J. Fluid Mech. (1980), *vol.* 101, *part* 2, *pp.* 225–242
Printed in Great Britain

On the thermodynamics of nonlinear constitutive relations in gasdynamics

By L. C. WOODS
Mathematical Institute, Oxford University

(Received 10 April 1979 and in revised form 19 May 1980)

The thermodynamics of irreversible processes is normally limited to processes that can be adequately described by linear constitutive relations, like those of Fourier and Newton in a simple gas. In this paper we use thermodynamic arguments to derive the (nonlinear) Burnett equations for a monatomic gas, thus avoiding the complicated kinetic theory by which the equations were discovered and which somewhat obscures the origin of the various terms in the equations. Expressions are given for the entropy, its flux and its production rate correct to second-order in Knudsen number. The theory involves five phenomenological parameters, and as there are eleven coefficients in the second-order terms of Burnett's equations, we are able to deduce several necessary constraints between these coefficients. Compact forms for the equations are found that clarify their physical significance. The general method we have developed is applicable to media other than simple gases.

In a final section we use our theory of Burnett's equations to draw some general conclusions concerning the second law of thermodynamics. It is shown that the Clausius–Duhem inequality holds only for the linear theory of constitutive relations; and that axiomatic generalizations of the inequality to nonlinear processes – common in continuum mechanics – fail because the vital distinction between reversible and irreversible processes is not made.

1. Linear constitutive relations

In a monatomic gas the classical linear constitutive relations for the viscous stress $\boldsymbol{\pi}_1$ and the heat flux vector $\mathbf{q}_1$ are given by

$$\left.\begin{aligned} &\boldsymbol{\pi}_1 = -2\mu\mathring{\mathbf{e}}, \quad \mathbf{q}_1 = -\kappa T\mathbf{g} \quad (\mathring{\mathbf{e}} \equiv \mathring{\nabla}\mathbf{v}, \quad \mathbf{g} \equiv \nabla T/T) \\ \text{where} \qquad &\mathring{\mathbf{e}} = \tfrac{1}{2}(\mathbf{e}+\mathbf{e}) - \tfrac{1}{3}\overset{\times}{e}\mathbf{I} \quad (\mathbf{e} = \nabla\mathbf{v}, \quad \overset{\times}{e} = \mathbf{I}:\nabla\mathbf{v} = \nabla.\mathbf{v}) \end{aligned}\right\} \qquad (1.1)$$

is the deviator of the velocity gradient tensor, $T\mathbf{g}$ is the temperature gradient, μ is the shear viscosity and κ is the thermal conductivity. The subscript '1' in (1.1) denotes a term $O(\epsilon)$, where ϵ is the Knudsen number, i.e. the ratio of a molecular mean free time to a macroscopic scale time (or a similar ratio of length scales). Certain variables† will be expanded in a Knudsen number series, typically

$$\phi = \phi_0 + \phi_1 + \phi_2 + \dots \quad (\phi_n = O(\epsilon^n)).$$

---

† Since dissipation is the transfer of energy from macroscopic to microscopic length scales, ϵ is the natural expansion parameter for all those functions whose values are determined by dissipation.

0022-1120/80/4554-2420 $02.00

For example, the pressure tensor is

$$\mathbf{p} = \mathbf{p}_0+\boldsymbol{\pi}_1+\boldsymbol{\pi}_2+\ldots, \quad \mathbf{p}_0 = p\mathbf{I}, \quad \boldsymbol{\pi}_1 = -2\mu\mathring{\mathbf{e}}, \quad \ldots \quad (p = R\rho T), \tag{1.2}$$

where p is the thermodynamic pressure and $\mathbf{I}$ the unit tensor. We shall also employ the classical relations

$$\kappa = \tfrac{15}{4}R\mu, \quad p\tau_1 = \mu = aT^{\varsigma} \quad (a, \varsigma \text{ are constants}), \tag{1.3}$$

where τ_1 is the microscopic free time associated with molecular momentum transfer.

Let $u = \frac{3}{2}p/\rho$ denote the internal specific energy, then the zero-order entropy

$$s_0 = \tfrac{3}{2}R\ln(p/\rho^{\frac{5}{3}})+\text{const.} = -R\ln(p/(RT)^{\frac{5}{2}})+\text{const.}, \tag{1.4}$$

satisfies the Gibbs relation

$$TDs_0 = Du+pD\rho^{-1} \quad \left(D \equiv \frac{\partial}{\partial t}+\mathbf{v}.\nabla\right), \tag{1.5}$$

D being the material time derivative.† The total entropy, $s = s_0+s_1+s_2+\ldots$, must satisfy the well-known stability condition $s-s_0 \leqslant 0$.‡ Now s_1 must be linear in $\boldsymbol{\pi}_1$ and $\mathbf{q}_1$. Continuity of the space derivatives of s_1, expected on physical grounds, rules out dependence on $|\boldsymbol{\pi}_1|$ and $|\mathbf{q}_1|$, and therefore s_1 may have either sign. We conclude that for thermodynamic stability it must vanish. Hence

$$s = s_0+s_2+\ldots, \quad s_2 \leqslant 0. \tag{1.6}$$

Of course this argument would fail in any region where $|s_1| < |s_2|$, but later we shall find that s_2 depends only on the products $\boldsymbol{\pi}_1{:}\boldsymbol{\pi}_1$ and $\mathbf{q}_1.\mathbf{q}_1$, so that, if s_1 did exist, it would have the unphysical property of doing so only for gradients $\mathring{\mathbf{e}}$ and $\mathbf{g}$ large enough to prevent $|s_1|$ exceeding $|s_2|$. Notice that (1.6) means that the error term in (1.5) is $O(\epsilon^2)$, and not $O(\epsilon)$ as might be expected. This is why 'local thermodynamic equilibrium' is usually a successful hypothesis.

It is generally true (e.g. see Woods 1975, p. 148) that

$$\rho Du+\mathbf{p}{:}\nabla\mathbf{v}+\nabla.\mathbf{q}-\psi = 0,$$

or

$$(\rho Du+p\nabla.\mathbf{v})+(\boldsymbol{\pi}_1{:}\mathring{\mathbf{e}}+\nabla.\mathbf{q}_1-\psi)+(\boldsymbol{\pi}_2{:}\mathring{\mathbf{e}}+\nabla.\mathbf{q}_2)+O(\epsilon^3) = 0, \tag{1.7}$$

where ψ is the radiant heat density. By (1.5), (1.7) correct to $O(\epsilon)$, and continuity, viz.

$$D\rho+\rho\nabla.\mathbf{v} = 0, \tag{1.8}$$

we find

$$\rho TDs_0 = -\boldsymbol{\pi}_1{:}\,\mathring{\mathbf{e}}-\nabla.\mathbf{q}_1+\psi.$$

As $\mathbf{g} = \nabla T/T$ this may be written

$$\rho TDs_0 = -\boldsymbol{\pi}_1{:}\,\mathring{\mathbf{e}}-\mathbf{q}_1.\mathbf{g}+\nabla.\mathbf{J}_{s1}+\psi, \tag{1.9}$$

where

$$\mathbf{J}_{s1} = \mathbf{q}_1/T \tag{1.10}$$

is the first-order entropy flux. For a monatomic gas $\boldsymbol{\pi}$ has zero trace, i.e. $\boldsymbol{\pi} = \mathring{\boldsymbol{\pi}}$, so that $\boldsymbol{\pi}{:}\,\mathbf{e} = \mathring{\boldsymbol{\pi}}{:}\,\mathring{\mathbf{e}}$, which explains the appearance of the deviator $\mathring{\mathbf{e}}$ in (1.7).

---

† The arguments in this section and in § 5 can be made more precise by also expanding D in a Knudsen number series; see appendix A.

‡ Often ignored in axiomatic continuum mechanics, see § 7.

Let $\sigma = \sigma_1 + \sigma_2 + \ldots$ be the entropy created per unit volume and $\mathbf{J}_s = \mathbf{J}_{s1} + \mathbf{J}_{s2} + \ldots$ be the entropy flux; then entropy balance at a point $P(\mathbf{r}, t)$ requires that

$$\sigma = \rho Ds + \nabla . \mathbf{J}_s - \psi/T, \tag{1.11}$$

and in particular that

$$\sigma_1 = \rho Ds_0 + \nabla . \mathbf{J}_{s1} - \psi/T + O(\epsilon^2). \tag{1.12}$$

From (1.9) and (1.12) we have for the first-order 'dissipation'

$$T\sigma_1 = -\boldsymbol{\pi}_1 : \mathring{\mathbf{e}} - \mathbf{q}_1 . \mathbf{g} \geqslant 0, \tag{1.13}$$

where the added inequality – often termed the 'Clausius–Duhem inequality' – is a local form of the second law of thermodynamics. And the first-order theory is completed by noting that, for an isotropic medium, (1.13) leads to the linear constitutive relations (1.1). This approach is elaborated in de Groot & Mazur (1962) and in Woods (1975) for more general fluids, including mixtures and plasmas.

Our present task is to generalize the standard theory to the nonlinear constitutive relations for a monatomic gas first given by Burnett (1935). Burnett's theory is based on the Chapman–Enskog series (in powers of ϵ) treatment of Boltzmann's kinetic equation. It yields values for $\boldsymbol{\pi} = \boldsymbol{\pi}_1 + \boldsymbol{\pi}_2$, $\mathbf{q} = \mathbf{q}_1 + \mathbf{q}_2$, where the eleven $O(\epsilon^2)$ terms in $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ are quadratic in $\mathring{\mathbf{e}}$ and ∇T and linear in $\nabla . \mathring{\mathbf{e}}$, $D\mathring{\mathbf{e}}$, $\overline{\nabla \overset{\circ}{\nabla} T}$ and $D(\nabla T)$. The coefficients of these terms are proportional to $\mu^2/p = \mu\tau_1 = p\tau_1^2$, τ_1 being the time defined in (1.3*b*).

