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NEAR-FROZEN QUASI-ONE-DIMENSIONAL FLOW
II. DE-EXCITATION SHOCKS

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CONTENTS

The possible existence of compression regions, analogous to condensation shocks, in expanding non-equilibrium nozzle flows is noted. For power-law nozzle shapes the structure and position of these 'de-excitation shocks' are derived when the relaxation frequency decays algebraically with temperature. The asymptotic limiting solutions downstream of the de-excitation shocks are also discussed. For certain nozzle shapes it appears that this limiting solution is an infinite sequence of such shocks separated in part by regions of near-frozen flow.

1. Introduction

In part I of this paper it was noted that near-frozen solutions for non-equilibrium nozzle flow were not necessarily uniformly valid at downstream infinity, even though the relaxation frequency vanished in this limit. For a given nozzle shape this difficulty occurs only for those relaxation frequencies which decay sufficiently slowly with temperature. In particular, for a power-law nozzle, i.e.

$$A \sim x^{\nu} \tag{1·1}$$

far downstream, the near-frozen solution does not remain valid if the relaxation frequency decays no faster than some power of the translational temperature. Throughout the present paper (part II) it is assumed that

$$\Omega \sim T^{\delta}, \tag{1·2}$$

as $T \to 0$, where $\delta \geqslant 0$.

Whether this model is likely to be physically correct is not easily assessed and the theoretical form of (1·2) depends greatly on the assumed form of the interaction potential. The

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classical Landau–Teller (1936) theory predicts a much faster decay than (1·2). Widom (1957), however, has suggested various alternative expressions which may be more appropriate at low temperatures, all of which adopt the limiting form (1·2). More recently, some numerical computations (Benson & Berend 1966) have shown that the Landau–Teller result, although applicable over most of the temperature range, is not valid for either 'large' or 'small' temperatures (a convenient measure of the size of T is the characteristic temperature of vibration). For low temperatures, Benson & Berend show that the decay is indeed slower than the classical result. Experimental evidence on this point, as noted in part I, is inadequate. In this paper the consequences of the assumption that (1·2) holds for sufficiently low temperatures will be examined in detail.

For a dissociating gas the corresponding rate function is, in fact, generally assumed to vary as some power of the temperature, and many of the results derived herein are applicable, with only a slight modification in the analysis, to such a gas. Differences do, however, arise in the eventual limiting form of the solution (see § 7). For simplicity only a vibrationally relaxing gas is considered here.

An important quantity with regard to the asymptotic analysis is the pseudo-entropy

$$-\int^{\sigma(x)} \frac{d\sigma}{T}. \tag{1·3}$$

Broer (1951) defined the pseudo-entropy with respect to an equilibrium isentropic flow. Here, it is defined with respect to the isentropic frozen flow. It was noted in part I, § 3 that this integral, evaluated from the near-frozen solution,† is not always bounded for large x, and a necessary condition on ν and δ for its convergence was given there. Note that for a given δ the integral (1·3) is unbounded for sufficiently small ν, that is for nozzles which grow slowly enough. This result also follows immediately from physical considerations; in the limit $\nu = 0$ a return to equilibrium conditions will occur.

However, (1·3) is not directly associated with the rate equation. This latter equation implies that a return towards equilibrium may occur if

$$\int^{x} \frac{dx}{\tau} \tag{1·4}$$

is unbounded at large distances. For $\delta \geqslant 0$ the divergence of (1·4) implies that (1·3) is also divergent, but the converse is not true. Indeed, when (1·4) converges but (1·3) does not, the asymptotic solution is not obvious. Cheng & Lee (1966) have also pointed out that the corresponding integrals for a dissociating gas play an important role in the determination of the eventual limiting solution far downstream. It is shown here that the convergence or otherwise of these integrals also dictates the behaviour of the solution between the initial frozen state and this limiting state.

A convenient way of discussing these asymptotic solutions, which include the region upstream of the limiting state, is to examine their gross features in terms of certain domains in the $(1/\nu, \delta)$ plane. In this plane (see figure 1)

$$l = 1-\nu\{2-\gamma+(\gamma-1)\,\delta\} > 0 \tag{1·5}$$

corresponds to the divergence of the pseudo-entropy integral (1·3) (see I, § 3). When $l < 0$

† This should be understood throughout this section, unless stated otherwise.

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both the integrals (1·3) and (1·4) are convergent and the near-frozen solution outlined in part I is then, as noted there, uniformly valid.

For $l > 0$ it can be shown, § 2, that the pseudo-entropy (or heat input) will cause a local increase, at large distances, in the translational temperature if $\nu < 1$. (Note that for $\nu < 1$, $x \to \infty$, dA/dx is a monotonically decreasing function of x.) In nozzle flows with heat addition, which are exactly analogous to the present non-equilibrium flows, this situation is obviously

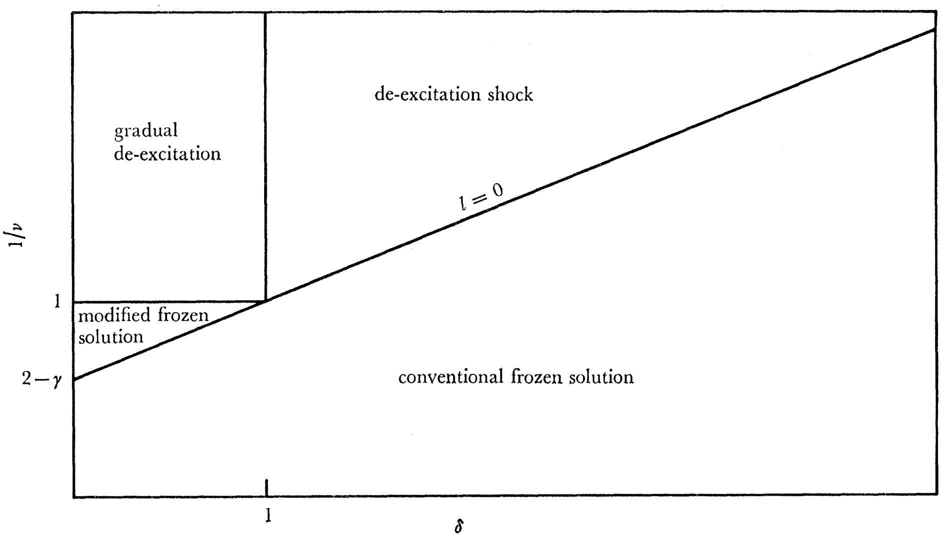

FIGURE 1. Gross features of the asymptotic solutions.

in general possible and the divergence of (1·3) indicates that the heat input, in comparison with the area change, becomes locally important at large distances downstream. This increase in the translational temperature leads to a de-excitation of the vibrational mode. Moreover, the local value of the relaxation frequency increases, and, under certain circumstances, this de-excitation takes place quickly.

In particular if $\delta > 1$ an equivalent phenomenon to the condensation shock (Wegener & Mack 1958) occurs. This 'shock', which is a supersonic-supersonic transition, corresponds to a region of sudden heat release, or, in the present case, to a rapid de-excitation of the internal mode. The structure of the 'de-excitation shock' is controlled by a local return to equilibrium in which the translational temperature can again become comparable with the reservoir temperature; in the neighbourhood of the shock the effect of the area change is negligible. Across the shock there is a finite increment of pressure and density. A feature of the analysis is that the position of the shock is clearly defined in terms of the initial reservoir conditions and the parameters ν and δ.

If $\delta < 1$ and $\nu < 1$, the de-excitation takes place more slowly. An equivalent statement is that the rate of decrease of the relaxation time, or increase of the relaxation frequency, is less marked in this case (and becomes even slower as $\delta \to 0$). The temperature maximum is no longer defined by local equilibrium conditions, and the effects of the heat input and the area change are of a comparable order of magnitude in this neighbourhood. In general, at the position of the temperature maximum, the departure from equilibrium will be $O(1)$. Although the temperature still attains some local maximum for all ν and δ in this region

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(see figure 1), the precise conditions under which compressions occur for $\delta < 1$ are not easily established. Some comments on this point are made in § 6.

For $\nu > 1$, $l > 0$, which is the small triangular domain in figure 1, no temperature increase occurs, though the decay does not follow the usual isentropic pattern far downstream (see § 2). The vibrational mode now asymptotes to some modified frozen state, in which the departure of the vibrational energy from its initial value remains 'small'.

The preceding phenomena by no means provide an exhaustive description, for $\nu < 1$, of the asymptotic solutions. An obvious and important question to ask is what type of decay downstream of the shock, or, for $\delta < 1$, the local temperature maximum, can be expected. Again, it is useful to discuss the various possibilities with the aid of a similar diagram to figure 1.

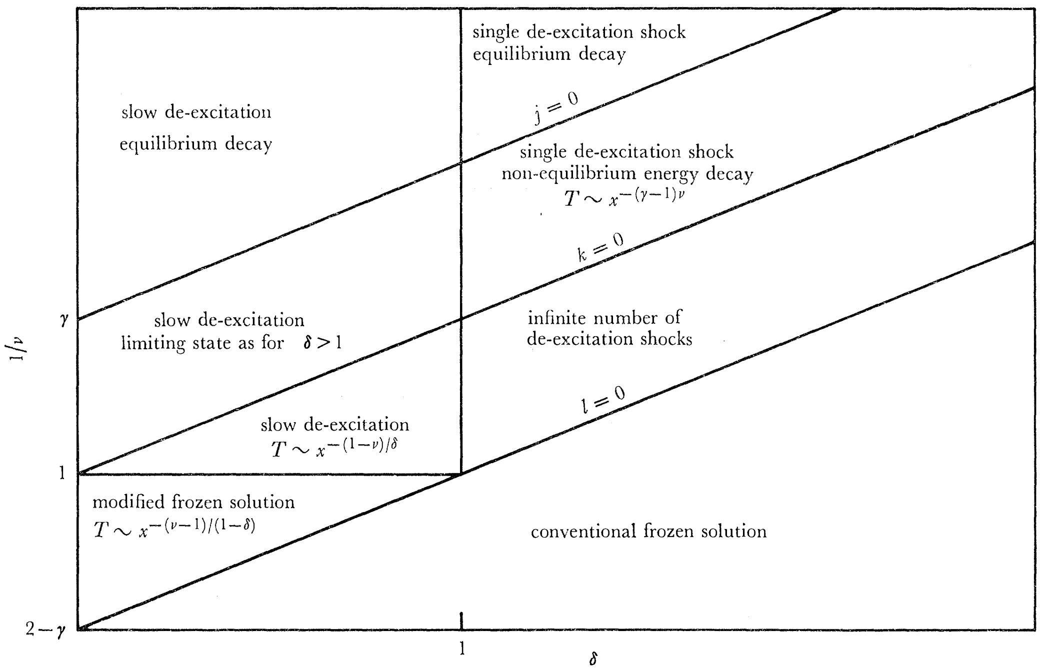

FIGURE 2. Detailed features of the asymptotic solutions.

