)$ is

$$\mathbf{u}_i = \omega\delta_i C'_i \hat{\mathbf{R}} + \mathscr{T}'_i \mathscr{F}'_* + \mathbf{v}' - \mathbf{v} + \int_{t'}^{t} \mathbf{F}\, dt. \tag{2.10}$$

Let $\mathsf{T} \equiv t - t'$ denote the transit time between P' and Q, then by (2.1) and (2.9)

$$\left.\begin{aligned} \mathbf{r} &= \mathbf{r}' + \mathsf{T}\mathbf{u}'_i + \int_{t'}^{t}\int_{t'}^{t} \mathbf{F}_\sigma\, dt_\sigma\, dt_s, \\ \mathbf{r} &= \bar{\mathbf{r}} + \mathsf{T}(\mathbf{u}'_i - \mathbf{v}' + \mathbf{v}) + \int_{t'}^{t}\int_{t'}^{t_s} (\mathbf{F}_\sigma - \mathbf{a}_p)\, dt_\sigma\, dt_s \\ \text{and} \qquad R &= |\mathbf{r} - \bar{\mathbf{r}}| = \hat{\boldsymbol{\alpha}}.(\mathbf{r} - \bar{\mathbf{r}}), \end{aligned}\right\} \tag{2.11}$$

the subscript σ denoting a value of s, and $\mathbf{a}_p$ being the acceleration of the fluid element P. Of course T and R will depend on ω and i. We shall require (2.11) when in § 3 we expand in powers of K, the average transit time being proportional to K.

2.2. *The transit probability*

We require an expression for the probability that a molecule colliding in the volume element $d\nu'$ at P' subsequently passes through the target at Q. There are three distinct mean free paths invoved, depending on whether it is particle (λ_0), momentum (λ_1) or energy (λ_2) that our typical molecule is required to transport from P' to Q. And correpondingly there are three distinct probabilities, say $\mathscr{P}_i$, $i = 0,\ 1,\ 2$. The values of λ_i at P', s and Q will be denoted by λ'_i, λ_{si} and λ_i respectively. In general λ_i will depend on ρ, T and ω.

Provided $\hat{\mathbf{R}}.\mathbf{u} > 0$ and no solid boundaries intervene, the molecule S can overtake the fluid element Q and, granted this, the probability that any molecule leaving $d\nu'$ along $\hat{\mathbf{R}}$ will reach the target before experiencing a collision is

$$\exp\left(-\int_0^R ds/\lambda_{si}\right),$$

where ds is an element of distance measured along the trajectory.

Let n' be the molecular number density at P', then the collision rate in $d\nu'$ is $(n'C'_i/\lambda'_i)\, d\nu'$ and, assuming that the angular distribution of the collided molecules is isotropic (see § 2.3), we shall have a fraction $\mathbf{n}.\hat{\mathbf{R}}/(4\pi R^2)$ of these leaving P' in the correct direction to cross the target $\mathbf{n}\Sigma$ at Q. (Because of the relative motion of P, and Q, it is the 'final' distance $R = |\mathbf{r} - \bar{\mathbf{r}}|$ rather than the 'initial' distance $|\mathbf{r} - \mathbf{r}'|$

that is required in calculating the solid angle subtended by the target; to see this, redraw figure 1, with P' stationary and Q moving.)

Combining the above results, we conclude that $\mathbf{n}.\hat{\mathbf{R}}n'C'_i\,\mathscr{P}_i\,dv'$ molecules experience a collision each second in the volume element dv' and subsequently pass through the target, where $\mathscr{P}_i$ are the probability densities

$$\mathscr{P}_i = \frac{\exp\left[-\int_0^R ds/\lambda_{si}\right]}{4\pi R^2\lambda'_i}, \quad i = 0,\,1,\,2. \tag{2.12}$$

The volume element $d\bar{v}$ at $\bar{P}$ can be expressed

$$d\bar{v} = d\varpi\, R^2 dR, \tag{2.13}$$

where $d\varpi$ is the element of solid angle subtended at Q by $d\bar{v}$. And since (differentiating the lower limit)

$$\frac{d}{dR}\left(\exp\left[-\int_0^R ds/\lambda_{si}\right]\right) = \frac{-1}{\lambda'_i}\exp\left[-\int_0^R ds/\lambda_{si}\right],$$

it follows that

$$\int_V \mathscr{P}_i\,d\bar{v} = 1, \tag{2.14}$$

where the integral is over the fluid volume V, assumed here to extend over the whole of physical space.

2.3. *The various mean free paths*

As remarked in § 1.3, 'persistence of velocity' plays an important role in molecular transport. Its effect is to increase the distance between the source from which the molecules transport momentum and energy and the target Q. Thus, referring to figure 1, if we take P' to be not the position at which the molecule S had its last collision, but the point from which S is effectively transporting the local fluid momentum, then it will be displaced some distance further away from Q. Equivalently we can replace the mean free path λ_0 for particle transport by a larger mean free path λ_1 for momentum transport. With energy transport velocity persistence is even more effective in stretching the mean free path, yielding a length λ_2 substantially greater than λ_1. With these transport processes we have different mean free times τ_i defined by

$$\lambda_i = c\tau_i = \omega\delta_i C_i \tau_i = \omega\delta_i \Lambda_i \quad (\Lambda_i \equiv C_i\tau_i), \tag{2.15}$$

where Λ_i are the average mean free paths introduced in § 1.

It is important for our model that λ_i and τ_i be independent of macroscopic gradients, i.e. have values at a given point determined only by the temperature and density at that point. Thus the persistence of velocity introduced above is defined as in the text by Jeans (1921) or Chapman & Cowling (1970), so the lengthening of the mean free paths will remove only that anisotropy at P' due to persistence under uniform conditions. Anisotropy in the molecular velocity due to gradients is represented by the term $\mathscr{T}'_i\mathscr{F}'_*$ appearing in (2.10), and a basic assumption in this paper is that there are no other similar terms. Certainly, as will be demonstrated in § 3, $\mathscr{T}'_i\mathscr{F}'_*$ is correct to $O(K^2)$.

Mass transport is to be distinguished from particle transport. By λ_0 we mean the average distance that an identifiable molecule moves between collisions, i.e. the usual

	Speed	Mean-free path	Free time
Particles	$C_0 = \bar{c}$	$\lambda_0 = (2\pi n\sigma^2)^{-\frac{1}{2}}$	$\tau_0 = \lambda_0/\bar{c}$
Momentum	$C_1 = (\frac{3}{8}\pi)^{\frac{1}{2}}\,\bar{c}$	$\lambda_1 = (6/\pi)^{\frac{1}{2}}\,\lambda_0$	$\tau_1 = (4/\pi)\,\tau_0$
Energy	$C_2 = (\frac{5}{3})^{\frac{1}{4}}\,C_1$	$\lambda_2 = \frac{3}{2}(\frac{5}{3})^{\frac{1}{4}}\lambda_1$	$\tau_2 = \frac{3}{2}\tau_1$
Mass	$\bar{c}$	∞	∞

TABLE 1. Maxwellian molecules.

mean-free path. On the other hand the mean-free path for mass transport is infinite because at each collision between identical particles there is no reduction in the mass being transported in any direction, many particles becoming involved in this transport in a cascade process. This fact explains a paradox occurring in Meyer's mean-free-path theory (Jeans 1921), namely that his theory is (almost) correct only if collisions between like particles are ignored, which is equivalent to giving such collisions an infinite mean free path.

For Maxwellian molecules we shall adopt the values for C_i, λ_i and τ_i set out in table 1. In the second column σ is the effective molecular diameter, which, for the molecular force law $\kappa r^{-\nu}$ and a relative velocity v_r between colliding molecules, is easily shown to satisfy

$$v_r\sigma^2(v_r) \propto v_r^{(\nu-5)/(\nu-1)} = v_r^{2(1-\delta)}, \quad \delta \equiv \frac{1}{2}+\frac{2}{\nu-1}.$$

Then the free time is given by

$$n\tau_0 = \frac{1}{\pi v_r\sigma^2(v_r)} \propto v_r^{2(\delta-1)}, \tag{2.16}$$

which is constant for $\nu = 5$ (Maxwellian molecules). When v_r results from collisions between molecules in a Maxwellian velocity distribution $v_r = \sqrt{2}\,\bar{c} \propto T^{\frac{1}{2}}$, so

$$n\tau_0 \propto T^{\delta-1} \quad (\delta = 1 \quad \text{for Maxwellian molecules}), \tag{2.17}$$

and we arrive at the value of λ_0 given in table 1.