While the kinetic theory gives precise values for the eleven Burnett coefficients, our thermodynamic approach requires five phenomenological coefficients, although, by tracing the physical origins of the various terms, we are able to give estimates for these numbers very close to their true values. From our coefficients we have deduced certain necessary relations between the Burnett coefficients, akin to the so-called† Onsager relations of the linear theory, although with quite different physical origin. Another important consequence of our new derivation of the Burnett equations is a clear physical interpretation of the various terms, which has been lacking hitherto (see Woods 1979). And our method, being simpler and in some aspects more general than the kinetic theory approach, is capable of various other applications.

2. The Burnett constitutive relations

These relations are usually expressed in the forms (Chapman & Cowling 1970)

$$\left.\begin{aligned} \boldsymbol{\pi}_2 &= \mu\tau_1 \left\{ \varpi_1 \overset{\times}{e}\mathring{\mathbf{e}} + \varpi_2 (D\mathring{\mathbf{e}} - 2\overset{\circ}{\overline{\mathbf{e} . \mathring{\mathbf{e}}}}) + \varpi_3 \overline{R\nabla \overset{\circ}{\nabla} T} + \varpi_4 \frac{R}{p} \overline{\nabla p \overset{\circ}{\nabla} T} + \varpi_5 \frac{R}{T} \overline{\nabla T \overset{\circ}{\nabla} T} + \varpi_6 \overset{\circ}{\overline{\mathring{\mathbf{e}} . \mathring{\mathbf{e}}}} \right\}, \\ \mathbf{q}_2 &= \mu\tau_1 R \left\{ \theta_1 \overset{\times}{e} \nabla T + \theta_2 (D\nabla T - \mathbf{e} . \nabla T) + \theta_3 \frac{T}{p} \mathring{\mathbf{e}} . \nabla p + \theta_4 T\nabla . \mathring{\mathbf{e}} + \theta_5 \mathring{\mathbf{e}} . \nabla T \right\}, \end{aligned}\right\} \tag{2.1}$$

where for the special case of Maxwellian molecules

$$\left.\begin{aligned} &\varpi_1 = \tfrac{4}{3}(\tfrac{7}{2} - \eth), \quad \varpi_2 = 2, \quad \varpi_3 = 3, \quad \varpi_4 = 0, \quad \varpi_5 = 3\eth, \quad \varpi_6 = 8, \\ &\theta_1 = \tfrac{15}{4}(\tfrac{7}{2} - \eth), \quad \theta_2 = \tfrac{45}{8}, \quad \theta_3 = -3, \quad \theta_4 = 3, \quad \theta_5 = 3(\tfrac{35}{4} + \eth). \end{aligned}\right\} \tag{2.2}$$

In the derivation of (2.1) it is assumed that the radiant heating ψ is zero.

---

† For a critique of the reciprocal relations see Woods (1975, chapter 7).

The form of these equations is rather uninstructive concerning the physical origin of the various terms, and we shall now group these terms into a more coherent pattern. By (1.1), (1.8) and $u = \frac{3}{2}RT$, equation (1.7), with zero ψ, can be written

$$\frac{1}{T}DT = -\tfrac{2}{3}\nabla.\mathbf{v}+2\xi \quad \left(\xi \equiv \tfrac{2}{3}\tau_1\mathring{\mathbf{e}}:\mathring{\mathbf{e}}-\frac{1}{3p}\nabla.\mathbf{q}_1 = O(\epsilon)\right). \tag{2.3}$$

Hence (1.8), (2.3) and $p = R\rho T$ yield

$$\frac{1}{p}Dp = -\tfrac{5}{3}\nabla.\mathbf{v}+O(\epsilon) = \frac{5}{2T}DT+O(\epsilon), \tag{2.4}$$

i.e. $pT^{-\frac{5}{2}}$ = constant + $O(\epsilon)$ at a fluid particle. By (1.4) this constant is $R^{\frac{5}{2}}e^{-s_0/R}$. Thus as $\epsilon \to 0$ we attain isentropic flow and, assuming continuity in the flow field so that this constant becomes independent of position, we arrive at

$$\frac{1}{p}\nabla p = \frac{5}{2T}\nabla T+O(\epsilon). \tag{2.5}$$

From (1.1) and (1.3)

$$\left.\begin{aligned} R\left(\nabla\nabla T+\frac{\delta}{T}\nabla T\nabla T\right) &= \frac{R}{\mu}\nabla(\mu\nabla T) = \frac{-4}{15\mu}\nabla\mathbf{q}_1 \\ \text{and} \qquad D\mathring{\mathbf{e}} &= \frac{-1}{2\mu}D\boldsymbol{\pi}_1+\tfrac{2}{3}\delta e\mathring{\mathbf{e}}. \end{aligned}\right\} \tag{2.6}$$

We also need the identities

$$\mathbf{e} = \mathring{\mathbf{e}}-\boldsymbol{\omega}\times\mathbf{I}+\tfrac{1}{3}\check{e}\mathbf{I}, \quad \boldsymbol{\omega}\times\mathbf{I} = \tfrac{1}{2}(\mathbf{e}-\mathbf{e}) = \mathring{\mathbf{e}}-\mathbf{e}+\tfrac{1}{3}\check{e}\mathbf{I} \quad (\boldsymbol{\omega} \equiv \tfrac{1}{2}\nabla\times\mathbf{v}), \tag{2.7}$$

where $2\boldsymbol{\omega}$ is the fluid vorticity, and the term $-\boldsymbol{\omega}\times\mathbf{I}$ in (2.7*a*) corresponds to a rigid-body rotational motion of the fluid particle P with angular velocity $\boldsymbol{\omega}$. Let $\mathscr{D}\mathbf{a}$, $\mathscr{D}\mathbf{A}$ denote the rates of change of a vector $\mathbf{a}$ and a tensor $\mathbf{A}$ in a frame fixed at P but rotating with an angular velocity $-\boldsymbol{\omega}$ with respect to the frame in which these derivatives are $D\mathbf{a}$ and $D\mathbf{A}$, then

$$\mathscr{D}\mathbf{a} = D\mathbf{a}+\boldsymbol{\omega}\times\mathbf{a}, \quad \mathscr{D}\mathbf{A} = D\mathbf{A}+\boldsymbol{\omega}\times\mathbf{A}-\mathbf{A}\times\boldsymbol{\omega}.$$

By (2.7) and the assumption that $\mathbf{A}$ is symmetric we have

$$\mathscr{D}\mathbf{a} = D\mathbf{a}+(\mathring{\mathbf{e}}-\mathbf{e}+\tfrac{1}{3}\check{e}\mathbf{I}).\mathbf{a}, \quad \mathscr{D}\mathbf{A} = D\mathbf{A}+2(\mathring{\mathbf{e}}-\mathbf{e}+\tfrac{1}{3}\check{e}\mathbf{I}).\mathbf{A}. \tag{2.8}$$

From (2.3)–(2.8) and relations similar to (2.6) involving $\nabla.\boldsymbol{\pi}_1$, and $D\mathbf{q}_1$, we find that for Maxwellian molecules (2.1) can be written succinctly as

$$\left.\begin{aligned} \boldsymbol{\pi} &= \boldsymbol{\pi}_1+\boldsymbol{\pi}_2 = \overset{\circ}{\overline{\mathbf{R}_1.\boldsymbol{\pi}_1}}-\alpha p\tau_1\mathscr{D}(\boldsymbol{\pi}_1/p)-\tau_0\overset{\circ}{\overline{\nabla\mathbf{q}_1}}, \\ \mathbf{q} &= \mathbf{q}_1+\mathbf{q}_2 = \mathbf{R}_2.\mathbf{q}_1-\beta p\tau_2T^{\frac{1}{2}}\mathscr{D}(\mathbf{q}_1/pT^{\frac{1}{2}})-\tfrac{15}{8}\tau_0RT\nabla.\boldsymbol{\pi}_1, \end{aligned}\right\} \tag{2.9}$$

where†

$$\mathbf{R}_1 = \mathbf{I}-2\tau_1\mathring{\mathbf{e}}, \quad \mathbf{R}_2 = \mathbf{I}-(\tau_2+4\tau_1-\tfrac{5}{2}\tau_0)\mathring{\mathbf{e}}, \tag{2.10}$$

and

$$\tau_0 = \tfrac{4}{5}\tau_1, \quad \tau_2 = \tfrac{3}{2}\tau_1, \quad \alpha = 1, \quad \beta = 1. \tag{2.11}$$

In the more general theory to be given below (2.9) and (2.10) remain true, but none of the relations in (2.11) apply.

---

† The reader should note that the subscripts in (2.10) and (2.11) relate to different microscopic time scales, and not to different orders in Knudsen number.