For $\delta > 1$, when the asymptotic solution is characterized by a de-excitation shock, it can be shown, § 4, that the initial behaviour downstream of the shock is that of a near-equilibrium flow with T and σ decaying accordingly. It is apparent that in general this near-equilibrium solution will not remain valid at large distances, since the local relaxation time again increases and some transition towards a frozen flow may occur. The structure of the solution in this case corresponds to the usual analysis of the breakdown of a near-equilibrium flow (Blythe 1964*b*): the transition from the equilibrium solution is characterized by the existence of a freezing point (Bray 1959; Blythe 1964*a*). Note, however, that if the exponent

$$j = 1-\nu\{\gamma+(\gamma-1)\,\delta\} > 0 \tag{1·6}$$

no freezing point exists, and the flow remains close to equilibrium, for all x, downstream of the shock. The limit $\nu \to 0$, for a given δ, is obviously included in (1·6): the line $j = 0$ is shown in figure 2. When $j < 0$, which, for a fixed value of δ, implies a greater rate of growth of A

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(larger ν) than for $j > 0$, a freezing point exists and the flow downstream of this point is not in thermodynamic equilibrium.

If the integral (1·4), evaluated from the asymptotic behaviour of the equilibrium solution† downstream of the shock, is divergent, which requires that

$$k = 1 - \nu\{1 + (\gamma - 1)\,\delta\} > 0, \tag{1·7}$$

then the vibrational energy eventually decays to ground level, the ambient equilibrium state at infinity. The line $k = 0$ is shown in figure 2.

For still larger values of ν, when $k < 0$, the integral (1·4), again evaluated from the equilibrium solution, is convergent for large x. In this case, downstream of the freezing point, the vibrational mode will freeze. The initial effect of this frozen behaviour on the temperature distribution is negligible. However, it is apparent that this state cannot describe the asymptotic limiting solution for precisely those reasons that led to the breakdown of the initial near-frozen solution, and the pseudo-entropy again becomes important. It transpires that the asymptotic limiting solution is in fact an infinite sequence of de-excitation shocks. Each cycle contains a shock followed first by a region of near-equilibrium flow, and then by a much larger region of near-frozen flow, which again terminates in a de-excitation shock. The strength of each successive shock decreases rapidly in magnitude. In the neighbourhood of the shocks, the equilibrium term in the rate equation is always locally important.

For $\delta < 1$, when the de-excitation takes place more slowly, it appears that the temperature profile may have any finite number of stationary values. In the domain $j > 0$ there is only one such maximum (cf. $\delta > 1$), downstream of which the decay is eventually influenced by the local equilibrium behaviour. Similarly for $j < 0$, $k > 0$ only one maximum occurs and the asymptotic limiting decay is as outlined for $\delta > 1$ (see figure 2). When $k < 0$, $\nu < 1$ more than one local temperature maximum may occur. It is not possible to give precise conditions on the actual number of these maxima without resort to numerical calculations. The limiting decay downstream of the final temperature maximum is given by the non-isentropic behaviour $T \sim x^{-(1-\nu)/\delta}$ (see § 6).

It is conventional in deriving the asymptotic limiting solution in non-equilibrium nozzle flow to assume that the equilibrium term in the rate equation is negligible (Blythe 1964*a*; Cheng & Lee 1966). Apparently this assumption will give erroneous results, for the rate equation used here, in either the domain $j > 0$, or the domain $k < 0$, $l > 0$, $\delta > 1$. Elsewhere it will enable the appropriate limiting decay to be found (downstream of any temperature maxima). As noted above, in the neighbourhood of a de-excitation shock the equilibrium term is never negligible. A full discussion of the implications of neglecting this term for large x is given in § 7. It is shown there that under a suitable set of approximations a simple model equation can be derived which will describe the asymptotic solution whenever the equilibrium term is negligible. Although this equation is not strictly valid for $\delta > 1$, $l > 0$, $k < 0$ (see figure 2), the type of asymptotic solution it predicts for this region is, somewhat remarkably, qualitatively similar to that found from the full equations. For the corresponding domain when $\delta < 1$ this equation shows clearly that only a finite number of

† The limiting form of the equilibrium solution for the translational temperature, density and velocity is similar to that for an isentropic flow with zero vibrational energy, e.g. $T \sim x^{-(\gamma-1)\nu}$, though certain of the constants that arise are not the same in these two cases, in particular, the limiting velocity. Consequently the criterion (1·7) emerges for both frozen and equilibrium flows (see I, § 3).

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temperature maxima can be expected, as opposed to the infinite number of shocks for $\delta > 1$. The equation also provides a useful qualitative description in various other domains of the $(1/\nu, \delta)$ plane, and, apart from the multiple shock domain and $j > 0$, it will predict the correct limiting decay downstream of any temperature maxima. However, it should be stressed that it does not provide a quantitative description of the whole of the asymptotic solution when $l > 0$.

Unless otherwise stated, the notation used is as in part I. Equation numbers prefixed by the roman numeral I refer to that equation in part I.

2. The cumulative effects of de-excitation

Near frozen solutions of the system of equations (I, 2·1) to (I, 2·4) were presented in part I. It was shown that the conventional expansion

$$\left.\begin{aligned}\sigma &= \sigma_\infty + \Lambda\sigma_1(x) + \Lambda^2\sigma_2(x) + \ldots,\\ T &= T_0(x) + \Lambda T_1(x) + \Lambda^2 T_2(x) + \ldots,\end{aligned}\right\} \tag{2·1}$$

is a valid solution for $x = O(1)$ only if $u_\infty \neq 0$. The extension to $u_\infty = 0$ was given in part I. It follows from the results derived there that T_1/T_0 is unbounded for large x if $l > 0$ (see I, § 3), irrespective of the initial value of u. For $u_\infty \neq 0$

$$\frac{T}{T_0} \sim 1 + \Lambda\frac{(\gamma-1)\,\sigma_\infty}{u_0(\infty)}\left(\frac{m_0}{u_0(\infty)}\right)^{(1-l)/\nu}\frac{x^l}{l} + \ldots \tag{2·2}$$

as $x \to \infty$ $(l > 0)$, where

$$u_0^2(\infty) = u_\infty^2 + 2\gamma/(\gamma-1). \tag{2·3}$$

The extension of this result to include $u_\infty = 0$ is straightforward and is described in appendix I; the only effect on the subsequent analysis is a change in the magnitude of the error term.

Similarly, the downstream expansion of the solution for the vibrational energy distribution can be written $(k \neq 0)$

$$\sigma_\infty - \sigma = \Lambda\left[\epsilon_1(\infty) + \frac{\sigma_\infty}{u_0(\infty)}\left(\frac{m_0}{u_0(\infty)}\right)^{(1-k)/\nu}\frac{x^k}{k} + \ldots\right] + o(\Lambda), \tag{2·4}$$

where $\epsilon_1(\infty)$ is the finite part, as $x \to \infty$, of the integral defining ϵ_1 (see I, § 5). The terms inside the square bracket are written in descending order of magnitude for $k < 0$. If $k > 0$ $\epsilon_1(x)$ is unbounded for large x and x^k is then the leading term in its asymptotic expansion.

It is convenient to assume that any constant factors that may in general occur in (1·1) and (1·2) are unity. This can be accomplished, if necessary, by suitably re-defining m_0 and Λ. It is also convenient here to replace Λ by the parameter

$$\lambda = \frac{\Lambda}{u_0(\infty)}\left(\frac{m_0}{u_0(\infty)}\right)^{(1-k)/\nu}. \tag{2·5}$$

This new rate parameter is scaled with respect to a flow time based on $u_0(\infty)$, which is more appropriate far downstream; the second factor is then chosen for simplicity so that

$$\Lambda F_0 \sim \lambda x^{k-1}$$

for large x. In equation (2·5) it should be understood that Λ and m_0 are modified to accord with (1·1) and (1·2).

Since $l > k$ it would appear from (2·2) that difficulties first arise with the near-frozen expansion when $x = O(\lambda^{-1/l})$. This length scale can also be deduced directly from the

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'entropy-production' equation (I, 2·2a), together with the rate equation (I, 2·4), as defining the region in which the pseudo-entropy gradient is important.

If
$$Y = \lambda^{1/l} x \tag{2·6}$$
equations (2·3) and (2·4) become
$$\left.\begin{aligned} \frac{T}{T_0} &\sim 1 + \frac{(\gamma-1)\,\sigma_\infty}{l}\left(\frac{u_0(\infty)}{m_0}\right)^{\gamma-1} Y^l + \dots, \\ \sigma_\infty - \sigma &\sim \lambda\epsilon_1(\infty) + \lambda^b \frac{\sigma_\infty}{k} Y^k + \dots, \end{aligned}\right\} \tag{2·7}$$
where
$$b = (\gamma-1)\,\nu/l. \tag{2·8}$$
Note that $k > 0$ implies that $b < 1$ and $\sigma_\infty - \sigma$ is then $O(\lambda^b)$ (see remarks above on the expansion (2·4)). Moreover, since $T_0 = O(\lambda^b)$ when $Y = O(1)$, an appropriate set of dependent variables in this region is
$$\left.\begin{aligned} \rho &= \lambda^{\nu/l} \frac{m_0}{u_0(\infty)} \Pi(Y,\lambda), \\ u &= u_0(\infty)\, V(Y,\lambda), \\ T &= \lambda^b \left(\frac{m_0}{u_0(\infty)}\right)^{\gamma-1} \Theta(Y,\lambda), \\ \sigma &= \sigma_\infty - \lambda\epsilon_1(\infty) - \lambda^b \Sigma(Y,\lambda). \end{aligned}\right\} \tag{2·9}$$

To simplify the ensuing discussion it is assumed that the error terms in (1·1) and (1·2) are $O(x^{\nu-1})$ and $O(T^{\delta+1})$ respectively. However, some of the results obtained below can be derived in a more general manner by suitably scaling A and Ω. Substituting (2·9) into the full equations gives, for the zero-order terms
$$\left.\begin{aligned} &\Pi_0 V_0 Y^\nu = 1, \\ &\frac{1}{\Pi_0}\frac{d\Pi_0}{dY} - \frac{1}{\gamma-1}\frac{1}{\Theta_0}\frac{d\Theta_0}{dY} = -\left(\frac{u_0(\infty)}{m_0}\right)^{\gamma-1}\frac{1}{\Theta_0}\frac{d\Sigma_0}{dY}, \\ &V_0 = 1, \\ &\frac{d\Sigma_0}{dY} = \frac{\Pi_0 \Theta_0^\delta \sigma_\infty}{V_0}, \end{aligned}\right\} \tag{2·10}$$
where
$$\Pi(Y,\lambda) = \Pi_0(Y) + o(1), \text{ etc.,}$$
and the terms neglected, including the case $u_\infty = 0$ (see appendix), are $O(\lambda^b, \lambda^{1/l}, \lambda, \lambda^{2n/(n+1)})$. The system of equations (2·10) describes a constant velocity, near-frozen flow (since $\sigma_\infty - \sigma = o(1)$) in which the local entropy production now plays a dominant role in the determination of the temperature profile.

