



MINISTRY OF TECHNOLOGY
AERONAUTICAL RESEARCH COUNCIL
CURRENT PAPERS

On the Breakdown of Near-Equilibrium Quasi-One-Dimensional Flow

By
P. A. Blythe

LIBRARY
ROYAL AIRCRAFT ESTABLISHMENT
BEDFORD.

LONDON HER MAJESTY'S STATIONERY OFFICE

1967

SIX SHILLINGS NET

On the breakdown of near-equilibrium
quasi-one-dimensional flow

C.P. No. 923*
January, 1964

by

P. A. Blythe

January 1964

Summary

The limitations of near-equilibrium solutions in expanding non-equilibrium flows are discussed. The breakdown of this type of solution far downstream is investigated for a vibrationally relaxing gas. It is shown that valid asymptotic solutions can be derived by the use of matching techniques. Asymptotic frozen levels of the vibrational energy are obtained for a particular flow model.

1. Introduction

In recent years a large body of literature has been devoted to the effects of finite rate processes on expanding quasi-one-dimensional flows. The importance of this problem stems from its application to the flow in hypersonic wind tunnels, rocket nozzles, etc. Relatively simple solutions can be obtained when the rate parameter Λ (ratio of the time scale of the flow to the time scale of the rate process), based on some characteristic conditions, is large. Under these circumstances a perturbation of the equilibrium solution, for which the time scale of the rate process is identically zero, would seem to be appropriate.

However, near-equilibrium analyses of expanding flows suffer from two limitations. This type of perturbation solution is in general singular at any position in the flow where conditions are specified (for $\Lambda \gg 1$ the order of the equations is reduced by one). Bloom and Ting (1960) (see also Napolitano (1962)) showed that it was possible to obtain a uniformly valid solution of this problem by using conventional "boundary-layer" techniques.

In addition, for an expanding flow, the perturbation solution will also become invalid far downstream where the local ratio of the flow time scale to the time scale of the rate process

*Replaces N.P.L. Aero Report 1090 - A.R.C.27 588.

Only a single rate process is considered here.

becomes small. The departure from equilibrium becomes "large" in such regions and the assumption of "small" deviations from an equilibrium solution is no longer valid. (The precise meaning of "large" and "small" will be outlined in the main body of the paper). It is this breakdown of the perturbation solution with which the present paper is concerned.

Associated with this breakdown is the freezing of the energy, σ' , in the lagging mode, i.e. σ' tends asymptotically to some constant non-zero value, though the equilibrium distribution $\bar{\sigma}'$, corresponding to the local translational temperature, approaches zero. This freezing phenomenon was brought to light in the early numerical work on this problem and much effort has been devoted to obtaining the asymptotic frozen levels for various types of rate process. Because of the complexity of the exact numerical calculations many approximate methods for obtaining this asymptotic level have been devised, see e.g. Bray (1959) Rosner (1962), and Stollery and Park (1963). Analytical investigations (Blythe 1963a,b) have shown that the phenomenon of freezing is associated with a turning point of the appropriate rate equation. An example of the type of equation considered there can be written

$$\frac{1}{N} \frac{ds}{d\xi} + P(\xi, N)s = Q(\xi, N) \quad \dots (1.1)$$

with $s = 0$ at $\xi = \xi_0$

where $N \gg 1$, $P(\xi, N)$ and $Q(\xi, N)$ are $O(1)$ and $s = \frac{\sigma' - \bar{\sigma}'}{\bar{\sigma}'}$ is the relative departure from equilibrium. The turning point behaviour is given by the zero of $P(\xi, N)$, which is defined by $\xi = 1$. For $\xi < 1$, $P(\xi, N) > 0$ and a perturbation solution of the type

$$s = \frac{Q(\xi, N)}{P(\xi, N)} + O\left(\frac{1}{N}\right) \quad \dots (1.2)$$

is valid. This solution breaks down at $\xi = 1$ and it is necessary to modify the solution there by including the derivative term (see section 4). Note that for $N \gg 1$ the order of (1.1) is reduced by one and, in general, (1.2) will not satisfy the boundary condition imposed on (1.1).

These analytical investigations were confined to the case where σ' is small compared with the stagnation enthalpy H_0' . Under this assumption by neglecting terms $O\left(\frac{\sigma'}{H_0'}\right)$ etc. it is

possible to show that as a first approximation the equations governing the flow are uncoupled from the rate-equation. In the present paper no assumption is made regarding the magnitude of σ' and in general the flow equations

and the rate equation will be coupled. It will, however, be assumed that the rate parameter Λ , based on initial conditions where the flow is assumed to be in equilibrium, is large. It can then be expected that a near-equilibrium perturbation solution (expansion in inverse powers of Λ) will be valid in some region. This solution may need modification, in the manner outlined by Bloom and Ting (1960), near the initial equilibrium station. As noted above this perturbation solution will also break down sufficiently far downstream. It follows for $\Lambda \gg 1$ that this will be a "large" distance downstream. In fact the rate equation again exhibits the turning point behaviour found in the uncoupled case. In addition, for $\Lambda \gg 1$, it follows that immediately upstream of this transition region σ' is "small" and "near" to its equilibrium value $\bar{\sigma}'$ ($\sigma'/\bar{\sigma}' - 1$ is $O\left(\frac{1}{\Lambda}\right)$) and far downstream $\bar{\sigma}'/H_0' \ll 1$. Consequently in the vicinity of the turning point, and downstream of it, the flow equations and the rate equation are again uncoupled to a first approximation. Hence, within and downstream of this region the approach used in the uncoupled case (Blythe 1963b) should be valid. The technique used there was to obtain valid solutions (of equation (1.1)) applicable to each of the regions of interest, i.e. the region upstream of the turning point, the region in the vicinity of the turning point, and finally the region downstream of the turning point (from which the asymptotic frozen level was determined). Boundary conditions for the solutions in the various regions were determined by means of appropriate matching procedures. As is well known matching or patching techniques form a very useful tool for dealing with turning point problems of this type which involve a large parameter.

Similar techniques are again used here. In the present case the solution valid immediately upstream of the turning point must be matched, at its upstream "edge", to the behaviour of the near-equilibrium solution far downstream. Essentially there are no major differences in the overall pictures for σ'/H_0' arbitrary with $\Lambda \gg 1$ and for $\frac{\sigma'}{H_0'}$ small: the effect of the coupling in the former case enters via the upstream matching conditions for the solution in the vicinity of the turning point. Various types of rate equation can be treated and solutions of these equations which have been obtained previously for the uncoupled case can be carried over by utilising this modification on the matching conditions. The asymptotic levels of σ so determined are influenced by the coupling in the perturbation region. Considerable interest centres on these asymptotic levels and even though they are influenced by the coupling, it again follows, as in the uncoupled case, that these values are not in agreement with those derived by the "sudden-freeze" approximation (Bray, 1959).

The analysis is carried out in detail for a vibrationally relaxing gas. It is assumed that the gas can be represented by a system of harmonic oscillations and that the Landau-Teller rate equation is valid (Landau and Teller (1936), Shuler (1959)).

2. Basic equations

2.1 Thermodynamic model

It is assumed that the translation and rotational modes of the gas are fully excited, that the vibrational mode can be represented by a system of harmonic oscillators, and that dissociation, ionization and similar phenomena are negligible.

