Non-equilibrium flow through a nozzle

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(Received 12 February 1963)

Vibrationally relaxing flow through a nozzle is examined in the case when the amount of energy in the lagging mode is small. It is shown that there exists a 'boundary-layer' region in which relatively large departures from equilibrium occur. The position of this region is given by the type of criterion that has previously been used to predict the onset of 'freezing'. An analytical solution for the distribution of the vibrational energy in the nozzle is obtained for a particular nozzle geometry, and an expression for the final asymptotic 'frozen' value of the vibrational energy far downstream is found. This asymptotic solution can be obtained from conditions at the 'freezing' point provided a suitable boundary condition is applied there.

1. Introduction

It is well known that when a gas is disturbed from a state of equilibrium the re-distribution of energy among the various modes is not instantaneous. Much work has been done on examining the effects that such time lags can have on various flows. In recent years considerable attention has been given to non-equilibrium expanding flows, especially the quasi-one-dimensional flow through a nozzle (see, for example, Bray 1959; Freeman 1959; Hall & Russo 1959; and Stollery & Smith 1962). Such flows are of considerable practical importance with regard to the performance of hypersonic wind tunnels, rocket nozzles, etc. In particular, in this report vibrationally relaxing flow through a divergent nozzle (as in a shock tunnel) will be considered in detail.

The important parameter in non-equilibrium flow is the ratio of the time scale of the flow to the relaxation time (i.e. a time characterizing the rate of adjustment of the lagging mode to the ambient conditions). In an expanding flow this parameter will decrease and consequently the lagging mode will find it increasingly difficult to adjust to its local equilibrium state. In fact as the flow expands the relaxation time will become large and the energy in the lagging mode will 'freeze out' at some constant value, greater than the equilibrium value, since the rate of change of energy in the lagging mode will approach zero as the relaxation time approaches infinity. Numerical calculations (see above references) confirm this general picture. They show, for dissociational or vibrational relaxation starting from equilibrium conditions, that the energy in the lagging mode at first remains near to its equilibrium value but that at sufficiently large distances downstream it breaks away from the equilibrium distribution and rapidly approaches some final constant, 'frozen', value (see figure 1). From these results it appears that a solution far enough upstream of the breakaway can be obtained by perturbing about the equilibrium solution. Downstream of the breakaway a suitable asymptotic solution can be constructed by including only the dominant terms in the rate equation (see § 3.4). In general such an asymptotic solution will contain an unknown constant which has to be determined by a suitable matching procedure to the solution upstream of the breakaway. Bray (1959) attempted to do this in a very simple manner for dissociation. By a suitable qualitative argument he obtained an equation which defined the breakaway or sudden 'freezing' position. Upstream of this point the flow was assumed to be in equilibrium, while downstream of it the energy in the lagging mode was assumed to remain constant at its equilibrium value at the 'freezing' point (see figure 1). This approximate solution was in reasonable agreement with the exact numerical solution.

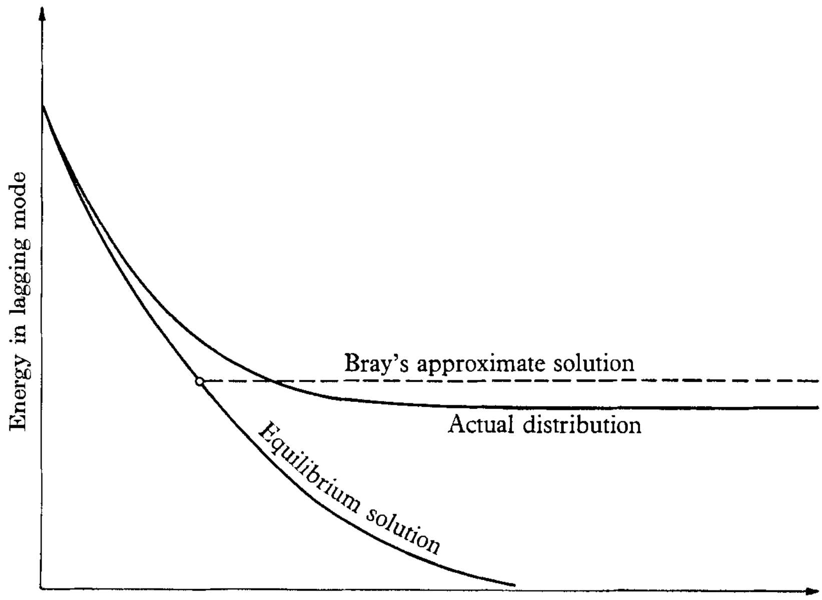

FIGURE 1. Schematic representation of variation of vibrational energy in a nozzle.