The equations (2·10) have the solution ($\delta \neq 1$)
$$\left.\begin{aligned} &V_0 = 1, \quad \Pi_0 = Y^{-\nu}, \\ &\Theta_0^{1-\delta} = KY^{-(\gamma-1)\nu(1-\delta)} + \frac{(1-\delta)(\gamma-1)\,\sigma_\infty}{l}\left(\frac{u_0(\infty)}{m_0}\right)^{\gamma-1} Y^{1-\nu}, \\ &\Sigma_0 = \sigma_\infty \int_{Y_0}^{Y} S^{-\nu}\Theta_0^\delta(S)\, dS + L, \end{aligned}\right\} \tag{2·11}$$
where K and L are arbitrary constants, S is a dummy variable, and the lower limit in the integral defining Σ_0 has been inserted for convenience.

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As $Y \to 0$

$$\Theta_0 \sim K^{1/(1-\delta)} Y^{-(\gamma-1)\nu},$$

and it is easily verified that this matches with the downstream expansion of the near-frozen solution, $T_0 \sim (m/u_0(\infty))^{\gamma-1} x^{-(\gamma-1)\nu}$, if

$$K = 1. \tag{2·12}$$

For $k > 0$ the integral defining Σ_0 converges as $Y \to 0$, and, putting $Y_0 = 0$, matching with the near-frozen solution, equations (2·7) and (2·9), shows that

$$L = 0. \tag{2·13a}$$

If $k < 0$ the leading term in the inner expansion ($Y \to 0$) of Σ_0 certainly matches with the appropriate leading term in the downstream expansion (2·7). This is not in itself sufficient to define L: such a term might now arise from a higher order term in the near-frozen solution. However, it would be necessary for this higher order term to be $O(\lambda^b)$—a term which will not in general occur in the near-frozen expansion. L is then defined as the finite part of

$$\sigma_\infty \int_Y^{Y_0} S^{-\nu} \Theta_0^\delta \, \mathrm{d}S \tag{2·13b}$$

as $Y \to 0$. In the special case when terms $O(\lambda^b)$ do occur in the near-frozen solution (for example, if b is a positive integer other than unity) this expression must be modified to include any contribution from the higher order term. The choice of Y_0 is apparently arbitrary but some care must be exercised since the integral does not necessarily remain bounded for all finite Y.

In fact it is the latter difficulty which is of especial interest here. It is convenient to divide the discussion into three parts.

(*a*) $\delta > 1$

When $\delta > 1$, $\nu < 1$ for all $l > 0$ (see figure 1). It follows immediately from (2·11) and (2·12) that the temperature becomes infinite at the point

$$Y = Y_s = \left[\frac{l}{(\delta-1)(\gamma-1)\sigma_\infty}\left(\frac{m_0}{u_0(\infty)}\right)^{\gamma-1}\right]^{1/l}. \tag{2·14}$$

(Hence Y_0 is any constant such that $0 < Y_0 < Y_s$.) In the neighbourhood of this singularity it is necessary to seek an alternative expansion. The region is characterized by the temperature becoming $O(1)$: its structure is analysed in § 3. Physically, the occurrence of this singularity corresponds to a compression through which there is a return towards local equiibrium. This phenomenon is termed a de-excitation shock.

(*b*) $\delta < 1$, $\nu < 1$

Equation (2·11) now indicates that

$$\Theta_0 \sim Y^{(1-\nu)/(1-\delta)}, \tag{2·15}$$

as $Y \to \infty$, and the temperature is unbounded in this limit. Although there is certainly a partial return towards equilibrium for large Y, where an alternative solution has to be sought (see § 6), the overall effect of the de-excitation, or heat addition, is much less marked than for $\delta > 1$.

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(c) $\delta < 1, \nu > 1$

The temperature distribution for large Y is again described by (2·15), through the exponent $(1-\nu)(1-\delta)^{-1}$ is negative in this case and the solution (2·11) remains physically plausible. In addition, Σ_0 tends asymptotically to some constant value. Here the cumulative effect of de-excitation transfers the flow from the initial near-frozen state to an alternative frozen one in which the temperature decay is no longer given by the usual isentropic law.

A summary of the various domains and their characteristic features was given in the introduction in figure 1.

3. De-excitation shocks

Here, and subsequently in §§ 4 and 5, the solution for the domain $\delta > 1$, $l > 0$ (see figures 1 and 2) is outlined both for the neighbourhood of the shock, $Y = Y_s$, and the region downstream of the shock.

Upstream of the shock the limiting behaviour as $Y \to Y_s$ is, from equation (2·11),

$$\Theta \sim (Y_s - Y)^{1/(\delta-1)},$$

apart from some constant factor. An appropriate length scale, consistent with the assumption that T and ϵ, the departure from a fully frozen flow, become $O(1)$ near $Y = Y_s$, is defined by

$$Y = Y_s(1+\lambda^d y), \tag{3·1}$$

where

$$d = b(\delta-1) \tag{3·2}$$

and b was defined in equation (2·8). The downstream expansion of (2·11), as $Y \to Y_s$, can be written in terms of y as

$$\left.\begin{aligned} T &\sim \left(\frac{m}{u_0(\infty)}\right)^{\gamma-1} l^{-1/(\delta-1)} Y_s^{-(\gamma-1)\nu}(-y)^{-1/(\delta-1)}, \\ \sigma_\infty - \sigma &\sim \sigma_\infty(\delta-1)\, l^{-\delta/(\delta-1)} Y_s^k (-y)^{-1/(\delta-1)}, \end{aligned}\right\} \tag{3·3}$$

where only terms $O(1)$ with respect to λ have been retained. The corresponding expressions for ρ and u adopt particularly simple forms and the order of magnitude of these quantities remains unchanged. These relations provide upstream matching conditions for the solution in the neighbourhood of Y_s.

For this region the correct dependent variables are T, σ, V and Π. From the continuity equation (I, 2·1) it follows immediately that, for $y = O(1)$, the effect of the area of change is negligible to zero order. Consequently, in terms of the above variables, neglecting terms $o(1)$, the full equations (I, 2·1) to (I, 2·3) can be integrated to give the one-dimensional relations

$$\left.\begin{aligned} \Pi V &= Y_s^{-\nu}, \\ \Pi(T/u_0^2(\infty) + V^2) &= Y_s^{-\nu}, \\ \gamma T/(\gamma-1) + \tfrac{1}{2}u_0^2(\infty) V^2 + \sigma &= \tfrac{1}{2}u_0^2(\infty) + \sigma_\infty. \end{aligned}\right\} \tag{3·4}$$

The rate equation (I, 2·4) becomes

$$\frac{d\sigma}{dy} = Y_s \frac{\Pi\Omega^*(T)}{V}[\bar{\sigma}(T) - \sigma], \tag{3·5}$$

where

$$\Omega^* = (u_0(\infty)/m_0)^{(\gamma-1)\delta}\Omega(T). \tag{3·6}$$

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$\Omega(T)$ is now, of course, given by any appropriate expression, valid for $T = O(1)$ (see, for example, equations (I, 2·9a) and (I, 2·9b)), which adopts the limiting form (1·2) as $T \to 0$.

The constants on the right-hand side of (3·4) follow formally by matching with the expansion (3·3) as $y \to -\infty$, or, more simply, by straightforward continuity arguments. Since these equations now correspond to flow through a constant area duct and the flow variables are controlled solely by the rate process, the equations may be thought of as governing the flow through a fully dispersed shock wave,† with the particular upstream conditions that the flow is out of equilibrium, that the density and velocity are finite, but that the temperature is zero. The overall transition across this one-dimensional region can be evaluated without resort to any detailed calculations of the structure of the region (see below). A return to local equilibrium defines the downstream limit $y \to +\infty$.

In general, non-equilibrium one-dimensional flows can be conveniently discussed in terms of the Rayleigh-line relations (Johannesen 1961) since these flows are completely equivalent to one-dimensional flow with heating. For the conventional case of a normal partly dispersed shock in an initially equilibrium flow the phenomenon corresponds to heat subtraction: here it corresponds to heat addition. A similar phenomenon occurs in condensation shocks (see, for example, Wegener & Mack 1958) and the transition across the present one-dimensional region, where $y = O(1)$, is formally equivalent to the transition across such shocks, with a suitable modification in the mechanism of the heat input. By analogy this region, through which the vibrational energy decays monotonically, is termed a de-excitation shock. These shocks fall into the general class of aerothermodynamic shocks discussed by Polachek & Seeger (1958).

A considerable simplification can be made in the usual relations given for such shocks since the upstream (matching) conditions correspond here to the limit of infinite Mach number. The appropriate solution of the algebraic relations (3·4) which matches with (3·3) is

$$\left.\begin{aligned} V = \frac{Y_s^{-\nu}}{\Pi} &= \frac{\gamma+\surd(1-Q)}{\gamma+1}, \\ \frac{T}{u_0^2(\infty)} &= \frac{\{\gamma+\surd(1-Q)\}\{1-\surd(1-Q)\}}{(\gamma+1)^2}, \end{aligned}\right\} \tag{3·7}$$

where
$$Q = \frac{2(\gamma^2-1)\,(\sigma_\infty-\sigma)}{u_0^2(\infty)}. \tag{3·8}$$

This solution is valid only if the Mach number remains supersonic, or alternatively if $Q < 1$. For a diatomic gas Q can certainly be no greater than

$$(\gamma-1)^2\frac{\gamma+1}{\gamma} = \frac{48}{175}$$

for $\gamma = \frac{7}{5}$.

Conditions at the downstream limit of the shock are, as noted above, defined by $\sigma = \bar{\sigma}(T)$ and can be found independently of the rate equation by means of an iterative solution of equations (3·7) and (I, 2·7) (Johannesen 1961). A plot of this final equilibrium temperature,

† The term is used here in the sense that this compression region is governed solely by the dissipative effects of relaxation (Lighthill 1956). It should not be taken to imply the conventional condition that u lies between the two sound speeds.

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as a function of the initial conditions, is shown in figure 3 for convergent-divergent nozzles ($u_\infty = 0$). Note that these limiting values, apart from the density, are independent of the rate parameter, the shape exponent ν, the frequency exponent δ, and are governed solely by the initial reservoir conditions. (The particular simplicity of figure 3 follows, for $u_\infty = 0$, from $\sigma_\infty = \bar{\sigma}_\infty$, which is independent of the initial pressure level for a vibrationally relaxing gas.) However, higher order terms in the solution for $y = O(1)$, which include the effects of the area change in this region and give a measure of the 'small' departure from equilibrium that exists for large y, will depend on λ.

