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Asymptotic solutions in non-equilibrium nozzle flow

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Analytical solutions for the quasi-one-dimensional flow of a gas not in thermodynamic equilibrium are presented for two distinct types of rate equation, namely, the linear rate equation which governs vibrational relaxation, and the non-linear rate equation which governs dissociation. The solutions are derived for the case when, to a first approximation, the rate equation is uncoupled from the remaining flow equations.

There are, in general, three distinct regions in non-equilibrium nozzle flow. First, a so-called near equilibrium region where a perturbation solution is expected to hold. This region is followed by a narrow transition-layer in which there is a rapid departure from equilibrium. Finally, downstream of this layer, the energy in the lagging mode tends asymptotically to some constant 'frozen-out' value. The solutions applicable to each of these three regions are derived for both rate equations, the boundary conditions for the transition-layer solution and the asymptotic solution are obtained from appropriate matching procedures.

In particular the structures of the asymptotic solutions are discussed. Several approximate methods for determining the asymptotic frozen level of the energy in the lagging mode have been proposed in the literature. For the present case, when there is only a small amount of energy in the lagging mode, it is shown that none of these approximate methods is mathematically correct.

1. Introduction

There exist many numerical solutions to the problem of non-equilibrium quasi-one-dimensional flow through a nozzle. These solutions have been obtained for several types of rate process. Non-equilibrium dissociation has been treated, for example, by Bray (1959), Freeman (1959), and Hall & Russo (1959); non-equilibrium ionization has been discussed, for example, by Smith (1958), Bray & Wilson (1961), Eschenroeder (1962), and Rosner (1962); the effects of vibrational relaxation have been investigated by Stollery & Smith (1962), and Stollery & Park (1963). All these papers showed quite clearly the characteristic feature of this type of flow, namely, the eventual 'freezing-out' of the energy σ in the lagging mode. In detail, the numerical solutions showed that initially σ followed closely its local equilibrium value $\bar{\sigma}$, but that at sufficiently large distances downstream there was a rapid increase in the departure from equilibrium and σ quickly approached some final asymptotic non-zero value (see figure 1).

This effect has important practical consequences since, for example, it can lead to appreciable departures from equilibrium in hypersonic wind tunnels, shock tunnels, etc., and also to loss of thrust in rocket nozzles, etc. Consequently, several of the above-named authors have presented approximate methods for obtaining this asymptotic frozen value.

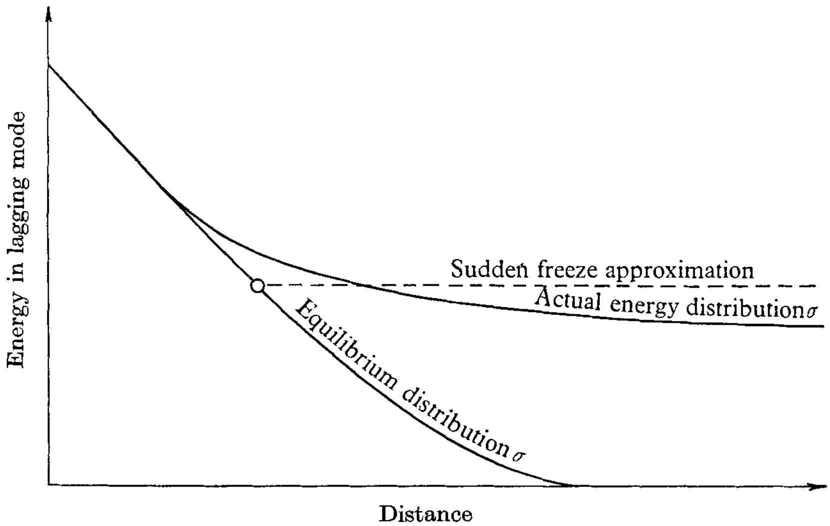

FIGURE 1. Distribution through the nozzle of the energy in the lagging mode (schematic). ○, Freezing point.

The 'sudden-freeze' approach discussed by Bray (1959), is perhaps the simplest of these approximate methods and is probably the one most widely used in practice. The approach is based on the prediction, by qualitative arguments, of a 'freezing point' which characterizes the position of the region where the rapid departure from equilibrium occurs. Upstream of this point it is assumed that σ is equal to its equilibrium value, while downstream of the freezing point it is assumed that σ remains constant at its equilibrium value at the freezing point (see figure 1). Hall & Russo (1959) and, for example, Tsuchiya (1962) have also used Bray's approach: the difference between the respective treatments is in the definition of the freezing point.

Both Smith (1958) and Rosner (1962) (see also Eschenroeder 1962) have pointed out that in order to obtain the correct asymptotic solution one must consider the asymptotic form of the rate equation when $\sigma \gg \bar{\sigma}$. However, they also assumed that this asymptotic solution could be matched directly to the equilibrium solution at some suitable point, which was defined by matching both the asymptotic solution for σ and its derivative to the equilibrium solution.

More recently Stollery & Park (1963) have proposed a further criterion for predicting the asymptotic frozen value. This criterion, which was applied in particular to the linear rate equation governing vibrational relaxation, is empirical in form and is based on the results of their numerical solutions. Essentially the criterion implies that the relaxation length suitably non-dimensionalized, is independent of the (dimensionless) rate parameter, at some freezing point.

Although comparison with exact numerical solutions would lead one to believe that these solutions are reasonable numerical approximations, there is obviously a need for obtaining a mathematically valid asymptotic solution even if only to determine the order of magnitude of the error in the approximate solutions.

In the present paper a thorough investigation of the solutions of the appropriate rate equations for dissociation, ionization, and vibrational relaxation is carried out for the case when, to a first approximation, the rate equation is uncoupled from the remaining flow equations. In order to justify such an assumption it is necessary to assume that σ is small in comparison with the total enthalpy. When σ is sufficiently small it follows (see e.g. Spence 1961) that the first approximation to the solution for the flow variables (velocity, pressure, etc.) is given by the usual isentropic solution with $\sigma = 0$. The first approximation to the distribution of σ is then found by integrating the rate equation using the basic isentropic values of the flow variables. In this limiting case the rate equations for dissociation and ionization are similar in form, both being Ricatti equations. The rate equation governing vibrational relaxation is assumed to be the usual linear one, which is a valid assumption provided that the vibrational mode can be represented by a system of harmonic oscillators and that only a small fraction of the oscillators are excited.

The solution to the linear rate equation governing vibrational relaxation has already been obtained by the author (Blythe 1963) for this uncoupled case. It was shown that the solution for the departure from equilibrium $\sigma - \overline{\sigma}$ depended on an integral of the steepest-descents type. The main contribution to this type of integral comes from the region near the stationary value of the exponential term, i.e. the saddle point (Jeffreys & Jeffreys 1946, p. 472). This saddle point corresponds to the region where freezing becomes important. Upstream of this region the contribution from the integral is small and hence the departure from equilibrium is small. Downstream of the region the integral tends to some constant value and the asymptotic value of the energy σ can be determined. It is interesting to note that the position of the saddle point is given by the type of criterion used by Bray, and by Hall & Russo, etc., to define their freezing points.

However, the behaviour of the solution of this rate equation can be more readily observed by considering the rate equation in terms of a different dependent variable. By using the relative departure from equilibrium $s \equiv (\sigma - \overline{\sigma})/\overline{\sigma}$ as the dependent variable it can be shown that the position of the saddle point is given by the zero of the coefficient of s in the transformed rate equation (see equation (2.10)). Because of the temperature dependence of $\overline{\sigma}$ the transformed equation is simplified if the reciprocal of the translational temperature $T(x)$, rather than the distance x, is used as the independent variable. If the variables are suitably non-dimensionalized with respect to their values at the saddle point, i.e. at the zero of the coefficient of s, it follows that the rate equation takes the form (see §2.1)

$$N^{-1}(ds/d\xi) + [G(\xi) - 1]s = 1, \tag{1.1}$$

where ξ is the appropriate dimensionless form of T^{-1}, i.e. $\xi = 1$ at the saddle points. Near $\xi = 1$ the function $G(\xi)$ can be expanded in the form

$$G(\xi) = 1 + \sum_{n=1}^{\infty} a_n(\xi - 1)^n. \tag{1.2}$$

In general $G(\xi)$ is a decreasing function of ξ and as $\xi \to \infty$, $G(\xi) \to 0$. The definition of N is, for the moment, not important, save that N should be interpreted as a large parameter which increases as the position of the saddle point moves downstream. Equation (1.1) is a simple example of a common type of differential equation in which the coefficient of the highest-order derivative is a small parameter (N^{-1}) and the coefficient of a lower order term possesses a zero (such that a perturbation solution would be singular at this zero).

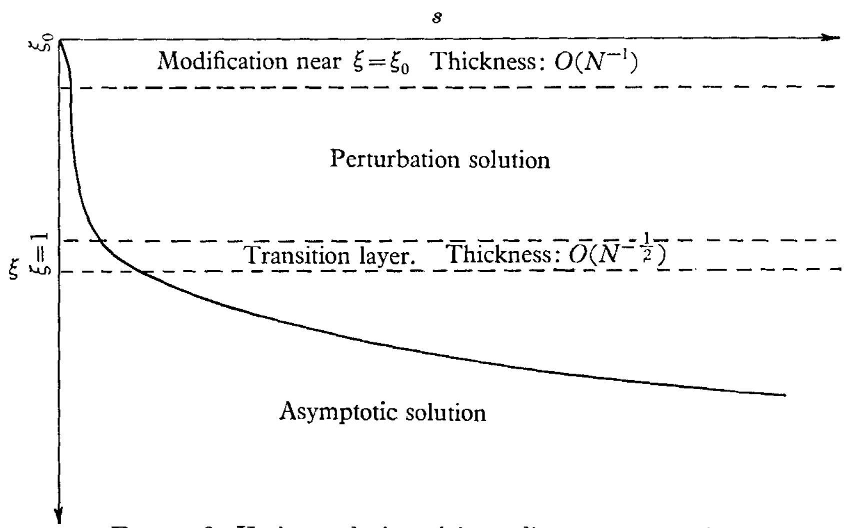

Figure 2. Various solution régimes: linear rate equation.

It is apparent from equation (1.1) that there are three distinct regions of interest. First, there is the region $\xi < 1$ upstream of the saddle point. In this region a perturbation solution is apparently appropriate and this solution corresponds to the usual near equilibrium solution which is expected to hold upstream of the saddle point. Such a solution may need modification near the initial equilibrium station where $s = 0$ if $G(\xi)$ is finite there (Bloom & Ting 1960). This effect (see § 2.2) is confined to a narrow region whose thickness is $O(N^{-1})$. The perturbation solution also breaks down near $\xi = 1$ which is the region corresponding to the rapid transition from the equilibrium solution. The saddle point $\xi = 1$ will henceforth be termed the freezing point in the present analysis. Near $\xi = 1$ the appropriate independent variable is $N^{\frac{1}{2}}(\xi - 1)$. Within this narrow region the derivative term in equation (1.1) becomes important and s grows rapidly. For $\xi > 1$, $G(\xi) \to 0$ and s becomes exponentially large ($\bar{\sigma}$ becomes exponentially small), though σ remains finite and tends to some asymptotic non-zero value. A schematic representation of this picture is given in figure 2.