For a system of harmonic oscillators the equilibrium energy content $\bar{\sigma}'$ is given by

$$\bar{\sigma}' = \frac{R\theta'}{e^{\theta'/T'} - 1} \quad \dots (2.1)$$

where θ' is the characteristic temperature of vibration, T' is the translational temperature, and R the gas constant. The rate equation governing the variation of the vibrational energy σ' is assumed to have the form (see e.g. Landau and Teller (1936), Shuler (1959) Herzfeld and Litovitz (1959))

$$\frac{D\sigma'}{Dt'} = \frac{1}{\tau'(\rho', T')} [\bar{\sigma}'(T') - \sigma'] \quad \dots (2.2)$$

Here $\frac{D}{Dt'}$ denotes the usual convective operator, ρ' is the density, and τ' is the local relaxation time. In general

$$\frac{1}{\tau'} = \rho' \Omega'(T') \quad \dots (2.3)$$

(see e.g. Johannesen (1961)). Several expressions for $\Omega'(T')$ have been derived, each of which shows some measure of qualitative agreement with the available experimental data (Herzfeld and Litovitz (1959), Widom (1957)). In an example presented in section 5 it is assumed that

$$\Omega'(T') = A \exp b'T'$$

There is some theoretical justification for this choice (Widom (1957)). However, it should at best be regarded as an empirical fit to the experimental data (Stollery and Park (1963)). It is more convenient to re-write the above expression in the form

$$\Omega'(T') = A \exp b \left(\frac{T'}{\theta'} \right) \quad \dots (2.4)$$

where b is now dimensionless and is assumed to be $O(1)$. [For O_2 , for which (2.4) fits the experimental data very well, $b \approx 3.6$. For N_2 , $b \approx 2$. These values were derived using Blackman's (1956) experimental data.]

The assumption that the rate equation has the form (2.2) is open to question. In general, it can be shown that (2.2) is valid for a system of harmonic oscillators when only small a fraction of the oscillators is excited (Shuler, 1959). In the present analysis this latter assumption is certainly violated. However, no suitable alternative equation has yet been proposed and, in fact, it is usual to assume that (2.2) remains valid (Stollery and Park (1963)) though some evidence does exist to the contrary (Johannesen and Zienkiewicz (1963)). Modifications to the form of (2.2) can easily be included in the analysis provided that the characteristic feature of the rate equation, namely that the rate of change of vibrational energy is proportional to the local departure from equilibrium, remains unchanged. It can be shown that any such modification would be of direct importance only in the coupled near-equilibrium region (see section 3): far downstream the rate equation would again reduce to the form (2.2) (for $\Lambda \gg 1$), since there the fraction of excited oscillators would be small, though the boundary conditions (matching conditions) for the solution far downstream would be influenced by the form of the rate equation upstream.

2.2 Flow equations

The equations governing the quasi-one-dimensional flow of a vibrationally relaxing gas can be written

Continuity

$$\rho v A = m \quad \dots (2.5)$$

Momentum

$$v \frac{dv}{dx} = - \frac{1}{\gamma \rho} \frac{dp}{dx} \quad \dots (2.6)$$

Energy

$$\frac{\gamma}{\gamma-1} \frac{p}{\rho} + \sigma + \frac{\gamma}{2} v^2 = \frac{\gamma}{\gamma-1} \bar{e} + \frac{\gamma}{2} v_e^2 \quad \dots (2.7)$$

State

$$p = \rho T \quad \dots (2.8)$$

The variables have been non-dimensionalized by putting

$$\left. \begin{aligned} p &= \frac{p'}{p'_e}, \quad \rho = \frac{\rho'}{\rho'_e}, \quad T = \frac{T'}{T'_e}, \quad v = \frac{v'}{a'_{fe}} \\ \sigma &= \frac{\sigma'}{RT'_e}, \quad A = \frac{A'}{A'_t}, \quad m = \frac{m'}{\rho'_e a'_{fe} A'_t}, \quad x = \frac{x'}{\ell'} \end{aligned} \right\} \dots (2.9)$$

where p' is the pressure, v' the velocity, $A'(x')$ the cross-sectional area at any station x' , ℓ' is some characteristic length associated with the nozzle, γ is the ratio of specific heats neglecting vibration (frozen specific heat ratio) and a'_{fe} is the frozen speed of sound. The suffix t denotes conditions at the cross-section of minimum area and the suffix $'e$ denotes conditions at the initial equilibrium station. All flows considered here will start from equilibrium conditions. These conditions may or may not coincide with stagnation conditions.

2.3 Transformed equations

The rate equation and the equation governing the distribution of $\bar{\sigma}'$ can be recast in non-dimensional form as

$$\frac{d\sigma}{dx} = \Lambda \frac{\rho\Omega}{v} [\bar{\sigma} - \sigma] \quad \dots (2.10)$$

$$\bar{\sigma} = \frac{\theta}{\exp\left(\frac{\theta}{T}\right) - 1} \quad \dots (2.11)$$

where

$$\bar{\sigma} = \frac{\bar{\sigma}'}{RT'_e}, \quad \theta = \frac{\theta'}{T'_e}, \quad \Omega = \frac{\Omega'(T')}{\Omega'_e(T'_e)} \quad \dots (2.12)$$

and

$$\Lambda = \frac{\ell \rho'_e \Omega'_e}{a'_{fe}} \quad \dots (2.13)$$

Λ is termed the rate parameter and represents some initial ratio of the flow time scale to the time scale of the rate process (for v_e finite it may be better to use v'_e rather than a'_{fe} as the scaling velocity). $\Lambda \frac{\rho\Omega}{v}$ is the local value of this ratio. For $\Lambda \gg 1$ it can be expected that, initially, the

energy distribution will follow, in some sense, the equilibrium distribution. This near-equilibrium behaviour can be expected to break down where $\frac{\Lambda \rho \Omega}{v}$ becomes $O(1)$, i.e. where the time scale of the rate process becomes of the same order of magnitude as the time scale of the flow. $\Lambda \ll 1$ implies that near-frozen conditions will hold everywhere. It is assumed that $\Lambda \gg 1$ for all initial conditions considered here.

The exponential temperature dependence of $\bar{\sigma}$ makes it more convenient to use a new independent variable

$$z = \frac{1}{T} \quad \dots (2.14)$$

rather than the dimensionless distance (Blythe 1963b). Equations (2.5), (2.6), (2.7), (2.10) and (2.11) become

$$pzvA = m \quad \dots (2.15)$$

$$v \frac{dv}{dz} = \frac{1}{\gamma z} \frac{dp}{p dz} \quad \dots (2.16)$$

$$\frac{\gamma}{\gamma-1} \frac{1}{z} + \sigma + \frac{\gamma}{2} v^2 = \frac{\gamma}{\gamma-1} + \bar{\sigma}_e + \frac{\gamma}{2} v_e^2 \quad \dots (2.17)$$

$$\frac{d\sigma}{dz} = \Lambda F(z, \sigma) [\bar{\sigma}(z) - \sigma] \quad \dots (2.18)$$

where

$$F(z, \sigma) = \frac{zp\Omega(z)}{v} \frac{dx}{dz} \quad \dots (2.19)$$

$$\bar{\sigma}(z) = \frac{\theta}{e^{\theta z} - 1} \quad \dots (2.20)$$

The equation of state

$$p = \frac{\rho}{z} \quad \dots (2.21)$$

has been used to eliminate ρ .

A more meaningful dependent variable than σ is the relative departure from equilibrium s , defined by

$$s = \frac{\sigma - \bar{\sigma}}{\bar{\sigma}} \quad \dots (2.22)$$

In terms of s equation (2.18) becomes

$$\frac{ds}{dz} + \left[\Lambda F(z,s) + \frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} \right] s = - \frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} \quad \dots (2.23)$$

The structure of this equation should be noted. It can be seen that for $\Lambda \gg 1$, z finite, s is $O\left(\frac{1}{\Lambda}\right)$. However, as $z \rightarrow \infty$ $F \rightarrow 0$ and this perturbation solution is singular at infinity. In fact the term in square brackets passes through a zero for large z . This zero is termed a turning point, or transition point of the differential equation and associated with it is a rapid growth in the relative departure from equilibrium s . In the neighbourhood of this zero the perturbation solution will become invalid.