In the first column the speeds are those defined in (2.2); as will be shown in §§ 3.4–3.6, C_1 and C_2 arise naturally on taking averages over

$$\mu_c = \tfrac{1}{3}\rho c^2\tau_1, \quad \kappa_c = \tfrac{1}{6}\rho c^4\tau_2/T, \tag{2.18}$$

where μ_c, κ_c are the contributions to μ and κ from molecules of speed c and for Maxwellian molecules $\rho\tau_1$, $\rho\tau_2$ are independent of c. Notice that (2.18) yields the averages

$$\left.\begin{aligned} \mu &= \tfrac{1}{3}\rho C_1^2\tau_1 = \tfrac{1}{3}\rho C_1\lambda_1 = \tfrac{1}{2}\rho\bar{c}\lambda_0 = \tfrac{1}{2}\rho\bar{c}^2\tau_0, \\ \text{and}\qquad \kappa &= \frac{1}{6}\frac{\rho}{T}C_2^2\tau_2 = \frac{5}{2}\frac{3k}{2m}\tfrac{1}{3}\rho C_1^2\tau_1 = \theta c_v\mu \quad (\theta = \tfrac{5}{2}). \end{aligned}\right\} \tag{2.19}$$

The value $\theta = \frac{5}{2}$ has a high accuracy for all molecular force laws, so if for the general case average times $\bar{\tau}_1$, $\bar{\tau}_2$ are defined by $\overline{c^2\tau_1} = C_1^2\bar{\tau}_1$, $\overline{c^4\tau_2} = C_2^4\bar{\tau}_2$, it is necessary that $\bar{\tau}_2 = \frac{3}{2}\bar{\tau}_1$.

It may be thought that table 1 can be established only by adopting the known results of classical kinetic theory but this is not so. Jeans (1921) showed that for momentum transport with hard molecules persistence of velocity lengthens Maxwell's mean free path by a factor 1·382 ($\approx (6/\pi)^{\frac{1}{2}}$), but he failed with similar arguments to prove that θ should be $\frac{5}{2}$, obtaining instead a value near $\frac{3}{2}$. In § 3.5 we shall establish the correct value of θ using only mean-free-path arguments, so table 1 can be constructed independently of the Chapman–Enskog theory.

2.4. *The stress transfer time*

In (2.10) for the molecular velocity we introduce the impulsive velocity $\mathscr{T}'_i \mathscr{F}'_*$ without giving a value for the 'stress transfer time' $\mathscr{T}'_i$. That $\mathscr{T}_i$ is approximately equal to the free time τ_i defined in § 2.3 follows by comparing the fluid and molecular motions after a time $\delta t \gg \tau_i$. For in this period the change in the mean velocity of a molecule is $(\delta t/\tau_i)\,\mathscr{T}_i \mathscr{F}_*$, whereas, for the fluid element in which it moves, the velocity change is $\delta t \mathscr{F}$, and for these motions to be in accord it is necessary that the non-dimensional number β_i defined in

$$\mathscr{T}_i = \beta_i \tau_i$$

be approximately unity. From the theory for β_i given below, we find that it contributes only about 10 % to one of the nonlinear terms in Burnett's equation, so it represents a comparatively unimportant effect. On the other hand the correction of $\mathscr{F}$ to $\mathscr{F}_*$ given in (2.7) is quite significant, reducing two linear terms in Burnett's equation by one third.

That $\beta_i \neq 1$ is due to the anisotropy created at P' by molecules arriving at P' with different speeds depending on the locations of their previous collisions. These collisions will be distributed, on average, over a sphere Γ of radius λ' centred at P', so that temperature and fluid velocity gradients will result in different initial velocities for the molecules converging on P'. Ideally we should trace the molecules back in their trajectories over several previous collisions, but in a fluid model such details would not be justified.

The impulsive velocity $\mathscr{T}_i \mathscr{F}_*$ is due to collisions between our representative molecule S – which subsequently moves along $\hat{\mathbf{R}}$ and molecules coming from various points on Γ. Suppose that $\tilde{S}$ is a typical molecule colliding in $d\nu'$ with S, and that it comes from P'' on Γ, then because S must have a final velocity along $\hat{\mathbf{R}}$, the points P'' will not be found uniformly distributed over Γ. In fact if S were stationary at P' before the collision, P'' would have to lie on the hemisphere γ of Γ lying furthest from the target Q, i.e. with $\hat{\mathbf{R}}$ as normal to its flat surface, in order that $\tilde{S}$ could subsequently impel S along $\hat{\mathbf{R}}$. And in this special case P'' would be distributed uniformly over γ. Now P' is a fluid particle, i.e. relative to P' the molecules in the element $d\nu'$ have an average (vectorial) velocity of zero. So to simplify our determination of β' it seems reasonable to assume that S is stationary in $d\nu'$ prior to collision, so that $\tilde{S}$ comes from points P'' uniformly distributed over γ.

A molecule $\tilde{S}$ arriving at P' from a point P'' on γ will have a velocity $\tilde{\mathbf{u}}'_i$ given by a formula like (2.10), namely

$$\tilde{\mathbf{u}}'_i = \omega\delta_i C''_i \hat{\mathbf{R}}' + \mathscr{T}''_i \mathscr{F}''_* + \mathbf{v}'' - \mathbf{v}' + \int_{t''}^{t'} \mathbf{F}\,dt,$$

then, if U'_i denotes the average of $|\tilde{\mathbf{u}}'_i|$ taken over γ, on average $\tilde{S}$ will have the velocity $U'_i \hat{\mathbf{R}}$, and will experience a head-on collision with S. Now suppose that the 'macroscopic stress' between $\tilde{S}$ and S were to be transferred uniformly during the free time

τ'_i, then the average work done on $\tilde{S}$ in this time would be $U'_i \tau'_i |\hat{\mathbf{R}} . \mathscr{F}'_*|$, while that done on S would be $C'_i |\hat{\mathbf{R}} . (\mathscr{T}'_i \mathscr{F}'_*)|$. Equating these we get

$$\mathscr{T}'_i = \beta'_i \tau'_i, \quad \beta'_i \equiv U'_i / C'_i. \tag{2.20}$$

Admittedly, since $\tilde{S}$ has the speed U'_i and S the speed C'_i, they could not remain in contact during our hypothetical drawn-out encounter; our model merely secures the overall requirement that work is transferred without loss.

2.5. *Conservation of mass*

In § 2.2 we found that each second $\mathbf{n} . \hat{\mathbf{R}} n' C'_i \mathscr{P}_i dv'$ molecules with relative velocity ω experience a collision in dv' at P' and subsequently pass through the target. The rate at which they cross the target is obtained by replacing the initial velocity $\hat{\mathbf{R}} C'_i$ by the arrival velocity $\mathbf{u}_i$. Hence the number flux of molecules of mass m (and relative velocity ω) through the target is

$$dN'_i = \frac{1}{m} \rho' \mathbf{n} . \mathbf{u}_i \mathscr{P}_i dv', \quad i = 0, 1, 2, \tag{2.21}$$

where $\rho' = mn'$ is the fluid density.

It is tempting to assume that $m dN_0$ is the *mass* flux of such molecules through the target, and to suppose that its double integral over the Maxwellian for ω and over the whole fluid must vanish. But this is to confuse mass transport with particle transport, which, as mentioned in § 2.3, have very different mean free paths. For mass transport the mean free path extends back from the target Q to the fluid boundary, and the integral just mentioned would reduce to a surface integral.

There is however another form of mass conservation that plays an essential role in our theory, namely that the mass of the fluid particle P is constant (see figure 1). This enables us to write

$$\rho(\mathbf{r}', t') \, dv(\mathbf{r}', t') \equiv \rho' dv' = \bar{\rho} d\bar{v} \equiv \rho(\bar{\mathbf{r}}, t) \, dv(\bar{\mathbf{r}}, t), \tag{2.22}$$

so that in the integrals for $\mathbf{p}$ and $\mathbf{q}$ to be given below, we are free to replace $\rho' dv'$ by $\bar{\rho} d\bar{v}$. The importance of this move is that in (2.13) we have a simple expression for the volume element $d\bar{v}$, independent of the molecule's flight time, which is not true of dv'.

2.6. *Momentum and energy flux*

By equations (2.7), (2.10) and (2.20)

$$u_i = \omega \delta_i \, C'_i \hat{\mathbf{R}} + \beta'_i \, \tau'_i \, \mathscr{F}' + \omega \delta_1 \, \beta'_i \tau_i \frac{1}{\rho'} (\nabla \boldsymbol{\pi})' : \hat{\mathbf{R}} \hat{\mathbf{R}} + \mathbf{v}' - \mathbf{v} + \int_{t'}^{t} \mathbf{F} \, dt. \tag{2.23}$$

These velocities $\mathbf{u}_i$ and the probabilities $\mathscr{P}_i$ defined in (2.12) depend on the relative velocity ω, and the volume integrals for $\mathbf{p}$ and $\mathbf{q}$ to be given shortly must also involve integrals over the Maxwellian (2.3). As this second integration is straightforward, and merely produces the appropriate coefficients for various terms in the theory, to simplify the appearance of our formulae we shall indicate it by a bar over the volume integral sign; and we shall omit further reference to the ω dependence and its elimination by integration, save where the consequences are not immediately obvious.