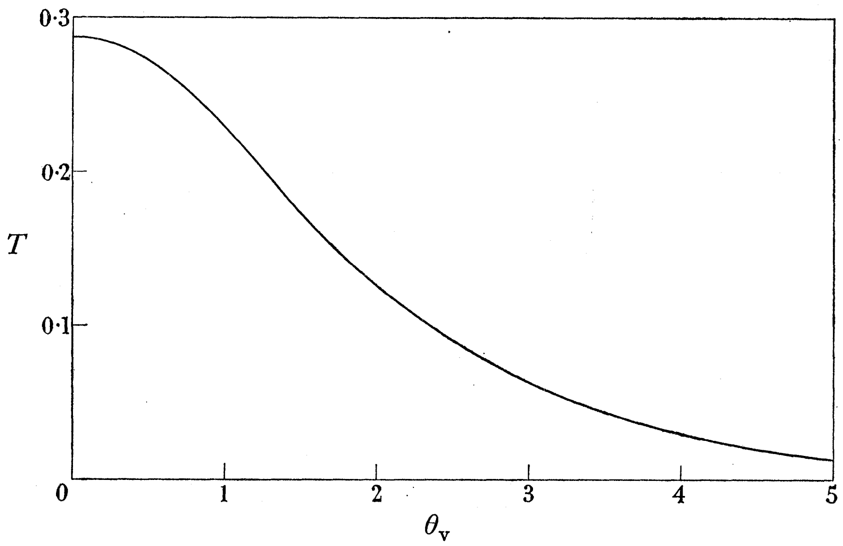

FIGURE 3. Limiting temperatures in de-excitation shocks.

The actual shock structure is easily determined by a numerical integration of (3·5) in conjunction with equations (3·7). Although the temperature and internal energy profiles, as functions of y, are also independent of λ to zero order, they are, as opposed to the zero order limiting values of T and σ, influenced by the parameters ν and δ.

4. The solution downstream of the shock

For $Y > Y_s$ and $O(1)$ the appropriate dependent variables are σ, T, Π and V. The conservation equations remain unchanged and the rate equation can be written

$$\frac{d\sigma}{dY} = \lambda^{-d}\frac{\Pi\Omega^*(T)}{V}[\bar{\sigma}(T)-\sigma]. \tag{4·1}$$

Note that λ is now replaced by an effective rate parameter λ^{-d}. Since $d > 0$, this effective rate parameter is large and equation (4·1) indicates that a near-equilibrium solution is appropriate in this region. Near-equilibrium nozzle flows have been considered elsewhere and the difficulties inherent in that problem are again present here. As the details of the solution for $Y > Y_s$ are practically equivalent to those given in Blythe (1964*b*) it does not seem necessary to do more than outline that approach in this paper. The salient features are given below and in § 5.

For $Y = O(1)$, but downstream of the shock, the basic solution is given by the equilibrium

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relations with the initial conditions defined by the downstream limit, $y \to +\infty$, of the shock solution. If, for convenience, the full expressions for the mass flow m and the scaled area ratio $\lambda^{-\nu/l}A$ are formally retained, higher order terms in the solution can be obtained by a conventional near-equilibrium expansion (Napolitano 1962) in inverse powers of the effective rate parameter,

$$\left.\begin{aligned} \sigma &= \bar{\sigma}_e + \lambda^d \sigma_{e_1} + \dots, \\ T &= T_e + \lambda^d T_{e_1} + \dots, \end{aligned}\right\} \tag{4·2}$$

where $\bar{\sigma}_e = \bar{\sigma}(T_e)$ and T_e, etc., define the local equilibrium solution. In general σ_{ei} and T_{ei} are $O(1)$ though they will depend implicitly on λ, since, for example, $m = m(\lambda)$. One could expand each of these terms so that

$$\bar{\sigma}_e = \bar{\sigma}_e^0(x) + O(\lambda^{2n/(n+1)}, \lambda, \lambda^{1/l}),$$

but the expansion is more easily derived as in (4·2). Higher order terms in this expansion can be shown to match with the perturbation to the shock solution.†

The near-equilibrium solution is not necessarily uniformly valid as $Y \to \infty$. In order to obtain a solution valid for large Y it is convenient to re-write the rate equation in the form

$$\frac{\mathrm{d}s}{\mathrm{d}Y} + \left(\lambda^{-d}\frac{\Pi\Omega^*}{V} + \frac{1}{\bar{\sigma}}\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}Y}\right)s = -\frac{1}{\bar{\sigma}}\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}Y}, \tag{4·3}$$

where

$$s = (\sigma - \bar{\sigma})/\bar{\sigma} \tag{4·4}$$

is the relative departure from equilibrium. As $Y \to \infty$ the behaviour of the factor

$$\lambda^{-d}\frac{\Pi\Omega^*}{V} + \frac{1}{\bar{\sigma}}\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}Y} \tag{4·5}$$

dominates the structure of the solution. From the downstream expansion of the equilibrium solution this factor has a zero for large Y if

$$j = 1 - \nu\{\gamma + (\gamma - 1)\delta\} < 0. \tag{4·6}$$

In the neighbourhood of this point, usually termed the freezing point (Blythe 1964 *b*), it is apparent that the near-equilibrium solution no longer holds as both terms in (4·5) are now of the same order of magnitude (see § 5).

If $j > 0$ the flow remains close to equilibrium since the term

$$\lambda^{-d}\Pi\Omega^*/V$$

is then dominant even as $Y \to \infty$. For a given value of δ, j is always positive for sufficiently small ν; for these cases the above result implies that the asymptotic decay downstream of the shock is, to zero order, that of an equilibrium flow. This limiting state is certainly correct for $\nu = 0$ and it seems plausible that a similar result will hold for some finite range of ν.

† In certain situations this type of perturbation solution is singular near any boundary where some initial conditions are prescribed (Bloom & Ting 1960). Here these boundary conditions are replaced by matching with the downstream near-equilibrium limit of the shock solution and this difficulty does not arise.

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5. $\delta > 1, j < 0$: THE FREEZING DOMAIN DOWNSTREAM OF THE SHOCK

For $j < 0$, as noted in § 4, (4·5) passes through a zero when $Y = O(\lambda^{d/j})$. In this case a suitable independent variable, for Y large, is defined by

$$Y = \lambda^{d/j}\phi\xi, \tag{5·1}$$

where ϕ is some constant (see appendix II) chosen so that $\xi = 1$ at the freezing point (zero of (4·5)). When $\xi = O(1)$ the conventional near-equilibrium expansion breaks down.

For $\xi < 1$, $s = O(1)$ and $T = O(\lambda^v)$, where

$$v = -(\gamma - 1)\,d\nu/j. \tag{5·2}$$

It follows that σ is exponentially small with respect to λ in this region. Moreover, since σ is a monotonically decreasing function of ξ, the value of σ upstream of the freezing point will provide an upper bound for an estimate of its magnitude for all $\xi = O(1)$. If such exponentially small terms are neglected in the conservation relations then these equations reduce to the usual isentropic form, with $\sigma = 0$, and are uncoupled from the rate equation. Any arbitrary constants that occur in the solution for the flow variables are found by matching with the downstream limit of the near-equilibrium solution. For these values of the temperature, density, etc., the internal energy distribution can be found either by formally integrating the rate equation or by a further application of matching techniques. This latter approach yields more insight into the nature of the solution. The full details need not concern us here and can be found in Blythe (1964*b*); the principal results are indicated below.

For $\xi = O(1)$, the structure of the solution for σ can be split into three regions. When $\xi < 1$ a modified perturbation solution, in which both of the terms in the factor (4·5) are important, is valid. This solution matches with the downstream expansion of the near-equilibrium solution for s. In the neighbourhood of the freezing point (the transition layer) this perturbation solution breaks down and there is a rapid departure from equilibrium. Within the layer, whose thickness with respect to ξ is $O(\lambda^{\frac{1}{2}v})$, $s = O(\lambda^{-\frac{1}{2}v})$. Downstream of the layer, $\xi > 1$, the solution is usually found by neglecting the equilibrium term in the rate equation.

In the present case this latter approach gives, for $\xi > 1$, $(k \neq 0)$.

$$\sigma = D\exp\left\{-\frac{\lambda^{-v}}{kg}(\xi^k - 1)\right\}; \tag{5·3}$$

where g is a positive constant (see appendix II) and only the dominant terms have been retained. Matching with the transition layer solution (Blythe 1964*b*) shows that

$$D = \sqrt{\frac{2\pi}{(-jg)}}\,\theta_v\lambda^{\frac{1}{2}v}\exp\left\{-\frac{\lambda^{-v}}{(\gamma-1)\nu g}\right\} \tag{5·4}$$

and again only the dominant terms are included.

For $k > 0$, which implies that (1·4) is unbounded, equation (5·3) indicates that σ always decays to zero in an exponential non-equilibrium manner. If $j < 0$ this exponential decay is always slower than the equilibrium (exponential) decay. Since the pseudo-entropy gradient, evaluated from this solution, remains negligible at large distances (and hence the conservation and rate equations remain uncoupled) it is apparent that (5·3) describes the limiting asymptotic decay for this case. Note that a similar analysis does not hold for $j > 0$. In particular the decay (5·3) is then apparently faster than the equilibrium decay, but, as pointed out in § 4, the equilibrium term cannot be neglected for large ξ.