The solution for finite z also exhibits a further type of singular behaviour namely that usually associated with the behaviour of perturbation solutions of this type (for which the order of the equation is reduced by one) near some boundary along which conditions are specified, i.e. $s = 0$ on $z = 1$. At $z = 1$ the perturbation solution gives $s = \frac{1}{\Lambda F(1,0)} + O\left(\frac{1}{\Lambda^2}\right)$ which, for $v_e \neq 0$, is in general non zero. [For $v_e = 0$, i.e. flow starting from equilibrium stagnation conditions, it can be shown that no modification near $z = 1$ is necessary.] The necessary modification to this type of solution in the neighbourhood of $z = 1$ has been considered previously by Bloom and Ting (1960) and Napolitano (1962). The solution appropriate here is briefly outlined in the appendix.

It is convenient to write down here two relationships which, in principle, together with equation (2.5) determine F as a function of z and s . From equations (2.16) and (2.17) it can be shown that

$$p = z^{-\frac{\gamma}{\gamma-1}} \exp \left\{ \int_1^z y^{-\frac{\gamma}{\gamma-1}} \left[\bar{\sigma}(1+s) \right] dy \right\} \quad \dots (2.24)$$

$$v = \left[v_e^2 + \frac{2}{\gamma-1} \left(1 - \frac{1}{z} \right) + \frac{2}{\gamma} \left(\bar{\sigma}_e - \bar{\sigma}(1+s) \right) \right]^{\frac{1}{2}} \quad \dots (2.25)$$

where y is a dummy variable. $x = x(z,s)$ then follows from (2.15), for any specified $A(x)$, and hence $F(z,s)$, can be obtained from equation (2.19).

3. Perturbation solution

3.1 $v_e \neq 0$: Bloom and Ting's approach

For $v_e \neq 0$ the foregoing system of equations can be reduced to two first order differential equations of the form

$$\left. \begin{aligned} \frac{1}{\Lambda} \frac{d\sigma}{dz} &= f(z, \sigma, p) \\ \frac{dp}{dz} &= g(z, \sigma, p) \end{aligned} \right\} \dots (3.1)$$

with $p = 1, \sigma = \bar{\sigma}_e$ at $z = 1$, where $f(1, \bar{\sigma}_e, 1) = 0$ Bloom and Ting (1960) and Napolitano (1962) have presented techniques for obtaining the solution to a similar system of equations. A solution of the type

$$\sigma = \sum_{i=0} \Lambda^{-i} \sigma_i(z) \quad \dots (3.2)$$

etc.

is sought. The degenerate case obtained by putting $\frac{1}{\Lambda} = 0$ gives the equilibrium solution. Such a solution is singular at $z = 1$, where the boundary conditions gives $\frac{d\sigma}{dz} = 0 \neq \left(\frac{d\sigma}{dz}\right)_{z=1}$

The necessary modification to the perturbation solution is found by considering the behaviour in a layer near $z = 1$ whose thickness is $O\left(\frac{1}{\Lambda}\right)$. A solution of the form

$$\sigma = \sum_{i=0} \Lambda^{-i} \sigma_i^*(\nu) \quad \dots (3.3)$$

etc.

with

$$\sigma_0^* = \bar{\sigma}_e, \quad \sigma_i^* = 0 (i \geq 1) \quad \text{at } z = 1,$$

where $\nu = \Lambda(z-1)$, is sought in this region. A uniformly valid solution can then be written down via the usual technique associated with inner and outer expansions. The solution near $z = 1$, in terms of the independent variable s , is outlined in the appendix. The solution for s ($z > 1$) is presented in detail in section 3.3. It is sufficient to note here that a solution of the type (3.2) forms a valid outer limit of the solution (3.3) which is valid near $z = 1$.

3.2 $v_e = 0$: convergent-divergent nozzle

This is an important exception when the system of equation cannot be reduced to the form (3.1). In this case the mass flow is not known a priori; in general it is a function of Λ (see below) and the equations reduce to the form

$$\left. \begin{aligned} \frac{1}{\Lambda} \frac{d\sigma}{dz} &= f^*\left(z, \sigma, p, \frac{1}{\Lambda}\right) \\ \frac{dp}{dz} &= g(z, \sigma, p) \end{aligned} \right\} \dots (3.4)$$

with $\sigma = \bar{\sigma}_e$, $p = 1$ at $z = 1$.

The value of $f^*\left(1, \bar{\sigma}_e, 1, \frac{1}{\Lambda}\right)$ is indeterminate ab initio.

However it can be shown that

$$\dots \lim_{z \rightarrow 1} f^*\left(z, \sigma, p, \frac{1}{\Lambda}\right) = \frac{1}{\Lambda} \left(\frac{d\bar{\sigma}}{dz} \right)_{z=1}$$

and it follows that a formal perturbation solution of the type (3.2) is not singular, in this case, at $z = 1$.

The perturbation solution is not so readily found as for $v_e \neq 0$. It is necessary to determine the appropriate value of the mass flow at each stage of the approximation. Details of the actual determination are given in section 3.3. Both cases ($v_e \neq 0$, $v_e = 0$) are treated, but special emphasis is placed on the latter since the former case ($v_e \neq 0$) has been dealt with at length by Napolitano (1962). The solutions are presented using s , rather than σ , as the independent variable; this is more convenient with regard to the behaviour for large z .

3.3 Solution for finite z

A formal solution of the type

$$\left. \begin{aligned} s &= s_0(z) + \frac{1}{\Lambda} s_1(z) + \dots \\ p &= p_0(z) + \frac{1}{\Lambda} p_1(z) + \dots \end{aligned} \right\} \dots (3.5)$$

etc.

is sought. In accordance with these expansions the function

$F(z,s)$ will have an expansion of the form

$$F(z,s) = F_0(z) + \frac{1}{\Lambda} F_1(z) + \dots \quad \dots (3.6)$$

From equations (3.5), (3.6) and (2.23)

$$\left. \begin{aligned} s_0 &= 0 \\ s_1 &= -\frac{1}{F_0} \cdot \frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} \\ i \geq 2 \\ s_i &= -\frac{1}{F_0} \left[\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} s_{i-1} + \frac{ds_{i-1}}{dz} \right] + \frac{1}{F_0} \sum_{k=1}^{i-1} F_k s_{i-k} \end{aligned} \right\} \dots (3.7)$$

Note that s_i depends only on the F_{i-k} ($k \geq 1$) which can be assumed known insofar as computing s_i is concerned ($s_0 = 0$). From equations (2.24), (2.25) and (3.7)

$$\left. \begin{aligned} p_0 &= z^{-\frac{\gamma}{\gamma-1}} \exp \left\{ \int_1^z y \frac{d\bar{\sigma}}{dy} dy \right\} \\ p_1 &= p_0 \int_1^z y \frac{d}{dy} \left(-\frac{1}{F_0(y)} \frac{d\bar{\sigma}}{dy} \right) dy \end{aligned} \right\} \dots (3.8)$$

etc.

(y is a dummy variable) and

$$\left. \begin{aligned} v_0 &= \left[v_e^2 + \frac{2}{\gamma-1} \left(1 - \frac{1}{z} \right) + \frac{2}{\gamma} (\bar{\sigma}_0 - \bar{\sigma}) \right]^{\frac{1}{2}} \\ v_1 &= \frac{1}{\gamma F_0 v_0} \frac{d\bar{\sigma}}{dz} \end{aligned} \right\} \dots (3.9)$$

etc.