The molecular momentum at the target $\mathbf{n}\Sigma$ is $m\mathbf{u}_1$ and, provided there are no solid boundaries in the fluid, the integral of $m\mathbf{u}_1 dN'_1$ over the fluid volume V is the rate at which momentum is transferred across $\mathbf{n}\Sigma$. By definition this is also $\mathbf{n}.\mathbf{p}$, hence by (2.21) and (2.22)

$$\mathbf{p} = \overline{\int}_V \bar{\rho}\mathbf{u}_1\mathbf{u}_1\mathscr{P}_1 d\bar{\nu}; \tag{2.24}$$

the influence of solid boundaries on (2.24) will be described shortly.

Since the trace of the viscous stress tensor, $\boldsymbol{\pi} = \mathbf{p} - p\mathbf{1}$, is zero for monatomic molecules, $p = \frac{1}{3}$ trace $\mathbf{p}$, i.e.

$$\left.\begin{aligned} p &= \frac{1}{3}\overline{\int}_V \bar{\rho}u_1^2\mathscr{P}_1 d\bar{\nu} \\ \text{and} \qquad \boldsymbol{\pi} &= \overline{\int}_V \bar{\rho}\mathbf{u}_1\overset{\circ}{}\mathbf{u}_1\mathscr{P}_1 d\bar{\nu} \quad (\mathbf{u}_1\overset{\circ}{}\mathbf{u}_1 \equiv \mathbf{u}_1\mathbf{u}_1 - \tfrac{1}{3}u_1^2\mathbf{1}) \end{aligned}\right\} \tag{2.25}$$

For monatomic molecules the energy transferred from P' to Q per molecule is the difference between the energy $\frac{1}{2}mu_2^2$ actually arriving at Q and the local value of the kinematic energy at Q, namely $\frac{1}{2}mC_2^2$. It follows that the integral of $\frac{1}{2}m(u_2^2 - C_2^2)\,dN_2'$ over the fluid volume gives $\mathbf{n}.\mathbf{q}$, where $\mathbf{q}$ is the heat flux vector. Hence by (2.21)

$$\mathbf{q} = \frac{1}{2}\overline{\int}_V \bar{\rho}(u_2^2 - C_2^2)\,\mathbf{u}_2\mathscr{P}_2 d\bar{\nu}. \tag{2.26}$$

As the volume integral of $\bar{\rho}\mathbf{u}_2\mathscr{P}_2$ is not zero, we cannot replace the integral in (2.26) by $\bar{\rho}u_2^2\mathbf{u}_2\mathscr{P}_2$, despite the fact that this would appear to be in accord with standard kinetic energy. For this latter theory there is no problem, since $\mathbf{q} = \frac{1}{2}\rho\overline{\mathbf{c}c^2} = \frac{1}{2}\rho\overline{\mathbf{c}(c^2 - C_2^2)}$, $\bar{c}$ being zero, but this applies at a single point in space. The physical meaning of $\mathbf{q}$ is that it is the *net* energy transferred; hence the form given in (2.26). A related point is that Jeans's (1921) model of heat transport, an improved version of Meyer's much earlier mean-free-path treatment, failed, not because, as he suggests, his model did not give zero mass flux at the target, but simply because of his gross underestimate of the influence of the persistence of velocity on the flux of molecular energy.

Finally note that in order to calculate $\mathbf{p}$ and $\mathbf{q}$ we need to know the fluid velocity $\mathbf{v}$, density ρ and (for C_i) the temperature T at all points in the flow field. Thus (2.24) and (2.26) taken with the basic conservation laws,

$$\left.\begin{aligned} &\frac{d\rho}{dt} + \rho\nabla.\mathbf{v} = 0, \quad \rho\frac{d\mathbf{v}}{dt} + \nabla.\mathbf{p} = \rho\mathrm{F}, \\ \text{and} \qquad &\rho c_v\frac{dT}{dt} + p\nabla.\mathbf{v} + \mathbf{p}:\overset{\circ}{\nabla\mathbf{v}} + \nabla.\mathbf{q} = 0, \end{aligned}\right\} \tag{2.27}$$

are integro-differential equations for $\mathbf{v}$, ρ and T, of which the Navier–Stokes equations and the Burnett equations are special cases. These are the equations of our generalized fluid dynamics. Boltzmann's equation is non-local in velocity space, our equations are non-local in real space, a feature that somewhat complicates each approach. It is not obvious at this stage whether the models are equally intractable; however, where fluid variables only are required, our approach does have the merit of suppressing unwanted kinetic details. It should also be noted that Boltzmann's equation evades being non-local in real space only by virtue of approximations we have not required, approximations involving the range of the interparticle potential and the distance of boundary surfaces.

2.7. *Boundary conditions*

The interaction between a gas and a solid surface is a very complicated phenomenon, and we do not propose here to give more than a brief account of the simplest method of dealing with boundary conditions in our generalized fluid dynamics. Cercignani's (1975) text contains a useful survey of the problem for classical kinetic theory, but of course if we had to resort to this theory to cope with boundary conditions, the mean-free-path approach developed above would be somewhat undermined.

We shall consider only the two limiting cases of diffuse and specular reflexion. First with specular reflexion molecules will retain perfectly their various transport properties after reflexion and the theory needs merely to cope with the geometric problem that boundaries introduce by abruptly altering the trajectories. The use of image sources suggests itself, especially with plane boundaries, and the theory presented above is very little altered.

Diffuse reflexion is a little more complicated. Let the point Q'' lie on a boundary at the point $\mathbf{r}''$, t'' and let ρ'', T'' denote the density and temperature at Q'', assumed *pro tempore* to be known. The molecular velocity of molecules leaving Q'' and arriving at a point Q in the fluid is

$$\mathbf{V}_i = \omega\delta_i C_i'' \hat{\mathbf{R}} + \beta_i'' \tau_i'' \mathscr{F}_*'' + \mathbf{v}'' - \mathbf{v} + \int_{t''}^{t} \mathbf{F}\, dt \quad (i = 1, 2), \tag{2.28}$$

in a notation obvious by comparison with (2.23). Here $\mathbf{v}''$ is the wall velocity and the value of C_i'' can be deduced from T''. Suppose that the surface element dA'' at Q'' emits molecules isotropically, then we can generalize (2.24) to

$$\mathbf{p} = \bar{\int}_V \rho' \mathbf{u}_1 \mathbf{u}_1 \mathscr{P}_1 dv' + \bar{\int}_A \rho'' \mathbf{V}_1 \mathbf{V}_1 \frac{\exp\left[-\int_0^R ds/\lambda_{s1}\right]}{4\pi R^2} dA'', \tag{2.29}$$

where any regions in V and A hidden from Q must be omitted from the integration domains. A similar formula for $\mathbf{q}$ has the subscript 1 replaced by 2, and $\frac{1}{2}(u_2^2 - C_2^2)\,\mathbf{u}_2$, $\frac{1}{2}(\mathbf{V}_2^2 - C_2^2)\,\mathbf{V}_2$ replacing $\mathbf{u}_1\mathbf{u}_1$ and $\mathbf{V}_1\mathbf{V}_1$ in the integrands. By taking Q to lie on the wall itself we can obtain expressions for $\mathbf{p}''$ and $\mathbf{q}'$, and from these values and the nature of the wall we can deduce ρ'' and T'', thus closing the system of equations.

This is admittedly an incomplete account of boundary conditions, but, one hopes, adequate to show how they could be incorporated in our generalized fluid dynamics.

3. Derivation of the Burnett equations

3.1. *Expansions in powers of the Knudsen number*

In order to obtain formulae for $\mathbf{p}$ and $\mathbf{q}$ similar in form to those deduced by Burnett (1935) from the Chapman–Enskog theory, and thereby to test our theory, we shall develop expansions for the integrals given in § 2.6 for $\mathbf{p}$ and $\mathbf{q}$, retaining terms $O(K^2)$, where for a given macroscopic variable $\phi(\mathbf{r}, t)$, K is the Knudsen number

$$K \equiv |\lambda\nabla\phi/\phi|,$$

λ being the appropriate mean free path. For time rates of change the number corresponding to K is $\tau_n \equiv \tau(d\phi/dt)/\phi$, where τ is the free time. The numbers K and τ_n will be assumed to be similar in magnitude, so that $O(K^2)$ can be used to indicate terms $O(\tau_n^2)$, $O(\tau_n K)$ as well as $O(K^2)$.