It is shown in § 2 that the transition layer solution near $\xi = 1$ can be matched on to the perturbation solution (which in turn forms a valid outer limit of the solution near $\xi = \xi_0$ where $s = 0$) by a suitable choice of the arbitrary constant of integration. Moreover, the asymptotic solution, where s is exponentially large, can be matched as $\xi \to 1$ to the transition layer solution at the downstream edge of the transition region. The asymptotic frozen value of the vibrational energy can then be determined. Although the formal solution to (1.1) can be written down, more insight into the problem can probably be obtained by examining the structures of these various regions. In addition, since the full solution of equation (1.1) is known, the validity of the solutions in these various regions can be assessed. This method of solution of equation (1.1) also forms a very useful introduction to the method of solution of the non-linear equations governing dissociation and ionization for which a formal solution cannot be written down.

It was pointed out above that both these non-linear equations, in the present uncoupled case, are Ricatti equations of the same type and consequently the solution for either a dissociating gas or an ionizing gas can be deduced from a single study of such a Ricatti equation. As in the linear case it is preferable to use s as the dependent variable. In terms of s the non-linear rate equation becomes a second Ricatti equation. In the transformed Ricatti equation the coefficient of s again possesses a zero and this zero corresponds to the freezing point (saddle point) in the linear case. The expression defining this zero is again similar in form to the criteria defining the freezing points of Bray, etc. The transformed equation takes the form (see §3.1)

$$N^{-1}(ds/d\xi) + \{H(\xi,N) - Q(\xi,N)\}s + \tfrac{1}{2}H(\xi,N)s^2 = Q(\xi,N), \tag{1.3}$$

where $\xi = 1$ corresponds to the zero of the coefficient of s (the freezing point) and N is again to be interpreted as a large parameter. Also

$$\left.\begin{aligned} H(\xi,N) &= f(\xi)\exp N(1-\xi), \\ Q(\xi,N) &= 1 + N^{-1}\kappa(\xi). \end{aligned}\right\} \tag{1.4}$$

Near $\xi = 1$, $f(\xi)$ and $\kappa(\xi)$ have expansions of the form

$$\left.\begin{aligned} f(\xi) &= 1 + \sum_{n=1}^{\infty} b_n(\xi-1)^n, \\ \kappa(\xi) &= \sum_{n=1}^{\infty} c_n(\xi-1)^n. \end{aligned}\right\} \tag{1.5}$$

In general $\kappa(\xi)$ is bounded and tends to a finite limit as $\xi \to \infty$; $f(\xi)$ is a monotonically decreasing function of ξ and approaches zero as $\xi \to \infty$. Note, however, that $f(\xi_0)$ ($\xi = \xi_0$ at $s = 0$) is not necessarily finite.

The dominant feature in equation (1.3) is the exponential dependence of $H(\xi,N)$ (equation (1.4)) and the solution is naturally more complex in form than in the linear case. However, the solution is still characterized by three distinct regions. For $\xi < 1$ a perturbation type of solution holds and this again corresponds to the usual near-equilibrium solution which is expected to hold in this region. The dominant terms in this region are the linear term $H(\xi,N)s$ on the left-hand side of equation (1.3) and $Q(\xi,N)$ on the right-hand side. This solution, as in the linear case, needs modification near $\xi = \xi_0$, where $s = 0$, if $f(\xi_0)$ is finite. The thickness of this region near $\xi = \xi_0$ is $O(N^{-1}\exp\{-N(1-\xi_0)\})$ (and not $O(N^{-1})$ as in the linear case). The perturbation solution breaks down as $\xi \to 1$ and this region, as before, is characterized by the energy distribution breaking away from the equilibrium distribution. Within this transition region near $\xi = 1$ the appropriate independent variable is $N(\xi - 1)$ and all the terms in equation (1.3) are of the same order of magnitude. Downstream of the freezing point it can be shown that s becomes exponentially large and that the energy in the lagging mode tends asymptotically to some constant value. The overall picture is sketched out in figure 3.

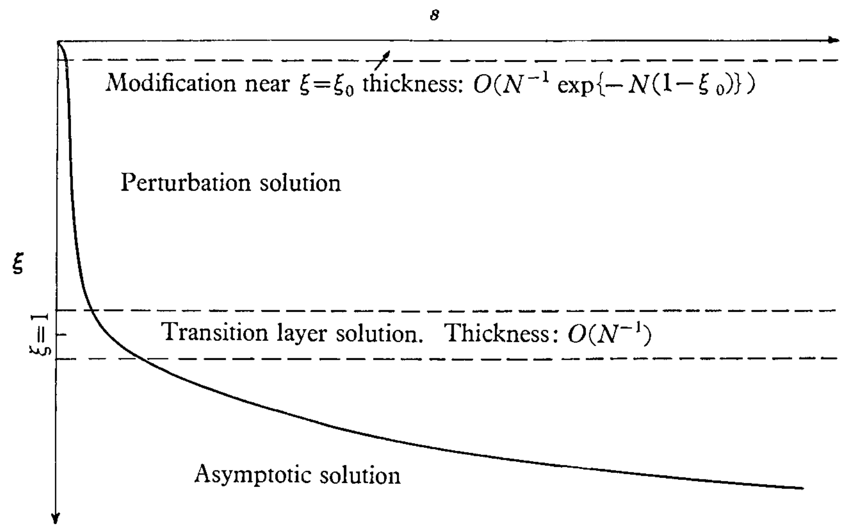

FIGURE 3. Various solution régimes: non-linear rate equation.

In §3 it is shown that the solutions in the various regions can again be matched on to each other by appropriate choice of the arbitrary constants of integration. In particular, in §3.4, the correct value of the asymptotic frozen level of the energy in the lagging mode is derived for either a dissociating or an ionizing gas.

It is apparent from the present analysis that, for both types of rate equation the effect of the transition layer must be taken into account in order to determine correctly the asymptotic frozen level. It is not correct to match the asymptotic solution directly to the equilibrium solution. The implications of this result are considered in detail in §4 with respect to the various approximate asymptotic solutions proposed in the literature.

2. Vibrational relaxation

2.1. *Transformation of rate equation*

This section of the paper is concerned with the quasi-one-dimensional flow of a vibrationally relaxing diatomic gas. The thermodynamic model used assumes that the translational degrees of freedom are fully excited and in a state of local equilibrium, that the gas can be represented in conventional fashion by means of a system of harmonic oscillators, and furthermore that only a small fraction of the oscillators is excited. Under these circumstances the rate equation governing the flow is linear (Shuler 1959) and can be written (Johannesen 1961)

$$v'(d\sigma'/dx') = \rho'\Omega'(T')(\bar{\sigma}'(T') - \sigma'), \tag{2.1}$$

where σ' is the vibrational energy and $\bar{\sigma}'(T')$ its total equilibrium value corresponding to the transitional temperature T', ρ' is the density, v' is the velocity, x' is the distance along the nozzle axis measured from some suitable datum point, and $\Omega'(T')$ is termed the relaxation frequency. The assumption that only a small fraction of the oscillators is excited implies that the translational temperature is much less than the characteristic temperature of vibration. Under this assumption it thus follows that to a first approximation the rate equation is uncoupled from the remaining flow equations since

$$\sigma = \sigma'/RT_0' \ll 1$$

and hence the energy equation, to a first approximation, is independent of σ. Here T_0' is the translational temperature at the initial equilibrium station and R is the usual gas constant. The initial equilibrium station may coincide with upstream stagnation conditions in a convergent-divergent nozzle, or it may represent the initial conditions in a uniform supersonic stream which then undergoes expansion through a divergent nozzle.

In this uncoupled case ($\sigma \ll 1$) the flow variables v', p', etc., are known functions of x', given by the usual isentropic solution for the quasi-one-dimensional flow of an ideal gas, provided the nozzle area distribution is specified (Blythe 1963). Consequently, in this case, equation (2.1) can be rewritten in dimensionless form as

$$d\sigma/dx = \Lambda F_1(x)[\bar{\sigma}(x) - \sigma], \tag{2.2}$$

where

$$\left.\begin{aligned} \sigma = \sigma'/RT_0', \quad \bar{\sigma} = \bar{\sigma}'/RT_0', \\ F_1(x) = \rho(x)\,\Omega(x)/v(x), \quad \Lambda = l\rho_0'\,\Omega_0'/a_0', \\ \rho = \rho'/\rho_0', \quad \Omega = \Omega'/\Omega_0', \quad v = v'/a_0', \quad x = x'/l. \end{aligned}\right\} \tag{2.3}$$

Here l is some suitable nozzle dimension, a' is the frozen speed of sound, and the suffix 0 denotes the value at the initial equilibrium station. Λ is a dimensionless rate parameter and represents the ratio of the flow time scale to the time scale of the relaxation process.

For a system of harmonic oscillators the equilibrium vibrational energy is given by

$$\bar{\sigma}' = R\Theta_v'/(\exp(\Theta_v'/T') - 1), \tag{2.4}$$

where Θ_v' is the characteristic temperature of vibration. A dimensionless characteristic temperature of vibration is defined by $\Theta_v = \Theta_v'/T_0'$ and the basic assumption that only a small fraction of the oscillators is excited implies that $\Theta_v \gg 1$. Hence, from (2.4)

$$\bar{\sigma} = \Theta_v \exp(-\Theta_v/T)[1 + O(\exp(-\Theta_v/T))], \tag{2.5}$$

where $T = T'/T_0'$ and $T \leqslant 1$. The exponential form of this function is of fundamental importance in the analysis and accordingly a new independent variable, defined by

$$z = [T(x)]^{-1}, \tag{2.6}$$

is chosen. Note that $z \geqslant 1$. In terms of this variable the rate equation (2.2) becomes

$$d\sigma/dz = \Lambda F(z)\,[\bar{\sigma}(z)-\sigma], \tag{2.7}$$

where

$$\left.\begin{aligned} F(z) &= \frac{z^{-1/(\gamma-1)}\,\Omega(z)}{[v_0^2+2(\gamma-1)^{-1}(1-z^{-1})]^{\frac{1}{2}}}\frac{dx}{dz},\\ \bar{\sigma}(z) &= \Theta_v \exp(-\Theta_v z). \end{aligned}\right\} \tag{2.8}$$

and

Here γ is the ratio of the specific heats neglecting vibration, i.e. the specific heat ratio corresponding to the basic isentropic flow: $\gamma = \frac{7}{5}$ for a diatomic gas. The known isentropic solution (see, e.g. Shapiro 1953) has been used to express the density and velocity as functions of z. Exponentially smaller terms have been omitted in the expression for $\bar{\sigma}$.

In place of σ a more meaningful dependent variable is the relative departure from equilibrium, s, which is defined by

$$s = (\sigma-\bar{\sigma})/\bar{\sigma}. \tag{2.9}$$

Substitution into equation (2.7) gives

$$\frac{ds}{dz}+\left(\Lambda F(z)+\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{dz}\right)s = -\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{dz}. \tag{2.10}$$

The first term in a conventional near-equilibrium solution (expansion in inverse powers of Λ) is given by balancing the term $\Lambda F(z)s$ on the left-hand side of equation (2.10) with the expression on the right-hand side. This perturbation scheme will apparently break down in the neighbourhood of

$$\Lambda F(z)+\bar{\sigma}^{-1}\,d\bar{\sigma}/dz = 0. \tag{2.11a}$$

(The approach may also break down near $z=1$, where the flow is in equilibrium, since $s = 0$ there but ds/dz may be finite, see §2.3.) The zero of this equation is termed the freezing point since it is characteristic of the region where s becomes large, that is, where the energy distribution breaks away from the equilibrium distribution. In fact, because of the exponential form of $\bar{\sigma}$, equation (2.11a) simplifies to

$$\Lambda F(z) = \Theta_v. \tag{2.11b}$$

The solution of this equation is written as $z = \Phi$ and a further independent variable is defined by $\xi = z/\Phi$. Using equation (2.8) and rearranging equation (2.10), that is scaling with respect to the values at the freezing point, gives

$$N^{-1}\,ds/d\xi+[G(\xi)-1]\,s = 1, \tag{2.12}$$

where

$$N = \bar{\sigma}^{-1}\,d\bar{\sigma}/d\xi = \Theta_v\,\Phi, \tag{2.13}$$

and

$$G(\xi) = F(z)/F(\Phi). \tag{2.14}$$

The simplicity in form of equation (2.12) is worthy of note. Although the corresponding equation derived in Blythe (1963), using the Mach number as the basic independent variable, is similar in structure it is more complex in detail and the advantage of using T^{-1} as the basic independent variable is obvious. In what follows it is assumed that N is a large parameter. This is consistent with the basic assumption that $\Theta_v \gg 1$ and requires that Φ is at least $O(1)$: if $\Phi < 1$ then it is to be expected that near-frozen conditions will hold everywhere since there will be no solution of (2.11*b*) which lies in the nozzle where $z \geqslant 1$.