In order to complete the determination of the F_1 (and hence the s_{i+1}) it is necessary to compute the A_i where

$$A = A_0(z) + \frac{1}{\Lambda} A_1(z) + \dots \quad \dots (3.10)$$

The A_1 are easily found from (2.15) if the mass flow m is known.¹ For $v_e \neq 0$ m follows immediately from the boundary conditions at $z = 1$, i.e. $m = v_e A_e$, and

$$\left. \begin{aligned} A_0 &= \frac{m}{\rho_0 z v_0} \\ A_1 &= -A_0 \left(\frac{p_1}{p_0} + \frac{v_1}{v_0} \right) \end{aligned} \right\} \dots (3.11)$$

etc.

Hence for any given $A(x)$ the $\Gamma_{\pm}(z)$ follow (equation (3.11) gives $x = x(z, \Lambda)$).

For $v_e = 0$ the mass flow cannot be determined from conditions at $z = 1$ (for any non-zero mass flow $(A)_{z=1}$ is infinite). In this case the mass flow can be found from conditions at the throat. From the continuity, momentum and energy equation it can be shown that

$$\frac{1}{\gamma-1} (v^2 z - 1) = z^2 \left(v^2 z \frac{1}{\gamma} \right) \frac{d\sigma}{dz} + \frac{v^2 z^2}{A} \frac{dA}{dz} \dots (3.12)$$

At the throat $\frac{dA}{dz} = 0$ and thus

$$\frac{1}{\gamma-1} (v^2 z - 1) = z^2 \left(v^2 z \frac{1}{\gamma} \right) \frac{d\sigma}{dz} \dots (3.13)$$

there*. It is assumed that the throat lies in the region of validity of the perturbation solution. Consequently the position of the throat $z = z_t$ is given by an expression of the form

$$z_t = z_0 + \frac{1}{\Lambda} z_1 + \dots \dots (3.14)$$

where z_0 is given, from (3.13), (3.9) and (3.7) as the root of

$$\frac{1}{\gamma-1} (z v_0^2(z) - 1) = z^2 \left(v_0^2(z) - \frac{1}{\gamma} \right) \frac{d\bar{\sigma}}{dz} \dots (3.15)$$

*The usual results for frozen and equilibrium flow follows from equation (3.13), i.e. the velocity at the throat is equal to the appropriate sound speed.

and

$$z_1 = \frac{\gamma z_0^2 \left[z_0 v_0^2(z_0) - \frac{1}{\gamma} \right]^2 \left[\frac{d}{dz} (\bar{\sigma}_{11})_{z=z_0} - 2z_0 v_0(z_0) v_1(z_0) \right]}{\left[\frac{d}{dz} (v_0^2 z) \right]_{z=z_0} - \gamma \left[z_0 v_0^2(z_0) - \frac{1}{\gamma} \right]^2 \left[\frac{d}{dz} \left(z^2 \frac{d\sigma}{dz} \right) \right]_{z=z_0}}$$

etc. ... (3.16)

It is expected that the mass flow m will be given by an expansion of the form

$$m = m_0 + \frac{1}{\Lambda} m_1 + \dots \quad \dots (3.17)$$

Equations (2.15) and (3.17) give

$$\left. \begin{aligned} A_0 &= \frac{m_0}{p_0 z v_0} \\ A_1 &= A_0 \left(\frac{m_1}{m_0} - \frac{p_1}{p_0} - \frac{v_1}{v_0} \right) \end{aligned} \right\} \dots (3.18)$$

etc.

The m_i are now found by considering the conditions on the A_i at the throat. At the throat

$$\begin{aligned} A(z_t) &= A_0(z_0) + \frac{1}{\Lambda} \left[A_1(z_0) + z_1 \left(\frac{dA}{dz} \right)_{z=z_0} \right] \\ &+ \frac{1}{\Lambda^2} \left[A_2(z_0) + z_1 \left(\frac{dA_1}{dz} \right)_{z=z_0} + z_2 \left(\frac{dA_0}{dz} \right)_{z=z_0} \right. \\ &\quad \left. + \frac{1}{2} z_1^2 \left(\frac{d^2 A_0}{dz^2} \right)_{z=z_0} \right] + \dots \end{aligned} \quad \dots (3.19)$$

But at the throat

$$A(z_t) = 1, \quad \left(\frac{dA}{dz} \right)_{z=z_t} = 0. \quad \dots (3.20)$$

and it follows that

$$\left. \begin{aligned} A_0(z_0) &= 1 \\ A_1(z_0) &= 0 \\ A_2(z_0) &= \frac{1}{2} z_1^2 \left(\frac{d^2 A_0}{dz^2} \right)_{z=z_0} \end{aligned} \right\} \dots (3.21)$$

etc.

From which

$$\begin{aligned}
 m_0 &= p_0(z_0) z_0 v_0(z_0) \\
 m_1 &= m_0 \left[\frac{p_1(z_0)}{p_0(z_0)} + \frac{v_1(z_0)}{v_0(z_0)} \right] \dots (3.22)
 \end{aligned}$$

etc.

Hence, for any given $A(x)$, the $F_1(z)$ follow.

For $v_e \neq 0$ the perturbation solution needs modification, near $z = 1^e$ for the reason outlined in section 3.1. This modification is derived in the appendix.

4. Solution for large z

4.1 Outline of approach

The class of functions $F(z, s)$ considered here are such that for large z $F \rightarrow 0$. It follows that the perturbation (near-equilibrium) solution is singular at infinity. Examination of equation (2.23) shows the manner of this breakdown. Since $\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} < 0$ and approaches $-\theta$ as $z \rightarrow \infty$, then at some point in the flow

$$\Lambda F(z, s) + \frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz} = 0 \dots (4.1)$$

Let the value of z satisfying this equation be Φ . Equation (4.1) defines the order of magnitude of Φ with respect to Λ . Since $F(z, s)$ is a decreasing function of z and $\Lambda \gg 1$, then $\Phi \gg 1$.

In the neighbourhood of this zero, which is a turning point of the differential equation, the relative departure from equilibrium grows rapidly and it is no longer valid to assume that s is "small". However, upstream of this region $\sigma = \bar{\sigma}(1+s)$ is $o(1)$ for large z since $\bar{\sigma}(z)$ becomes exponentially small as z increases. Hence, as σ is a monotonically decreasing function of z (equation 2.18), $\sigma \ll 1$ within and downstream of the region near $z = \Phi$. If terms of $O(\sigma, \bar{\sigma})$ etc. are neglected for large z the flow equations governing the distribution of pressure, velocity etc. are of closed form and can be solved independently of the rate equation. (This solution is of course, influenced by the known coupled solution for $z = O(1)$.) The distribution of σ and s is then found from the rate equation utilising this basic solution for the flow variables. Solutions of a similar system of equations have been given in Blythe (1963a,b). These papers were concerned with the case $\sigma \ll 1$ for all z . The techniques used there can be extended to the present case where $\sigma \ll 1$ only for $z \gg 1$.