Our first task is to find the expansion for the molecular velocity $\mathbf{u}_i$ given by (2.23). We shall omit the subscript i denoting the transport property until required, and also further simplify matters by omitting the factor $\omega\delta_i$ accompanying C_i. Later we shall find that restoring $\omega\delta_i$ and then averaging over ω makes small changes to only two $O(K^2)$ coefficients, which indicates that just two thermal speeds (C_1, C_2) provide a good description even to $O(K^2)$. However for $K > 1$, the thermal spread of molecular velocities is very important, as we shall establish in a later paper. Thus (see (2.15)) we write λ in place of λ_i, and simplify (2.23) to

$$\mathbf{u} = C'\hat{\mathbf{R}} + \beta'\tau'\mathscr{F}' + \beta'\tau'\frac{1}{\rho'}(\nabla\boldsymbol{\pi})' : \hat{\mathbf{R}}\hat{\mathbf{R}} + \mathbf{v}' - \mathbf{v} + \int_{t'}^{t}\mathbf{F}\,dt. \tag{3.1}$$

Next we assume that

$$|\mathbf{v}' - \mathbf{v}|/C = O(K), \quad |\mathscr{F}|\tau/C = O(K), \quad |\mathbf{F}|\tau/C = O(K). \tag{3.2}$$

We shall find that, for any variable $\phi(\mathbf{r}, t)$,

$$\phi' = \phi(1 + O(K)); \quad \text{and} \quad \beta' = 1 + O(K), \quad \hat{\mathbf{R}}\hat{\mathbf{R}} : \boldsymbol{\pi} = O(K), \tag{3.3}$$

so that after division by C, the first right-hand term in (3.1) is $O(1)$ and the rest $O(K)$.

Notice that (3.2*a*) constrains the theory to weak shocks, and furthermore, since the hypothesis $|\mathbf{v}' - \mathbf{v}|/C = (\tau^{-1}|\mathbf{v}' - \mathbf{v}|)\tau/C = O(1)$, would require $|\mathscr{F}|\tau/C$ also to be $O(1)$, there is no alternative to (3.2) allowing the possibility of an expansion in powers of K that would avoid this constraint on shock wave strength. In other words all expansions in powers of K are valid only if $K < 1$ and, if just a few terms are retained, accuracy requires that $K \ll 1$. The natural scales in the sequel are λ and τ and terms of rth degree in λ, τ and their products are $O(K^r)$.

An important parameter in expansions in powers of K is the transit time $\mathsf{T} = t - t'$ of a typical molecule moving from P' to Q. By (2.5)

$$\mathbf{F}_\sigma - \mathbf{a}_p = -\mathscr{F}_\sigma + (\mathbf{a}_\sigma - \mathbf{a}_p) = -\mathscr{F}_\sigma + O(\mathsf{T}),$$

since the difference in fluid accelerations will be proportional to the distance σ and hence to the transit time $(t_\sigma - t')$, which has T as its upper bound. Hence (2.7), (2.11) and (3.3) yield the expansions

$$\mathbf{r} = \mathbf{r}' + \mathsf{T}\mathbf{u}' + \tfrac{1}{2}\mathsf{T}^2\mathbf{F}' + O(\mathsf{T}^3) \tag{3.4}$$

and $$R\hat{\boldsymbol{\alpha}} = \mathbf{r} - \bar{\mathbf{r}} = \mathsf{T}(C'\hat{\mathbf{R}} + \tau\mathscr{F}) - \tfrac{1}{2}\mathsf{T}^2\mathscr{F} + O(K^3) + O(\mathsf{T}^3).$$

The scalar products of the latter expansion with $\hat{\boldsymbol{\alpha}}$ and $\hat{\mathbf{R}}$ lead to

$$\mathsf{T} = x\tau(C/C')\{1 + \tau(\tfrac{1}{2}x - 1)\hat{\mathbf{R}}.\mathscr{F}/C\} + O(K^3) + O(\mathsf{T}^3), \tag{3.5}$$

and $$\hat{\boldsymbol{\alpha}} = \hat{\mathbf{R}} + \tau(1 - \tfrac{1}{2}x)(\mathscr{F} - \hat{\mathbf{R}}\hat{\mathbf{R}}.\mathscr{F})/C + O(K^3) + O(\mathsf{T}^3), \tag{3.6}$$

where we have introduced the non-dimensional distance

$$x \equiv R/\lambda = R/\tau C. \tag{3.7}$$

By (3.3) $C'/C = 1 + O(K)$, so $\mathsf{T} = xO(\tau) = xO(K)$. It is true that $0 \leqslant x < \infty$, but as all the expansions given below will subsequently be multiplied by a factor e^{-x} coming from $\mathscr{P}$ in (2.12), we can freely omit powers of x from the error terms, and write the error terms in (3.5) and (3.6) as $O(K^3)$ alone.

The volume integrals for $\mathbf{p}$ and $\mathbf{q}$ will reduce to integrals of the type (see (2.12) and (2.13))

$$\left.\begin{aligned} \frac{1}{4\pi}\int_0^\infty \left(\int_{\mathrm{R}} \hat{\mathbf{R}}\hat{\mathbf{R}}\,d\varpi\right) x^n e^{-x}\,dx &= \tfrac{1}{3}n!\,\mathbf{1}, \\ \frac{1}{4\pi}\int_0^\infty \left(\int_{\hat{\mathrm{R}}} \underset{\longleftarrow\text{odd}\longrightarrow}{\hat{\mathbf{R}}\hat{\mathbf{R}}\ldots\hat{\mathbf{R}}}\,d\varpi\right) x^n e^{-x}\,dx &= 0, \\ \frac{1}{4\pi}\int_0^\infty \int_{\hat{\mathrm{R}}} \hat{\mathbf{R}}\hat{\mathbf{R}}\hat{\mathbf{R}}\hat{\mathbf{R}}\,d\varpi\Big) x^n e^{-x}\,dx &= \tfrac{2}{15}n!(\mathring{\mathbf{K}}+\tfrac{5}{6}\mathbf{11}). \end{aligned}\right\} \tag{3.8}$$

Here $\mathbf{1}$ is the unit tensor and $\mathring{\mathbf{K}}$ is a fourth-order tensor (see Woods, 1975, p. 189) with the property of generating the deviator $\mathring{\mathbf{A}}$ of any second-order tensor $\mathbf{A}$, $\mathring{\mathbf{K}}:\mathbf{A} = \mathring{\mathbf{A}}$. Note from (3.8) that integrals containing $(1-x)$ and $(x-\frac{1}{2}x^2)$ in the integrands will vanish, for which reason we find that the terms involving $\mathscr{F}$ in (3.5) and (3.6) make no contributions to the final results. (The vector $\hat{\boldsymbol{\alpha}}$ only occurs as $x\hat{\boldsymbol{\alpha}}$).

3.2. *Expansion for the molecular velocity*

For any function $\phi(\mathbf{r}, t)$,

$$\phi(\mathbf{r}', t') \equiv \phi' = \phi - \mathsf{T}\,d\phi/d\mathsf{T} + \tfrac{1}{2}\mathsf{T}^2\,d^2\phi/d\mathsf{T}^2 + O(K^3),$$

the right-side being evaluated at $\mathbf{r}$, t. Hence by (2.8), (3.3), (3.4) and $T = t-t'$,

$$\phi' = \phi - \mathsf{T}\left(\mathbf{u}'.\nabla + \frac{d}{dt}\right)\phi + \tfrac{1}{2}\mathsf{T}^2\left[\left(C\hat{\mathbf{R}}.\nabla + \frac{d}{dt}\right)^2 - \mathbf{F}.\nabla\right]\phi + O(K^3), \tag{3.9}$$

where

$$\mathbf{u}' = C'\hat{\mathbf{R}} + \mathbf{v}' - \mathbf{v} + \tau\mathscr{F} + O(K^2),$$

and ∇ and d/dt denote the gradient and material derivative at Q. As described at the end of § 3.1 we can write (3.5) as

$$\mathsf{T} = x\tau(C/C') + O(K^3), \tag{3.10}$$

without committing an error in our final results.

Particular cases of (3.9) are

$$\mathbf{v}' - \mathbf{v} = -x(\lambda\hat{\mathbf{R}}.\nabla\mathbf{v} + \tau\mathbf{a}) + O(K^2), \tag{3.11}$$

and

$$C' = C\left\{1 - \frac{x}{2T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right)\right\} + O(K^2), \tag{3.12}$$

where we have used $C \propto T^{\frac{1}{2}}$ in the second expansion.