As will become apparent later, the terms in (2.9) containing $\mathscr{D}$ and ∇ arise from changes in the second-order entropy ($\mathscr{D}s_2$) and changes in the second-order entropy flux ($\nabla\,.\,\mathbf{J}_{s2}$). And we shall establish in § 3 that the operators $\mathbf{R}_1$ and $\mathbf{R}_2$ result from fluid element shear over a mean free path; in fact (1.2) can be expressed

$$\mathbf{p} = p\mathbf{I} + \boldsymbol{\pi}_1 + O(\epsilon^2) = (\mathbf{I} - 2\tau_1\mathring{\mathbf{e}}).p\mathbf{I} + O(\epsilon^2), \tag{2.12}$$

showing that $\mathbf{p}$ differs from $p\mathbf{I}$ because of this effect.

Parity under reversal of molecular motions plays an important role in linear phenomenological theory. Irreversible equations like (1.1), viz.

$$\overset{(+)}{\boldsymbol{\pi}_1} = -2\mu\overset{(-)}{\mathring{\mathbf{e}}}, \quad \overset{(-)}{\mathbf{q}_1} = -\kappa T\overset{(+)}{\mathbf{g}} \quad (+\text{, positive parity; } -\text{, negative parity})$$

always contain terms of opposite parity and, as explained in Woods (1975), the reciprocal relations ensure that all the terms in σ_1 have positive parity. As it stands in (1.13) σ_1 appears to have negative parity, but when the constitutive relations (1.1) are substituted into (1.13), its parity becomes positive. Now an interesting feature of (2.1) is that they reveal $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ to have parities opposite to the right-hand sides of $\boldsymbol{\pi}_1$ and $\mathbf{q}_1$, which we can indicate as follows:

$$\overset{(+)}{\mathbf{p}} = \overset{(+)}{p\mathbf{I}} - 2\mu\overset{(-)}{\mathring{\mathbf{e}}} + \mu\tau_1\overset{(+)}{\boldsymbol{\Pi}}, \quad \overset{(-)}{\mathbf{q}} = -\kappa T\overset{(+)}{\mathbf{g}} + \mu\tau_1 R\overset{(-)}{\mathbf{Q}},$$

the parities ascribed to $\mathbf{p}$ and $\mathbf{q}$ following from their kinetic theory (i.e. reversible) definitions. We infer that $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ are due to *reversible* effects, so that, although they can change the entropy of a fluid element, they cannot increase the dissipation in the element.

It has long been known that the Burnett equations fail when applied to shock waves and other situations in which ϵ much exceeds 0·2. In a recent paper (Woods 1979) the author discusses the reason for this, and incidently as part of a check on a general theory for fluid dynamics for unconstrained ϵ, gives a mean-free-path treatment of the equations. The value of our present study lies not in the equations obtained, but in the generality of the approach and the possibility of applying it to more complicated media. It also offers an interesting example of nonlinear constitutive equations with which one can check the basic equation of thermodynamics and the Clausius–Duhem inequality.

3. Fluid particle distortion

In this section we shall use elementary mean-free-path arguments to obtain expressions for the influence of fluid particle distortion on dissipation and entropy flux. The distortion we are concerned with is due to the change in fluid velocity that occurs during the flight of a typical molecule S from one collision to the next. We shall assume that S moves a distance λ between collisions, at a speed C and so takes a time $\tau = \lambda/C$. We have chosen a single molecular speed for our molecules rather than a Maxwellian distribution of speeds, for, provided the mean free time τ and the mean free path λ are given different values for the transport of entropy, momentum and energy, there is no loss in accuracy in the single-speed model, at least in a theory valid only $O(\epsilon^2)$ (Woods 1979). We shall introduce three distinct microscopic time scales, τ_0, τ_1, τ_2, and (later) two ratios α, β of time-scales, making five phenomenological parameters in all. Kinetic theory yields precise values for these constants once the nature of the force law between molecules has been specified.

Let $P(\mathbf{r}, t)$ and $P'(\mathbf{r}', t')$, where $\mathbf{r}' = \mathbf{r} - \lambda\hat{\boldsymbol{\alpha}}$, $t' = t - \tau$ and $\hat{\boldsymbol{\alpha}}$ is unit vector, be points in the fluid moving with fluid velocities $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ and $\mathbf{v}' = \mathbf{v}(\mathbf{r}', t')$. As shown in figure 1, P' is displaced from P in distance and time so that an average molecule S moving along a unit vector $\hat{\mathbf{R}}$ (relative to P') correctly chosen can move from a first collision at P' to a second collision at P. The microscopic scales λ and τ will depend on what property S is transporting from P' to P; subscripts will be added later to indicate these properties.

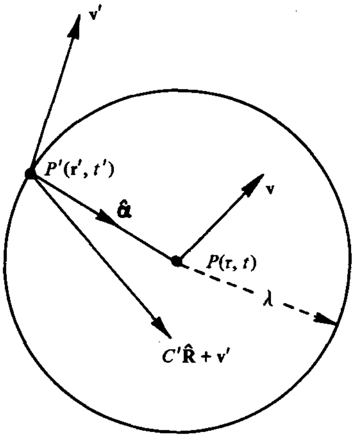

FIGURE 1. Fluid particle distortion.

If $\phi(\mathbf{r}, t)$ is a fluid property, then

$$\phi' = \phi(\mathbf{r} - \lambda\hat{\boldsymbol{\alpha}}, t - \tau) = \phi(\mathbf{r}, t) - \lambda\hat{\boldsymbol{\alpha}}.\nabla\phi - \tau D\phi + O(\epsilon^2), \tag{3.1}$$

where the derivatives are evaluated at P. For example if C' is the average molecular speed at P' and C is its value at P, then since $C \propto T^{\frac{1}{2}}$, (3.1) gives

$$C' = C\left\{1 - \frac{1}{2T}(\lambda\hat{\boldsymbol{\alpha}}.\nabla T + \tau DT) + O(\epsilon^2)\right\}. \tag{3.2}$$

During its passage from P' to P, S will experience the body force $\mathbf{F}$ per unit mass acting on the fluid, which by Euler's equation of motion is related to the fluid acceleration, $\mathbf{a} = D\mathbf{v}$, by

$$\mathbf{F} = \mathbf{a} + \frac{1}{\rho}\nabla p + O(\epsilon).$$

Let S leave P' with a thermal velocity $C'\hat{\mathbf{R}} + \mathbf{w}$, where $\mathbf{w}$ is a small anisotropic correction due to pressure and temperature gradients and which will be assigned a value shortly. Relative to P, which moves with a velocity $(\mathbf{v} - \mathbf{v}')$ relative to P', S arrives with the velocity

$$\mathbf{u} = C'\hat{\mathbf{R}} + \mathbf{w} + \mathbf{v}' - \mathbf{v} + \tau\mathbf{F} = C'\hat{\mathbf{R}} + \mathbf{w} + \mathbf{v}' - \mathbf{v} + \tau\mathbf{a} + \tau\nabla p/\rho + O(\epsilon^2),$$

since variations of $\mathbf{F}$ with distance can add only a term $O(\epsilon^2)$ to this result. Applying (3.1) and noting that $\hat{\boldsymbol{\alpha}} = \hat{\mathbf{R}} + O(\epsilon)$, we find

$$\mathbf{u} = C\hat{\mathbf{R}}.\left\{\mathbf{I}\left(1 - \frac{\tau}{2T}DT - \frac{\lambda}{2T}\hat{\mathbf{R}}.\nabla T\right) - \tau\nabla\mathbf{v} + \frac{\tau}{\rho C}\hat{\mathbf{R}}\nabla p\right\} + \mathbf{w} + O(\epsilon^2). \tag{3.3}$$

A molecule $\bar{S}$ approaching P from the opposite direction will have a velocity $\bar{\mathbf{u}}$ relative to P obtained by reversing the sign of $\hat{\mathbf{R}}$ in (3.3) and since the centre of mass M of the colliding molecules must remain at P on the average, we may take the collision between S and $\bar{S}$ as typical. However because of the ∇T and ∇p terms in (3.3), M will drift from P unless we choose $\mathbf{w}$ to eliminate these terms. Doing this, and using (2.4) to write

$$\frac{DT}{2T} = -\tfrac{1}{3}\nabla . \mathbf{v} + O(\epsilon) = -\tfrac{1}{3}\overset{\times}{e} + O(\epsilon),$$

we get (see (1.1) and (2.7))

$$\mathbf{u} = C\hat{\mathbf{R}} . \{\mathbf{I} - \tau(\mathring{\mathbf{e}} - \boldsymbol{\omega} \times \mathbf{I})\} + O(\epsilon^2) \quad (\boldsymbol{\omega} \equiv \tfrac{1}{2}\nabla \times \mathbf{v}).$$

Below we shall be concerned only with the thermodynamic effects of fluid particle distortion and, as $\boldsymbol{\omega}$ corresponds to a rigid body rotation of P, the term $\tau\boldsymbol{\omega} \times \mathbf{I}$ has no thermodynamic role for P, and can be omitted. Also note that $\hat{\mathbf{u}} \equiv C\mathbf{R}$ is the average speed of molecules at P *after* collision. Hence we can write

$$\left.\begin{aligned} \mathbf{u} &= \hat{\mathbf{u}} . \{\mathbf{I} - \tau\mathring{\mathbf{e}}\} + O(\epsilon^2) \\ \text{and} \qquad \hat{\mathbf{u}} &= \mathbf{u} . \{\mathbf{I} + \tau\mathring{\mathbf{e}}\} + O(\epsilon^2) \end{aligned}\right\} \tag{3.4}$$

for the relations between molecular velocities before ($\mathbf{u}$) and after ($\hat{\mathbf{u}}$) collision at P. From (3.4*b*) we see that fluid particle shear supplies a factor $(\mathbf{I} + \tau\mathring{\mathbf{e}})$. to the velocities of colliding molecules at P. This is because, during the passage of molecules from points on the sphere $|\mathbf{r}' - \mathbf{r}| = \lambda$ to P, the fluid at P has time to acquire a velocity increment that differs from the earlier average value over the sphere.