4.2 Solution for the flow variables

From equation (2.24)

$$\begin{aligned}
 p &= z^{-\frac{\gamma}{\gamma-1}} \exp \int_1^z y \frac{d}{dy} \left\{ \bar{\sigma}(1+s) \right\} dy \\
 &= z^{-\frac{\gamma}{\gamma-1}} \exp \int_1^z y \frac{d\sigma}{dy} dy
 \end{aligned}$$

The integral in this expression is re-written

$$\int_1^z z \frac{d\sigma}{dz} = \int_1^{z^*} y \frac{d}{dy} \left(\bar{\sigma}(1+s) \right) dy + \int_{z^*}^z y \frac{d\sigma}{dy} dy$$

where z^* is large, but is assumed to be in the domain where the near-equilibrium solution is valid, i.e. $z^* < \Phi$. For large z , σs , where s is given by equation (3.7), becomes exponentially small and the upper limit in the first term in the above expression can be replaced by infinity (neglecting terms which are exponentially small). The second term contains the contribution from the region in the neighbourhood of and downstream of the turning point, where the near-equilibrium perturbation solution is no longer valid. This term is negligible if $z \frac{d\sigma}{dz}$ approaches zero "quickly enough" for large z . Such a requirement is somewhat more restrictive than merely asking that terms $O(\sigma)$ be negligible. However, this assumption can be justified, a posteriori, when the precise orders of magnitude of the various terms can be written down. [It turns out to be necessary to assume that terms $O(\sigma \log \sigma)$ are negligible in this region]. It then follows that

$$p = P(\Lambda) z^{-\frac{\gamma}{\gamma-1}} \quad \dots (4.2)$$

where

$$P(\Lambda) = \exp \left\{ \int_1^\infty z \frac{d}{dz} \left[\bar{\sigma}(1+s) \right] dz \right\}, \quad \dots (4.3)$$

s is given by (3.2), and

$$P(\Lambda) = P_0 + \frac{1}{\Lambda} P_1 + \dots \quad \dots (4.4)$$

where

$$\left. \begin{aligned} P_0 &= \exp \left\{ \int_1^\infty z \frac{d\bar{\sigma}}{dz} dz \right\} = (1 - e^{-\theta}) e^{-\bar{\sigma}_0} \\ P_1 &= P_0 \int_1^\infty z \frac{d}{dz} \left(-\frac{1}{F_0} \frac{d\bar{\sigma}}{dz} \right) dz \end{aligned} \right\} \dots (4.5)$$

etc.

From equation (2.25) for $z \gg 1$, neglecting terms $O(\sigma)$

$$v = \left[v_0^2 + \frac{2}{\gamma-1} \left(1 - \frac{1}{z} \right) + \frac{2\bar{\sigma}_0}{\gamma} \right]^{\frac{1}{2}} \dots (4.6)$$

Note that this expression is independent of Λ , though it does depend on conditions at $z = 1$. For any given $A(x)$, $x = x(z, \Lambda)$ follows from equations (2.15), (4.2) and (4.6). Similarly the asymptotic expansion for $F(z, s)$ is given by*

$$F(z, s) = F_{0A}(z) + \frac{1}{\Lambda} F_{1A}(z) + \dots \dots (4.7)$$

where the $F_{iA}(z)$ are the asymptotic expansions of the $F_i(z)$ (neglecting terms $O(\sigma)$ etc.).

The retention of terms $O(\Lambda^{-1})$, though neglecting terms $O(\sigma)$ etc., can also be justified a posteriori, since it is shown that for $z \gg 1$ σ is exponentially small with respect to Λ .

4.3 Form of rate equation for z large

Under similar assumptions the rate equation becomes

$$\frac{ds}{dz} + \left[\Lambda F_A(z, \Lambda) - \theta \right] s = \theta \dots (4.8)$$

where $F_A(z, \Lambda)$ is given by equation (4.7). A new independent

*It is assumed that $x = x(z, \Lambda)$ has a valid expansion of the type $x = \sum \frac{1}{\Lambda^i} x_i(z)$ for large z , which e.g. requires that $\frac{x_{i+1}(z)}{x_i(z)}$ is at most $O(1)$ for large z .

variable $\xi = z/\Phi$ is defined, where Φ is now to be interpreted as the root of

$$\Lambda F_A(z, \Lambda) - \theta = 0 \quad \dots (4.9)$$

In terms of ξ equation (4.8) can be written

$$\frac{1}{N} \frac{ds}{d\xi} + [G(\xi, N, \Lambda) - 1]s = 1 \quad \dots (4.10)$$

where

$$N = \theta\Phi \quad \dots (4.11)$$

and

$$G(\xi, N, \Lambda) = \frac{F_A(z, \Lambda)}{F_A(\Phi, \Lambda)} \quad \dots (4.12)$$

Note for $\Lambda \gg 1$, $N \gg 1$. Equation (4.10) is simply a first order linear differential equation and the general solution can be written down in terms of the appropriate integral (Blythe 1963a). The solution in any region can then be obtained via suitable expansions, for $N \gg 1$, of this integral. A second approach is to consider the behaviour of the differential equation rather than the integral, in the various regions of interest (Blythe, 1963b). This latter approach probably yields more insight into the structure of the solution and the technique can be applied to equations of greater complexity than (4.11) (e.g. the non-linear asymptotic form of the rate equations governing dissociation and ionization Blythe 1963b). The second approach will be described here because of this greater generality. As already noted this technique has previously been applied to the solution of a similar type of equation (Blythe 1963b), though in that case $\theta \gg 1$ and Φ was $O(1)$. Here θ is $O(1)$ but $\Phi \gg 1$. Both cases satisfy $N \gg 1$.

In general

$$G(\xi, N, \Lambda) = \sum_{i=0}^{\infty} \Lambda^{-i} G_i(\xi, N) \quad \dots (4.13)$$

where $G_0(1, N) = 1$ and $G_i(1, N) = 0$, $i \geq 1$ [The remarks on the validity of the expansion of $x = x(z, \Lambda)$ for large z ensure the validity of the expansion for G]. In order to proceed further it is necessary to know the expansions of the $G_i(\xi, N)$ for $N \gg 1$. In fact the exact details of the approach depend completely on the form of the $G_i(\xi, N)$. As an example,

the class of functions $G_i(\xi, N)$ which have expansions of the form

$$G_i(\xi, N) = G_{i0}(\xi) + \frac{1}{N} G_{i1}(\xi) + \frac{1}{N^2} G_{iR}(\xi, N) \dots \quad (4.14)$$

[where $G_{iR}(\xi, N)$ is $O(1)$, $G_{ij}(1) = 0$, save for $i = j = 0$, when $G_{00}(1) = 1$] will be considered. This is a fairly general class of functions and includes, for a suitable temperature dependence of the relaxation frequency, flows in which $A \sim x^n$ for large z (provided $\gamma < 3/2$). Types of temperature dependence permissible include, for example, the exponential form given in (2.4), any power law dependence, and also combinations of both these forms, i.e. $\Omega \sim T^{-r} e^{bT}$. Note that if $A \sim x^n$ for large z it follows that N is $O(\Lambda^{\frac{1}{m}})$ where $m = \frac{n\gamma-1}{n(\gamma-1)}$.

Associated with equation (4.10) are three regions of interest. Firstly the region $\xi < 1$ where $G(\xi, N) - 1$ is $O(1)$. It appears that in this case some suitable perturbation solution (expansion in inverse powers of N for the leading terms, if (4.14) is valid) is applicable. The system of equations in this region is again of lower order than (4.10). The region $\xi \sim 1$, where $G(\xi, N) - 1$ is now "small", is a transition region in which s can be expected to increase rapidly. Finally, for $\xi > 1$, it can be shown that s becomes exponentially large, though $\bar{\sigma}s$ remains finite. The solutions applicable to each of these three regions are derived below.

4.4 Solution for $\xi < 1$

In the region $\xi < 1$ a perturbation solution of the type

$$\begin{aligned} s = & E_{00}(\xi) + \frac{1}{N} E_{01}(\xi) + \dots \\ & + \frac{1}{\Lambda} (E_{10}(\xi) + \frac{1}{N} E_{11}(\xi) + \dots \\ & + \frac{1}{\Lambda^2} (\dots) \dots \quad (4.15) \end{aligned}$$

is sought. [This form of expansion may only be applicable to the leading terms, see equation (4.14). The general term depends on the form of $G_{iR}(\xi, N)$]. It follows from (4.10)

and (4.14) that

$$E_{00}(\xi) = \frac{1}{G_{00}(\xi)-1}, \quad E_{01}(\xi) = \frac{G'_{00}(\xi)}{[G_{00}(\xi)-1]^{\frac{3}{2}}}$$

$$E_{10}(\xi) = \frac{-G_{10}(\xi)}{[G_{00}(\xi)-1]^2}$$

... (4.16)

etc.