At this stage some comment on the function $G(\xi)$ seems desirable. There is considerable uncertainty as to what is the correct temperature dependence of $\Omega(T)$. In general it would appear that Ω may contain a dependence on Θ_v (see, e.g., the Landau–Teller theory or the more complex quantum-mechanical calculations of Herzfeld *et al.*; a survey of these theories is given in Herzfeld & Litovitz 1959). Hence, strictly $G = G(\xi, N)$ and consequently the solution presented below for $G = G(\xi)$, although mathematically valid, is subject to the physical limitation that it implies the relaxation frequency to be independent of the characteristic temperature of vibration. Nevertheless, it is felt worth while to examine the solution of equation (2.12) since this equation is the simplest possible case of the type under consideration. The method of approach is easily adapted to cases where $G = G(\xi, N)$.

2.2. *Formal solution*

The full solution of equation (2.12) satisfying the boundary condition $s = 0$ on $\xi = \xi_0 = \Phi^{-1}$ can be written

$$s = N \exp\{N\eta(\xi)\} \int_{\xi_0}^{\xi} \exp\{-N\eta(\psi)\}\, d\psi, \tag{2.15}$$

where
$$\eta(\xi) = \int_1^{\xi} \{1 - G(\psi)\}\, d\psi.$$

The implications of this solution have been considered elsewhere (Blythe 1963). It is sufficient to say here that the integral occurring in (2.15) is of the steepest descents type (Jeffreys & Jeffreys 1946, p. 472) with a dominant contribution from the region near $\xi = 1$. It can be shown that equation (2.15) reduces to the usual near-equilibrium solution upstream of the freezing point. Near $\xi = 1$ the integral grows as an error function, i.e.

$$s \sim \frac{N^{\frac{1}{2}}\pi^{\frac{1}{2}} \exp\{-\frac{1}{2}NG'(1)(\xi-1)^2\}}{(-2G'(1))^{\frac{1}{2}}} [1 + \operatorname{erf}\{N^{\frac{1}{2}}(-\tfrac{1}{2}G'(1))^{\frac{1}{2}}(\xi - 1)\}], \tag{2.16}$$

where the prime denotes differentiation with respect to ξ. Furthermore, it can be seen that asymptotically far downstream of the freezing point

$$\left.\begin{aligned} s &\sim K \exp\{N(\xi-1)\}, \\ \text{or} \qquad \sigma/\bar{\sigma}_f &\to K, \end{aligned}\right\} \tag{2.17}$$

where
$$K = N \exp\left\{-\int_1^{\infty} NG(\psi)\, d\psi\right\} \int_{\xi_0}^{\infty} \exp\{-N\eta(\psi)\}\, d\psi, \tag{2.18}$$

and the suffix f denotes the value at the freezing point. Evaluating the integral by the method of steepest descents gives

$$K = N^{\frac{1}{2}} \left(\frac{2\pi}{-G'(1)}\right)^{\frac{1}{2}} \exp\left\{-\int_1^{\infty} NG(\psi)\, d\psi\right\} \times \left[1 + \frac{1}{4G'(1)} \left\{\frac{G'''(1)}{2G'(1)} + \frac{7}{9}\left(\frac{G''(1)}{G'(1)}\right)^2\right\} \frac{1}{N} + O\left(\frac{1}{N^2}\right)\right]. \tag{2.19}$$

In the subsequent analysis the solution of equation (2.12) will be obtained from an alternative approach. The perturbation solution, valid for $\xi < 1$, of equation (2.12) will be presented, including any necessary modification near $z = 1$. It will be shown that this solution is the correct upstream limit for a solution in the neighbourhood of the freezing point and a matching procedure is developed. The asymptotic solution downstream of the freezing point is then derived. The arbitrary constant in this solution is found by matching the solution, as $\xi \to 1$, to the downstream edge of the transition layer solution which holds in the neighbourhood of the freezing point.

Whilst the various solutions in the different regions can be derived quite easily from (2.15) the analysis presented below is of interest since it shows clearly, for an elementary case, why the near equilibrium solution breaks down, how the rapid transition from the equilibrium solution occurs, and emphasizes that it is not correct to match the asymptotic solution directly to the equilibrium solution. Moreover, this analysis forms a very useful introduction to the similar approach used in §3 for the non-linear rate equation governing dissociation for which the full solution cannot be written down. The existence of the exact solution (2.15) also enables the validity of the matching techniques to be assessed.

2.3. *Perturbation solution*

Upstream of the freezing point a solution of the form

$$s = E_0(\xi) + N^{-1}E_1(\xi) + \dots \tag{2.20}$$

is sought. It follows from equation (2.12) that

$$\left.\begin{aligned} E_0 &= [G(\xi)-1]^{-1}, \\ E_1 &= G'(\xi)\,[G(\xi)-1]^{-3}, \end{aligned}\right\} \tag{2.21}$$

and so on. Such a solution will need modification near $\xi = \xi_0$, where $s = 0$, when $G(\xi_0)$ is finite. The region near $\xi = \xi_0$ must then be considered separately (Bloom & Ting 1960) and an appropriate independent variable is

$$\nu = N(\xi - \xi_0). \tag{2.22}$$

Equation (2.12) can be written

$$ds/d\nu + [G_0 - 1 + \nu N^{-1}G_0' + \dots]\,s = 1, \tag{2.23}$$

where $\quad G_0 = G(\xi_0), \quad G_0' = (dG/d\xi)_{\xi=\xi_0}$, etc.

A solution of (2.23) of the form

$$s = \zeta_0(\nu) + N^{-1}\zeta_1(\nu) + \dots \tag{2.24}$$

is sought, and it is found that

$$\left.\begin{aligned} \zeta_0 &= (G_0-1)^{-1}\,[1-\exp\{-(G_0-1)\,\nu\}], \\ \zeta_1 &= \frac{G_0'}{(G_0-1)^3}[1-\exp\{-(G_0-1)\,\nu\}] - \frac{\nu G_0'}{(G_0-1)^2} + \frac{1}{2}\frac{\nu^2 G_0'}{(G_0-1)}\exp\{-(G_0-1)\,\nu\}, \\ &\qquad \text{etc.,} \end{aligned}\right\} \tag{2.25}$$

using the boundary conditions $\zeta_t = 0$ on $\nu = 0$. By considering the limiting behaviour of (2.21) as $\xi \to \xi_0$ and the limiting behaviour of (2.25) as $\nu \to \infty$ it is readily seen that the solutions represented by equations (2.20) and (2.24) do indeed match at the downstream edge of this 'boundary-layer' region near $\xi = \xi_0$. For the case when $G(\xi_0)$ is not finite, i.e. when $G(\xi) \sim B(\xi-\xi_0)^{-n}$ as $\xi \to \xi_0$, it can be shown that (2.21) is a valid solution up to and including $\xi = \xi_0$.

It is apparent from equation (2.21) that the perturbation solution breaks down as $\xi \to 1$ where $G(\xi) \sim 1+(\xi-1)\,G'(1)+\ldots$. In general the perturbation solution is only a valid solution for $1 > \xi > \xi_0$. Note that this solution although it corresponds to the usual near-equilibrium solution (expansion in inverse powers of Λ) only completely reduces to that solution where $G(\xi) \gg 1$. It can be shown from the exact solution (2.15), by integration by parts, that (2.20) and (2.21) do indeed represent a valid solution in the region $1 > \xi > \xi_0$, and also that equations (2.24) and (2.25) represent a valid solution where $N(\xi-\xi_0)$ is $O(1)$.

2.4. *Transition layer solution*

As $\xi \to 1$ the perturbation solution breaks down since the derivative term becomes important in this region. Near $\xi = 1$ the appropriate independent variable is

$$u = N^{\frac{1}{2}}(\xi-1), \tag{2.26}$$

and equation (2.12) can be written

$$\frac{ds}{du}+\left[uG'(1)+\frac{u^2}{2N^{\frac{1}{2}}}G''(1)+\ldots\right]s = N^{\frac{1}{2}}. \tag{2.27}$$

The solution to this equation is assumed to have the form

$$s = N^{\frac{1}{2}}S_0(u)+S_1(u)+\ldots \tag{2.28}$$

and it follows that

$$\left.\begin{aligned} &dS_0/du+G'(1)\,uS_0 = 1,\\ &dS_1/du+G'(1)\,uS_1 = -\tfrac{1}{2}u^2G''(1)\,S_0, \quad \text{etc.}\end{aligned}\right\} \tag{2.29}$$

Note that $G'(1) < 0$. The solutions to equations (2.29) can be written

$$\left.\begin{aligned} S_0 &= B_0\exp\{-\tfrac{1}{2}G'(1)\,u^2\}+\frac{\pi^{\frac{1}{2}}\exp\{-\tfrac{1}{2}G'(1)\,u^2\}}{(-2G'(1))^{\frac{1}{2}}}\left[1+\operatorname{erf}\left\{\left(-\frac{G'(1)}{2}\right)^{\frac{1}{2}}u\right\}\right],\\ \frac{2}{G''(1)}S_1 &= (B_1-\tfrac{1}{3}B_0u^3)\exp\{-\tfrac{1}{2}G'(1)\,u^2\}-\frac{\pi^{\frac{1}{2}}u^3\exp\{-\tfrac{1}{2}G'(1)\,u^2\}}{3\,(-2G'(1))^{\frac{1}{2}}}\\ &\quad\times\left[1+\operatorname{erf}\left\{\left(-\frac{G'(1)}{2}\right)^{\frac{1}{2}}u\right\}\right]+\frac{u^3}{3G'(1)}-\frac{2}{3[G'(1)]^2}.\end{aligned}\right\} \tag{2.30}$$

As $u \to -\infty$, i.e. as the upstream edge of the transition layer is approached, it is seen that

$$\left.\begin{aligned} S_0 &\sim B_0\exp\{-\tfrac{1}{2}G'(1)\,u^2\}+\frac{1}{G'(1)}\frac{1}{u}+\frac{1}{[G'(1)]^2}\frac{1}{u^3}+\ldots,\\ \frac{2}{G''(1)}S_1 &\sim (B_1-\tfrac{1}{3}B_0u^3)\exp\{-\tfrac{1}{2}G'(1)\,u^2\}-\frac{1}{[G'(1)]^2}-\frac{1}{[G'(1)]^3}\frac{1}{u^2}-\ldots,\end{aligned}\right\} \tag{2.31}$$

but from the perturbation solution it follows that, as $\xi \to 1$,

$$s \sim N^{\frac{1}{2}}\left(\frac{1}{G'(1)}\frac{1}{u}+\frac{1}{[G'(1)]^2}\frac{1}{u^3}+\ldots\right)-\frac{G''(1)}{2}\left(\frac{1}{[G'(1)]^2}+\frac{1}{[G'(1)]^3}\frac{1}{u^2}+\ldots\right). \quad (2.32)$$

From equations (2.28) and (2.31) it is seen that the transition layer solution matches with the perturbation solution at the upstream edge of the transition layer provided the $B_i = 0$. Consequently the solution within the layer can be written

$$s = N^{\frac{1}{2}}L(u)+\frac{G''(1)}{2}\left[-\tfrac{1}{3}u^3L(u)+\frac{1}{3}\frac{u^2}{G'(1)}-\frac{\frac{2}{3}}{[G'(1)]^2}\right]+O(N^{-\frac{1}{2}}), \quad (2.33)$$

where $$L(u) = \frac{\pi^{\frac{1}{2}}\exp\{-\frac{1}{2}G'(1)\,u^2\}}{(-2G'(1))^{\frac{1}{2}}}[1+\operatorname{erf}\{(\tfrac{1}{2}\{G'(1)\})^{\frac{1}{2}}u\}]. \quad (2.34)$$

It can be seen that the first term in (2.33) is in complete agreement with (2.16) which was derived from the full solution (2.15). It is easily shown that the higher-order terms also agree with the appropriate expansion of the exact solution.