Functions of the molecular speed will have each velocity vector modified in this way. For example (2.12) can be written

$$\hat{\mathbf{p}} \equiv p\mathbf{I} = (\mathbf{I} + \tau_1\mathring{\mathbf{e}}) . \mathbf{p} . (\mathbf{I} + \tau_1\mathring{\mathbf{e}}),$$

where $\hat{\mathbf{p}}$ is the (isotropic) pressure tensor for collided molecules and $\mathbf{p}$ is the pressure tensor for uncollided molecules.

Below we shall use the rule given in (3.4*b*) to obtain expressions for the 'collided' values of the first-order entropy production rate σ_1 and of the first-order flux $\mathbf{J}_{s1}$, namely $\hat{\sigma}_1$ and $\hat{\mathbf{J}}_{s1}$. We need these values because it is our claim that σ and $\mathbf{J}_s$ are given by the *collided* values of $\Sigma = -(\boldsymbol{\pi} \colon \mathring{\mathbf{e}} + \mathbf{q} . \acute{\mathbf{g}})/T$ and $\boldsymbol{\zeta} = \mathbf{q}/T$, i.e.

$$\sigma = \Sigma + O(\epsilon^3), \quad \mathbf{J}_s = \boldsymbol{\zeta} + O(\epsilon^3), \tag{3.5}$$

or since the collision operator $\wedge$ adds a factor $(1 + O(\epsilon))$,

$$T\sigma = T\hat{\sigma}_1 - (\boldsymbol{\pi}_2 : \mathring{\mathbf{e}} + \mathbf{q}_2 \cdot \acute{\mathbf{g}}) + O(\epsilon^3), \quad \mathbf{J}_s = \hat{\mathbf{J}}_{s1} + \frac{\mathbf{q}_2}{T} + O(\epsilon^3). \tag{3.6}$$

The meaning of (3.5) is that, while $\mathbf{p}$ and $\mathbf{q}$ at P are determined by the sequence of *earlier* collisions, σ and $\mathbf{J}_s$ depend additionally on the collisions occurring at P itself. In other words $\mathbf{p}$ and $\mathbf{q}$ at P are fixed in value by the *incoming* molecules, whereas σ and $\mathbf{J}_s$ are determined by the outgoing (i.e. collided) molecules at P. That dissipation is due to the randomizing effect of collisions is well understood, and (3.5) ensures that collisions occurring at the point of interest P are included in the entropy production and transport processes.

Let τ_0 denote the entropy transport time, then since the flux $\mathbf{J}_{s1}$ involves only one molecular speed,† we infer from (3.4*b*) that

$$\hat{\mathbf{J}}_{s1} = \mathbf{J}_{s1}.(\mathbf{I}+\tau_0\mathring{\mathbf{e}}). \tag{3.7}$$

The viscous stress tensor $\boldsymbol{\pi}_1$ contains two molecular speeds, and the microscopic time-scale is that for momentum transport, hence

$$\hat{\boldsymbol{\pi}}_1 = \boldsymbol{\pi}_1.(\mathbf{I}+2\tau_1\mathring{\mathbf{e}}). \tag{3.8}$$

The heat flux vector $\mathbf{q}_1$ involves three molecular speeds, and guided by the form of (2.10*b*) we shall write

$$\hat{\mathbf{q}}_1 = \mathbf{q}_1.\{\mathbf{I}+(\tau_2'+2\tau_1)\mathring{\mathbf{e}}\}, \tag{3.9}$$

where τ_2' is a mean free time for energy transport. Finally ∇T has two molecular speeds but, as the associated time scale exceeds τ_1, we can define a time τ_0' by its appearance in the relation

$$\widehat{\nabla T} = \nabla T.\{\mathbf{I}+(\tau_0'+2\tau_1)\mathring{\mathbf{e}}\} \tag{3.10}$$

following the pattern for $\hat{\mathbf{q}}_1$. Below we shall find that τ_0', τ_2' appear only in the combination $(\tau_0'+\tau_2')$, and therefore it is expedient to write

$$\tau_2 \equiv (\tau_2'+\tau_0')-\tau_0, \tag{3.11}$$

which, since τ_0 is defined by (3.7), provides the definition of the time τ_2 for energy transport.

Our theory does not yield relations between the mean free times τ_0, τ_1 and τ_2 introduced above, which are therefore independent parameters in our approach. For Maxwellian molecules kinetic theory gives the relations given in (2.11).

4. Entropy flux and production rate

By (3.6) and (3.7), correct to $O(\epsilon^2)$,

$$\mathbf{J}_s = \mathbf{J}_{s1}+\mathbf{J}_{s2} = \mathbf{J}_{s1}.(\mathbf{I}+\tau_0\mathring{\mathbf{e}})+\frac{\mathbf{q}_2}{T} = \frac{\mathbf{q}}{T}+\tau_0\frac{\mathbf{q}_1}{T}.\mathring{\mathbf{e}}, \tag{4.1}$$

since $\mathbf{q} = \mathbf{q}_1+\mathbf{q}_2+O(\epsilon^3)$. For a Maxwellian gas $\tau_0 = \frac{4}{5}\tau_1$, and by (1.3) the term in (4.1) due to shear, viz. $\mathbf{J}_{s2}-\mathbf{q}_2/T$, can be expressed

$$\mathbf{J}_{s2}-\frac{\mathbf{q}_2}{T} = -\frac{3\mu^2R}{pT}\nabla T.\mathring{\mathbf{e}}, \tag{4.2}$$

in agreement with a result obtained by Shavit & Zvirin (1970) from kinetic theory.

The value of $\hat{\sigma}_1$ follows from that of σ_1, given in (1.13), viz.

$$T\sigma_1 = -\boldsymbol{\pi}_1:\mathring{\mathbf{e}}-\mathbf{q}_1.\mathbf{g},$$

plus use of (3.8), (3.9) and (3.10). Thus, neglecting terms $O(\epsilon^3)$,

$$\begin{aligned} T\hat{\sigma}_1 &= -\hat{\boldsymbol{\pi}}_1:\mathring{\mathbf{e}}-\hat{\mathbf{q}}_1.\mathbf{g}-\mathbf{q}_1.\hat{\mathbf{g}} \quad (\hat{\mathbf{g}} = \widehat{\nabla T}/T) \\ &= -\boldsymbol{\pi}_1.\{\mathbf{I}+2\tau_1\mathring{\mathbf{e}}\}:\mathring{\mathbf{e}}-\mathbf{q}_1.\{\mathbf{I}+(\tau_2'+2\tau_1)\}\mathring{\mathbf{e}}.\mathbf{g}-\mathbf{q}_1.\{\mathbf{I}+(\tau_0'+2\tau_1)\mathring{\mathbf{e}}\}.\mathbf{g}, \end{aligned}$$

---

† In kinetic theory $\mathbf{J}_s$, $\mathbf{p}$, $\mathbf{q}$ and RT are the averages $-k\langle\mathbf{c}(\ln f-1)\rangle$, $\rho\langle\mathbf{cc}\rangle$, $\frac{1}{2}\rho\langle\mathbf{cc}.\mathbf{c}\rangle$ and $\frac{1}{3}\langle\mathbf{c}.\mathbf{c}\rangle$ respectively.

i.e. by (3.11)

$$T\hat{\sigma}_1 = T\sigma_1 - 2\tau_1 \boldsymbol{\pi}_1 . \mathring{\mathbf{e}} : \mathring{\mathbf{e}} - (\tau_0 + 4\tau_1 + \tau_2)\, \mathbf{q}_1 . \mathring{\mathbf{e}} . \mathbf{g},$$

or

$$T\hat{\sigma}_1 = T\sigma_1 + \frac{4\mu^2}{p}\left(\mathring{\mathbf{e}} : \overset{\circ}{\overline{\mathring{\mathbf{e}} . \mathring{\mathbf{e}}}} + a\frac{R}{T}\nabla T . \mathring{\mathbf{e}} . \nabla T\right) \quad \left(a \equiv \frac{15}{16}\left(4 + \frac{\tau_0 + \tau_2}{\tau_1}\right)\right). \tag{4.3}$$

For a Maxwellian gas it follows from (2.11) that $a = 189/32$, a curiously large number unless its origin is exposed by mean-free-time arguments as above.

Finally, we have from (3.6a) that the entropy source term, correct to $O(\epsilon^2)$, is given by

$$\left.\begin{aligned} T\sigma &= -\boldsymbol{\pi} : \mathring{\mathbf{e}} - \mathbf{q} . \mathbf{g} + \frac{4\mu^2}{p}\left(\mathring{\mathbf{e}} : \overset{\circ}{\overline{\mathring{\mathbf{e}} . \mathring{\mathbf{e}}}} + a\,\frac{R}{T}\nabla T . \mathring{\mathbf{e}} . \nabla T\right) \\ \text{or}\qquad T\sigma &= -\boldsymbol{\pi} : \mathring{\mathbf{e}} . (\mathbf{I} + 2\tau_1 \mathring{\mathbf{e}}) - \mathbf{q}\mathbf{g} : \{\mathbf{I} + (\tau_0 + 4\tau_1 + \tau_2)\mathring{\mathbf{e}}\}. \end{aligned}\right\} \tag{4.4}$$

Note from (4.1) that $\mathbf{J}_s$ is not equal to $\mathbf{q}/T$ in nonlinear theory, although in the literature of continuum mechanics this is generally assumed to be the case. Also we see from (4.4) that the bilinear form for σ familiar in linear theory does not hold in the nonlinear case, and that, unlike σ_1, the second-order entropy production rate, $\sigma_2 = \sigma - \sigma_1$, can have either sign, which means that $\sigma_1 \geqslant 0$ does not generalize to $\sigma = \sigma_1 + \sigma_2 \geqslant 0$, as generally supposed.