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For $k < 0$ equation (5·3) predicts that the vibrational energy becomes frozen for large ξ. It is apparent, however, that the vibrational mode cannot remain in this state as $\xi \to \infty$, since any near-frozen behaviour will break down for precisely those reasons already advanced in § 2: the pseudo-entropy will again influence the asymptotic solution for large ξ.† As this frozen value of the vibrational energy is exponentially small, it follows that the pseudo-entropy gradient will only become important exponentially far downstream. The corresponding length scale to (2·6) is defined by

$$Y_1 = [\lambda^{-v}\sigma(\infty)]^{1/l}Y, \tag{5·5}$$

where $\sigma(\infty)$ is the frozen value defined by (5·3) and (5·4). In the region $Y_1 = O(1)$ the equations reduce, under suitable transformations, to a similar form to those described in the preceding sections for $Y = O(1)$, with the parameter λ replaced by $\lambda^{-v}\sigma(\infty)$. It is apparent

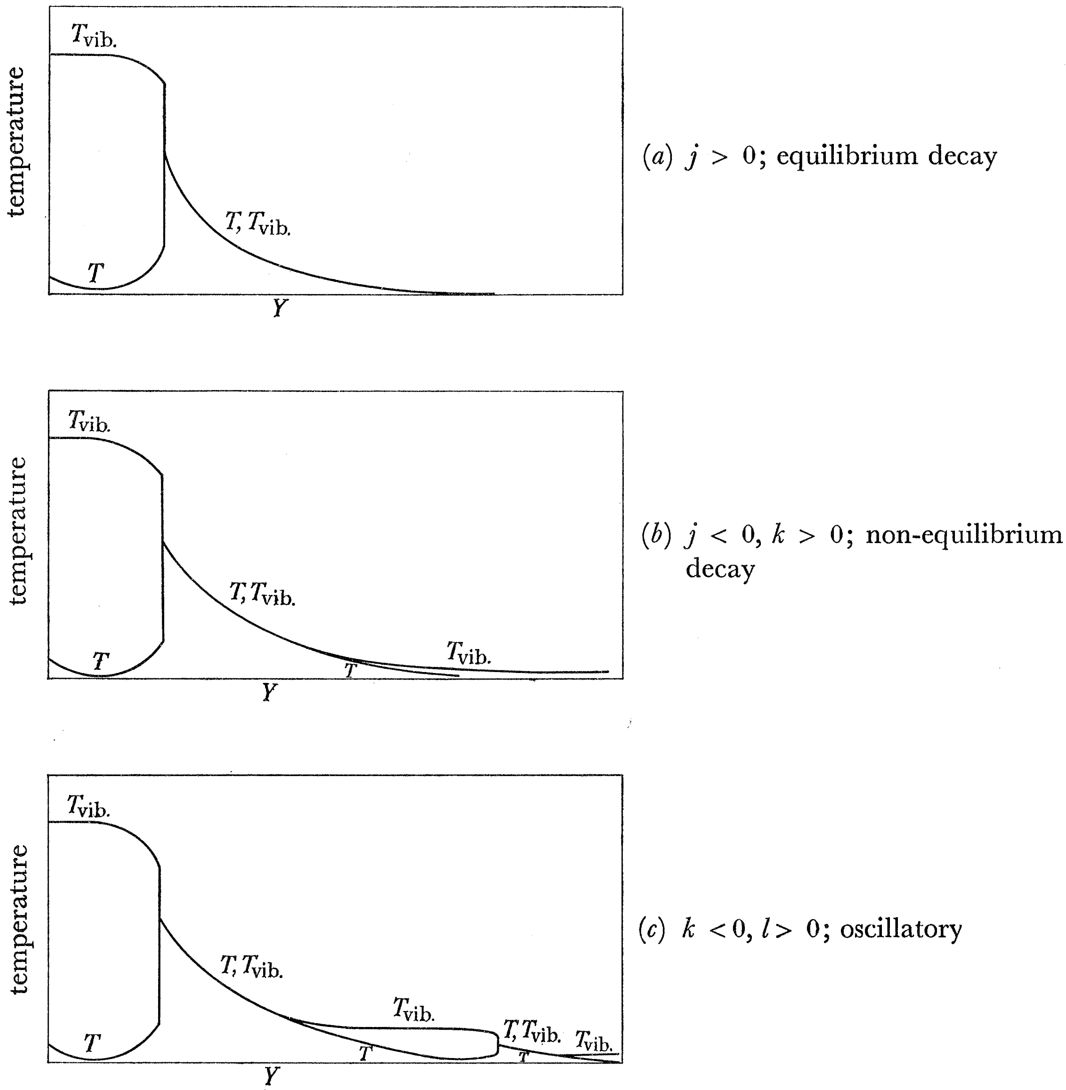

FIGURE 4. Temperature profiles (schematic) for $l > 0$, $\delta > 1$.

† The solution outlined in Blythe (1964*b*) is not uniformly valid as $\xi \to \infty$ for $k < 0$, $l > 0$. It is assumed in that paper that $\int^{\sigma(x)} \frac{d\sigma}{T}$ converges.

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that the whole cycle repeats an infinite number of times with successively smaller values of an appropriate local rate parameter. Since the non-uniformity that occurs when $Y_1 = O(1)$ is already exponentially far downstream, and is characterized by an exponentially small value of σ, any further repetition of this pattern will probably be of little practical significance.

A summary of the various types of solution possible for $\delta > 1$, and their position in the $(1/\nu, \delta)$ plane was given in figure 2 (see § 1). Note that, for a fixed δ, the equilibrium decay $(j > 0)$, the non-equilibrium decay $(j < 0, k > 0)$ and the repetitive pattern of near-frozen flow bounded by de-excitation shocks occur for successively larger values of ν. This latter result seems intuitively obvious; even larger values of ν, for which $l > 0$, imply that the near-frozen solution for $x = O(1)$ remains valid at downstream infinity.

Another useful way of summarizing the asymptotic states for $\delta > 1$ is to plot the translational and vibrational temperature profiles as functions of distance through the nozzle. This is done schematically in figure 4. In each case de-excitation shocks are represented simply as discontinuities. A more detailed picture would include their structure.

6. Gradual de-excitation: the domain $\delta < 1$, $\nu < 1$

It is apparent from § 2, cases (*b*) and (*c*), that the sudden de-excitation encountered for finite Y when $\delta > 1$ does not occur for $\delta < 1$. In particular, as noted in § 2 (*c*), if $\nu > 1$ the effect of the pseudo-entropy, or heat input, is to transfer the initial frozen state to some modified frozen state with a non-isentropic temperature decay. A small degree of de-excitation does take place but the vibrational energy remains finite and $O(1)$ at downstream infinity. For smaller values of $\nu < 1$ the asymptotic solution is not so readily deduced and it is this case which is considered in the present section.

When $\nu < 1 (\delta < 1)$ the limiting behaviour as $Y \to \infty$ of the solution for $Y = O(1)$ (equation (2·15)) indicates that the translational temperature again becomes significant at large distances downstream. From (2·15) it follows that $T = O(1)$ when $Y = O(\lambda^{d/(1-\nu)})$ or $x = O(\lambda^{-1/(1-\nu)})$ (note: $d < 0$ for $\delta < 1$). Hence, a suitable length scale is defined by

$$x = \lambda^{-1/(1-\nu)} \hat{Y}. \tag{6·1}$$

In this region, $\hat{Y} = O(1)$, $\rho = O(\lambda^{\nu/(1-\nu)})$ and it is convenient to write

$$\rho = \lambda^{\nu/(1-\nu)} \hat{\rho}. \tag{6·2}$$

The remaining dependent variables T, σ and u are $O(1)$ in this region, and it is implied that a significant degree of de-excitation of the vibrational mode will occur. For the domain $\nu < 1$, $\delta < 1$, the downstream expansions of equations (2·11) give

$$\left.\begin{aligned} T &\sim \Delta_1 \hat{Y}^{(1-\nu)/(1-\delta)}, \quad & \sigma &\sim \sigma_\infty - \Delta_2 \hat{Y}^{(1-\nu)/(1-\delta)}, \\ \hat{\rho} &\sim \hat{Y}^{-\nu}, & V &\sim 1, \end{aligned}\right\} \tag{6·3}$$

where again only the dominant terms are included and

$$\left.\begin{aligned} \Delta_1 &= \left(\frac{m_0}{u_0(\infty)}\right)^{\gamma-1} \left[\frac{(\gamma-1)(1-\delta)\,\sigma_\infty}{l} \left(\frac{u_0(\infty)}{m_0}\right)^{\gamma-1}\right]^{1/(1-\delta)}, \\ \Delta_2 &= \left(\frac{1-\delta}{1-\nu}\right)\sigma_\infty \left\{\left(\frac{u_0(\infty)}{m_0}\right)^{\gamma-1} \Delta_1\right\}^{\delta}. \end{aligned}\right\} \tag{6·4}$$

These relations provide initial conditions, as $\hat{Y} \to 0$, for the solution when $\hat{Y} = O(1)$.

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In terms of the dependent variables T, σ, V and $\hat{\rho}$ and the independent variable $\hat{Y}$ there is little simplification in the full equations. (To zero order $\lambda^{\nu/(1-\nu)}A$ can be replaced by $\hat{Y}^{\nu}$ and the mass flow can be assumed given by its fully frozen value.) Detailed conclusions regarding the solution in this region are not possible. However, a few qualitative observations can be made. It is apparent that the region is characterized by both the heat input and the area change effects being important at the same time.

The asymptotic limiting solutions as $\hat{Y} \to \infty$ are easily found (see § 7). For $k < 0$ ($l > 0$) it can be shown that ($\delta \neq 0$)

$$T \sim q\hat{Y}^{-(1-\nu)/\delta}, \quad \sigma \sim -\frac{kq}{1-\nu}\hat{Y}^{-(1-\nu)/\delta}, \tag{6·5}$$

where

$$\left.\begin{aligned} q &= \left\{\frac{u_e(\infty)}{u_0(\infty)}\frac{1-\nu}{\delta m_0}\left(\frac{m_0}{u_0(\infty)}\right)^{(1-l)/\nu}\right\}^{1/\delta}, \\ u_e^2(\infty) &= u_0^2(\infty) + 2\sigma_\infty. \end{aligned}\right\} \tag{6·6}$$

and

For $k > 0$ the limiting solutions are similar to those found for $\delta > 1$. When $j < 0$ σ decays exponentially, though $\bar{\sigma}$ is negligible, and the temperature decays algebraically as in the frozen solution ($T \sim \hat{Y}^{-(\gamma-1)\nu}$), but its magnitude is not given by that solution. For $j > 0$ the limiting solution for σ is always influenced by the equilibrium term.

A discussion of the corresponding limiting solutions for a dissociating gas has recently been given by Cheng & Lee (1966).

Since this final limiting behaviour is one in which the translational temperature decays it is apparent from (6·3) that T must pass through at least one maximum value. By analogy with $\delta > 1$ (see figure 2) it might be expected that several stationary points would occur for $k < 0$, but that for $k > 0$ there would only be a single maximum value. It is possible by considering the integral curves of a simple model equation to give some support to this conjecture; this is dealt with in § 7.

The density and pressure profiles in this region are unfortunately not so readily deduced. Equations (6·3) show that the density gradient is always negative initially but that the pressure gradient is positive if

$$1/\nu > 2-\delta. \tag{6·7}$$

When $\delta > \nu$, for which $\mathrm{d}^2T/\mathrm{d}\hat{Y}^2 > 0$ initially, this inequality is automatically satisfied. If $\delta < \nu$, $\mathrm{d}^2T/\mathrm{d}\hat{Y}^2 < 0$ initially, but (6·7) will still hold for some ν and δ. In those cases when (6·7) is not satisfied it is not clear whether the pressure gradient will become positive before the asymptotic limiting decay is attained. Similarly, it does not seem possible to determine analytically whether the density gradient will become positive in some region of the flow. It would seem necessary to resort to numerical computations in order to establish more precisely the conditions under which compressions occur. (The model equation of § 7 is not sufficiently detailed to provide information on this point.) In general it can be expected that the form of $\Omega(T)$, for $T = O(1)$, will have some bearing on this question.