While it is convenient to derive the solution in this form it is necessary to know the relative orders of magnitude of N and Λ in order to write down the error involved in stopping at any given term, i.e. if one used only the terms given in (4.16) the error term is either $O\left(\frac{1}{N^2}\right)$ or $O\left(\frac{1}{\Lambda^2}\right)$. This relationship is supplied by equation (4.9) for a given $F_A(z)$.

By considering the behaviour of this solution for small ξ , where G becomes large, and the behaviour of the near equilibrium perturbation solution of section 3 for large z it can readily be shown that the two solutions match provided terms $O(\sigma)$ etc. are neglected in the near equilibrium solution for large z . Thus (4.16) represents a valid outer limit of the near equilibrium solution.

4.5 Solution near $\xi = 1$

As $\xi \rightarrow 1$ the perturbation solution breaks down, since $G_{00}(1) = 1$, and in this region the derivative term becomes important. It is appropriate to seek a solution of the form (Blythe, 1963b)

$$s = N^{\frac{1}{2}}S_{00}(u) + S_{01}(u) + O(N^{-\frac{1}{2}})$$

$$+ \frac{1}{\Lambda} (N^{\frac{1}{2}}S_{10}(u) + S_{11}(u) + \dots)$$

$$+ \dots \quad \dots (4.17)$$

where

$$u = N^{\frac{1}{2}}(\xi-1) \quad \dots (4.18)$$

In the neighbourhood of $\xi = 1$

$$G_0(\xi, N) = 1 + \frac{u}{N^{\frac{1}{2}}} G'_{00}(1) + \frac{1}{2} \frac{u^2}{N} G''_{00}(1) + \dots$$

$$+ \frac{1}{N} \left(\frac{u}{N^{\frac{1}{2}}} G'_{01}(1) + \dots \right)$$

$$+ \dots \quad \dots (4.19)$$

and for $i \geq 1$

$$\begin{aligned}
 G_i(\xi, N) &= \frac{u}{N^{\frac{1}{2}}} G'_{i0}(1) + \frac{1}{2} \frac{u^2}{N} G''_{i0}(1) + \dots \\
 &+ \frac{1}{N} \left(\frac{u}{N^{\frac{1}{2}}} G'_{i1}(1) + \dots \right) \\
 &+ \dots \qquad \qquad \qquad \dots \quad (4.20)
 \end{aligned}$$

From equations (4.10) and (4.17) through (4.20) it follows that

$$\left. \begin{aligned}
 \frac{dS_{00}}{du} + G'_{00}(1) u S_{00} &= 1 \\
 \frac{dS_{01}}{du} + G'_{00}(1) u S_{01} &= -\frac{1}{2} G''_{00}(1) u^2 S_{00}
 \end{aligned} \right\} \dots (4.21)$$

$$\frac{dS_{10}}{du} + G'_{00}(1) u S_{10} = -G'_{10}(1) u S_{00} \qquad \dots (4.22)$$

etc.

The solutions of these equations can be written

$$\left. \begin{aligned}
 S_{00} &= B_{00} \exp\left\{-\frac{1}{2} G'_{00}(1) u^2\right\} + \frac{\exp\left\{-\frac{1}{2} G'_{00}(1) u^2\right\}}{\left(\frac{-2G'_{00}(1)}{\pi}\right)^{\frac{1}{2}}} \left[1 + \operatorname{erf}\left\{\left(\frac{-G'_{00}(1)}{2}\right)^{\frac{1}{2}} u\right\}\right] \\
 \frac{2}{G''_{00}(1)} S_{01} &= (B_{01} - \frac{1}{3} u^3 B_{00}) \exp\left\{-\frac{1}{2} G'_{00}(1) u^2\right\} \\
 &- \frac{1}{3} u^3 \frac{\exp\left\{-\frac{1}{2} G'_{00}(1) u^2\right\}}{\left(\frac{-2G'_{00}(1)}{\pi}\right)^{\frac{1}{2}}} \left[1 + \operatorname{erf}\left\{\left(\frac{-G'_{00}(1)}{2}\right)^{\frac{1}{2}} u\right\}\right] \\
 &+ \frac{1}{3} \frac{u^2}{G'_{00}(1)} - \frac{2}{3} \cdot \frac{1}{[G'_{00}(1)]^{\frac{3}{2}}}
 \end{aligned} \right\} \dots (4.23)$$

$$\frac{1}{G'_{10}} S_{10} = (B_{10} - \frac{1}{2}u^2 B_{00}) \exp \{-\frac{1}{2} G'_{00}(1)u^2\} - \frac{1}{2} \left(u^2 + \frac{1}{G'_{00}(1)} \right) \frac{\exp\{-\frac{1}{2}G'_{00}(1)u^2\}}{\left[\frac{-2G'_{00}(1)}{\pi} \right]^{\frac{1}{2}}} \left[1 + \operatorname{erf} \left\{ \left(\frac{-G'_{00}(1)}{2} \right)^{\frac{1}{2}} u \right\} \right] - \frac{u}{2G'_{00}(1)} \dots (4.24)$$

etc.

The undetermined constants B_{ij} are found by considering conditions at the upstream edge of this layer. From equations (4.22) and (4.24), as $u \rightarrow -\infty$

$$\left. \begin{aligned} S_{00} &\sim B_{00} \exp\{-\frac{1}{2}G'_{00}(1)u^2\} + \frac{1}{G'_{00}(1)} \cdot \frac{1}{u} + \frac{1}{[G'_{00}(1)]^2} \cdot \frac{1}{u^3} + \dots \\ \frac{2}{G'_{00}(1)} S_{01} &\sim (B_{01} - \frac{1}{3}u^3 B_{00}) \exp\{-\frac{1}{2}G'_{00}(1)u^2\} - \frac{1}{[G'_{00}(1)]^2} - \frac{1}{[G'_{00}(1)]^3} \cdot \frac{1}{u^2} \dots \\ \frac{1}{G'_{10}(1)} S_{10} &\sim (B_{10} - \frac{1}{2}u^2 B_{00}) \exp\{-\frac{1}{2}G'_{00}(1)u^2\} - \frac{1}{[G'_{00}(1)]^2} \cdot \frac{1}{u} \dots \end{aligned} \right\} \dots (4.25)$$

However, by considering the behaviour of the solution given by (4.16) as $\xi \rightarrow 1$ it follows that the solutions match only if the $B_{ij} = 0$. Thus within the transition layer the solution can be written

$$s = N^{\frac{1}{2}} L(u) + \frac{G''_{00}(1)}{2} \left[-\frac{u^3}{3} L(u) + \frac{1}{3} \frac{u^2}{G'_{00}(1)} - \frac{2/3}{[G'_{00}(1)]^2} \right] + O(N^{-\frac{1}{2}}) + \frac{G'_{10}(1)}{\Lambda} \left\{ N^{\frac{1}{2}} \left[-\frac{1}{2} \left(u^2 + \frac{1}{G'_{00}(1)} \right) L(u) - \frac{u}{2G'_{00}(1)} \right] + O(1) \right\} + O\left(\frac{N^{\frac{1}{2}}}{\Lambda^2}\right) \dots (4.26)$$

where

$$L(u) = \frac{\exp\{-\frac{1}{2}G'_{00}(1)u^2\}}{\left(\frac{-2G'_{00}(1)}{\pi}\right)} \left[1 + \operatorname{erf} \left\{ \left(\frac{-G'_{00}(1)}{2} \right)^{\frac{1}{2}} u \right\} \right] \dots (4.27)$$

4.6 Solution for $\xi > 1$

As ξ increases s becomes exponentially large and including only the dominant terms the rate equation reduces to

$$\frac{1}{N} \frac{ds}{d\xi} + \left[\sum_{i=0} \Lambda^{-i} G_1(\xi, N) - 1 \right] s = 0 \dots (4.28)$$

The next term in the asymptotic solution for $\xi > 1$ could apparently be derived by a formal expansion of the type

$$s = s_{A0} + \bar{\sigma} s_{A1} + \dots$$

but the higher order terms cannot justifiably be found from (4.10) since terms which are exponentially small have already been neglected in deriving this equation.