5. The generalized Gibbs' relation

By (1.2) and (1.8) equation (1.5), which has an error term $O(\epsilon^2)$, can be written

$$\rho T D s_0 = \rho D u + \mathbf{p}_0 : \mathbf{e} + O(\epsilon^2); \tag{5.1}$$

we shall now generalize this fundamental equation of thermodynamics, reducing the error term to $O(\epsilon^3)$. On the left-hand side we shall write $\rho T D s = \rho T D(s_0 + s_2) + O(\epsilon^3)$, so the first step is to find an expression for s_2.

Consider a fluctuation of a small fluid particle system P, occurring on such a short time scale that the energy and density of P remain constant. As the latter can change only on the macroscopic time scale, it follows that the fluctuation must occur in a time comparable to the mean free times $\tau_1, \tau_2, \ldots$ introduced earlier. Suppose that $\psi = 0$ and we can treat $\mathbf{q}_1$ and $\boldsymbol{\pi}_1$ as being constant across P, although varying with time during the fluctuation. In this case by (1.5) and (4.1) Ds_0 and $\nabla . \mathbf{J}_s$ are zero during the fluctuation and (1.11) reduces to

$$\rho T D s_2 = T\sigma_1 = -(\boldsymbol{\pi}_1 : \mathring{\mathbf{e}} + \mathbf{q}_1 . \mathbf{g}) \geqslant 0, \tag{5.2}$$

since σ_2 can be ignored compared with σ_1. Now suppose that P is initially in its normal state in the fluid, but that at $t = 0$ it is suddenly isolated and its gradients $\nabla\mathbf{v}$ and ∇T permitted to relax to zero. The mismatch apparent in (5.2) between the orders of the left- and right-hand sides of the equation requires that $D = O(\epsilon^{-1})$, i.e. that the rates of change be rapid.

The two terms of σ_1 in (5.2) will relax at different rates. We shall consider first the thermal dissipation term and write (5.2) as

$$\rho T S_2'(t) = -\mathbf{Q}(t) . \boldsymbol{G}(t), \tag{5.3}$$

where $S_2(t)$ is the value of the second-order entropy function and $\mathbf{Q}(t)$, $T\mathbf{G}(t)$ are the values of the heat flux and of the temperature gradient during the relaxation process. The initial conditions are

$$S_2(0) = s_2, \quad \mathbf{Q}(0) = \mathbf{q}_1, \quad \mathbf{G}(0) = \mathbf{g}, \quad \rho T S_2'(0) = -\mathbf{q}_1 \cdot \mathbf{g}, \tag{5.4}$$

retaining the symbols s_2, $\mathbf{q}_1$, $\mathbf{g}$ to denote values in the original steady state. The relaxation process will be completed at $t = \infty$; hence

$$S_2(\infty) = 0, \quad \mathbf{Q}(\infty) = 0, \quad \mathbf{G}(\infty) = 0. \tag{5.5}$$

To complete the set of equations constitutive relations are needed for $\mathbf{Q}'(t)$ and $\mathbf{G}'(t)$. These we shall assume take the usual form for relaxation processes,

$$\mathbf{Q}'(t) = -\mathbf{Q}(t)/c\tau_2, \quad \mathbf{G}'(t) = -\mathbf{G}(t)/b\tau_2, \tag{5.6}$$

where c, b are constants that we expect to be close to unity, since the mean free time (τ_2) for energy transport will be the appropriate time scale for the decay of $\mathbf{q}_1$ and ∇T. Equations (5.3)–(5.6) yield

$$\rho T S_2(t) = \tfrac{1}{2}\beta\tau_2 \mathbf{q}_1 \cdot \mathbf{g} \exp(-2t/\beta\tau_2) \quad \left(\beta \equiv \frac{2cb}{c+b}\right)$$

and therefore
$$\rho T s_2 = \tfrac{1}{2}\beta\tau_2 \mathbf{q}_1 \cdot \mathbf{g}, \tag{5.7}$$

where $\beta \sim 1$.

A similar argument applied to the viscous dissipation term in (5.2), with relaxation times chosen proportional to the momentum-transport mean free time τ_1, yields a second term for s_2, which added to (5.7) gives

$$\rho T s_2 = \tfrac{1}{2}\alpha\tau_1 \boldsymbol{\pi}_1 : \mathring{\mathbf{e}} + \tfrac{1}{2}\beta\tau_2 \mathbf{q}_1 \cdot \mathbf{g} \quad (\alpha, \beta \sim 1). \tag{5.8}$$

By (1.1) and (1.3) this formula can be written

$$\rho T s_2 = -\frac{\mu^2}{p}\left\{\alpha \mathring{\mathbf{e}} : \mathring{\mathbf{e}} + \gamma \frac{R}{T} \nabla T . \nabla T\right\} \quad \left(\gamma = \frac{15}{8}\frac{\tau_2}{\tau_1}\beta\right). \tag{5.9}$$

By employing the general formula for entropy given by kinetic theory (see de Groot & Mazur 1962, p. 182) Shavit & Zvirin (1970) have shown that for Maxwellian molecules $(\tau_2/\tau_1 = \frac{2}{3})$ $\rho T s_2$ is given by the special case

$$\alpha = 1, \quad \beta = 1, \tag{5.10}$$

of our formulae (5.9).

As indicated by (2.4) we can employ the adiabatic relations in (5.9) without significant error. Thus in differentiating (5.9) we may use (1.3) and (2.4) to obtain

$$\rho T D s_2 = (2\varsigma - 5)\frac{\mu^2}{\rho p T}\frac{DT}{T} = \tfrac{4}{3}(\varsigma - \tfrac{5}{2})\frac{\mu^2}{p^2} Du,$$

since $u = \frac{3}{2}RT$. Hence

$$\rho T D s_2 = -\frac{4\mu^2}{3p^2}(\varsigma - \tfrac{5}{2})(\xi_1 + \xi_2)\rho Du - \frac{\mu^2}{p}(D\xi_1 + D\xi_2), \tag{5.11}$$

where
$$\xi_1 = \alpha \mathring{\mathbf{e}} : \mathring{\mathbf{e}}, \quad \xi_2 = \gamma \frac{R}{T} \nabla T . \nabla T,$$

play the role of internal co-ordinates (Woods 1975, p. 66) in our thermodynamic system. Another form of (5.11) that we shall need shortly is

$$\rho T D s_2 = -\frac{2\mu^2}{p}\left\{(\mathscr{s}-\tfrac{5}{2})\,\alpha\mathring{\mathbf{e}}:\mathring{\mathbf{e}}+(\mathscr{s}-3)\,\gamma\frac{R}{T}\nabla T\,.\,\nabla T\right\}\frac{DT}{T}$$
$$-\frac{2\mu^2}{p}\left\{\alpha\mathring{\mathbf{e}}:D\mathring{\mathbf{e}}+\gamma\frac{R}{T}\nabla T\,.\,D\nabla T\right\}. \qquad (5.12)$$

Adding (5.11) to (5.1) and including two further terms on the right-hand side for a reason to be given shortly, we arrive at our generalized Gibbs' relation:

$$\rho T D s = \left[1-\frac{4\mu^2}{3p^2}(\mathscr{s}-\tfrac{5}{2})\,(\xi_1+\xi_2)\right]\rho\, Du+(\mathbf{p}_0+\boldsymbol{\pi}_2):\mathbf{e}+\mathbf{q}_2\cdot\mathbf{g}-\frac{\mu^2}{p}D\xi_1-\frac{\mu^2}{p}D\xi_2+O(\epsilon^3). \qquad (5.13)$$

The new $O(\epsilon^2)$ terms included are $\boldsymbol{\pi}_2:\mathbf{e}$ and $\mathbf{q}_2\cdot\mathbf{g}$, which by the discussion at the end of § 2 represent reversible work and reversible heat transfer respectively. The specific entropy (considered as a function of state) is changed by the addition of reversible work, the basic work term, $\mathbf{p}_0:\mathbf{e} = p\nabla.\mathbf{v} = \rho p\, d(\rho^{-1})/dt$ being of this nature, and therefore the term $\boldsymbol{\pi}_2:\mathbf{e}$ is properly included. In local thermodynamics, as distinct from global thermodynamics, heat and work are entirely equivalent forms of energy transport and so the reversible heating in $\mathbf{q}_2\cdot\mathbf{g}$ must also be included in the '$T\,ds$' equation. With all these effects (internal energy, work, heat and internal co-ordinates) accounted for, there remain no further possibilities of $O(\epsilon^2)$ terms, permitting us to advance the error term in (5.13) to $O(\epsilon^3)$.