One such computation, with $\delta = 0·5$, $\nu = 0·9$, (therefore $l > 0$, $k < 0$) $\theta_v = 1$ and $u_\infty = 0$, shows that both the density and pressure gradients are negative throughout the flow. The inequality (6·7) is not satisfied for this case. For the numerical solution only terms $O(1)$ were retained in the equation. The explicit expression used for $\Omega(T)$ was of the form (I, 2·9b) with $D_1 = 5$. (It should be stressed that the values $\delta = \frac{1}{2}$, $D_1 = 5$ were chosen to give an

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example of a solution for $\delta < 1$; it should not be taken to imply any correlation of the low-temperature experimental data.) Figure 5 shows the translational temperature and vibrational energy distributions. It is interesting to note that the magnitude of the temperature maximum of which there is only one, is numerically very small. The initial rate of growth

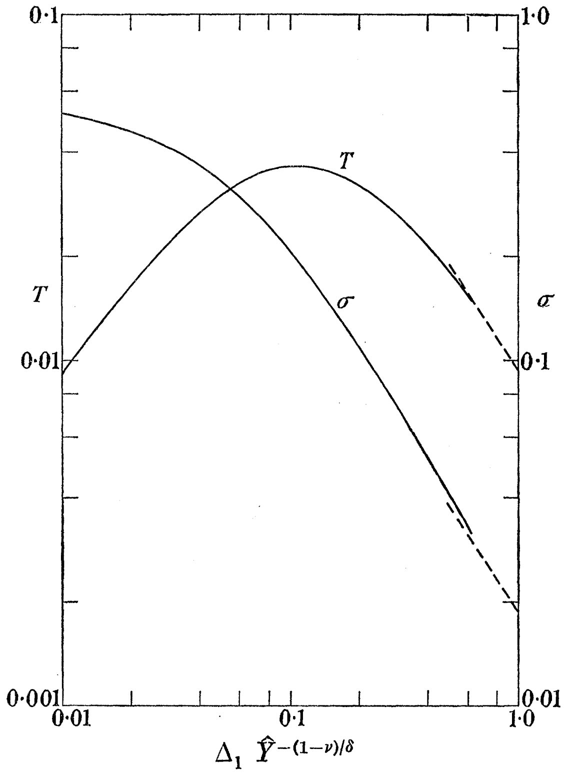

Figure 5. Temperature and energy profiles far downstream for the gradual de-excitation case $\delta = 0{\cdot}5$, $\nu = 0{\cdot}9$, with $\theta_v = 1$, $u_\infty = 0$ and $D_1 = 5$. The broken lines denote the asymptotic limiting solution (equation (6·5)).

$T \sim \hat{Y}^{(1-\nu)/(1-\delta)} = \hat{Y}^{\frac{1}{5}}$, is small in this particular case. In fact, the equilibrium term can be neglected throughout for this asymptotic solution without incurring any significant numerical error, although it is not mathematically correct to do so in general for $\delta < 1$. Presumably for smaller values of $1-\delta$ the temperature maximum is numerically larger.

7. Asymptotic solutions, a model equation

7·1. *The model equation*

It is usual when discussing the limiting form of the solution far downstream to argue that the equilibrium term in the rate equation is negligible (Rosner 1962; Cheng & Lee 1966). Since the temperature again becomes $O(1)$ for all $l > 0$ ($\delta \geqslant 0$) this assumption may, in this domain, lead to erroneous results. However, downstream of any temperature maxima the assumption will have some validity, though obviously it can never lead to a uniformly valid description if $l > 0$, $k < 0$, $\delta > 1$ (see figure 2). In other cases, apart from $j > 0$ when the equilibrium term dominates the asymptotic behaviour, the correct final limiting decay

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can be deduced from the ensuing relations. Consequently, it is useful to consider this approach in some detail; the qualitative features of the solutions that can be obtained are surprising.

As $T \to 0$ it is apparent from the energy equation that the velocity asymptotes to some constant value provided that the vibrational energy either freezes or decays to ground level. By using this result and by neglecting the equilibrium term in the rate equation, we can reduce the governing equations (I, 2·1) to (I, 2·4) to the following coupled differential equations

$$-\frac{\nu}{x}-\frac{1}{\gamma-1}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}x}=\frac{1}{T}\frac{\mathrm{d}\sigma}{\mathrm{d}x}, \tag{7·1}$$

$$\mathrm{d}\sigma/\mathrm{d}x=-\lambda x^{-\nu}T^{\delta}\sigma, \tag{7·2}$$

where λ now includes any contributions from the constant speed u and the mass flow m. The relaxation frequency has been replaced by its behaviour at low temperatures, which is consistent with the preceding approximations. Equations (7·1) and (7·2) can be combined to give the single second-order relation ($l>0$, $\delta \neq 1$, $\nu \neq 1$, $k \neq 0$)

$$w^{-\beta}\frac{\mathrm{d}w}{\mathrm{d}z}=-z^{b}\frac{\mathrm{d}^2w}{\mathrm{d}z^2}, \tag{7·3}$$

where $$w=[Tx_1^{\nu(\gamma-1)}]^{1-\delta},\quad x_1=\lambda^{1/(1-\nu)}x,\quad z=l^{-l/k}x_1^{l}, \tag{7·4}$$

and $$\beta=\delta/(\delta-1); \tag{7·5}$$

the exponent b was defined in equation (2·8). The model equation (7·3) will apparently give a meaningful description only in those regions where the temperature is small and the vibrational mode is nearly frozen.

A further transformation ($\delta \neq 0$)

$$\eta=-z^{1+\mu}\,\mathrm{d}w/\mathrm{d}z,\quad \zeta=z^{\mu}w, \tag{7·6}$$

reduces (7·3) to $$\frac{\mathrm{d}\eta}{\mathrm{d}\zeta}=\eta\frac{\zeta^{-\beta}-(1+\mu)}{\eta-\mu\zeta}, \tag{7·7}$$

where $$\mu=-k/l\beta. \tag{7·8}$$

The parameters μ and β, and therefore implicitly ν and δ, play an important role in determining the integral curves of equation (7·7).

7·2. $l>0,\quad k<0,\quad \delta>1$

For this particular case (see figure 2) the solution of the full equations, as $\lambda \to 0$, predicts a repetitive pattern of de-excitation shocks. Obviously the model equation will not give a uniformly valid description of this solution for large x, though the equation will be valid in certain regions of the flow. The structure of the solution of (7·7) in this case is, however, particularly informative.

Under these conditions $\beta>1$, $\mu>0$ and both η and ζ are positive. The integral curves of equation (7·7) are sketched for the positive quadrant in figure 6. These curves are dominated by the behaviour near the singular point

$$\eta=\mu(1+\mu)^{-1/\beta},\quad \zeta=(1+\mu)^{-1/\beta} \tag{7·9}$$

and are spirals which eventually asymptote to the η, ζ axes. The direction x (or z) increasing is shown by the arrows. This follows directly from the relations (7·6). Note that the singular

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point corresponds to a decaying solution

$$T \sim x^{-(1-\nu)/\delta}, \quad \sigma \sim x^{-(1-\nu)/\delta} \tag{7·10}$$

of equations (7·1) and (7·2)†. (The constant factors have been omitted in (7·10.) Since the solution always moves away from this point, (7·10) cannot describe the limiting behaviour for large x.

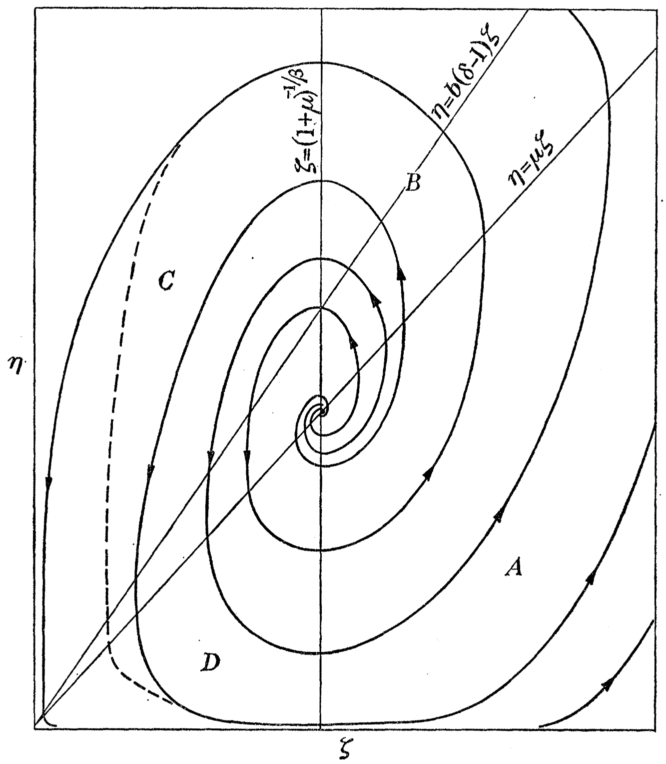

FIGURE 6. Integral curves of the model equation for $l > 0$, $k < 0$, $\delta > 1$.

The limiting behaviour of T and σ, predicted by the model equation, is not immediately apparent from these integral curves. In general it can be shown that the translational temperature takes stationary values on

$$\eta = b(\delta-1)\zeta; \tag{7·11}$$

this line is shown in figure 6. For the present range of the parameters $b(\delta-1) > \mu$. On integral curves which approach this line from below the stationary value is a minimum, on curves which approach the line from above it is a maximum. Any integral curve will intersect this line an infinite number of times. In particular, it is a trivial matter to show that the successive temperature minima decrease in magnitude.

It is apparent that the model equation, as well as the full equations, predicts an oscillatory temperature profile for $l > 0$, $k < 0$ and $\delta > 1$, even though the model equation cannot, in this case, give a uniformly valid quantitative description for large x. However, the behaviour of the model equation and that of the full equations coincide in the sector A (see figure 6), where, for η 'small', the flow is essentially frozen. In sector B the temperature gradient

† A second apparent limiting behaviour is a frozen solution in which $T \sim x^{-(1-\nu)/(\delta-1)}$; it is easily shown, for example, that this implies negative values of σ and is consequently inadmissible.