It is useful to consider here the behaviour of s as the downstream edge of the transition layer is approached, i.e. as $u \to +\infty$. From (2.34) it follows that

$$L(u) \sim \left(\frac{2\pi}{-G'(1)}\right)^{\frac{1}{2}}\exp\{-\tfrac{1}{2}G'(1)\,u^2\} \quad (2.35)$$

as $u \to \infty$. In terms of the ξ co-ordinate it is seen that $L(u)$ becomes exponentially large with respect to N (since $G'(1) < 0$) and hence from equation (2.34) s also becomes exponentially large.

2.5. *Asymptotic solution*

The asymptotic solution downstream of the freezing point can perhaps be most easily derived by considering the rate equation with $\sigma/\bar{\sigma}_f$ as the dependent variable; the suffix f denotes the value at the freezing point. It follows from equations (2.7), (2.13) and (2.14) that

$$dA/d\xi = NG(\xi)[\bar{A}-A], \quad (2.36)$$

where $$A = \sigma/\bar{\sigma}_f, \quad \bar{A} = \bar{\sigma}/\bar{\sigma}_f = \exp N(1-\xi). \quad (2.37)$$

Downstream of the freezing point, $G(\xi) \to 0$, $\bar{A}$ becomes exponentially small, and (2.36) reduces to

$$dA/d\xi = -NG(\xi)A. \quad (2.38)$$

In general the error term in (2.38) is expected to be exponentially small and one might expect that a formal solution of (2.36) for $\xi > 1$ could be written

$$A = A_0(\xi,N)+\bar{A}A_1(\xi,N)+\ldots, \quad (2.39)$$

where the equations for the A_i are obtained by equating like powers of $\bar{A}$. However, the exponential form of $\bar{A}$ is an approximation to the full expression (2.4) and it follows that for $i \geqslant 1$ one should strictly take into account the higher-order terms in $\bar{A}$ (though the solution (2.39) would be perfectly valid for the assumed exponential form of $\bar{A}$). Furthermore, the inclusion of the perturbation to the flow variables would also affect the A_i's for $i \geqslant 1$. The equation satisfied by A_0 (i.e. (2.38)) is not affected by the higher-order terms in $\bar{A}$ nor by the perturbation to the flow variables, and it follows that a first approximation to the asymptotic solution is given by

$$A_0 = K' \exp\left\{-N\int_1^{\xi} G(\psi)\, d\psi\right\}. \tag{2.40}$$

The terms neglected are exponentially small for $\xi > 1$ and in fact as $\xi \to \infty$ these terms approach zero. Thus it is expected that (2.40) will give the correct value for the asymptotic frozen level of the vibrational energy. The solution (2.40) can also be deduced by assuming that s is exponentially large for $\xi > 1$. Neglecting terms which are exponentially small compared to s in equation (2.12) gives, as a first approximation to s in this region,

$$ds/d\xi + N[G(\xi) - 1]\, s = 0. \tag{2.41}$$

Hence
$$s = K' \exp\left\{N\int_1^{\xi} [1 - G(\psi)]\, d\psi\right\}. \tag{2.42}$$

Since $s+1 = \exp\{N(\xi-1)\}A$, it follows, neglecting exponentially small terms, that the arbitrary constants in (2.40) and (2.42) are the same.

As $\xi \to 1$, equation (2.42) gives

$$s \sim K' \exp\{-\tfrac{1}{2}G'(1)\, u^2\}\left[1 - \frac{G''(1)\, u^3}{6N^{\frac{1}{2}}} + \dots\right] \tag{2.43}$$

(writing $u = N^{\frac{1}{2}}(\xi - 1)$). From equations (2.33), (2.34) and (2.35) the behaviour at the downstream edge of the transition layer is seen to be given by

$$s \sim (-2\pi/G'(1))^{\frac{1}{2}} \exp\{-\tfrac{1}{2}G'(1)\, u^2\}\, [N^{\frac{1}{2}} - \tfrac{1}{6}G''(1)\, u^3 + O(N^{-\frac{1}{2}})], \tag{2.44}$$

where only the exponentially large terms have been retained. Comparison of (2.43) and (2.44) shows that the solutions match provided

$$K' = (-2\pi/G'(1))^{\frac{1}{2}}\, N^{\frac{1}{2}} + O(N^{-\frac{1}{2}}). \tag{2.45}$$

Higher-order terms in K' can be computed by obtaining S_2, S_3, etc., in the transition-layer solution. Note that it is not necessary to compute the A_i for $i \geqslant 1$ in order to do this, though the terms which are exponentially smaller must of course still match. The asymptotic solution given by (2.42) and (2.45) is seen to be in agreement with the expression (2.19) derived from the exact solution (2.15).

It follows that the asymptotic value of σ is given by

$$\sigma/\bar{\sigma}_f = (-2\pi/G'(1))^{\frac{1}{2}}\, [N^{\frac{1}{2}} + O(N^{-\frac{1}{2}})] \exp\left\{-N\int_1^{\infty} G(\xi)\, d\xi\right\}. \tag{2.46}$$

Hence the asymptotic value of σ is not $O(\bar{\sigma}_f)$, which would be a consequence of the sudden-freeze approximation, i.e. the assumption that up to the freezing point the flow is in equilibrium while beyond it the flow is frozen with σ remaining constant at its value at the freezing point. The sudden-freeze and other approximations for the asymptotic solution will be discussed in §4.

2.6. *Summary of solutions*

In order to assist the reader a list of the independent and dependent variables which are appropriate to the various regions is given in table 1.

Region	Independent variable	Dependent variable	Solution (equation no.)
Initial 'boundary-layer' region	$\nu = N(\xi-\xi_0)$	$s = \zeta_0+N^{-1}\zeta_1+\ldots$	(2.25)
Perturbation solution $1>\xi>\xi_0$	ξ	$s = E_0+N^{-1}E_1+\ldots$	(2.21)
Transition layer solution $\xi \sim 1$	$u = N^{\frac{1}{2}}(\xi-1)$	$s = N^{\frac{1}{2}}S_0+S_1+\ldots$	(2.33)
Asymptotic solution $\xi > 1$	ξ	s is exponentially large	(2.42), (2.45)

TABLE 1. Breakdown of solutions: linear rate equation

3. Non-equilibrium dissociation and ionization

3.1. *Transformation of the rate equation*

Because of the linear form of the rate equation the analysis of §2 was comparatively straightforward. However, for dissociation or ionization the rate equation is non-linear, even when there is only a small amount of energy in the lagging mode. This non-linear behaviour is particularly important with regard to the structure of the asymptotic solution.

Molecular dissociation of a diatomic gas will be considered first. In order to simplify the problem as much as possible it is assumed that the translational and rotational modes are fully excited and that the translational, rotational and vibrational modes are in a state of local equilibrium throughout the flow. The effects of electronic excitation, etc., are assumed to be negligible. The assumption that the vibrational mode is in equilibrium implies that the vibrational relaxation time is much less than that for dissociation, a condition which can only be expected to hold over a limited temperature range (see e.g. Heims 1958).

Freeman (1958) has derived a suitable rate equation for molecular dissociation under these conditions. This equation can be written in the form

$$v'\frac{d\alpha}{dx'} = C'(\alpha, T')\frac{\rho'_D}{\rho'^2}\left\{\frac{1-\alpha}{1-\alpha_e}\alpha_e^2-\alpha^2\right\}, \tag{3.1}$$

where $\alpha_e = \alpha_e(\rho', T')$ is given by

$$\alpha_e^2/(1-\alpha_e) = \rho'_D/\rho'\exp(-D'_e/kT'). \tag{3.2}$$

Here α is the dissociation fraction (ratio by mass of the dissociated atoms), α_e is the local equilibrium value of α corresponding to the translational temperature T' and the density ρ', ρ'_D is a characteristic 'density of dissociation' (see Lighthill 1957), D'_e is the energy of dissociation and k is Boltzmann's constant. $C'(\alpha, T')$

is termed a rate function. The precise dependence of C' upon α and T' is rather uncertain. Freeman (1958) suggested that the main variation will be some inverse power law dependence on temperature. At constant temperature, from the calculations of Wood (1956), one might expect that

$$C' = b\alpha + d(1-\alpha),$$

where b and d are of the same order of magnitude. Thus for $\alpha \ll 1$, $C' \sim d$. Consequently for the present uncoupled case, where $\alpha \ll 1$, the assumption

$$C' = C_1 T'^{-r} \tag{3.3}$$

should be valid. In fact all that is strictly necessary for the present analysis to hold is that, to a first approximation for $\alpha \ll 1$,

$$C' = C'(T').$$

The characteristic density ρ'_D is in general a function of temperature (Lighthill 1957), though its variation with temperature is in many cases very slight.

By suitably non-dimensionalizing the variables with respect to the equilibrium conditions (as in §2) and by utilizing the condition $\alpha \ll 1$ equation (3.1) becomes

$$d\alpha/dx = \Lambda F_1(x)\,[\alpha_e^2(x) - \alpha^2], \tag{3.4}$$

where

$$F_1(x) = \rho^2 C(T)/v\rho_D, \tag{3.5}$$

$$\Lambda = lC'(T_0)\,\rho_0'^2/a_0'\rho_D' \tag{3.6}$$

and $\rho_D = \rho'_D/\rho'_{D_0}$, $C(T) = C'(T')/C'_0(T'_0)$, and the other symbols are as previously defined in §2. The functions F_1 and α_e are known functions of x from the basic isentropic solution, i.e. the solution when $\alpha = 0$ and the flow remains in thermodynamic equilibrium. Using the assumption $\alpha_e \ll 1$ equation (3.2) can be written

$$\alpha_e^2 \approx \rho'_{D_0}\rho_D/\rho'_0\rho \exp(-\Theta_D/T), \tag{3.7}$$

where $\Theta_D = D_e/kT'_0$ is a dimensionless characteristic temperature of dissociation.