Equations (3.10) to (3.12) enable us to write (3.9) as

$$\begin{aligned} \phi' = \phi - x\lambda\hat{\mathbf{R}}.\nabla\phi - x\tau\frac{d\phi}{dt} + x^2\tau\lambda\hat{\mathbf{R}}.\nabla\mathbf{v}.\nabla\phi - \frac{x^2\tau}{2T}\frac{d\phi}{dt}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right) \\ + \tfrac{1}{2}x^2\tau^2\mathbf{a}.\nabla\phi + (\tfrac{1}{2}x^2 - x)\tau^2\mathscr{F}.\nabla\phi + x^2\psi + \ldots, \end{aligned}$$

where

$$\begin{aligned} \psi &= \tfrac{1}{2}\tau^2\left(C\hat{\mathbf{R}}.\nabla + \frac{d}{dt}\right)^2\phi = \tfrac{1}{2}\tau^2\left\{(C\hat{\mathbf{R}}+\mathbf{v})^2 : \nabla\nabla\phi + 2(C\hat{\mathbf{R}}+\mathbf{v}).\nabla\frac{\partial\phi}{\partial t} + \frac{\partial^2\phi}{\partial t^2}\right\} \\ &= \tfrac{1}{2}\lambda^2\hat{\mathbf{R}}\hat{\mathbf{R}}\colon \nabla\nabla\phi + \tau\lambda\left(\hat{\mathbf{R}}.\nabla\frac{d\phi}{dt} - \hat{\mathbf{R}}.\nabla\mathbf{v}.\nabla\phi\right) + \tfrac{1}{2}\tau^2\left(\frac{d^2\phi}{dt^2} - \mathbf{a}.\nabla\phi\right). \end{aligned}$$

Hence, omitting terms containing $(\frac{1}{2}x^2-x)$ as described at the end of § 3.1, we arrive at the expansion

$$\phi' = \phi - x\lambda\hat{\mathbf{R}}.\nabla\phi - x\tau\frac{d\phi}{dt} - \frac{x^2\tau}{2T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right)\frac{d\phi}{dt} + x^2\tau\lambda\,\hat{\mathbf{R}}.\nabla\frac{d\phi}{dt} + \tfrac{1}{2}x^2\lambda^2\hat{\mathbf{R}}\hat{\mathbf{R}}:\nabla\nabla\phi + \tfrac{1}{2}x^2\tau^2\frac{d^2\phi}{dt^2} + \ldots. \tag{3.13}$$

To deal with the integral in (3.1), we shall apply (3.13) to $\mathbf{F}$, shortening the distance x to $x(1-s/R)$, s being distance measured along the molecular trajectory (see figure 1). This amounts to linear interpolation. Thus

$$\mathbf{F}_s = \mathbf{F} - x\left(1-\frac{s}{R}\right)\left(\lambda\hat{\mathbf{R}}.\nabla\mathbf{F} + \tau\frac{d\mathbf{F}}{dt}\right) + O(K^2); \tag{3.14}$$

and similarly from (3.10) and (3.12)

$$t_s = t' + \frac{xs}{R}\tau\left\{1 + \frac{xs}{2TR}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right)\right\} + O(K^3). \tag{3.15}$$

Hence

$$\int_{t'}^{t}\mathbf{F}_s\,dt_s = x\tau\mathbf{F}\left\{1 + \frac{x}{2T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau + \tau\frac{dT}{dt}\right)\right\} - \tfrac{1}{2}x^2\tau\left(\lambda\hat{\mathbf{R}}.\nabla\mathbf{F} + \tau\frac{d\mathbf{F}}{dt}\right) + O(K^3).$$

Adding this to the case $\phi = \mathbf{v}$ of (3.13) we get

$$\mathbf{v}' - \mathbf{v} + \int_{t'}^{t}\mathbf{F}_s\,dt_s = -x\lambda\hat{\mathbf{R}}.\nabla\mathbf{v} - x\tau\mathbf{F} - \frac{x^2\tau}{2T}\mathscr{F}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right) + \tfrac{1}{2}x^2\tau\lambda\hat{\mathbf{R}}.\nabla\mathbf{a} + \tfrac{1}{2}x^2\tau\lambda\hat{\mathbf{R}}.\nabla\mathscr{F} + \tfrac{1}{2}x^2\tau^2\frac{d\mathscr{F}}{dt} + \tfrac{1}{2}x^2\hat{\mathbf{R}}\hat{\mathbf{R}}:\nabla\nabla\mathbf{v} + \ldots. \tag{3.16}$$

Correct to $O(K)$, equations (3.3), (3.12) and (3.16) enable us to write (3.1) as

$$\mathbf{u} = C\hat{\mathbf{R}}\left\{1 - \frac{x}{2T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right)\right\} - x\lambda\hat{\mathbf{R}}.\nabla\mathbf{v} + \tau(1-x)\mathscr{F} + O(K^2). \tag{3.17}$$

Then with the help of the expressions for $\mathscr{P}_0$ and $\bar{p}$ given below in (3.30) and (3.33), this expansion substituted into (2.24) and (2.26) enables us to calculate $\mathbf{p}$ and $\mathbf{q}$ correct to $O(K)$, which in turn allows us to find the expansion for $\mathbf{u}$ correct to $O(K^2)$. We shall be giving both the $O(K)$ and $O(K^2)$ calculations of $\mathbf{p}$ and $\mathbf{q}$ below, so for brevity here we will merely quote the results of the first iteration required to proceed to the second. These are

$$\mathscr{F} = -\frac{1}{\rho}\nabla.\mathbf{p} = -\frac{1}{\rho}\nabla p + O(K) = -\frac{1}{\rho}\nabla\rho + \frac{1}{\rho}\nabla.(2\mu\nabla\mathring{\mathbf{v}}) + O(K^2), \tag{3.18}$$

$$p = \tfrac{1}{3}\rho C_1^2, \quad \mu = \tfrac{1}{3}\rho C_1\lambda = p\tau_1, \quad \kappa = \theta c_v\mu, \tag{3.19}$$

$$d\rho/dt = -\rho\nabla.\mathbf{v}, \quad dp/dt = -\tfrac{5}{3}p\nabla.\mathbf{v} + O(K), \quad dT/dt = -\tfrac{2}{3}T\nabla.\mathbf{v} + O(K), \tag{3.20}$$

$$\frac{\nabla p}{p} = \frac{5}{3}\frac{\nabla\rho}{\rho} + O(K) = \frac{5}{2}\frac{\nabla T}{T} + O(K). \tag{3.21}$$

Equations (3.12) and (3.21) follow from the adiabatic relations, $p \propto T^{\frac{5}{2}}$, etc., which are exact when μ and κ are zero. In (3.19) θ has the value $\frac{5}{2}$, but as we plan to prove this from our mean-free-path theory, independently of table 1, we make no commitment about its value at this stage.

First consider the term $\tau'\beta'\mathscr{F}'$ in (3.1). By (2.17) and $T \propto C^2$, we get

$$\frac{d(n\tau)}{n\tau} = (\mathscr{s}-1)\frac{dT}{T} = 2(\mathscr{s}-1)\frac{dC}{C}.$$

However this is not correct for our purpose of calculating the change between $\tau(\mathbf{r}', t')$ and $\tau(\mathbf{r}, t)$ experienced by a typical molecule S as it moves with *constant velocity* (correct to $O(K)$) along its path. Thus one of the Cs in $T \propto CC$ must be held constant, which reduces the coefficient of dC/C by unity. If in addition we eliminate n by $n \propto T^{\frac{3}{2}} + O(K)$ [cf. (3.20)], we arrive at

$$\left(\frac{d\tau}{\tau}\right)_s = (\mathscr{s}-2)\frac{dT}{T} + O(K).$$

Similarly, for $\lambda = \tau C$ and $\mu = p\tau$, (3.22)

$$(d\lambda/\lambda)_s = (\mathscr{s}-\tfrac{3}{2})\,dT/T + O(Kn),$$

and

$$(d\mu/\mu)_s = (\mathscr{s}+\tfrac{1}{2})\,dT/T + O(Kn).$$

By (3.13) and (3.23*a*),

$$\tau' = \tau\left\{1 - \frac{x(\mathscr{s}-2)}{T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right)\right\} + O(K^2). \tag{3.23}$$

The theory of the factor β' is given in § 2.4. We can use (3.17) to write down an expansion for $\tilde{\mathbf{u}}'$. Since P'' is one mean free path from P', x is unity in the present application. Thus

$$\tilde{u}' = C'\left\{1 - \frac{1}{2T}\left(\lambda\hat{\mathbf{R}}'.\nabla T + \tau\frac{dT}{dt}\right)\right\} - \lambda\hat{\mathbf{R}}'\hat{\mathbf{R}}' : \nabla\mathbf{v} + O(K^2),$$

where the vector $\hat{\mathbf{R}}'$ is to be averaged over the hemisphere γ. The averages of $\hat{\mathbf{R}}'$ and $\hat{\mathbf{R}}'\hat{\mathbf{R}}'$ are $\frac{1}{2}\hat{\mathbf{R}}$ and $\frac{1}{3}\mathbf{1}$; by (3.20*c*):

$$\mathbf{1} : \nabla\mathbf{v} = \nabla.\mathbf{v} = -\frac{3}{2}\frac{1}{T}\frac{dT}{dt} + O(K),$$

hence by (2.20)

$$\beta' = 1 - \frac{\lambda}{4T}\hat{\mathbf{R}}.\nabla T + O(K^2). \tag{3.24}$$

An application of (3.13) to $\mathscr{F}$ gives

$$\mathscr{F}' = \mathscr{F} - x(\lambda\hat{\mathbf{R}}.\nabla\mathscr{F} + \tau\, d\mathscr{F}/dt) + O(K^2). \tag{3.25}$$

Also (3.3), (3.18) and (3.22*c*) yield

$$\beta'\tau'\frac{1}{\rho'}(\nabla\pi)' : \hat{\mathbf{R}}\hat{\mathbf{R}} = -\frac{2\tau\mu}{\rho}\left\{\nabla\nabla\mathring{\mathbf{v}} + (\mathscr{s}+\tfrac{1}{2})\frac{1}{T}\nabla T\nabla\mathring{\mathbf{v}}\right\} : \hat{\mathbf{R}}\hat{\mathbf{R}} + O(K^3) \tag{3.26}$$