Note that if we subtract (5.11) from (5.13) we find (cf. (5.1))

$$\rho T D s_0 = \rho D u+(\mathbf{p}_0+\boldsymbol{\pi}_2):\mathbf{e}+\mathbf{q}_2\cdot\mathbf{g}+O(\epsilon^3), \qquad (5.14)$$

and if we use (1.7) to remove ρDu from (5.14) we get (cf. (1.12))

$$\sigma_1 = \rho D s_0+\nabla.\frac{\mathbf{q}}{T}-\frac{\psi}{T}+O(\epsilon^3). \qquad (5.15)$$

Finally, subtracting (5.15) from (1.11) and using (4.1), we arrive at

$$\sigma_2 = \rho D s_2+\nabla.[\tau_0\mathbf{q}_1.\mathring{\mathbf{e}}/T]. \qquad (5.16)$$

6. Derivation of Burnett's equations

We are now in a position to write down an equation in which the only unknowns are $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$, and from which we can therefore obtain expressions for these Burnett additions to the classical linear theory. Eliminating $(\hat{\sigma}_1-\sigma_1)$ and σ_2 from (3.6), (4.3) and (5.16), we obtain

$$\boldsymbol{\pi}_2:\mathring{\mathbf{e}}+\mathbf{q}_2\cdot\mathbf{g} = \frac{4\mu^2}{p}\left(\mathring{\mathbf{e}}:\mathring{\overline{\mathring{\mathbf{e}}.\mathring{\mathbf{e}}}}+a\frac{R}{T}\nabla T.\mathbf{e}.\nabla T\right)-\rho T D s_2-T\nabla.[\tau_0\mathbf{q}_1.\mathring{\mathbf{e}}/T]. \qquad (6.1)$$

By (1.3) and the adiabatic relations the last term can be written

$$-\frac{\tau_0}{\tau_1}T\nabla.\left(\frac{\mu}{pT}\mathring{\mathbf{e}}.\mathbf{q}_1\right) = -\tau_0\mathbf{q}_1.\nabla.\mathring{\mathbf{e}}-\tau_0(\mathscr{s}-\tfrac{7}{2})\,\mathbf{q}_1.\mathring{\mathbf{e}}.\nabla T/T-\tau_0\mathring{\mathbf{e}}:\nabla\mathbf{q}_1.$$

Using (2.4) to remove DT from (5.12) in favour of $\nabla.\mathbf{v}$ and substituting in (6.1), we arrive at our basic equation for $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$, namely

$$\begin{aligned}\boldsymbol{\pi}_2 : \mathring{\mathbf{e}} + \mathbf{q}_2 . \frac{\nabla T}{T} &= \frac{\mu^2}{p}\left[\tfrac{4}{3}\alpha(\tfrac{5}{2}-\delta)\,\nabla.\mathbf{v}\mathring{\mathbf{e}} + 2\alpha D\mathring{\mathbf{e}} + 4\overset{\circ}{\overline{\mathring{\mathbf{e}}.\mathring{\mathbf{e}}}}\right]:\mathring{\mathbf{e}} \\ &\quad + \frac{\mu^2}{p}R\frac{\tau_2}{\tau_1}\left[\tfrac{5}{2}\beta(3-\delta)\,\nabla.\mathbf{v}\,\nabla T + \tfrac{15}{4}\beta D\nabla T + \frac{15}{4}\frac{\tau_0}{\tau_2}T\nabla.\mathring{\mathbf{e}}\right].\frac{\nabla T}{T} \\ &\quad + \frac{15}{4}\frac{\mu^2}{pT}R\left(4 + \frac{(\tau_2 - \frac{5}{2}\tau_0)}{\tau_1} + \frac{\tau_0}{\tau_1}\delta\right)\nabla T.\mathring{\mathbf{e}}.\nabla T - \tau_0\nabla\mathbf{q}_1 : \mathring{\mathbf{e}}. \qquad (6.2)\end{aligned}$$

Notice that the third term in (6.2) and the part $\tau_0\nabla\kappa\nabla T : \mathring{\mathbf{e}}$ of the last term can be expressed either as $[\;] : \mathring{\mathbf{e}}$ or as $[\;].\nabla T$, which presents us with an ambiguity in deriving values for $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ from the equation.

We shall make use of the fact that the trace of $\boldsymbol{\pi}$, and hence of $\boldsymbol{\pi}_2$, is zero to remove this uncertainty. If $\boldsymbol{\pi}_2$ contains both $\nabla\mathbf{q}_1$ and $\nabla T\nabla T$, then to have zero trace it must also contain $\nabla.\mathbf{q}_1\mathbf{I}$ and $\nabla T.\nabla T\mathbf{I}$. Now if in the argument leading to (3.4) we had retained the term 2ξ in (2.3), the result would have been

$$\mathbf{u} = \hat{\mathbf{u}}.\mathbf{R}, \quad \mathbf{R} \equiv \mathbf{I}\left(1 - \tfrac{2}{3}\tau_1\tau\mathring{\mathbf{e}} : \hat{\mathbf{e}} + \frac{\tau}{3p}\nabla.\mathbf{q}_1 + O(\epsilon^2)\right) - \tau\mathring{\mathbf{e}} + O(\epsilon^2). \qquad (6.3)$$

Our interest here is in the nature of the term $\hat{\mathbf{u}}.\mathbf{I}\,O(\epsilon^2)$; we see that it at least contains $\nabla.\mathbf{q}_1$. Since the extension of the expansion for C' in (3.2) to terms $O(\epsilon^2)$ cannot yield an isotropic term of the form $\nabla T.\nabla T$, and there exists no other source for such a term, we conclude that (6.3) does not possess a term like $\hat{\mathbf{u}}.\mathbf{I}\,\nabla T.\nabla T\,O(\epsilon^2)$.

Following the method of accounting for the effect of fluid particle shear based on (3.4), we can write $\mathbf{p}^* = \mathbf{R}.\hat{\mathbf{p}}.\mathbf{R}$ for that part of $\mathbf{p}$ arising from shear, where $\hat{\mathbf{p}}$ is the pressure tensor for collided molecules. Although this is not a precise estimate, it is sufficient to reveal that $\mathbf{p}$ does contain $\nabla.\mathbf{q}_1\mathbf{I}$ but not $\nabla T.\nabla T\mathbf{I}$. We conclude that only the final term of (6.2) is to be written as $[\;] : \mathring{\mathbf{e}}$ and so included in the first right-hand expression.

Equation (6.2) is ambiguous in another way. This is because

$$\mathring{\mathbf{e}} : (\mathbf{e} - \tilde{\mathbf{e}}).\mathring{\mathbf{e}} = 0, \quad \nabla T.(\mathbf{e} - \mathbf{e}).\nabla T = 0, \qquad (6.4)$$

so by (2.7) terms $\boldsymbol{\omega} \times \mathring{\mathbf{e}}$ and $\boldsymbol{\omega} \times \nabla T$ can be included in $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ without affecting the right-hand side of (6.2). This is a reflexion of the fact that rigid body rotations make no contribution to the entropy production rate. In (3.3) we ignored changes in the unit vector $\hat{\mathrm{R}}$ between P' and P. If we replace $\hat{R}$ by its value at P', namely $\hat{\mathrm{R}}' = \hat{\mathrm{R}} - \tau D\hat{\mathrm{R}} - \lambda\hat{\mathrm{R}}.\nabla\hat{\mathrm{R}} + O(\epsilon^2) = \hat{\mathrm{R}} - \tau D\hat{\mathrm{R}} + O(\epsilon^2)$, and retain the $\boldsymbol{\omega} \times \mathbf{I}$ term, (3.4) becomes

$$\mathbf{u} = \hat{\mathbf{u}}.(\mathbf{I} - \tau\mathring{\mathbf{e}}) + \tau\hat{\mathrm{R}}DC - \tau(D\hat{\mathbf{u}} + \boldsymbol{\omega} \times \hat{\mathbf{u}}) + O(\epsilon^2).$$

The rule visible in the last term must apply to all fluxes constructed from $\mathbf{u}$, and shows that $D\nabla T$ must be accompanied by $\boldsymbol{\omega} \times \nabla T$ and $D\mathring{\mathbf{e}}$ by $\boldsymbol{\omega} \times \mathring{\mathbf{e}} - \mathring{\mathbf{e}} \times \boldsymbol{\omega} = 2\boldsymbol{\omega} \times \mathring{\mathbf{e}}$, $\mathring{\mathbf{e}} = -\boldsymbol{\pi}_1/2\mu$ being a dyadic product of fluxes. By (2.8) and (6.2) this requires the addition of

$$\alpha\frac{4\mu^2}{p}(\mathring{\mathbf{e}} - \mathbf{e} + \tfrac{1}{3}\check{e}\mathbf{I}).\mathring{\mathbf{e}} : \mathring{\mathbf{e}} + \beta\frac{15}{4}\frac{\mu^2}{pT}R\frac{\tau_2}{\tau_1}(\mathring{\mathbf{e}} - \mathbf{e} + \tfrac{1}{3}\check{e}\mathbf{I}) : \nabla T\nabla T$$

to (6.2), which now takes the form

$$\begin{aligned}\boldsymbol{\pi}_2 : \mathring{\mathbf{e}} + \mathbf{q}_2 . \frac{\nabla T}{T} = \frac{\mu^2}{p} \Big[& \tfrac{4}{3}\alpha(\tfrac{7}{2} - \eth)\, \nabla . \mathbf{v}\mathring{\mathbf{e}} + 2\alpha(D\mathring{\mathbf{e}} - 2\overset{\circ}{\overline{\mathbf{e} . \mathring{\mathbf{e}}}}) \\ & + \frac{15}{4}\frac{\tau_0}{\tau_1} R\, (\overset{\circ}{\overline{\nabla\nabla T}} + \eth\overset{\circ}{\overline{\nabla T \nabla T}}/T) + 4(1+\alpha)\overset{\circ}{\overline{\mathring{\mathbf{e}} . \mathring{\mathbf{e}}}} \Big] : \mathring{\mathbf{e}} \\ & + \frac{\mu^2}{p} R \Big[\frac{5}{2}\frac{\tau_2}{\tau_1}\beta(\tfrac{7}{2} - \eth)\, \nabla . \mathbf{v} \nabla T + \frac{15}{4}\frac{\tau_2}{\tau_1}\beta(D\nabla T - \mathbf{e} . \nabla T) \\ & + \frac{15}{4}\frac{\tau_0}{\tau_1} T\nabla . \mathbf{e} + \frac{15}{4}\left(4 + \frac{\tau_2}{\tau_1}(1+\beta) - \frac{5\tau_0}{2\tau_1} + \frac{\tau_0}{\tau_1}\eth\right) \mathring{\mathbf{e}} . \nabla T \Big] . \frac{\nabla T}{T}. \end{aligned} \tag{6.5}$$