Actually the precise conditions under which the rate equation is uncoupled from the remaining flow equations is not $\alpha \ll 1$ but $\alpha \log \alpha \ll 1$, since the energy equation, in dimensionless form, contains a term $\Theta_D \alpha$. This is to be compared with the energy equation for vibrational relaxation where the corresponding term is simply σ. Consequently, from (3.7), a necessary condition on Θ_D is

$$\Theta_D \gg \log(\Theta_D \rho'_{D_0}/\rho'_0). \tag{3.8}$$

Again it is the exponential form of α_e that is a dominant feature of the analysis and it is convenient to use as independent variable

$$z = [T(x)]^{-1}. \tag{3.9}$$

The rate equation becomes, in terms of this variable,

$$d\alpha/dz = \Lambda F(z)\,[\alpha_e^2(z) - \alpha^2], \tag{3.10}$$

where

$$F(z) = \frac{dx}{dz}\frac{\rho^2(z)\,C(z)}{v(z)\,\rho_D(z)}, \quad \alpha_e^2 \approx \frac{\rho'_{D_0}}{\rho'_0}\frac{\rho_D(z)}{\rho(z)}\exp(-\Theta_D z). \tag{3.11}$$

Neglecting exponentially smaller terms, α_e is expressed as

$$\alpha_e = h(z)\exp(-\tfrac{1}{2}\Theta_D z), \tag{3.12}$$

where

$$h(z) = [\rho'_{D_0}\rho_D(z)/\rho'_0\rho(z)]^{\frac{1}{2}}. \tag{3.13}$$

The functions $\rho(z)$, $h(z)$, etc., are determined from the basic isentropic solution. If it could be assumed that the translational, rotational and vibrational modes are all fully excited (or, e.g., that the ideal dissociating gas were a valid model) then this isentropic solution would be the usual constant γ solution with the appropriate value of γ. However, as z becomes large it is physically unrealistic to assume that the vibrational mode is fully excited and allowances have to be made for variations in γ.

An equation of the form (3.10) also governs the flow of a monatomic ionizing gas when α, now to be interpreted as the ionization fraction, is small (Rosner 1962, Eschenroeder 1962) (again it is necessary to assume that $\alpha \log \alpha \ll 1$). The equilibrium value of the ionization fraction has the usual exponential form with Θ_D replaced by a characteristic ionization temperature. Consequently the results obtained below for dissociation will also be applicable to ionization provided the necessary modifications are made to the functions $F(z)$ and $h(z)$.

Equation (3.10), as pointed out by Freeman (1959), is a Ricatti equation and can be transformed to a second-order linear equation by means of a suitable substitution. However, it does not appear possible to write down a formal solution to this transformed equation and it is necessary to proceed as in §2 and to obtain valid solutions within the various regions governing the flow. As before the appropriate dependent variable is

$$s = (\alpha - \alpha_e)/\alpha_e, \tag{3.14}$$

and equation (3.10) is transformed into a further Ricatti equation

$$ds/dz + (2\Lambda F\alpha_e + \alpha_e^{-1}d\alpha_e/dz)\,s + \Lambda F\alpha_e s^2 = -\alpha_e^{-1}d\alpha_e/dz. \tag{3.15}$$

The first term in the usual near equilibrium solution (expansion in inverse powers of Λ) is obtained by balancing the term $2\Lambda F\alpha_e s$ on the left-hand side of this equation with the expression on the right-hand side of this equation. Such a solution must break down near points where

$$2\Lambda F\alpha_e + \alpha_e^{-1}d\alpha_e/dz = 0. \tag{3.16}$$

Note that, as in §2, this is the type of freezing criterion derived by Bray (1959) from qualitative arguments. Note also that if equation (3.10) were linearized by assuming small departures from equilibrium then the analysis of §2 would still predict a breakdown of this near equilibrium solution in the region where (3.16) is satisfied, since the F of §2 would be replaced here by $2F\alpha_e$.

The solution of equation (3.16), for the position of what is termed the freezing point is written $z = \Phi$. A new independent variable is defined by $\xi = z/\Phi$ and equation (3.15) can be rearranged to give

$$N^{-1}ds/d\xi + [H(\xi,N) - Q(\xi,N)]\,s + \tfrac{1}{2}H(\xi,N)\,s^2 = Q(\xi,N), \tag{3.17}$$

where $$N = (-\alpha_e^{-1} d\alpha_e/d\xi)_{\xi=1} = \tfrac{1}{2}\Theta_D \Phi - \mu, \quad \mu = [(d/d\xi)\log h]_{\xi=1}, \tag{3.18}$$

$$H(\xi, N) = f(\xi)\exp\{N(1-\xi)\}, \quad f(\xi) = \frac{F(z)}{F(\Phi)}\frac{h(z)}{h(\Phi)}\exp\{\mu(1-\xi)\}, \tag{3.19}$$

and $$Q(\xi, N) = 1 + N^{-1}[\mu - (d/d\xi)\log h]. \tag{3.20}$$

As in §2, it is again assumed that N is a large parameter. This is consistent with the requirement on Θ_D provided that Φ is $O(1)$, since μ is $O(1)$: $\Phi < 1$ indicates that near-frozen conditions can be expected to hold everywhere, see §2.1. Apart from the non-linear term the important feature of equation (3.18), in comparison with the linear equation (2.12), is the exponential form of the function $H(\xi, N)$ and the equation is somewhat dominated by the rapid exponential decay of this function. Note that $Q(\xi, N)$ is $O(1)$ and that its derivatives are all $O(1/N)$.

3.2. *Perturbation solution*

For $\xi < 1$ it is seen from equation (3.17) that s is $O(\exp[-N(1-\xi)])$. Write

$$s = \epsilon \exp\{-N(1-\xi)\};$$

then from (3.17)

$$\epsilon = Q(\xi, N)/f(\xi) + \text{exponentially smaller terms.}$$

Accordingly a solution of the form

$$s = \epsilon_1 \exp\{-N(1-\xi)\} + \epsilon_2 \exp\{-2N(1-\xi)\} + \ldots \tag{3.21}$$

is sought. This will be a valid form of solution provided the ϵ_i are $o(\exp[N(1-\xi)])$. It is found that

$$\epsilon_1 = \frac{Q(\xi, N)}{f(\xi)}, \quad \epsilon_2 = \frac{Q(\xi, N)}{f^2(\xi)}\left\{\frac{Q(\xi, N)}{2} - \frac{Q'(\xi, N)}{NQ(\xi, N)} + \frac{f'(\xi)}{Nf(\xi)} - 1\right\}, \quad \ldots \tag{3.22}$$

Note that the ϵ_i's are all $O(1)$ for large N. It is correct to retain the dependence of the ϵ_i's on N since the $(i+1)$th term will be exponentially smaller than the ith. However, although, in relation to equation (3.17), these higher-order terms can be computed, in reality they are of little significance beyond the first term since the terms neglected in deriving (3.17) are of a similar order of magnitude to these higher-order terms. Note that ϵ_1 is equivalent to the first term in a conventional near-equilibrium solution.

This perturbation solution, as in §2, will need modification near $\xi = \xi_0$, where the boundary condition $s = 0$ has to be satisfied, if $H(\xi, N)$ remains finite there (Bloom & Ting 1960). This region near $\xi = \xi_0$, where the term involving the derivative in equation (3.17) is expected to be important, is

$$O(N^{-1}\exp\{-N(1-\xi_0)\})$$

in extent, and a new independent variable is defined by

$$w = N\exp\{N(1-\xi_0)\}(\xi - \xi_0), \tag{3.23}$$

and equation (3.17) becomes, near $\xi = \xi_0$,

$$\begin{aligned} ds/dw + [f_0 - \{(f_0 - N^{-1}f_0')\omega + Q_0\}\exp\{-N(1-\xi_0)\} + O(\exp\{-2N(1-\xi_0)\})]\,s \\ + \tfrac{1}{2}[f_0 - (f_0 - N^{-1}f_0')\omega\exp\{-N(1-\xi_0)\} + O(\exp\{-2N(1-\xi_0)\})]\,s^2 \\ = Q_0\exp\{-N(1-\xi_0)\} + O(\exp\{-2N(1-\xi_0)\}). \end{aligned} \tag{3.24}$$

A solution of the form

$$s = \exp\{-N(1-\xi_0)\} Z_1(\omega, N) + \exp\{-2N(1-\xi_0)\} Z_2(\omega, N) + \dots \tag{3.25}$$

is sought; it is assumed that the Z_i are $o(\exp\{N(1-\xi_0)\})$. It follows from equations (3.24) and (3.25) that

$$dZ_1/dw + f_0 Z_1 = Q_0, \text{ etc.} \tag{3.26}$$

The solution of this equation satisfying the boundary condition $Z_1 = 0$ on $w = 0$ is

$$Z_1 = (Q_0/f_0)[1-\exp(-f_0 w)], \tag{3.27}$$

which as $w \to \infty$ matches with the first term of the perturbation solution as $\xi \to \xi_0$. Higher-order terms can also be shown to match and, as in the linear case, the perturbation solution forms a valid outer limit of the solution near $\xi = \xi_0$. When $f(\xi) \sim \beta(\xi-\xi_0)^{-n}$ near $\xi = \xi_0$ it again follows that the perturbation solution is valid up to and including $\xi = \xi_0$.

3.3. *Transition layer solution*

As $\xi \to 1$ the coefficient of s in equation (3.17) approaches zero and it is apparent that sufficiently near to $\xi = 1$ the perturbation solution must break down. Near $\xi = 1$ it is appropriate to use the independent variable

$$y = N(\xi - 1), \tag{3.28}$$

and equation (3.17) can be rewritten, near $\xi = 1$,

$$\begin{aligned} ds/dy + [\{f(1) + N^{-1} y f'(1) + \dots\} e^{-y} - \{1 + O(N^{-2})\}]\, s \\ + \tfrac{1}{2}\{f(1) + N^{-1} y f'(1) + \dots\} e^{-y} s^2 = 1 + O(N^{-2}). \end{aligned} \tag{3.29}$$

Note that near $\xi = 1$, $Q = 1 + O(N^{-2})$. A formal solution of this equation can be expressed in the form

$$s = \Sigma_0(y) + N^{-1}\Sigma_1(y) + \dots, \tag{3.30}$$

and the equations satisfied by Σ_0 and Σ_1 are

$$d\Sigma_0/dy + [e^{-y} - 1]\Sigma_0 + \tfrac{1}{2} e^{-y} \Sigma_0^2 = 1, \tag{3.31}$$

$$d\Sigma_1/dy + [e^{-y} - 1 + e^{-y}\Sigma_0]\Sigma_1 = -f'(1)\, y\, e^{-y}\Sigma_0(1 + \tfrac{1}{2}\Sigma_0). \tag{3.32}$$

The equations for the higher-order terms are similar in form to (3.32), though with a more complex right-hand side. The simplicity of the right-hand side of equation (3.32) arises from the fact that within the transition layer

$$Q = 1 + O(N^{-2}).$$

To solve equation (3.31) one notes that it is a Ricatti equation, simpler in form than (3.17), and the solution is most easily obtained by transforming to an appropriate second-order linear differential equation. It is convenient to change both the dependent and independent variables and the transformation is defined by

$$t = \tfrac{1}{2} e^{-y}, \quad \Sigma_0 + 1 = -\beta^{-1} d\beta/dt, \tag{3.33}$$

and equation (3.31) becomes

$$t(d^2\beta/dt^2) + d\beta/dt - t\beta = 0, \tag{3.34}$$

which is Bessel's equation of zeroth order. The solutions are the zeroth-order Bessel functions (of imaginary argument) of the first and second kind, $I_0(t)$ and $K_0(t)$, respectively. It follows from (3.33) that

$$\Sigma_0 + 1 = [K_1(t) - \delta_0 I_1(t)]/[K_0(t) + \delta_0 I_0(t)], \tag{3.35}$$

where K_1 and I_1 are the corresponding Bessel functions of the first order and δ_0 is some arbitrary constant. Note that $\Sigma_0 + 1$ corresponds to α/α_e.