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becomes positive and the effects of the heat input, or pseudo-entropy, are important. This sector, where $\sigma_\infty - \sigma$ and T are still 'small', corresponds to the region described in § 2 and the model equation is also valid there. The de-excitation shock predicted by the full equations occurs in C. A possible shock path, together with the near-equilibrium region downstream of the shock, is sketched in figure 6. Through the shock the temperature will increase, at least initially, more slowly than (7·3) predicts. In the near-equilibrium region, the actual temperature decay is slower than that given by (7·3). For the full equations the temperature maxima are defined by local equilibrium conditions; for the model equation this is not so. Nevertheless, this latter equation does suggest that there is no simple limiting law in this case and the cyclic nature of the solution of the full equations can be inferred.

7·3. $l > 0, \quad k < 0, \quad \delta < 1, \quad \nu < 1$

In this domain, see figure 2, it appears (§ 6) that there are no regions of rapid de-excitation. The actual temperature profile is, however, not clear. It was noted in § 6 that there will be at least one maximum and it was conjectured, by analogy with $\delta > 1$, that there may be more than one when $k < 0$. Having noted the results of § 7·1, it is not surprising that the model equation, which will give the various decays outlined in § 6 for $j < 0$, also leads to some useful results in this case.

Here the parameters β and μ are negative, as is the co-ordinate η. It is convenient to define

$$\eta_1 = -\eta, \quad \beta_1 = -\beta, \quad \mu_1 = -\mu, \tag{7·12}$$

where $\mu_1 < 1$. Equation (7·7) becomes

$$\frac{d\eta_1}{d\zeta} = \eta_1 \frac{(1-\mu_1) - \zeta^{\beta_1}}{\eta_1 - \mu_1 \zeta}. \tag{7·13}$$

By considering the behaviour near the singular point corresponding to (7·9) it is seen that the integral curves depend implicitly on the magnitude of the parameter

$$c = \frac{1-\mu_1}{\mu_1}\beta_1 = \frac{1-\nu}{-k}\frac{\delta}{(1-\delta)^2}, \tag{7·14}$$

which is positive in the present domain but can range over all finite values. It follows that there are two cases to consider.

(*a*) $4c > 1$

Near the singular point, as in § 7·1, the integral curves are a right-handed family of spirals. Here, however, on $\zeta = 0 (\eta_1 > 0)$

$$d\eta_1/d\zeta = 1 - \mu_1 > 0.$$

There is one and only one curve which passes through the origin on which $d\eta_1/d\zeta = 1$. The integral curves are sketched in figure 7*a*, where the arrows again show the direction x (or z) increasing. Note that this direction is now towards the focus of the spiral, which again corresponds to the decay given by (7·10). This solution, in the present case, is the correct limiting solution ($\delta \neq 0$) downstream of any temperature maxima (see equation (6·5)). The line

$$\eta_1 = (1-\delta)\, b\zeta \tag{7·15}$$

is the counterpart of (7·11) and its intersection with the integral curves defines stationary values of the temperature profile.

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Initial frozen conditions correspond to values of η_1 and ζ which are both small but $\eta_1 = o(\zeta)$. Such points lie beneath the integral curve passing through the origin. It is apparent that integral curves passing through this region will intersect the line (7·15) a finite number of times. The model equation also predicts that successive maxima will decrease in magnitude. Without resort to detailed numerical calculations it is not possible to predict the number of

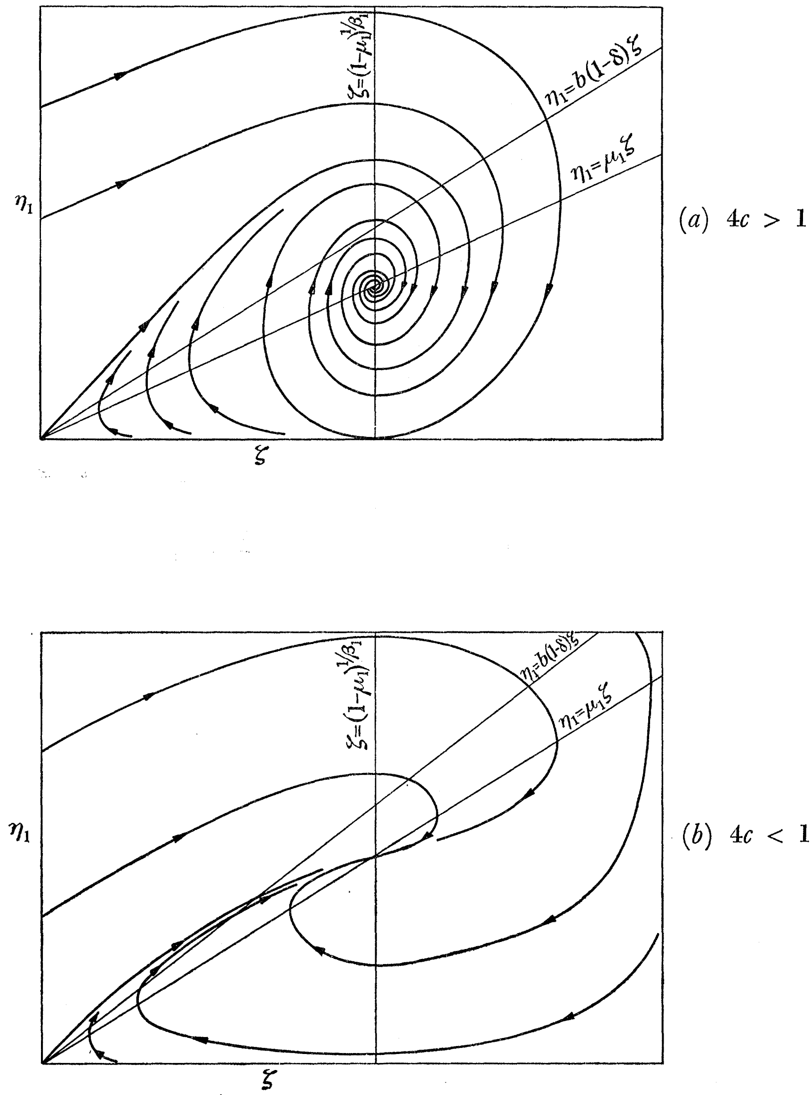

FIGURE 7. Integral curves of the model equation for $l > 0$, $k < 0$, $\delta < 1$.

stationary values that will occur in any given situation. (Such an investigation must be applied to the full equations to avoid any quantitative errors: in the neighbourhood of the maxima the equilibrium term would, in general, be important. See, however, § 6.) For the example given in § 6, in which $4c = 10$, only two stationary values, one maximum, occur. Nevertheless, the form of the integral curves clearly indicates the possibility, presumably for sufficiently large values of c, that there will be more than one local maximum.

In this context it is of interest to note the behaviour as $\delta \to 1$, since in this limit it follows from equation (7·14) that c becomes large. For $\delta = 1$ equation (7·3) is not valid but the corresponding relation is easily deduced from (7·1) and (7·2). The appropriate integral

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curves of that equation are closed loops and it can be inferred that the temperature profile will have an infinite number of stationary values, as for $\delta > 1$.

(*b*) $1 > 4c > 0$

The behaviour near the singular point is modified and the integral curves are shown in figure 7 (*b*). Initial frozen conditions are as in (*a*) and all integral curves passing through this region correspond to the temperature profile having two stationary values.

The limit $c \to 0$ is of interest. In the present domain the limiting case $c = 0$ is only possible as the marginal one in which $\nu \to 1$, $\delta \to 0$. For this case, an exact integral of (7·1) and (7·2) is

$$T = Ax^{-(\gamma-1)} + Bx^{-\lambda}, \tag{7·16}$$

where A and B are positive constants (for λ small). The temperature profile as for $\nu > 1$, has apparently no stationary values. Equation (7·15) shows clearly the type of non-uniformity that occurs for large x, in this limiting case, as $\lambda \to 0$.

7·4. $k > 0$

Irrespective of δ the denominator in (7·7) is now finite for all values of η and ζ that are of interest. The integral curves are easily obtained and figure 8 shows these curves for $\delta < 1$. It can again be argued that the temperature profile will have two stationary values on curves which pass through the near-frozen region.

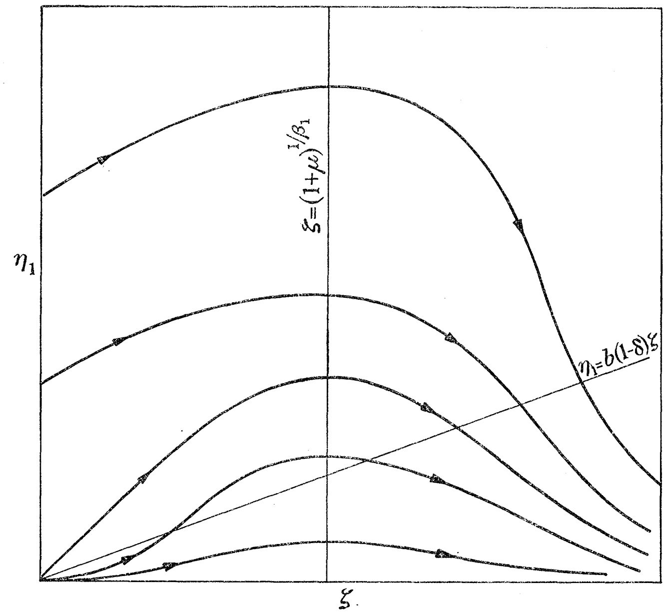

FIGURE 8. Integral curves for $k > 0$, $\delta < 1$.

For $\delta > 1$ the full equations predict a rapid de-excitation region in which the equilibrium term becomes important. In the region of the de-excitation shock the model equation is not quantitatively correct (similar errors may also arise in the neighbourhood of the temperature maximum for $\delta < 1$). Downstream of the temperature maximum both the model equation and the full equations predict, if $j < 0$, the decay (5·3) for the energy and $T \sim x^{-(\gamma-1)\nu}$, where any constant factor is not determined by the isentropic solution. This limiting decay also holds for $\delta < 1$.

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The model equation also predicts that σ decays according to (5·3) even if $j > 0$. This result is erroneous since the equilibrium term will be important for large x (see § 5).

8. Concluding remarks

When the nozzle shape and the relaxation frequency are described by the power law behaviours (1·1) and (1·2) respectively it would appear that there is a wide variety of possible asymptotic solutions. The different types of asymptotic behaviour were summarized in figures 1 and 2. Associated with these solutions is a somewhat bewildering array of length scales. These are listed in tables 1 and 2 with respect to the magnitude of $Y = \lambda^{1/l}x$.