It is now correct to equate coefficients and obtain the values for $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$ directly. For the coefficients defined in (2.1) we see from (6.5) that

$$\left.\begin{aligned} & \varpi_1 = \tfrac{4}{3}\alpha(\tfrac{7}{2} - \eth), \quad \varpi_2 = 2\alpha, \quad \varpi_3 = \frac{15}{4}\frac{\tau_0}{\tau_1}, \quad \varpi_5 = \eth\varpi_3, \quad \varpi_6 = 4(1+\alpha), \\ & \theta_1 = \frac{5}{2}\frac{\tau_2}{\tau_1}\beta(\tfrac{7}{2} - \eth), \quad \theta_2 = \frac{15}{4}\frac{\tau_2}{\tau_1}\beta, \quad \theta_3 = \varpi_3, \quad \tfrac{5}{2}\theta_3 + \theta_5 = \frac{15}{4}\left(4 + \frac{\tau_2}{\tau_1}(1+\beta) - \frac{5}{2}\frac{\tau_0}{\tau_1}\right) + \eth\varpi_3. \end{aligned}\right\} \tag{6.6}$$

The values of $\boldsymbol{\pi}$ and $\mathbf{q}$ that can be obtained from (6.5) can be written compactly in the forms given in (2.9) and (2.10). For Maxwellian molecules (see (2.11)) the coefficients reduce to the Burnett values given in (2.2). There are five phenomenological constants, so various relations exist between the coefficients, the most obvious of which is indicated by the appearance of ϖ_3 in four places.

7. General conclusions

The thermodynamic derivation of Burnett's equations given above is of interest as much for the light it can throw on the thermodynamics of irreversible processes in general, as for the particular details relating to the equations themselves. Several general points are worth noting, for misconceptions are widespread in the literature of continuum mechanics, especially in that branch to which the terms 'axiomatic' or 'rational' may be applied. First I shall sketch the general form of the linear theory, of which the account in § 1 is a special case.

The second law of thermodynamics may be expressed as a global inequality of the form

$$\int_{t_1}^{t} \int_V \sigma \, d\mathbf{x}\, dt \geqslant 0, \quad \begin{matrix}(V \geqslant \delta\mathbf{x}_1)\\ (t_2 - t_1 \geqslant \delta t),\end{matrix} \tag{7.1}$$

where σ is the local rate of entropy production, and the integral is taken over a fluid volume V, which must exceed a certain lower bound $\delta\mathbf{x}_1$ and over a time interval $t_2 - t_1$ likewise constrained. In gasdynamics the lower bound $\delta\mathbf{x}_1$ is a fluid element of smallest dimension l such that the Knudsen number $\epsilon = \lambda/l$ is much less than unity. The inequality is due to Clausius, and secures thermodynamic stability. It is statistical in its basis, applies only to large systems, so in (7.1) σ may have either sign, provided only that it is non-negative on average. The value of σ is not unique, but depends on the size of the fluid element regarded as being a (macroscopic) 'point' in the flow pattern.

If σ is expanded in a power series in Knudsen number ϵ, say $\sigma = \sigma_1 + \sigma_2 + \dots$, then continuum theory normally terminates at σ_1, a choice that by (7.1) imposes a lower bound on the size of the fluid element $d\mathbf{x}$. For σ_1 one can find a non-negative bilinear form

$$\sigma_1 = \sum_{\alpha} J_\alpha X_\alpha, \quad \sigma_1 \geqslant 0, \tag{7.2}$$

where J_α are the processes (thermodynamic forces) and X_α the affinities (fluxes). The inequality $\sigma_1 \geqslant 0$ is usually called the Clausius–Duhem inequality; it is a local form of the second law of thermodynamics.

From (7.2) can be inferred relations of the type

$$J_\alpha = \sum_{\beta} L_{\alpha\beta} X_\beta, \quad L_{\alpha\beta} = \eta_\alpha \eta_\beta L_{\beta\alpha}, \tag{7.3}$$

where η_α, η_β are the (molecular) motion reversed parities of X_α, X_β. As made clear by Woods (1975, chapter 7), the reciprocal relations (7.3 *b*) are a direct consequence of the irreversibility involved in σ_1. Finally, involved in the derivation of (7.2) there is a Gibbs relation of the type

$$T\,ds_0 = du + p\,dp^{-1} + \dots. \tag{7.4}$$

The question we wish to answer is 'how much of this theory also holds for nonlinear irreversible processes?' The answer is 'none, save the global inequality (7.1)'.

First consider (7.2). The bilinear form is certainly not preserved in the nonlinear theory (cf. (1.13) and (4.4)), for *both* the J_s and X_s are changed. Also the local inequality (7.2*b*) cannot be generalized to $\sigma \geqslant 0$, for the second term σ_2 may have either sign, and it is not difficult to see from (4.4) and (6.2) that – especially near boundaries – σ_2 could dominate σ_1 via second-order derivatives in T and $\mathbf{v}$, despite its having an additional factor ϵ. To make the nonlinear terms in the constitutive equations become important, we have, in effect, reduced the size of the fluid particle to such an extent that it becomes a *small* thermodynamic system, subject to fluctuations that are not bound by the second-law inequality. Of course we would expect $\sigma \geqslant 0$ to be true in most parts of the fluid most of the time, but contrary to a widely accepted axiom of rational continuum mechanics (Coleman & Noll 1963; Truesdell 1969; Eringen 1975) it is not true in general.

In the axiomatic thermodynamics of Coleman & Noll (1963), the authors claim that for (7.1) to hold it is necessary and sufficient for $\sigma \geqslant 0$ in V, but 'necessity' here is obviously false, unless the physics arising from the granular nature of matter is violated by imposing 'suitable smoothness assumptions.' Coleman (1964) in fact proves that the condition $\sigma \geqslant 0$ (which he calls the second law) holds if and only if ∇T does not appear in the functional for entropy, but concludes wrongly that this must mean that s is independent of ∇T. By (5.9), which shows that s does depend on ∇T, and Coleman's theorem we deduce that $\sigma \geqslant 0$ is *not* true in general, but fortunately this leaves the second law (7.1) intact.

It is not correct to generalize (7.3*a*) to read $J_\alpha = \phi_\alpha(X_1, X_2, \dots)$ for Burnett's equations make it clear that new affinities, not contained in the linear theory, appear at the second order. Nor is the entropy production rate σ any guide as to what these new affinities might be (e.g. see (4.4)). One cannot rewrite (7.3*b*) in the form

$$\frac{\partial J_\alpha}{\partial X_\beta} = \eta_\alpha \eta_\beta \frac{\partial J_\beta}{\partial X_\alpha}$$

and then claim that, when applied to the nonlinear theory, this correctly generalizes the reciprocal relations (e.g. as in Eringen 1975; Edelen 1974). In fact had a generalized 'Onsager relation' of this type been valid, we would have had no difficulty in allocating the penultimate term in (6.2) between $\boldsymbol{\pi}_2$ and $\mathbf{q}_2$, with a result quite different from that given in (6.5). The physical origin of the reciprocal relations lies in irreversibility, which is an attribute of σ_1, but not of $\sigma_1+\sigma_2$.

That the Gibbs relation (7.4) must be changed from the form it has in linear theory by the addition of further terms is well known, and reflects the fact that the extension of state space required by the nonlinear theory results in a reduction of the entropy. But it is essential to extend the relation in such a way as to secure thermodynamic stability, $s-s_0 \leqslant 0$ or equivalently $ds_0 \geqslant ds$, a constraint that appears to be ignored in axiomatic continuum mechanics. For example Green & Naghdi (1977) in pursuit of a finite, non-zero speed for second sound at room temperatures, postulated that $s = s_0 - \alpha T^{-1}\, dT/dt$ for heat conduction in a rigid solid, which material is thus unstable whatever the sign of α. They compound this error by writing $u = u_0 - c\, dT/dt$ for the internal energy, it being classical that stability requires $u \geqslant u_0$. In any case, unlike entropy, internal energy is a clearly defined physical property (although parts of it may be 'frozen' in certain circumstances), independent of the precision with which state space is delineated; in the Burnett theory $u = u_0$.