The upstream edge of the transition layer is defined by $y \to -\infty$ ($t \to +\infty$) and it should be possible to match the solution in this region to the downstream limit, as $\xi \to 1$, of the perturbation solution. For t large it follows from the asymptotic expansions of the Bessel functions that

$$\Sigma_0 + 1 \sim \frac{e^{-2t}[1 + 3/8t + \ldots] - \frac{1}{2}\delta_0[1 - 3/8t + \ldots]}{e^{-2t}[1 - 1/8t + \ldots] + \frac{1}{2}\delta_0[1 + 1/8t + \ldots]}. \tag{3.36}$$

However, from (3.21) and (3.22) as $\xi \to 1$

$$s \sim e^{y}\{1 - N^{-1}f'(1)\, y + O(N^{-2})\} + e^{2y}O(1) + \ldots, \tag{3.37}$$

or since $y = -\log(2t)$, equation (3.37) can be written

$$s \sim \tfrac{1}{2}t^{-1}\{1 + N^{-1}f'(1)\log 2t + O(N^{-2})\} + t^{-2}O(1) + \ldots. \tag{3.38}$$

By comparing the terms in t^{-1} which are $O(1)$ in equations (3.36) and (3.38), it is seen that the expressions do match provided $\delta_0 = 0$. It can also be shown that the terms in t^{-2}, etc., match and hence the first approximation to the solution within the layer is given by

$$\Sigma_0 + 1 = K_1(t)/K_0(t). \tag{3.39}$$

In terms of the independent variable t equation (3.32) can be integrated to give

$$\Sigma_1 = \frac{\delta_1}{tK_0^2(t)} + \frac{f'(1)}{tK_0^2(t)}\int t\log(2t)\{K_0^2(t) - K_1^2(t)\}\,dt, \tag{3.40}$$

where δ_1 is some arbitrary constant. In order to evaluate this integral it is convenient to make use of the result (Watson 1952, p. 135)

$$\begin{aligned}\int tK_n^2(t)\,dt &= \tfrac{1}{2}t^2[K_n^2(t) - K_{n-1}(t)\,K_{n+1}(t)]\\ &= \tfrac{1}{2}t^2[K_n^2(t) - K_{n+1}^2(t)] + ntK_n(t)\,K_{n+1}(t).\end{aligned} \tag{3.41}$$

It then follows from equation (3.40) that

$$\Sigma_1 = \frac{\delta_1}{tK_0^2(t)} + f'(1)\,t\,[\log 2t - 1]\,\frac{[K_0^2(t) - K_1^2(t) + t^{-1}K_0(t)\,K_1(t)]}{K_0^2(t)} + \frac{f'(1)}{2t}. \tag{3.42}$$

By considering the behaviour of this expression for large t ($y \to -\infty$) it is found that

$$\Sigma_1 \sim \delta_1 e^{-2t} + \tfrac{1}{2}t^{-1}f'(1)\log 2t + O(t^{-2}\log 2t). \tag{3.43}$$

Using this expression and equation (3.30) and comparing with equation (3.38) shows that terms of $O(1/N)$ match provided $\delta_1 = 0$. Hence Σ_1 is given by

$$\Sigma_1 = f'(1)\left\{\frac{1}{2t} + t(\log 2t - 1)\left[1 - \frac{K_1^2(t)}{K_0^2(t)} + \frac{K_1(t)}{tK_0(t)}\right]\right\}. \tag{3.44}$$

3.4. *Asymptotic solution*

The form of the asymptotic solution downstream of the freezing point is, as in § 2, most easily seen by considering the original form of the rate equation using $\alpha/\alpha_{ef} = A$ as the independent variable (α_{ef} denotes the value of α_e at the freezing point). In terms of A and ξ equation (3.10) becomes

$$\frac{dA}{d\xi} = \tfrac{1}{2}NG(\xi)\left[\frac{f(\xi)}{G(\xi)}\exp\{-2N(\xi-1)\}-A^2\right], \tag{3.45}$$

where $G(\xi) = F(z)/F(\Phi)$. The dominant feature of this equation is the rapid decay of the exponential term for $\xi > 1$ and a first approximation to this equation is, for $\xi > 1$,

$$dA/d\xi = -\tfrac{1}{2}NG(\xi)A^2. \tag{3.46}$$

As in § 2 a scheme for obtaining the higher-order terms in the asymptotic solution can be written down, but again it is expected that these terms, although mathematically derivable, will have little physical significance since they will be affected by the next approximation to the lagging energy distribution, i.e. by the inclusion of the effect of the perturbation to the flow variables, etc. The solution of equation (3.46) is certainly the first term in such an asymptotic solution, the higher-order terms being exponentially small. From equation (3.46)

$$A(\xi, N) = \left[D+\tfrac{1}{2}N\int_1^{\xi} G(\psi)\,d\psi\right]^{-1}, \tag{3.47}$$

where D is an arbitrary constant. It follows, either from (3.47) and the definition of s or from equation (3.17) assuming s is exponentially large, that

$$s+1 = \frac{G(\xi)\exp\{N(\xi-1)\}}{f(\xi)\left[D+\tfrac{1}{2}N\int_1^{\xi} G(\psi)\,d\psi\right]}. \tag{3.48}$$

As $\xi \to 1$, this equation becomes

$$s+1 \sim \frac{e^y[1+O(N^{-2})]}{D+\tfrac{1}{2}y+\tfrac{1}{4}N^{-1}f'(1)\,y^2}. \tag{3.49}$$

On the other hand from (3.39) as $y \to +\infty$, $t \to 0$ (downstream edge of transition layer) it is seen that

$$\Sigma_0+1 \sim \frac{e^y[1+O(y\,e^{-2y})]}{\tfrac{1}{2}y+\log 2+\tfrac{1}{2}F(0)} \tag{3.50}$$

where $F(r)$ denotes the digamma function. It is seen that the leading term of (3.50) matches with the leading term of (3.49), neglecting terms of $O(1/N)$, if

$$D = D_0 = \log 2+\tfrac{1}{2}F(0) \approx 0\cdot4045. \tag{3.51}$$

Note that (3.50) indicates that the next term in the asymptotic solution is of the form $A_1(\xi, N)\exp\{-2N(\xi-1)\}$. To obtain a better approximation to D it is necessary to consider the second approximation to the solution in the transition layer. From equation (3.42) it follows that for small t, i.e. $y \to +\infty$,

$$\Sigma_1 \sim f'(1)\,e^y\frac{[D_0^2-D_0+\tfrac{1}{2}-\tfrac{1}{4}y^2]}{(D_0+\tfrac{1}{2}y)^2}[1+O(y\,e^{-2y})].$$

From equation (3.49), writing $D = D_0 + N^{-1}D_1 + \ldots$, it is found that

$$s+1 \sim \frac{e^y}{D_0+\frac{1}{2}y}\left[1-\frac{(D_1+\frac{1}{4}f'(1)\,y^2)}{N(D_0+\frac{1}{2}y)}+O\left(\frac{1}{N^2}\right)\right].$$

Hence terms $O(N^{-1})$ match, provided

$$D_1 = -f'(1)\,[D_0^2-D_0+\tfrac{1}{2}] \approx -0{\cdot}2591f'(1). \tag{3.52}$$

From equations (3.48), (3.51) and (3.52) it is seen that the asymptotic solution is given by

$$\frac{\alpha}{\alpha_{ef}} = \left[\tfrac{1}{2}N\int_1^\xi G(\xi)\,d\xi + 0{\cdot}4045 - \frac{0{\cdot}2591f'(1)}{N}+O\left(\frac{1}{N^2}\right)\right]^{-1} \tag{3.53}$$

3.5. *Summary of solutions*

In order to assist the reader a list of the dependent and independent variables appropriate to each of the regions is given in table 2.

Region	Independent variable	Dependent variable	Solution (equation no.)
Initial 'boundary-layer' region $\xi \sim \xi_0$	$w = N(\xi-\xi_0)\,e^{N(1-\xi_0)}$	$s = Z_1\,e^{-N(1-\xi_0)}+\ldots$	(3.27)
Perturbation solution $\xi < 1$	ξ	$s = \epsilon_1\,e^{-N(1-\xi)}+\ldots$	(3.22)
Transition layer solution $\xi \sim 1$	$y = N(\xi-1)$	$s = \Sigma_0+N^{-1}\,\Sigma_1+\ldots$	(3.39), (3.44)
Asymptotic solution $\xi > 1$	ξ	$s+1 = \dfrac{G(\xi)}{f(\xi)}A(\xi,N)\,e^{N(\xi-1)}$	(3.47), (3.53)

TABLE 2. Breakdown of solutions: non-linear rate equation

3.6. *Numerical example*

As an example the above solutions have been evaluated for the case of the Lighthill ideal dissociating gas (Lighthill 1957). This model assumes that the vibrational mode is always half excited and leads to certain simplifications; in particular the specific heat ratio γ (for $\alpha = 0$) is independent of temperature and has the value $\frac{4}{3}$. A more exact thermodynamic model, assuming that the vibrational energy had its local equilibrium value, could have been used. This model would give $\gamma = \gamma(T)$. However, since the purpose of this example is to demonstrate the general behaviour of the solution, the Lighthill model is satisfactory.

For the example considered it was assumed that $C = T^{-r}$ with $r = 2{\cdot}5$ (Freeman 1958, p. 411), $\Theta_D = 10$ and $\rho_D(z) = 1$ (Lighthill ideal dissociating gas). The nozzle geometry was taken to be hyperbolic, i.e. the area ratio $= 1+x^2$. Under these conditions the function $F(z)$ and $h(z)$ are given by

$$F(z) = \frac{m}{4}\,\frac{|z-\frac{1}{2}(\gamma+1)|\,z^{r-(2\gamma-1)/(\gamma-1)}}{(1-z^{-1})^2\,[2^{-\frac{1}{2}}(\gamma-1)^{\frac{1}{2}}\,mz^{1/(\gamma-1)}(1-z^{-1})^{-\frac{1}{2}}-1]^{\frac{1}{2}}}, \tag{3.54}$$

$$h(z) = (\rho'_{D_0}/\rho'_0)^{\frac{1}{2}}\,z^{1/2(\gamma-1)}, \tag{3.55}$$

where $m = (2/(\gamma+1))^{(\gamma+1)/2(\gamma-1)}$ is the dimensionless mass flow rate defined by $m = \rho_t v_t$, where the suffix t denotes conditions at the throat. The functions $f(\xi)$, $Q(\xi, N)$, etc., follow immediately from equations (3.18), (3.19) and (3.20). $\int_1^\xi G(\psi)\,d\psi$ was evaluated over a range of ξ for various Φ.

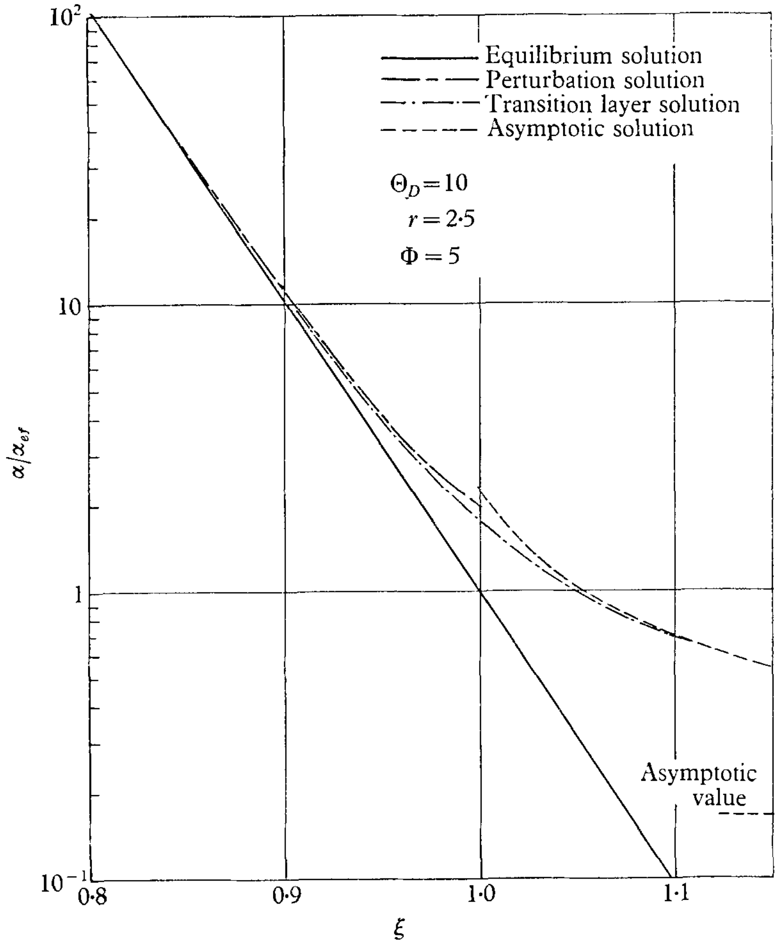

FIGURE 4. Dissociating flow through a hyperbolic nozzle.