From equation (4.28)

$$s = K \exp \left\{ N \int_1^{\xi} \left[1 - \sum_{i=0} \Lambda^{-i} G_i(\psi, N) \right] d\psi \right\} \dots (4.29)$$

where ψ is a dummy variable. In order to determine K consider the behaviour of (4.29) as $\xi \rightarrow 1$. It is seen that, in terms of the independent variable u

$$s \sim K \exp \left\{ -\frac{1}{2} G'_{00}(1) u^2 \right\} \left[1 - \frac{u^3}{6N^{\frac{1}{2}}} \cdot G''_{00}(1) + \dots \right. \\ \left. + \frac{1}{\Lambda} \left(-\frac{1}{2} u^2 G'_{10} + \dots \right) \right. \\ \left. + \dots \right] \dots (4.30)$$

By comparison with the behaviour of the transition layer

solution as $u \rightarrow \infty$ it follows that the expressions match if

$$K = \left[\frac{2\pi}{-G'_{00}(1)} \right]^{\frac{1}{2}} N^{\frac{1}{2}} + \dots \quad \dots (4.31)$$

where the error term is either $O(N^{-\frac{1}{2}})$ or $O\left[\frac{N^{\frac{1}{2}}}{\Lambda^2}\right]$. Note that K does not contain a term $O(N^{\frac{1}{2}}/\Lambda)$, but it does contain a term $O\left(\frac{1}{\Lambda}\right)$.

It follows from (4.31), and (4.29) that the asymptotic frozen level of Λ is given by

$$\frac{\sigma}{\bar{\sigma}_f} = \left[\frac{2\pi}{-G'_{00}(1)} \right]^{\frac{1}{2}} N^{\frac{1}{2}} \exp \left\{ -N \int_1^{\infty} G_{00}(\xi) d\xi - \frac{N}{\Lambda} \int_1^{\infty} G_{10}(\xi) d\xi - \int_1^{\infty} G_{01}(\xi) d\xi \right\} \quad \dots (4.32)$$

where $\bar{\sigma}_f$ is the value of $\bar{\sigma}$ at $\xi = 1$, i.e.

$$\bar{\sigma}_f = \theta e^{-N} \quad \dots (4.33)$$

4.7 Summary

The results of the foregoing analysis are summarized in the table given below

Domain	Independent variable	Dependent variable	Solution
$z \sim 1$	$v = \Lambda(z-1)$	$s = \sum_{i=0} \Lambda^{-i} \zeta_i(v)$	See Appendix
$z > 1$	z	$s = \sum_{i=0} \Lambda^{-i} S_i(z)$	See section 3.3
$z \gg 1$	$\xi < 1$ $\xi = z/\Phi$	$s = \sum_{i=j=0} \Lambda^{-i} N^{-j} E_{ij}(\xi)$	Equation 4.16
	$\xi \sim 1$ $u = N^{\frac{1}{2}}(\xi-1)$	$s = N^{\frac{1}{2}} \sum_{i=j=0} \Lambda^{-i} N^{-\frac{1}{2}j} S_{ij}(u)$	Equations 4.25
	$\xi > 1$	s is exponentially large	Equations (4.29) and (4.31)

5. Example: asymptotic frozen levels for flow through a hyperbolic nozzle

The specific case of flow through the hyperbolic nozzle

$$A = 1 + x^2 \quad \dots (5.1)$$

($v_e = 0$), is used to illustrate the approach. It is assumed that the relaxation frequency is given by an expression of the form (2.4), i.e.

$$\Omega(z) = \exp\left\{\frac{b}{\theta} \left(\frac{1}{z} - 1\right)\right\} \quad \dots (5.2)$$

It follows that

$$G_{00}(\xi) = \xi^{-\left(\frac{2\gamma-1}{2(\gamma-1)}\right)}$$

$$G_{01}(\xi) = \left(b + \frac{(3-2\gamma)\theta}{4\left[1 + \frac{\gamma-1}{\gamma}\bar{\sigma}_e\right]}\right) \left(\frac{1}{\xi} - 1\right) \xi^{-\left(\frac{2\gamma-1}{2(\gamma-1)}\right)} \quad \dots (5.3)$$

etc.

$$\text{and } G_{10} = G_{11} = G_{12} = 0 \quad i \geq 1 \quad (\gamma < \frac{3}{2})$$

From equation (4.32) it is seen that the asymptotic limiting values are given by

$$\frac{\sigma}{\bar{\sigma}_f} = c_0 \left(N^{\frac{1}{2}} + O(N^{-\frac{1}{2}})\right) \exp\{-c_1 N - c_2\} \quad \dots (5.4)$$

where

$$\left. \begin{aligned} c_0 &= \left\{ \frac{4\pi(\gamma-1)}{2\gamma-1} \right\}^{\frac{1}{2}} \\ c_1 &= 2(\gamma-1) \\ c_2 &= \frac{2(\gamma-1)}{2\gamma-1} - 2(\gamma-1) \left\{ b + \frac{3-2\gamma}{4\left(1 + \frac{\gamma-1}{\gamma}\bar{\sigma}_e\right)} \right\} \end{aligned} \right\} \quad \dots (5.5)$$

and

$$\bar{\sigma}_f = \theta \exp - N \quad \dots (5.6)$$

Also, using equation 4,9

$$\Lambda = Q_0 N^{\frac{2\gamma-1}{2(\gamma-1)}} \left[1 - \left\{ b + \frac{(3-2\gamma)\theta}{4(1+\frac{\gamma-1}{\gamma}\bar{\sigma}_e)} \right\} \frac{1}{N} + O\left(\frac{1}{N^2}\right) \right] \quad \dots (5.7)$$

where

$$Q_0 = \frac{2(\gamma-1) e^{b/\theta} \theta^{-\frac{1}{2(\gamma-1)}} \left[\frac{2}{\gamma-1} + \frac{2\bar{\sigma}_e}{\gamma} \right]^{\frac{3}{4}}}{(P_0 m_0)^{\frac{1}{2}}} \quad \dots (5.8)$$

Note that N is $O\left(\Lambda^{\frac{2(\gamma-1)}{2\gamma-1}}\right)$, i.e. N is $O\left(\Lambda^{4/9}\right)$ for

$\gamma = 7/5$. This fairly weak dependence of N on Λ implies that the asymptotic series will only converge rapidly for values of Λ that are numerically very large indeed.

In general, for nozzles which grow asymptotically as powers of x similar expressions hold* (though it is necessary to know the shape of the nozzle for $x = O(1)$ in order to determine the constants P_1 and m_1 ($i \geq 1$) etc.). It is interesting to note that for a nozzle which is asymptotically wedge shaped, with the relaxation frequency given by (5.2), $\sigma \rightarrow 0$ asymptotically, though it does depart from the equilibrium distribution for large z . This result is a consequence of the assumed temperature dependence of Ω . Any deviation from this dependence of the type

$$\Omega \sim z^{-s} \exp\left\{ -\frac{b}{z} (1 - 1) \right\} \quad s > 0 \quad \dots (5.9)$$

would invalidate this conclusion.