Green & Naghdi's main aim was to replace the Clausius–Duhem inequality by separate inequalities for work and heat dissipation. Thus for example instead of (1.13) they would have the two constraints

$$(A)\quad -\boldsymbol{\pi}_1 : \mathring{\mathbf{e}} \geqslant 0, \quad (B)\quad -\mathbf{q}_1 . \mathbf{g} \geqslant 0 \quad (\partial T/\partial t = 0, \quad \mathbf{v} = 0), \tag{7.5}$$

the second of which they restrict to steady temperature fields and zero fluid velocities. For materials with central symmetry (e.g. see Woods 1975, chapter 8) (1.13) does divide into (A) and (B), save that the constraints added to B are absent, but Green & Naghdi have not specifically confined their attention to such materials. And as they later apply the theory to mixtures (Green & Naghdi 1978), they include the case when the friction between diffusing components contributes to the irreversible work.

To demonstrate that the general principle involved in (7.5) is wrong, we need only to cite the phenomenon of thermal diffusion, in which a flow of matter is caused by a temperature gradient. In this case the dissipation is given by (de Groot & Mazur 1962, p. 26)

$$T\sigma_1 = -\boldsymbol{\pi}_1 : \nabla\mathbf{v} - \mathbf{q}_1 . \mathbf{g} + \sum_i \rho_i (\mathbf{v}_i - \mathbf{v}) . \mathscr{F}_i \geqslant 0 \quad (\mathscr{F}_i \equiv \mathbf{F}_i - T\nabla(g_i/T)), \tag{7.6}$$

where $\mathbf{v}_i$, $\mathbf{v}$ are the ith component and barycentric velocities, $\mathbf{F}_i$ is the body force on the ith component and ρ_i, g_i are the density and specific Gibbs functions for the ith component. The third right-hand term is the rate at which work is dissipated due to friction between species. The Green & Naghdi (1978) theory of mixtures (presented in a different notation) must necessarily encompass this case. Accepting their principle of separating the dissipated work, we have the inequality

$$-\boldsymbol{\pi}_1 : \nabla\mathbf{v} + \sum_i \rho_i (\mathbf{v}_i - \mathbf{v}) . \mathscr{F}_i \geqslant 0, \tag{7.7}$$

plus (7.5*b*). If we now assume that the mixture has central symmetry, the vectorial and tensorial terms may be separated giving

$$\sum_i \rho_i(\mathbf{v}_i-\mathbf{v}).\mathscr{F}_i \geqslant 0, \tag{7.8}$$

instead of

$$-\mathbf{q}_1.\mathbf{g}+\sum_i \rho_i(\mathbf{v}_i-\mathbf{v}).\mathscr{F}_i \geqslant 0, \tag{7.9}$$

which follows from (7.6). Now while (7.5*b*) and (7.8) lead to unconnected linear constitutive relations of the form

$$\mathbf{q} = -\kappa\nabla T \quad (\mathbf{v}_i = 0); \quad \rho_i(\mathbf{v}_i-\mathbf{v}) = \sum_j \beta_{ij}\mathscr{F}_j, \tag{7.10}$$

where κ and the principal minors of $|\beta_{ij}|$ are positive parameters, (7.9) yields

$$\mathbf{q} = -\kappa\nabla T+\sum_j \alpha_j\mathscr{F}_j; \quad \rho_i(\mathbf{v}_i-\mathbf{v}) = a_i\nabla T+\sum_j \beta_{ij}\mathscr{F}_j. \tag{7.11}$$

In other words the Green & Naghdi theory suppresses thermal diffusion altogether.

It might be thought that (7.10*a*) does not prevent the adoption of a separate constitutive assumption of the form

$$\mathbf{q} = -\kappa\nabla T+\sum_j b_j\rho_j(\mathbf{v}_j-\mathbf{v}) \quad (b_j \neq 0) \tag{7.12}$$

but, if we adhere to the Green & Naghdi hypothesis of non-negative dissipated work, it is easily shown that b_j in (7.12) must be zero. The work in question (ignoring other kinds for simplicity) is

$$\sum_j \rho_i(\mathbf{v}_i-\mathbf{v}).\mathscr{F}_i,$$

and, if this is non-negative, it follows from (7.11*b*) that $a_i = 0$. In this case (7.11*b*) and (7.12) yield

$$\rho_i(\mathbf{v}_i-\mathbf{v}) = \sum_j \beta_{ij}\mathscr{F}_j, \quad \mathbf{q} = -\kappa\nabla T+\sum_j \alpha_j\mathscr{F}_j \quad (\alpha_j = \sum_j b_i\beta_{ij}). \tag{7.13}$$

Now the reciprocal relations require that the coefficient of $\mathscr{F}_j$ in (7.13*b*) be equal to $(-T)$ times the coefficient of ∇T in (7.13*a*). Thus $\alpha_j = 0$ and, with $|\beta_{ij}| \neq 0$, we have $b_j = 0$.

That heat and work transfers are really inseparable for fluid particles is also very evident in Burnett's equations (2.9).

The work described above has been profitably discussed with Dr H. Troughton, recently of the Mathematical Institute, Oxford.

Appendix A. Use of multiple time scales

The theory presented in § 1 and § 5 may seem clearer to the reader if we adopt multiple time scales and expand the operator D as a Knudsen (or Enskog) series [cf. § 7.14 of Chapman & Cowling 1970]

$$D = D_0+D_1+D_2+\dots \quad (D_n = O(\epsilon^n)) \tag{A 1}$$

and then equate terms of the same order in ϵ, regarding the resulting equations as exact. Thus (1.5) becomes

$$TD_0 s_0 = D_0 u + pD_0\rho^{-1}, \quad TD_1 s_0 = D_1 u + pD_1\rho^{-1}, \qquad \text{(A 2)}$$
$$TD_2 s_0 = D_2 u + pD_2\rho^{-1} + \boldsymbol{\pi}_2 : \mathring{\mathbf{e}} + \mathbf{q}_2 \cdot \boldsymbol{\mathfrak{g}}, \quad \ldots,$$

where in the second-order relation we have added the *reversible* work and heat transfers in accord with the discussion following (5.13). Equations (1.7) and (1.8) yield (with ψ zero)

$$\left.\begin{aligned} &\rho D_0 u + p\rho D_0\rho^{-1} = 0, \quad \rho D_1 u + p\rho D_1\rho^{-1} + \boldsymbol{\pi}_1 : \mathring{\mathbf{e}} + \nabla . \mathbf{q}_1 = 0, \\ &\rho D_2 u + p\rho D_2\rho^{-1} + \boldsymbol{\pi}_2 : \mathbf{e} + \nabla . \mathbf{q}_2 = 0, \end{aligned}\right\} \qquad \text{(A 3)}$$

then from (1.9) and (1.11)

$$\left.\begin{aligned} \rho TD_1 s_0 + T\nabla . \mathbf{J}_{s1} &= T\sigma_1 = -\boldsymbol{\pi}_1 : \mathring{\mathbf{e}} - \mathbf{q}_1 \cdot \boldsymbol{\mathfrak{g}}, \quad J_{s1} = \mathbf{q}_1/T, \\ T\sigma_2 &= \rho T(D_2 s_0 + D_0 s_2) + \nabla . \mathbf{J}_{s2}. \end{aligned}\right\} \qquad \text{(A 4)}$$

Equation (2.3) gives

$$\frac{1}{T} D_0 T = -\tfrac{2}{3}\nabla . \mathrm{v}, \quad \frac{1}{T} D_1 T = 2\xi,$$

and in (2.9) $\mathscr{D}$ should be $\mathscr{D}_0 = D_0 + \boldsymbol{\omega}\times$.

From (A 2*c*), (A 3*c*) and (A 4*c*) we find (5.16) in the form

$$\sigma_2 = \rho D_0 s_2 + \nabla . (\mathbf{J}_{s2} - \mathbf{q}_2/T). \qquad \text{(A 5)}$$

Finally the generalized Gibbs' relation is obtained by adding $TD_0 s_2$ to the sum of (A 2):

$$T(D_0 s_0 + D_1 s_0 + D_2 s_0 + D_0 s_2) = TDs = Du + pD\rho^{-1} + TD_0 s_2 + \boldsymbol{\pi}_2 : \mathring{\mathbf{e}} + \mathbf{q}_2 \cdot \boldsymbol{\mathfrak{g}}, \qquad \text{(A 6)}$$

which is the same as (5.13).

REFERENCES

BURNETT, D. 1935 *Proc. Lond. Math. Soc.* **39**, 385–430; **40**, 382–435.

CHAPMAN, S. & COWLING, T. G. 1970 *The Mathematical Theory of Non-Uniform Gases*. Oxford University Press.

COLEMAN, B. D. 1964 *Arch. Rat. Mech. Anal.* **17**, 1–46, 230–254.

COLEMAN, B. D. & NOLL, W. 1963 *Arch. Rat. Mech. Anal.* **13**, 167–178.

EDELEN, D. G. B. 1974 *Zeitschrift für physikalische Chemie Neue Folge* **88**, 37–53.

ERINGEN, A. C. 1975 *Continuum Physics*, vol. II, pp. 115–126. Academic.

GREEN, A. E. & NAGHDI, P. M. 1977 *Proc. Roy. Soc.* A **357**, 253–270.

GREEN, A. E. & NAGHDI, P. M. 1978 *Quart. J. Mech. Appl. Math.* **31**, 265–293.

DE GROOT, S. R. & MAZUR, P. 1962 *Non-Equilibrium Thermodynamics*. North Holland.

SHAVIT, A. & ZVIRIN, Y. 1970 Haifa, *Technion Rep.* TME-110.

TRUESDELL, C. 1969 *Rational Thermodynamics*. McGraw-Hill.

WOODS, L. C. 1975 *The Thermodynamics of Fluid Systems*. Oxford University Press.

WOODS, L. C. 1979 *J. Fluid Mech.* **93**, 585–608.