The solutions corresponding to the different flow régimes are plotted in figure 4 for $\Phi = 5$. Only the first term of the perturbation solution, the first two terms of the transition layer solution, and the first three terms of the asymptotic solution were used. Upstream stagnation conditions are specified by $\xi = 0{\cdot}2$. It can be seen from figure 4 that there is no significant departure from the equilibrium solution until $\xi > 0{\cdot}85$, or from the perturbation solution until $\xi > 0{\cdot}9$. The asymptotic solution, in this case is apparently valid for $\xi > 1{\cdot}1$. The behaviour of the solutions in the vicinity of the freezing point is shown in figure 5. In figure 6, both the one-term and the two-term solutions applicable to the transition layer region are shown. The first, second, and third approximations

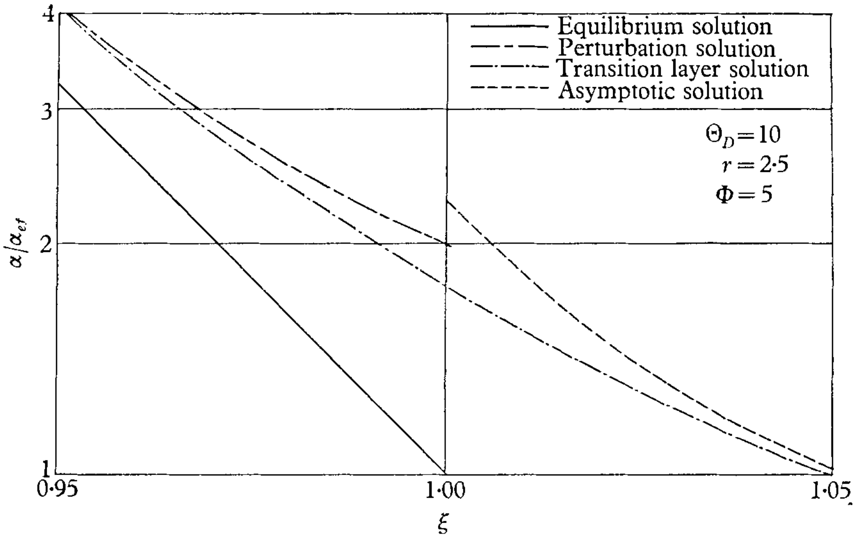

FIGURE 5. Solutions near the freezing point.

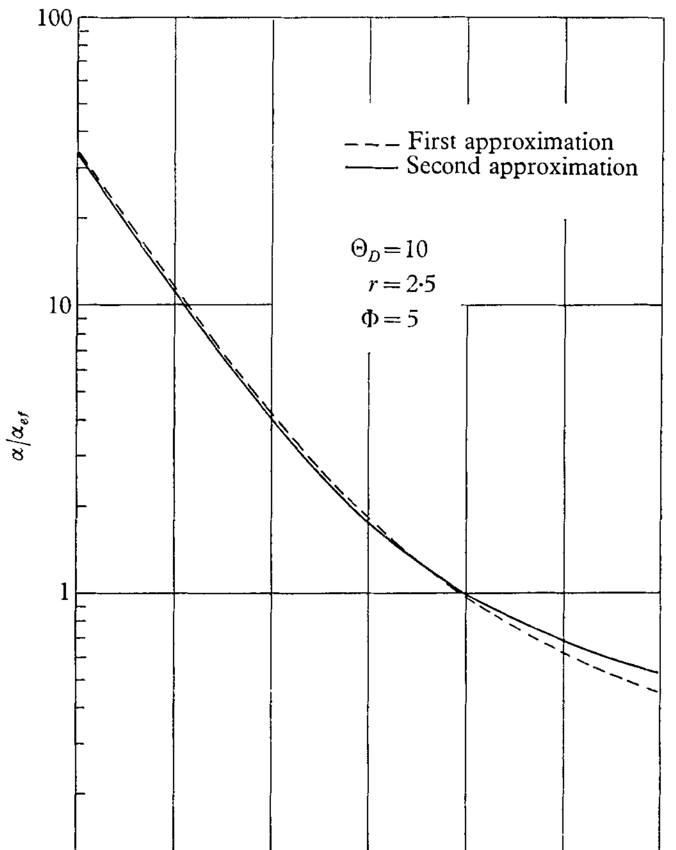

FIGURE 6. Transition layer solution.

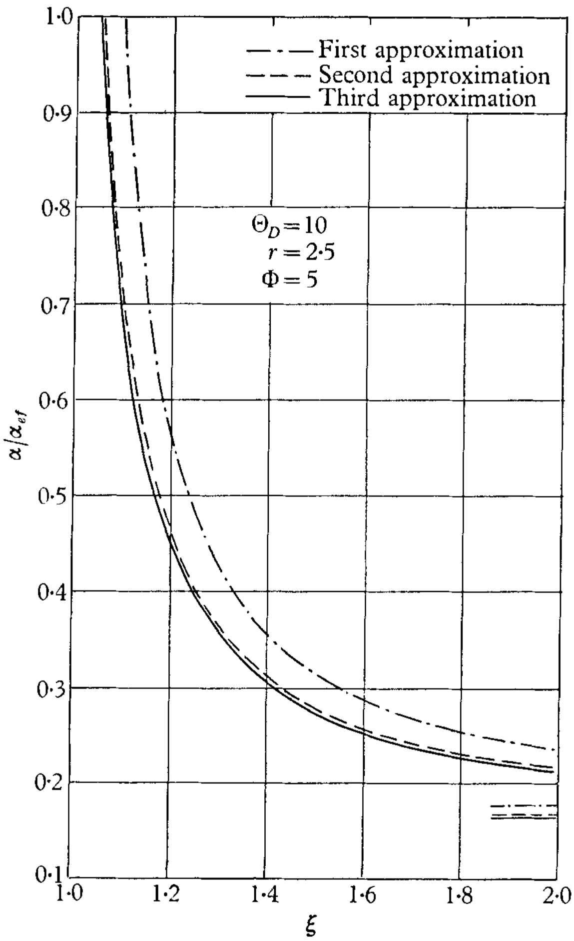

FIGURE 7. Asymptotic solution.

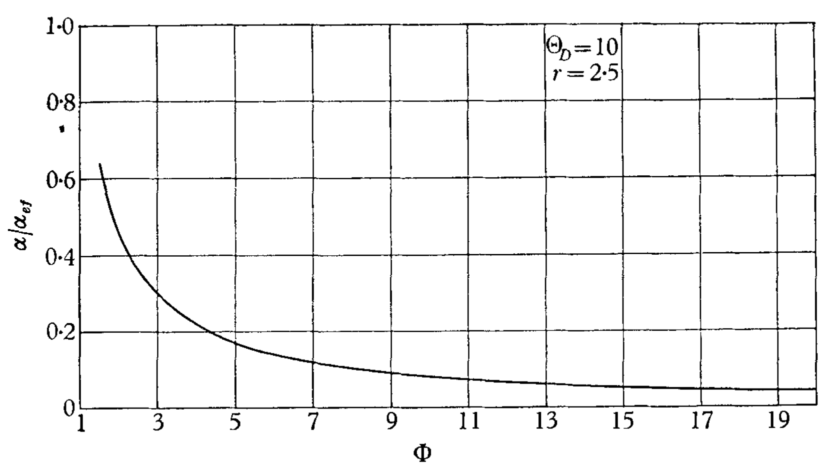

FIGURE 8. Asymptotic levels of the dissociation fraction.

to the asymptotic solution are shown in figure 7. It would appear that in this case the series representing the asymptotic solution converges fairly rapidly.

Φ	$\frac{1}{2}N\int_1^{\xi} G(\psi)\, d\psi$	D_0	$\frac{D_1}{N}$
10	11·877	0·405	0·016
5	5·580	0·405	0·035
2·5	2·347	0·405	0·086
1·5	0·921	0·405	0·240
1·2	0·420	0·405	0·651

TABLE 3. Asymptotic values

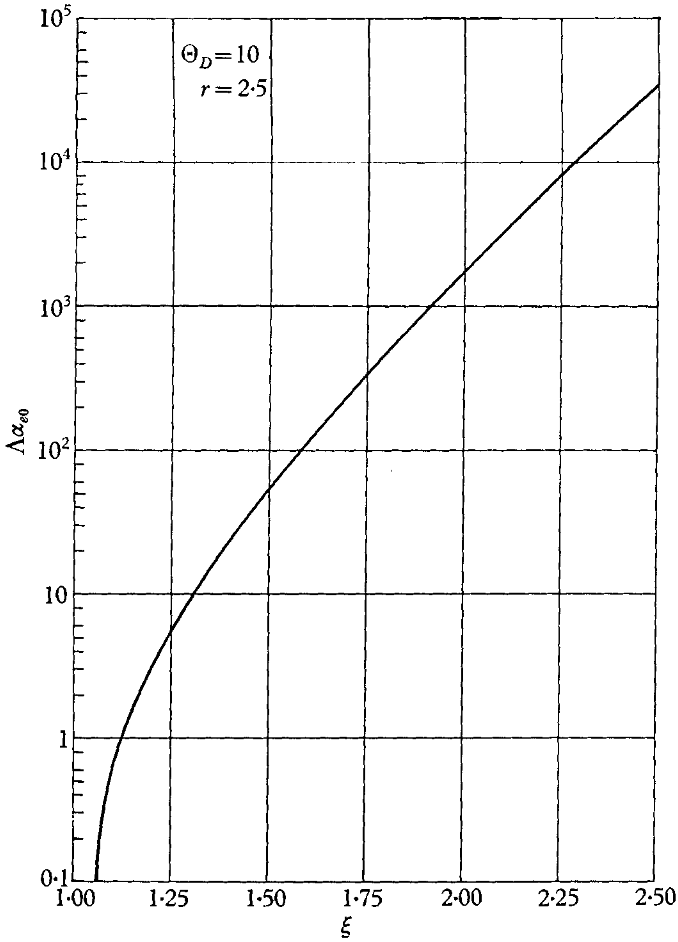

FIGURE 9. Rate parameter as a function of Φ.

Considerable interest is attached to the asymptotic levels of the dissociation fraction and these are shown in figure 8 as a function of Φ. As $\Phi \to 1$ the series representing the asymptotic solution breaks down, i.e. the series no longer converges since as $\Phi \to 1$, $f'(1) \to \infty$ ($f'(1) \sim -2/(\Phi-1)$ as $\Phi \to 1$). In table 3 numerical values of the first three terms in the asymptotic solution are given for various Φ. It is apparent that the approach is of little use for freezing points lying upstream of the nozzle throat ($\Phi < \frac{1}{2}(\gamma+1)$).