6. Concluding remarks

The error in neglecting $\int_{z^*}^{\infty} y \frac{d}{dy} \{ \bar{\sigma}(1+s) \} dy$ and

$\int_{z^*}^z y \frac{d\sigma}{dz} dy$ in equation (4.2), where s in these expressions is

given by the near-equilibrium solution and σ by the solution for $z \gg 1$, can be shown to be $O(N \exp\{-cN\})$ where

Provided $\int_{z^}^z y d\sigma$ remains small for large z .

$c = c(\xi^*)$ is $O(1)$, for the hyperbolic nozzle defined by (5.1). It follows that all the error terms in the various asymptotic solutions are exponentially small with respect to N and it is correct to retain terms $O(\Lambda^{-1}, N^{-1})$ etc.

The solution has been presented for a specific form of the $G_i(\xi, N)$. The extension to other cases, where $\Omega(z)$ and $A(x)$ are such that the $G_i(\xi, N)$ are not given by expansions of this form, can easily be carried out via similar matching procedures.

The asymptotic approach of σ to some constant non-zero value, or freezing of the energy in the lagging mode, has been the subject of much discussion. Many approximate methods exist for determining this asymptotic value, the most common of which is that due to Bray (1959). This approach, the sudden-freeze approach, is based on the prediction, by means of a qualitative argument of a "freezing point". Upstream of this point the flow is assumed to remain in equilibrium while downstream of it σ remains constant at its equilibrium value at the freezing point. It is interesting to note, that the position of Bray's freezing point is given by a criterion of the form which defines the turning point of the rate equation. However the analysis presented here shows that $\sigma/\bar{\sigma}_f$ is not $O(1)$ as $z \rightarrow \infty$ (see equations (4.29) and (4.31) for the present case. Extension to other cases e.g. the flow of a dissociating gas, also shows that $\sigma/\bar{\sigma}_f$ is not asymptotically of $O(1)$. Insofar as the flow of a dissociating gas is concerned it would appear that the sudden freeze approach gave good agreement with exact numerical calculations. This agreement, which is perhaps fortuitous, can probably be accounted for by the slow convergence of the asymptotic series in some practical cases.

Acknowledgement

This paper is published by permission of the Director, National Physical Laboratory.

Appendix

Solution near $z = 1$

At $z = 1$ $s = 0$, and for all finite $F(1,0)$ the perturbation solution is singular there. However, for the class of flows in which $v_e = 0$ (convergent-divergent nozzle) $F(1,0)$ is infinite (as $z \rightarrow 1$ $F \sim \frac{1}{(z-1)^n}$, apart from some numerical factor) and the perturbation solution is valid up to and including $z = 1$.

When F is finite at $z = 1$ it is necessary to modify the perturbation solution near $z = 1$. In this region the derivative term is important and the appropriate independent variable is (Bloom and Ting (1960), Napolitano (1962))

$$v = \Lambda(z-1) \quad \dots (A.1)$$

and a solution of the form

$$s = \frac{1}{\Lambda} \zeta_1(v) + \frac{1}{\Lambda^2} \zeta_2(v) + \dots \quad \dots (A.2)$$

is sought. The function $F(z,s)$ will still have an expansion of the form

$$F(z,s) = F_0(z) + O\left(\frac{1}{\Lambda}\right) \quad \dots (A.3)$$

where F_0 , as for $z > 1$, is given by the equilibrium solution. Consequently, in terms of v

$$F(z,s) = F_0(1) + O\left(\frac{1}{\Lambda}\right) \quad \dots (A.4)$$

and neglecting terms $O\left(\frac{1}{\Lambda}\right)$ in the rate equation gives

$$\frac{d\zeta_1}{dv} + F_0(1)\zeta_1 = \left(-\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz}\right)_{z=1} \quad \dots (A.5)$$

$$\zeta_1 = \frac{\left(-\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz}\right)_{z=1}}{F_0(1)} \left[1 - \exp\{-F_0(1)v\}\right] \quad \dots (A.6)$$

using the boundary condition that $s = 0$ on $v = 0$. It then

follows that as $\nu \rightarrow \infty$

$$s \sim \frac{\left(-\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz}\right)_{z=1}}{F_0(1)} + O\left(\frac{1}{\Lambda}\right)$$

which is in agreement with the first term of the outer solution (equation 3.7) as $z \rightarrow 1$. It can be shown in similar fashion that terms of $O\left(\frac{1}{\Lambda^2}\right)$ etc. match and it follows that (3.7) represents a valid outer limit of the solution valid near $z = 1$.

A uniformly valid solution for $z \geq 1$ can be written down using the usual technique, i.e.

Uniformly valid solution = Outer solution + Inner solution

- Inner expansion (Outer solution).

Thus, neglecting terms $O\left(\frac{1}{\Lambda^2}\right)$ a uniformly valid solution is

$$s = \frac{1}{\Lambda} \left[\frac{1}{F_0(z)} \left(-\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz}\right) - \frac{\left(-\frac{1}{\bar{\sigma}} \frac{d\bar{\sigma}}{dz}\right)_{z=1}}{F_0(1)} \exp\{-F_0(1)\nu\} \right] \dots \quad (A.7)$$

The solutions for v_1 , p_1 etc. follow, as before, from equations (2.24) and (2.25).

References

- BLACKMAN, V. H. - 1956, Vibrational relaxation in oxygen and nitrogen, J. Fluid Mech. 1, 61
- BLOOM, M. H. and TING, L. - 1960, On near-equilibrium and near-frozen quasi-one-dimensional flow AEDC-TN-60-156 PIBAL-R-525
- BLYTHE, P. A. - 1963a, Non-equilibrium flow through a nozzle, J. Fluid Mech. 17, 126
- BLYTHE, P. A. - 1963b, Asymptotic solutions in non-equilibrium nozzle flow NPL Aero Report 1071, ARC 25,105 Hyp 354
- BRAY, K. N. C. - 1959, Atomic recombination in a hypersonic wind tunnel nozzle, J. Fluid Mech. 6, 1
- HERZFELD, K. F. and LITOVITZ, T. A. - 1959, Absorption and Dispersion of Ultrasonic Waves, Academic Press
- LANDAU, L. and TELLER, E. - 1936, Zur Theorie der Schalldispersion Phys. Z. Sowjet 10, 34
- NAPOLITANO, L. G. - 1962, On two new methods for the solution of non-equilibrium flows. University of Naples I.A. Report No. 42
- ROSNER, D. E. - 1962, Estimation of electrical conductivity at rocket nozzle exit sections
- SHULLER, K. E. - 1959, Relaxation processes in multistate systems. Phys of fluids 2, 442
- STOLLERY, J. L. and PARK, C. - 1963, Computer solutions to the problem of vibrational relaxation in hypersonic nozzle flows. Imperial College, Aeronautics Department Report No. 115
- ZIENKIEWICZ, H. K. and JOHANNESSEN, N. H. - 1963, Departures from the linear equation for vibrational relaxation in shock waves in oxygen and carbon dioxide. J. Fluid Mech. 17, 499

© *Crown copyright 1967*

Printed and published by
HER MAJESTY'S STATIONERY OFFICE

To be purchased from
49 High Holborn, London W C 1
423 Oxford Street, London W 1
13A Castle Street, Edinburgh 2
109 St Mary Street, Cardiff
Brazenose Street, Manchester 2
50 Fairfax Street, Bristol 1
35 Smallbrook, Ringway, Birmingham 5
7 - 11 Linenhall Street, Belfast 2
or through any bookseller

Printed in England