Finally substituting (3.16), (3.23) to (3.26) into (3.1), and ignoring terms containing $(\frac{1}{2}x^2 - x)$ as justified at the end of § 3.1, we arrive at

$$\mathbf{u} = C'\hat{\mathbf{R}} - x\lambda\hat{\mathbf{R}}.\nabla\mathbf{v} + \tau(1-x)\mathscr{F} - \tau\mathscr{F}\left\{[x(\mathscr{s}-2) + \tfrac{1}{2}x^2]\frac{1}{T}\left(\lambda\hat{\mathbf{R}}.\nabla T + \tau\frac{dT}{dt}\right) + \frac{\lambda}{4T}\hat{\mathbf{R}}.\nabla T\right\}$$
$$+ \tfrac{1}{2}x^2\tau\lambda\hat{\mathbf{R}}.\nabla\mathbf{a} + \tfrac{1}{2}x^2\lambda^2\hat{\mathbf{R}}\hat{\mathbf{R}} : \nabla\nabla\mathbf{v} - \frac{2\tau\mu}{\rho}\left\{\nabla\nabla\mathring{\mathbf{v}} + (\mathscr{s}+\tfrac{1}{2})\frac{1}{T}\nabla T\nabla\mathring{\mathbf{v}}\right\} : \hat{\mathbf{R}}\hat{\mathbf{R}} + O(K^3), \tag{3.27}$$

where from $C^2 \propto T$ and (3.15)

$$C'^2 = C^2\left\{1-\frac{x}{T}\left(\lambda\hat{\mathbf{R}}.\nabla T+\tau\frac{dT}{dt}\right)-\frac{x^2\tau^2}{2T^2}\frac{dT}{dt}\left(\lambda\hat{\mathbf{R}}.\nabla T+\tau\frac{dT}{dt}\right)\right.$$
$$\left.+\frac{x^2\tau\lambda}{T}\hat{\mathbf{R}}.\nabla\left(\frac{dT}{dt}\right)+\frac{x^2\lambda^2}{2T}\hat{\mathbf{R}}\hat{\mathbf{R}}:\nabla\nabla T+\frac{x^2\tau^2}{2T}\frac{d^2T}{dt^2}+\ldots\right\}. \tag{3.28}$$

3.3. *Expansion of the transit probability and fluid density*

The number defined in (2.12), namely

$$\mathscr{P} = \frac{\exp\left[-\int_0^R ds/\lambda_s\right]}{4\pi R^2\lambda'}, \tag{3.29}$$

will be expanded in the form

$$\left.\begin{aligned} \mathscr{P} &= \mathscr{P}_0\{1+\vartheta_1+\vartheta_2+\ldots\}, \\ \text{where}\qquad \mathscr{P}_0 &\equiv \frac{e^{-x}}{4\pi R^2\lambda}, \end{aligned}\right\} \tag{3.30}$$

and ϑ_r is $O(K^r)$. Since the integrals of $\mathscr{P}$ and $\mathscr{P}_0$ over the whole fluid volume are both unity (see (2.14))

$$\int_V \mathscr{P}_0\vartheta_r d\bar{v} = 0, \quad r = 1, 2, \ldots, \tag{3.31}$$

and in a theory correct to $O(K^2)$ this has the fortunate consequence that the numbers ϑ_2, ϑ_3, ... are not required. Incidentally the zeros in (3.31) occur in fact because of the appearance of factors $(\frac{1}{2}x^2-x)$, $(\frac{1}{3}x^3-\frac{1}{2}x^2)$, ... in ϑ_1, ϑ_2, ...

To evaluate the integral in (3.29) we adopt the expansion

$$\frac{1}{\lambda_s} = \frac{1}{\lambda}\left\{1+\frac{x}{T}\left(1-\frac{s}{R}\right)(\mathscr{s}-\tfrac{3}{2})\left(\lambda\hat{\mathbf{R}}.\nabla T+\tau\frac{dT}{dt}\right)+\ldots\right\},$$

which follows from (3·22*b*) and linear interpolation as used in (3.14). Then

$$\exp\left[-\int_0^R ds/\lambda_s\right] = e^{-x}\left\{1-\frac{x^2}{2T}(\mathscr{s}-\tfrac{3}{2})\left(\lambda\hat{\mathbf{R}}.\nabla T+\tau\frac{dT}{dt}\right)+\ldots\right\}$$

whence

$$\mathscr{P} = \mathscr{P}_0\left\{1-(\tfrac{1}{2}x^2-x)(\mathscr{s}-\tfrac{3}{2})\frac{1}{T}\left(\lambda\hat{\mathbf{R}}.\nabla T+\tau\frac{dT}{dt}\right)+\ldots\right\}. \tag{3.32}$$

Finally we need an expression for $\bar{\rho} = \rho(\bar{\mathbf{r}}, t)$ in terms of $\rho(\mathbf{r}, t)$. From figure 1 and (3.6) it follows that

$$\bar{\mathbf{r}} = \mathbf{r}-R\hat{\boldsymbol{\alpha}} = \mathbf{r}-x\lambda\hat{\mathbf{R}}+\lambda\tau(\tfrac{1}{2}x^2-x)(\mathscr{F}-\hat{\mathbf{R}}\hat{\mathbf{R}}.\mathscr{F})/C+\ldots,$$

in which the term involving $(\frac{1}{2}x^2-x)$ can be omitted; thus

$$\bar{\rho} = \rho-x\lambda\hat{\mathbf{R}}.\nabla\rho+\tfrac{1}{2}x^2\lambda^2\hat{\mathbf{R}}\hat{\mathbf{R}}:\nabla\nabla\rho+O(K^3). \tag{3.33}$$

3.4. *The pressure tensor*

From (2.24) this tensor is (omitting integration over ω)

$$\mathsf{p} = \int_V \bar{\rho}\mathbf{u}_1\mathbf{u}_1\mathscr{P}_1 d\bar{v}, \tag{3.34}$$

where the quantities in the integrand appear in (3.27), (3.28), (3.32) and (3.33). The algebra that follows is straightforward, all integrals being of the type given in (3.8). We shall set out the integrand for the first-order theory only. We have, on dropping a term involving $(1-x)$,

$$\mathbf{p} = \rho C_1^2 \int_V \left\{\left[1-\frac{x}{T}\left(\lambda_1 \hat{\mathbf{R}}\,.\,\nabla T+\tau_1\frac{dT}{dt}\right)\right]\hat{\mathbf{R}}\hat{\mathbf{R}}-x\tau_1(\hat{\mathbf{R}}\hat{\mathbf{R}}\,.\,\nabla\mathbf{v}+\widetilde{\nabla\mathbf{v}}\,.\,\hat{\mathbf{R}}\hat{\mathbf{R}})\right\}$$
$$\times\left\{1-\frac{x\lambda_1}{\rho}\hat{\mathbf{R}}\,.\,\nabla\rho\right\}\mathscr{P}_0\,d\bar{v},$$

where the tilde denotes the transpose of a dyad. Thus, correct to $O(K)$,

$$\mathbf{p} = \tfrac{1}{3}\rho C_1^2\{\mathbf{1}(1+\tfrac{2}{3}\tau_1\nabla\,.\,\mathbf{v})-\tau_1(\nabla\mathbf{v}+\widetilde{\nabla\mathbf{v}})\},$$

or $\mathbf{p} = p\mathbf{1}+\boldsymbol{\pi}$, where (cf. (2.19))

$$p = \tfrac{1}{3}\rho C_1^2, \quad \boldsymbol{\pi} = -2\mu\overset{\circ}{\nabla}\mathbf{v}, \quad \mu\equiv p\tau_1 = \tfrac{1}{3}\rho C_1^2\tau_1 = \tfrac{1}{3}\rho C_1\lambda_1. \tag{3.35}$$