Table 1. Solutions for large x, $\delta > 1$, $l > 0$.

range of exponents	entropy production (§ 2)	position of 1st shock (§ 3)	near-equilibrium (§ 4)	transition (freezing point) (§§ 4 and 5)	frozen (§ 5)	asymptotic decay (§§ 4, 5, and 7)
$k < 0$	$Y = O(1)$	$Y = Y_s = O(1)$ $Y - Y_s = O(\lambda^{\mu})$	$Y > Y_s$ $Y = O(1)$	$Y = \lambda^{d/j}\phi\xi$ $\xi - 1 = O(\lambda^{\frac{1}{2}v})$	$\xi > 1$	pattern repeats
$k > 0$, $j < 0$	(as above)	(as above)	(as above)	$Y = \lambda^{d/j}\phi\xi$ $\xi - 1 = O(\lambda^{\frac{1}{2}v})$	no frozen region for large x	$\sigma \sim \exp\left\{-\dfrac{\lambda^{-v}\xi^k}{kg}\right\}$ $T \sim x^{-(\gamma-1)\nu}$
$k > 0$, $j > 0$	(as above)	(as above)	(as above)	no freezing point	no frozen region for large x	$\sigma \sim \bar{\sigma}$ $T \sim x^{-(\gamma-1)\nu}$

Table 2. Solutions for large x, $\delta < 1$, $l > 0$.

range of exponents	entropy production (§ 2)	gradual de-excitation (§ 6)	asymptotic decay (§§ 6 and 7)
$\nu > 1$	$Y = O(1)$	solution frozen for Y large	$\sigma \to$ constant $T \sim x^{-(\nu-1)/(1-\delta)}$
$\nu < 1$, $k < 0$	$Y = O(1)$	$Y = O(\lambda^{-\{(\gamma-1)\nu(1-\delta)\}/(1-\nu)})$	$\sigma \sim x^{-(1-\nu)/\delta}$ $T \sim x^{-(1-\nu)/\delta}$
$k > 0$, $j < 0$	$Y = O(1)$	(as above)	As for $\delta > 1$
$j > 0$	$Y = O(1)$	(as above)	As for $\delta > 1$

For $\delta > 1$ the asymptotic solutions are all characterized by de-excitation shocks. The structure of the solution for $k < 0 (\delta > 1)$ is repetitive, each cycle being characterized by successively smaller values of an effective rate parameter. In the second cycle this parameter is already exponentially small; it follows that the second de-excitation shock occurs exponentially far downstream and that the temperature jump across the shock is also transcendentally small. It seems, as noted in § 5, that any further repetition of this pattern will be negligible in practice. For $k > 0$ only a single de-excitation shock occurs, though the eventual limiting decay downstream of the shock depends on whether $j \gtrless 0$ (see figure 2 and table 1).

For $\delta < 1$ there are no regions of rapid de-excitation, but the eventual limiting decay still depends on the exponents k and j ($l > 0$). For $k > 0$ there is only one temperature maximum. Note, however, that although for $k < 0$ there may be several local maxima, the number of these maxima is now finite, as opposed to the corresponding situation for $\delta > 1$.

It is apparent that the conventional approach of neglecting the equilibrium term in the rate equation for large x can lead to important quantitative errors, in particular it will always

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do so in the domain $l > 0$, $k < 0$, $\delta > 1$. Nevertheless, this approach can still be used to predict some of the qualitative features of the asymptotic solutions; except in the above domain, and also for $j > 0$, it will yield the correct limiting decay downstream of any temperature maxima.

The author is grateful to Dr N. C. Freeman and Mr J. L. Stollery for some helpful comments.

Appendix I. Downstream expansion of the near-frozen solution for $u_\infty = 0$.

When $u_\infty = 0$ the near-frozen expansion for $x = O(1)$ was outlined in part I. For nozzles such that $A \sim |x|^n$ as $x \to -\infty$ the expansion (II, 2·1) is still valid to $O(\Lambda)$ if $n > 1$. If $n < 1$ the dominant perturbed quantity is $O(\Lambda^{2N})$, where $N = n/(n+1)$. For these terms the associated expressions T_{2N}, etc., are directly proportional to the fully frozen solution and the expansion for $x = O(1)$ can be written

$$\sigma = \sigma_f(\Lambda) + \Lambda\sigma_1(x) + \ldots,$$

$$T = T_f\,(x, \Lambda) + \Lambda T_1(x) + \ldots,$$

where
$$\sigma_f = \sigma_\infty - \Lambda^{2N} K_{2N}, \quad \frac{T_f}{T_0} = 1 + \frac{\gamma - 1}{\gamma}\Lambda^{2N} K_{2N}$$

(see equation (I, 5·25)). If T_0 and σ_∞ are now replaced by T_f and σ_f the results outlined in § 2 again follow.

Appendix II. The constants ϕ and g.

The zero approximation to the flow variables ρ, T, etc., for $\xi = O(1)$ is given by the local equilibrium solution with the initial conditions provided by the downstream limit of the shock solution. Since the freezing point ($j < 0$) occurs where $Y = O(\lambda^{\mu/j})$ the expansion of the equilibrium solution for Y large will define ϕ to zero order. This expansion gives

$$V_e \sim V_\infty = \frac{u_e(\infty)}{u_0(\infty)}, \quad \Pi_e \sim \frac{m_0}{V_\infty} Y^{-\nu}, \quad T_e \sim C_T Y^{-(\gamma-1)\nu},$$

where
$$u_e^2(\infty) = \frac{2\gamma}{\gamma - 1} + 2\sigma_\infty + u_\infty^2,$$

$$C_T = \left(\frac{1}{V_\infty \Pi_{se} S_e}\right)^{\gamma-1} T_{se},$$

and
$$S_e = \left\{1 - \exp\left(-\frac{\theta_v}{T_{se}}\right)\right\} \exp\left\{-\frac{\bar{\sigma}_{se}}{T_{se}}\right\}.$$

Here T_{se}, etc., are the downstream equilibrium limits of the zero order shock solution. It follows from this expansion and equations (4·5) and (5·1) that ϕ is defined by

$$\phi = \left[\frac{C_T^{\delta+1}}{(\gamma-1)\,\nu\theta_v V_\infty^2}\left(\frac{u_0(\infty)}{m_0}\right)^{(\gamma-1)\delta}\right]^{-1/j}.$$

From these results it is a relatively simple matter to show that

$$g = \frac{C_T \phi^{-(\gamma-1)\nu}}{(\gamma-1)\,\nu\theta_v}$$

(see equation (5·3)).

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Appendix III. Notation

A	area ratio.
a_i	constants, see (I, 3·5).
B	constant, see (I, 2·8).
b_i	constants, see appendix I, part I.
b	$(\gamma-1)\nu/l$.
C	constant, see (I, 4·16).
C_p	specific heat at constant pressure.
C_{pa}	specific heat at constant pressure for the active modes.
$C_{\text{vib.}}$	specific heat contribution from the vibrational mode.
C_T	constant, see appendix II, part II.
D	constant, see (II, 5·4).
D_0, D_1	constants, see (I, 2·9).
D	the operator $\mathrm{d}/\mathrm{d}X+\mathrm{d}Z/\mathrm{d}\lvert X\rvert$.
d	$b(\delta-1)$ (part II).
d_i	constants in outer solution (part I).
e_i	constants in outer solution (part I).
F	$\rho\Omega/u$.
$\mathscr{F}_i$	see (I, 5·21)
f_i	see (I, 5·21).
$G(\alpha, t)$	see (I, 4·14).
g	constant, see (II, 5·3) and appendix II, part II.
$g_2(x)$	see (I, 7·8).
$H_i(x)$	defined in (I, 5·15) and (I, 5·22).
h	nozzle length scale (e.g. throat height).
J	constant, see (I, 4·16).
j	exponent, $1-\nu[\gamma+(\gamma-1)\delta]$.
K	constant in pseudo-entropy solution (part II).
K_i	constants occurring in the outer solution (part I).
k	exponent, $1-\nu[1+(\gamma-1)\delta]$.
L	constant in pseudo-entropy solution (part II).
L_i	see (I, 6·5).
l	exponent, $1-\nu[2-\gamma+(\gamma-1)\delta]$.
M_i	see (I, 5·15) and (I, 5·22).
$\mathscr{M}_i$	see (I, 5·22).
m	mass flow.
N	$n/(n+1)$.
n	exponent associated with upstream nozzle shape.
Q	effective heat input, see (II, 3·8).
q	constant, see (II, 6·6).
R	gas constant.
$S_i(x)$	defined by (I, 5·15) and (I, 5·22).
$\mathscr{S}_i(x)$	see (I, 5·22).
s	dummy variable.
$\mathfrak{s}$	$(\sigma-\bar{\sigma})/\bar{\sigma}$, relative departure from equilibrium.
T	temperature.
t	dummy variable.
U	$\Lambda^{-n/(n+1)}u$, stretched velocity in inner layer (part I).
u	velocity.
v	exponent, see (II, 5·2).
V	$u/u_0(\infty)$.
w	$[Tx_1^{(\gamma-1)\nu}]^{1-\delta}$, see (II, 7·4).
X	$\Lambda^{1/(n+1)}x$, stretched inner variable.
x	distance through nozzle.
x_1	$\lambda^{1/(1-\nu)}x$.
Y	$\lambda^{1/l}x$, stretched co-ordinate for pseudo-entropy regime.
y	stretched distance co-ordinate for shock solution, see (II, 3·1).
Z	$k\lvert X\rvert^{n+1}$.
z	$l^{-l/k}x_1^l$.
α	parameter in (I, 4·14).
β	exponent in (I, 2·8).
$\Gamma(\alpha)$	Γ function.
$\gamma(\alpha, t)$	incomplete Γ function.
γ_e	Euler's constant.
γ	specific heat ratio for the active modes.
Δ_i	constants, see (II, 6·4).
δ	exponent associated with frequency decay, see (II, 1·2).
ϵ	$\sigma_\infty-\sigma$, departure from a fully frozen flow.
ζ	stretched co-ordinate in model equation, see (II, 7·6).
η	stretched co-ordinate in model equation, see (II, 7·6).

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Θ scaled temperature in pseudo-entropy regime, see (II, 2·9).
θ_v characteristic temperature of vibration.
κ constant, see (I, 4·19).
Λ rate parameter, see (I, 2·6).
λ modified rate parameter, see (II, 2·5).
μ $-k/l\beta$.
ν exponent associated with downstream nozzle shape.
ξ stretched nozzle co-ordinate near freezing point, see (II, 5·1).
π scaled density for pseudo-entropy, see (II, 2·9).
ρ density.
Σ see (II, 2·9).
σ vibrational energy.
$\bar{\sigma}$ local equilibrium value of vibrational energy.
τ relaxation time.
ϕ constant, see appendix II, part II.
Ω relaxation frequency.

Subscripts

$0, 1, n/(n+1), \ldots$, etc. denote perturbation quantities in the various solutions.

Dimensional quantities

All variables defined above are non-dimensionalized according to the scheme outlined in (I, 2·5). Any dimensional quantities are indicated by primed variables, e.g. σ', T', etc.

Equation numbers

The roman numeral I or II prefixed to an equation number refers to that equation in the respective part of this paper.

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