That this method of approach should break down as $\Phi \to 1$ is not surprising since under this condition the flow corresponds to a near frozen flow. In figure 9, a plot of $\Lambda\alpha_{e0}$, which is the appropriate rate parameter (see equation (3.4)), against Φ is shown. $\Lambda\alpha_{e0}$ small is the condition under which a near frozen solution can be expected to hold.

4. Resumé and discussion of previous work

Perhaps the most important feature of the theory presented above is the derivation of the correct asymptotic solution, subject to the limitation of only a small amount of energy in the lagging mode. Much has been written on the final, or frozen-out, value of the energy in the lagging mode and it is appropriate here to turn to the work of Bray (1959). Bray presented numerical solutions for the quasi-one-dimensional flow of an ideal dissociating gas, subject to a rate equation of the type (3.1), and also described an approximate method for deducing the asymptotic frozen value of α. In Bray's work, α was not small compared with unity and the rate equation could not be regarded as uncoupled from the remaining flow equations. Here, however, this approximate approach will be considered in the uncoupled limit. By means of a suitable qualitative argument Bray deduced that freezing would become important where (in the present notation)

$$d\alpha_e/dz \sim -\Lambda F\alpha_e^2,$$

$$d\alpha_e/dz = -P\Lambda F\alpha_e^2, \tag{4.1}$$

P being a constant of $O(1)$. This criterion is equivalent to the present definition of the freezing point when $P = 2$ (equation (3.16)). However, Bray assumed that (4.1), as well as indicating where freezing would set in, also gave the asymptotic frozen value of α: that is he assumed that upstream of the freezing point α was given by the equilibrium distribution, while downstream of the freezing point α remained constant at its equilibrium value at the freezing point—the so-called sudden-freeze approximation. A similar approach to Bray's involving a slight modification in P, was also given by Hall & Russo (1959). These sudden-freeze approximations seemed to give reasonable agreement with the exact numerical results.

The solution of equation (4.1) can be written

$$\xi_P = 1+N^{-1}\log\tfrac{1}{2}P+N^{-2}f'(1)\log\tfrac{1}{2}P+O(N^{-3}). \tag{4.2}$$

It follows that
$$\alpha_{eP}/\alpha_{ef} = (2/P)\,[1+O(N^{-1})], \tag{4.3}$$

where the suffix P denotes the value of α_e at the point ξ_P. It is apparent from equation (3.53) that the sudden-freeze approximation, i.e. α is $O(\alpha_{eP})$, is incorrect for P of $O(1)$. In fact it is necessary that P is $O(N)$ if α_{eP} is to give the correct asymptotic value. Note that this result is only true for $\alpha \ll 1$; nothing can be said on the order of magnitude of the asymptotic value for general values of α.

For the linear rate equation, the solution of the corresponding criterion, written in the form
$$P\Lambda F(z)+\bar{\sigma}^{-1}(d\bar{\sigma}/dz) = 0 \tag{4.4}$$

where P is $O(1)$ ($P = 1$ for the present definition of the freezing point, see equation (2.11*a*)), is given by the solution of

$$PG(\xi_P) = 1. \tag{4.5}$$

Also

$$\bar{\sigma}_P/\bar{\sigma}_f = \exp\{N(1-\xi_P)\} \tag{4.6}$$

and it follows from equation (2.19) that in order to obtain the correct asymptotic limit

$$\xi_P = 1 + \int_1^\infty G(\psi)\,d\psi - \tfrac{1}{2}N^{-1}\log\{(-2\pi/G'(1))\,N\} + O(N^{-2}) \tag{4.7}$$

which indirectly specifies P from equation (4.5). Note that in order to use such a criterion it is necessary to have $P = P(N)$, i.e. any P of $O(1)$ is not sufficient. Omission of the terms of $O(N^{-1}\log N)$ and $O(N^{-1})$ leads to significant errors, from a mathematical point of view, in the asymptotic value. Note that for this linear case the asymptotic frozen value is much more sensitive to the value of P than in the non-linear case. Again these conclusions are valid only when $\sigma \ll 1$.

Rosner (1962) (see also Smith 1958) recognized that the asymptotic form of the rate equation was given by neglecting the equilibrium term and that a more correct asymptotic solution would be obtained by integrating the resultant equation (i.e. equation (3.46)). Since Rosner considered the uncoupled problem for a monatomic ionizing gas his results are of direct interest here. As well as obtaining a numerical solution to an equation of the type (3.10) Rosner presented an approximate analytical solution for the distribution of α. To obtain this latter solution he considered the form of the rate equation when $\alpha_e \ll \alpha$, i.e. equation (3.46), and integrated this equation to give a result equivalent to equation (3.47). Rosner then assumed that the arbitrary constant, as yet undetermined in his asymptotic solution, could be derived by matching α and its derivative to the equilibrium solution at some point. It follows that this match point is defined by

$$d\alpha_e/dz = -\Lambda F(z)\,\alpha_e^2 \tag{4.8}$$

which is not the point associated with the singular behaviour of equation (3.15) though equation (4.8) is similar in form to (3.16). Moreover, it is obvious that this approach does not formally take into account the behaviour within the transition layer. If one obtains an asymptotic solution in this way it transpires that

$$\frac{\alpha}{\alpha_{ef}} = \left\{\frac{\alpha_{ef}}{\alpha_{eR}} + \tfrac{1}{2}N\int_{\xi_R}^{\xi} G(\psi)\,d\psi\right\}^{-1}, \tag{4.9}$$

where the suffix R denotes the value at Rosner's match point, which is given by equation (4.8). Equation (4.8) is equivalent to (4.1) with $P = 1$, and it follows from equation (4.2) that

$$\xi_R = 1 - N^{-1}\log 2 - N^{-2}f'(1)\log 2 + O(N^{-3}), \tag{4.10}$$

and hence, from equation (4.9),

$$\frac{\alpha}{\alpha_{ef}} = \left\{\tfrac{1}{2}N\int_1^{\xi} G(\psi)\,d(\psi) + \tfrac{1}{2}(1+\log 2) - \frac{f'(1)\,(\log 2)^2}{N} + O\left(\frac{1}{N^2}\right)\right\}^{-1}, \tag{4.11}$$

noting that $f'(1) = G'(1) + O(N^{-1})$. Comparison with equation (3.53) shows that the first term of this solution *is* correct but that the higher-order terms are *not*. It follows that Rosner's approach is a better approximation than the sudden-freeze approach. The above result also implies that the error in the sudden-freeze approximation lies not so much in matching directly to the equilibrium solution but in failing to take account of the correct asymptotic form of the rate equation. The effect of the transition layer determines the second and higher-order terms in the asymptotic solution.

Rosner also obtained an exact numerical solution of the full equation for a specific case and he compared both the sudden-freeze result and (effectively) the expression (4.9), as $\xi \to \infty$, with the exact asymptotic value. He concluded, as might be expected, that his solution gave closer agreement with the exact numerical solution than did the sudden-freeze approach. On the other hand the value given by the sudden-freeze assumption was still apparently of the same order of magnitude as the exact asymptotic solution, even though in this particular case $N \approx 11$. It soon becomes apparent that for this case the series of equation (3·53) converges only slowly. The convergence of the asymptotic solution is governed, apart from the magnitude of N, by the function $G(\xi)$ and the derivatives $f'(1)$, $f''(1)$, etc. In many cases the derivatives $f'(1)$, etc., are large and from the asymptotic series it would appear that the relevant parameter governing convergence is $N/f'(1)$. Consequently in some cases the asymptotic series will converge only slowly. In particular as

$$\Phi \to 1, \quad f'(1) \sim -2/(\Phi-1), \text{ etc.,}$$

and the relevant parameter governing convergence is $N(\Phi-1)$. As noted in §3.6 for $(\Phi-1)$ sufficiently small the asymptotic series no longer converges.

A similar approach to Rosner's applied to the linear rate equation is also mathematically incorrect for this uncoupled case. For the linear rate equation of §2, the asymptotic value of $\sigma/\overline{\sigma}_f$ is

$$O\left(N^{\frac{1}{2}} \exp\left\{-N\int_1^\infty G(\psi)\,d\psi\right\}\right),$$

while Rosner's approach gives $\sigma/\overline{\sigma}_f$ to be

$$O\left(\exp\left\{-N\int_1^\infty G(\psi)\,d\psi\right\}\right).$$

Note that in this case the approach does not give a good first approximation to the asymptotic value. Again, as was found for the non-linear rate equation, the convergence of the asymptotic series is slow in many cases.

Eschenroeder (1962) also considered the flow of an ionizing gas. He too noted that the asymptotic solution was given by neglecting the equilibrium term in the rate equation and integrating the subsequent equation. However, he assumed that the function $F_1(x)$ (equation (3.4)) was given by its asymptotic representation for large x, which is equivalent to assuming that $G(\xi)$ can be represented by its asymptotic form for large z and Φ. A necessary condition for such an assumption to be valid is that $\Phi \gg 1$. Eschenroeder examined two cases:

(i) where $\int^x F_1(x)\,dx$ was finite for all x, and (ii) where the integral was not bounded. For the first case he still assumed that the asymptotic solution could be represented by α = constant, that is, he neglected the variation with x as α approached its asymptotic limit, and he matched this solution to the equilibrium solution at the point defined by equation (3.16). Thus for case (i) Eschenroeder's approach was equivalent to the sudden-freeze approximation. In case (ii) Eschenroeder did include the asymptotic variation with x, since in this case $\alpha \to 0$ asymptotically, (though it does *not* follow the equilibrium distribution for large x). As before he matched this solution to the equilibrium solution at the freezing point defined by equation (3.16). For $\Phi \gg 1$ it follows that for this latter case the approach is equivalent to Rosner's but with an error term of $O(N^{-1}\Phi^{-1})$ instead of $O(N^{-2})$. However, for general values of Φ the approach does not give the first term of the asymptotic solution correctly, since $F_1(x)$ and hence $G(\xi)$ could not then be represented by its asymptotic expansion for all $\xi \geqslant 1$.

More recently Stollery & Park (1963) have derived a further freezing criterion which they specifically applied to a linear rate equation. The criterion is empirical in structure. Stollery & Park observed that in their numerical calculations the (dimensionless) relaxation length defined by conditions in the equilibrium flow at the point where the equilibrium energy equalled the asymptotic non-equilibrium frozen value (this is not in general the same freezing point as Bray's) appeared to be independent of the (dimensionless) rate parameter, i.e. for the rate equation of § 2,

$$NG(\xi_{St})\,(d\xi/dx)_{\xi_{St}} = \text{const. (independent of } N), \tag{4.12}$$

where ξ_{St} defines the value of ξ at the freezing point as given by Stollery & Park. Since ξ_{St} is defined by $\overline{\sigma}(\xi_{St}) = \sigma(\infty)$, where $\sigma(\infty)$ denotes the asymptotic value of σ, it follows that ξ_{St} is given by equation (4.7). Substitution of this expression in the left-hand side of equation (4.12) does not, in general, give an expression which is independent of N.

In conclusion it can be stated that none of the approximate methods of determining the asymptotic value of the energy in the lagging mode are mathematically correct in the limit when the energy is small compared with the total enthalpy (though Rosner's approach as applied to the non-linear rate equation (3.4) is a valid first approximation). However, no conclusions can be given concerning the validity of these approximate methods for arbitrary values of α, σ. Comparison with exact numerical calculations when α and σ are $O(1)$ would seem to indicate that the approximate methods may have some limited region of validity.

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