Correct to $O(K^2)$ our theory gives

$$\begin{aligned}\mathbf{p} = p\mathbf{1}&\left\{1-\tau_1\left(\frac{1}{T}\frac{dT}{dt}+\tfrac{2}{3}\nabla\,.\,\mathbf{v}\right)+\frac{\lambda_1^2}{3}\left(\frac{\nabla^2 T}{T}+\frac{\nabla^2\rho}{\rho}\right)+\frac{\tau_1^2}{T}\left(\frac{d^2T}{dt^2}-\frac{2}{T}\left(\frac{dT}{dt}\right)^2\right)\right.\\
&\left.+(\mathscr{s}-\tfrac{3}{2})\frac{\lambda_1^2}{3T^2}\nabla T\,.\,\nabla T+(\mathscr{s}+\tfrac{1}{2})\frac{\lambda_1^2}{3\rho T}\nabla\rho\,.\,\nabla T+\tfrac{2}{3}\tau_1^2\nabla\,.\,\mathbf{a}+\tfrac{2}{3}\tau_1^2\widetilde{\nabla\mathbf{v}}:\nabla\mathbf{v}\right\}\\
&-2\mu\overset{\circ}{\nabla}\mathbf{v}+\tfrac{2}{3}\lambda_1^2\left\{(\mathscr{s}-\tfrac{1}{2})\frac{1}{T}\frac{dT}{dt}\overset{\circ}{\nabla}\mathbf{v}+\overset{\circ}{\nabla}\mathbf{a}+\overset{\circ}{\overline{\widetilde{\nabla\mathbf{v}}\,.\,\nabla\mathbf{v}}}\right\}\\
&+\tfrac{2}{5}p\lambda_1^2\left\{\frac{1}{T}\overset{\circ}{\overline{\nabla\nabla T}}+\frac{1}{\rho}\overset{\circ}{\overline{\nabla\nabla\rho}}+(\mathscr{s}-\tfrac{3}{2})\frac{1}{T^2}\overset{\circ}{\overline{\nabla T\nabla T}}+(\mathscr{s}+\tfrac{1}{2})\frac{1}{\rho T}\overset{\circ}{\overline{\nabla\rho\nabla T}}\right\}.\end{aligned} \tag{3.36}$$

This may be simplified with the aid of (3.21), which enables us to write

$$\frac{\nabla\nabla\rho}{\rho} = \frac{3}{2}\frac{\nabla\nabla T}{T}+\frac{3}{10}\frac{\nabla p\nabla T}{pT}+O(K); \tag{3.37}$$

also

$$\frac{d}{dt}(\nabla\mathbf{v}) = \nabla\mathbf{a}-\nabla\mathbf{v}\,.\,\nabla\mathbf{v} \tag{3.38}$$

yields

$$\overset{\circ}{\nabla}\mathbf{a} = \frac{d}{dt}(\overset{\circ}{\nabla}\mathbf{v})+\overset{\circ}{\overline{\nabla\mathbf{v}\,.\,\nabla\mathbf{v}}}.$$

Then by (3.20), further use of (3.21) and $p\lambda_1^2 = \mu\tau_1 C_1^2 = 3\mu\tau_1 kT/m$, which follows from (3.19), the second part of (3.36) yields

$$\boldsymbol{\pi} = -2\mu\overset{\circ}{\nabla}\mathbf{v}+\mu\tau_1\mathbf{E},$$

where

$$\mathbf{E} = \tfrac{2}{3}(1-2\mathscr{s})\nabla\,.\,\mathbf{v}\overset{\circ}{\nabla}\mathbf{v}+2\frac{d}{dt}(\overset{\circ}{\nabla}\mathbf{v})+2\overset{\circ}{\overline{\nabla\mathbf{v}\,.\,\nabla\mathbf{v}}}+2\overset{\circ}{\overline{\widetilde{\nabla\mathbf{v}}\,.\,\nabla\mathbf{v}}}+3\frac{k}{m}\overset{\circ}{\overline{\nabla\nabla T}}+3\mathscr{s}\frac{k}{mT}\overset{\circ}{\overline{\nabla T\nabla T}}. \tag{3.39}$$

Burnett's (1935) theory leads to (e.g. see Ferziger & Kaper, 1972, p. 148)

$$\begin{aligned}\mathbf{E} = \varpi_1\nabla\,.\,\mathbf{v}\overset{\circ}{\nabla}\mathbf{v}+\varpi_2\left(\frac{d}{dt}(\overset{\circ}{\nabla}\mathbf{v})-2\overset{\circ}{\overline{\nabla\mathbf{v}\,.\,\overset{\circ}{\nabla}\mathbf{v}}}\right)+\varpi_3\frac{k}{m}\overset{\circ}{\overline{\nabla\nabla T}}&\\
+\varpi_4\frac{k}{mp}\overset{\circ}{\overline{\nabla p\nabla T}}+\varpi_5\frac{k}{mT}\overset{\circ}{\overline{\nabla T\nabla T}}+\varpi_6\overset{\circ}{\overline{\overset{\circ}{\nabla}\mathbf{v}\,.\,\overset{\circ}{\nabla}\mathbf{v}}}&\end{aligned} \tag{3.40}$$

For Maxwellian molecules Burnett gives the values

$$\varpi_1 = \tfrac{4}{3}(\tfrac{7}{2}-s), \quad \varpi_2 = 2, \quad \varpi_3 = 3, \quad \varpi_4 = 0, \quad \varpi_5 = 3s, \quad \varpi_6 = 8$$

and it is easily shown that with these values (3.39) and (3.40) are identical. For other molecular forces Burnett and others have found values for ϖ_i, $i = 1, \ldots, 6$, only slightly different from those given above. Our theory could be readily generalized as indicated in § 2.3.

Now τ_1 is independent of ω for a Maxwellian gas, so had we retained $\omega\delta_1$ in the theory, i.e. allowed for thermal spread in the molecular speeds, the only effect would have been to replace λ_1^2 in (3.36) by the average $\overline{\lambda_1^2} = \overline{\omega^2}\,\delta_1^2\,\lambda_1^2$ and, as (2.2) and (2.4) show this to be λ_1^2, our procedure is justified.

In the following section we shall show that the coefficient of $\mathbf{1}$ in (3.36) reduces to p, which means that the trace of $\boldsymbol{\pi}$ is zero. Alternatively we can argue that trace $\boldsymbol{\pi} = \overset{\times}{\pi}$ must be zero for physical reasons, and use the coefficient of $\mathbf{1}$ in (3.36) as an equation to determine the value of θ in (3.19).

3.5. *Trace of the viscous tensor*

In a tenuous gas it is well known that the bulk viscosity is zero, save that in certain circumstances an effective bulk viscosity due to relaxation effects can arise (e.g. see Woods, 1975; Clarke & McChesney, 1976). But in a simple monatomic gas, which has no internal molecular energy and hence no associated relaxation times, the bulk viscosity is certainly zero; and this means that $\overset{\times}{\boldsymbol{\pi}}$ is zero. By (3.36)

$$\frac{\overset{\times}{\pi}}{3p} = -\tau_1\left(\frac{1}{T}\frac{dT}{dt}+\tfrac{2}{3}\nabla.\mathbf{v}\right)+\frac{\lambda_1^2}{3}\left(\frac{\nabla^2 T}{T}+\frac{\nabla^2\rho}{\rho}\right)+\frac{\tau_1^2}{T}\left\{\frac{d^2T}{dt^2}-\frac{2}{T}\left(\frac{dT}{dt}\right)^2\right\}$$
$$+(s-\tfrac{3}{2})\frac{\lambda_1^2}{3T^2}\nabla T.\nabla T+(s+\tfrac{1}{2})\frac{\lambda_1^2}{3\rho T}\nabla\rho.\nabla T+\tfrac{2}{3}\tau_1^2\nabla.\mathbf{a}+\tfrac{2}{3}\tau_1^2\,\widetilde{\nabla\mathbf{v}}:\nabla\mathbf{v}. \quad (3.41)$$

To deal with the first term on the right-hand side of (3.41) we use the energy conservation equation (2.27), namely

$$\rho C_v\frac{dT}{dt}+p\nabla.\mathbf{v}+\boldsymbol{\pi}:\overset{\circ}{\nabla\mathbf{v}}+\nabla.\mathbf{q} = 0, \quad (3.42)$$

since $\mathbf{1}:\overset{\circ}{\mathbf{A}} = 0$. Anticipating the Fourier law (§ 3.6)

$$\mathbf{q} = -\kappa\nabla T+O(K^2) \quad (\kappa = \theta c_v\mu),$$

and using (3.35*b*) we can write (3.42) in the form

$$\frac{1}{T}\frac{dT}{dt}+\tfrac{2}{3}\nabla.\mathbf{v} = \tfrac{4}{3}\tau_1\,\overset{\circ}{\nabla\mathbf{v}}:\overset{\circ}{\nabla\mathbf{v}}+\frac{\theta}{\rho T}\nabla.(\mu\nabla T)+O(K^2).$$

By (3.21) and the trace of (3.37)

$$\frac{\nabla^2 T}{T}+\frac{\nabla^2\rho}{\rho} = \frac{5}{2}\frac{\nabla^2 T}{T}+\frac{3}{10}\frac{\nabla p.\nabla T}{pT} = \frac{5}{2\mu}\nabla.(\mu\nabla T)-s\frac{\nabla p.\nabla T}{pT}+\frac{3}{10}\frac{\nabla p.\nabla T}{pT},$$

since by (2.17) and (2.19) $\mu \propto T^{s}$. Equation (3.20*c*) and the trace of (3.38) yield

$$\frac{\tau_1^2}{T}\left\{\frac{d^2T}{dt^2}-\frac{1}{T}\left(\frac{dT}{dt}\right)^2\right\} = -\tfrac{2}{3}\tau_1^2\nabla.\mathbf{a}+\tfrac{2}{3}\tau_1^2\nabla\mathbf{v}:\nabla\mathbf{v}+O(K^3).$$

We substitute these values into (3.41) and, by using (3.20c) and noting from (3.35) that $\lambda_1/\mu = 3\tau_1/\rho$, we arrive finally at the conclusion that, correct to $O(K^2)$,

$$\overset{\times}{\pi} = (\tfrac{5}{2}-\theta)\, 3\frac{k}{m}\tau_1 \nabla . (\mu \nabla T).$$

But as $\overset{\times}{\pi}$ must be zero for the physical reason described earlier, we conclude that $\theta = \frac{5}{2}$, a result achieved completely by mean-free-path arguments, and without reference to 'persistence of velocities' for energy transport. Previous mean-free-path treatments, confined to $O(K)$ accuracy, have not obtained values for θ much larger than $\frac{3}{2}$.

3.6. *The heat flux vector*

Our general formula for the heat flux vector is (2.26):

$$\mathbf{q} = \frac{1}{2}\int_V \bar{\rho}(u_2^2 - C_2^2)\, \mathbf{u}_2 \mathscr{P}_2\, d\bar{v}. \tag{3.43}$$

From (3.27), (3.28) and

$$\hat{\mathbf{R}}\hat{\mathbf{R}} : \nabla \mathbf{v} = \hat{\mathbf{R}}\hat{\mathbf{R}} : \overset{\circ}{\nabla}\mathbf{v} + \tfrac{1}{3}\nabla . \mathbf{v} = \hat{\mathbf{R}}\hat{\mathbf{R}} : \overset{\circ}{\nabla}\mathbf{v} - \frac{1}{2T}\frac{dT}{dt} + O(K),$$

we obtain for $u_2^2 - C_2^2$ the expansion

$$\begin{aligned} u_2^2 - C_2^2 = C_2^2 \bigg\{ &-\frac{x\lambda_2}{T}\hat{\mathbf{R}} . \nabla T - 2x\tau_2 \hat{\mathbf{R}}\hat{\mathbf{R}} : \overset{\circ}{\nabla}\mathbf{v} + 2(1-x)\lambda_2\, \hat{\mathbf{R}} . \frac{\mathscr{F}}{C_2^2} \\ &+ \frac{x^2\tau_2\lambda_2}{2T}\left[\hat{\mathbf{R}} . \nabla\left(\frac{dT}{dt}\right) - \frac{1}{T}\frac{dT}{dt}\hat{\mathbf{R}} . \nabla T\right] - 2x(\jmath - \tfrac{3}{2})\frac{\tau_2\lambda_2}{T}\frac{dT}{dt}\hat{\mathbf{R}} . \frac{\mathscr{F}}{C_2^2} \\ &+ 2(x^2 - x)\,\tau_2\,\lambda_2\, \hat{\mathbf{R}} . \nabla \mathbf{v} . \mathscr{F}/C_2^2 + \tau_2\lambda_2 \hat{\mathbf{R}}\hat{\mathbf{R}}\hat{\mathbf{R}} \vdots [x^2 - g)\nabla\overset{\circ}{\nabla}\mathbf{v} \\ &+ (x^2 - g(\jmath + \tfrac{1}{2}))\overset{\circ}{\nabla}\mathbf{v}\nabla T/T] + \ldots \bigg\}, \end{aligned} \tag{3.44}$$

where $g = 4\mu/(\rho C_2 \lambda_2)$. This is to be multiplied by the expansion for $\mathbf{u}_2$, and had we retained the factors $\omega\delta_i$ (see (2.28)), then averaged $(u_2^2 - C_2^2)\,\mathbf{u}_2$ over ω, the effect would be to replace g in (3.44) by

$$\bar{g} = \frac{4\mu}{\rho C_2 \lambda_2}\overline{\omega^3}\,\delta_1\,\delta_2^2 = \frac{8}{9}\frac{4}{\sqrt{\pi}}\left(\frac{2}{5}\right)^{\frac{1}{2}}\left(\frac{4}{15}\right)^{\frac{1}{2}} \approx \tfrac{2}{3}(1 - 0{\cdot}008) \approx \tfrac{2}{3},$$

in which calculation we have used (2.2), (2.4) and (3.35). The approximation here introduces an error of less than 1 %. As we shall see later the exact value of the coefficient in question is $\frac{2}{3}$; without averaging we get $g = \frac{2}{3} \times 1{\cdot}017$, which is still very close.

The other term affected by averaging over ω is the one containing $\mathscr{F}$. In this case (again anticipating the multiplication by $\mathbf{u}_2$) $2\tau_2\lambda_2\mathscr{F}/C_2^2$ is replaced by the average of $2(\omega\delta_2)\,\tau_2(\omega\delta_2\,\lambda_2)\mathscr{F}/C_2^2)$. Since

$$\frac{3\mathscr{F}}{C_1^2} = -\frac{3\nabla p}{\rho C_1^2} + O(K) = -\frac{\nabla p}{p} + O(K) = -\frac{5}{2}\frac{\nabla T}{T} + O(K),$$

this average reduces to $-\alpha\tau_2\lambda_2\nabla T/T + O(K)$, with $\alpha = 1$. Without averaging $\alpha = 1{\cdot}291$; the exact value of α is $\frac{10}{9}$. The error our value of $\alpha = 1$ produces will be indicated shortly.

Substituting (3.44), (3.32) and (3.33) into (3.43), using

$$\nabla\left(\frac{dT}{dt}\right) = \frac{d}{dt}(\nabla T) + \nabla\mathbf{v}\,.\,\nabla T,$$

(3.2), the integrals in (3.8) and the averages just described, we obtain

$$\mathbf{q} = -\frac{\rho C_2^3\lambda_2}{6T}\nabla T + \frac{\rho C_2^2\lambda_2^2}{6T}\left[\frac{d}{dt}(\nabla T) - \nabla\mathbf{v}\,.\,\nabla T + (\delta - \tfrac{1}{2})\frac{1}{T}\frac{dT}{dt}\nabla T \right.$$
$$\left. + \tfrac{8}{15}T\nabla\,.\,\nabla\overset{\circ}{\mathbf{v}} + \frac{8}{15}\left(\frac{37{\cdot}5}{4} + \delta\right)\nabla\overset{\circ}{\mathbf{v}}\,.\,\nabla T - \frac{8}{15}\frac{T}{p}\nabla\overset{\circ}{\mathbf{v}}\,.\,\nabla p\right]. \qquad (3.45)$$

From the first term in (3.45) we obtain $\kappa = \frac{1}{6}\rho C_2^4\tau_2$, as stated in equation (2.19). By (3.20*c*) our result can be written

$$\mathbf{q} = -\kappa\nabla T + \frac{\mu^2}{\rho T}\mathbf{Q},$$

where

$$Q = \theta_1\nabla\,.\,\mathbf{v}\nabla T + \theta_2\left(\frac{d}{dt}(\nabla T) - \nabla\mathbf{v}\,.\,\nabla T\right) + \theta_3\frac{T}{p}\nabla\overset{\circ}{\mathbf{v}}\,.\,\nabla p + \theta_4 T\nabla\,.\,\nabla\overset{\circ}{\mathbf{v}} + \theta_5\nabla\overset{\circ}{\mathbf{v}}\,.\,\nabla T,$$

with $$\theta_1 = \tfrac{15}{4}(\tfrac{7}{2} - \delta), \quad \theta_2 = \tfrac{45}{8}, \quad \theta_3 = -3, \quad \theta_4 = 3$$

and $$\theta_5 = 3\left(\frac{37{\cdot}5}{4} + \delta\right).$$

In this calculation we have used

$$\frac{4}{135}\frac{\rho}{T}C_2^3\lambda_2\tau_2 = \frac{4}{15}\kappa\tau_2 = \frac{k}{m}\mu\tau_1 = \frac{\mu^2}{\rho T}.$$

Were 37·5 in θ_5 replaced by 35, our results would agree entirely with Burnett's expression for $\mathbf{q}$ for Maxwellian molecules. This error and the much smaller error in $\bar{g}$ removed above are unimportant considering both the simplicity of our model and its much greater generality than possible with the Chapman–Enskog series development.

4. Concluding remarks

We remind the reader that our purpose has not been yet another approach to the Burnett equations; it has been to construct a theory of fluid dynamics valid for all K values, and then to use Burnett's results as a first check on this theory at small values of K. As remarked in the introduction, tests of the theory at $K \approx 1$ and higher are important; these will be provided in later papers. Another important development, partially completed, is the extension of the expressions for $\mathbf{p}$ and $\mathbf{q}$ to molecules possessing internal energy. And boundary conditions certainly need further consideration.

Because mean-free-path arguments are independent of having accurate kinetic equations for velocity distribution functions, they may have some future in turbulent plasmas, where the effect of micro-instabilities is mainly to alter the collision times. Admittedly phenomenological in spirit, but perhaps such methods are the best that can be achieved at this stage in the development of plasma theory.

For a theory correct only to $O(K)$ one must accept that mean-free-path arguments are inferior to exact kinetic equation treatments, but at higher powers of K the mathematics of the exact theory not only becomes troublesome, but also largely confounds the objective by severely constraining the K range.

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