Such a solution gives no information on the detailed behaviour in the rapid transition region near the freezing point, and in general this behaviour must be known in order to determine the correct boundary condition to apply to the asymptotic solution. In the present paper an analytical solution for the variation of the energy in the lagging mode is derived for a relatively simple case, namely vibrational relaxation in a conical nozzle assuming that the amount of vibrational energy is small and that dissociation, etc., is negligible. The Mach number of the flow is assumed to be large everywhere. It is shown that a rapid transition or 'boundary-layer' region exists in which appreciable departures from equilibrium occur. Upstream of this region the flow remains near to equilibrium. The position of the boundary-layer region is given by the type of criterion used by Bray (1959) to define the freezing point. The analytical solution to be presented here is valid, neglecting error terms of a certain order, throughout the nozzle, and the correct asymptotic solution is easily found from this solution. It is shown that the asymptotic solution can be obtained from conditions at the freezing point provided a suitable boundary condition is applied there. Furthermore (see § 3.3) the solution contains the two limiting cases of near-equilibrium and near-frozen flow.

The simplicity of the solution derived here arises from the assumption that the amount of vibrational energy is small, i.e. that the fraction of excited oscillators is small. (This technique was earlier used by Spence (1961) in discussing unsteady shock propagation in a relaxing gas.) In this case it is permissible to use a linear rate equation (Shuler 1959) and to a first approximation the flow variables are given by their values neglecting vibration.† These values are then substituted into the rate equation and a first-order linear differential equation with known coefficients is obtained for the local departure from equilibrium. The solution of this equation can be expressed as the product of a known function and a certain integral. The integral is a typical steepest-descents type and can be evaluated in the usual way. The main contribution to the integral comes from the region near the saddle point and it is this point that is identified with the onset of freezing.

The relevant equations are written down in § 2 and the first approximation to the flow variables obtained. The rate equation is solved in § 3 and the distribution of the vibrational energy found for the case described above.

2. The governing equations and the approximation scheme

The translational and rotational degrees of freedom are assumed to be fully excited and in a state of local equilibrium throughout the flow. Dissociation and similar phenomena are assumed to be negligible. The rate equation for vibrational relaxation is taken to have the form

$$\frac{d\sigma'}{dt'} = \omega'(\rho', T')\{\bar{\sigma}'(T') - \sigma'\}, \tag{1}$$

where σ' is the vibrational energy, $\bar{\sigma}'$ its equilibrium value corresponding to the local translational temperature T'; ω' is termed the relaxation frequency (the reciprocal of the relaxation time) and is a function of the density ρ' and the temperature T'; t' is the time measured from some suitable datum value. Primed variables are in dimensional form. This rate equation can be shown to be valid for a system of harmonic oscillators when only a small fraction of the oscillators are excited (Shuler 1959), and this condition will be used here. Theoretically ω' takes the form

$$\omega' = \rho'\Omega'(T'),$$

and several expressions for Ω' exist. Here it will be assumed that $\Omega' \propto T'^s$. Although this type of variation is not in agreement with any of the theoretical predictions it does have the correct qualitative behaviour and furthermore it

† Some numerical work by Stollery & Smith (1962) has shown that this is a fair approximation for vibrational relaxation in a diatomic gas even when the fraction of excited oscillators is not small though the validity of the linear rate equation is then questionable.

leads to certain simplifications in the analytical solution to be presented later. Equation (1) is now re-written in dimensionless form as

$$\frac{d\sigma}{dx} = \Lambda \frac{\rho T^s}{u} (\bar{\sigma} - \sigma), \tag{2}$$

where all the variables have been non-dimensionalized with respect to their values at some suitable reference point (denoted by the suffix r, i.e., ρ'/ρ'_r, etc.) save for σ', $\bar{\sigma}'$ which are non-dimensionalized with respect to RT'_r where R is the gas constant; x' is the distance measured from this point, and $x = x'/l$, where l is some suitable nozzle dimension; u' is the velocity, and $\Lambda = l\omega'_r/u'_r$ is a representative value of the ratio of the time scale of the flow to the time scale of the relaxation process. Λ large implies that the flow is near equilibrium, while Λ small that the flow is nearly frozen (see Freeman 1959).

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

$$\bar{\sigma}' = \frac{R\theta'}{e^{\theta'/T'} - 1},$$

where θ' is the characteristic temperature of vibration. Let $\theta = \theta'/T'_r$, so that the above equation can be written in dimensionless form as

$$\bar{\sigma} = \frac{\theta}{e^{\theta/T} - 1}, \tag{3a}$$

and since it is assumed that the fraction of excited oscillators is small, $\theta \gg 1$, and

$$\bar{\sigma} \approx \theta\, e^{-\theta/T}. \tag{3b}$$

The equations governing the quasi-one-dimensional flow through the nozzle can be written in non-dimensional form as

$$\rho u A = 1, \tag{4}$$

$$u\frac{du}{dx} = -\frac{1}{\gamma_\alpha m_r^2 \rho}\frac{dp}{dx}, \tag{5}$$

$$\frac{\gamma_\alpha}{\gamma_\alpha - 1} T + \sigma + \tfrac{1}{2}\gamma_\alpha m_r^2 u^2 = \frac{\gamma_\alpha}{\gamma_\alpha - 1} + \sigma_r + \tfrac{1}{2}\gamma_\alpha m_r^2, \tag{6}$$

and the equation of state is

$$p = \rho T. \tag{7}$$

Here $A = A'/A'_r$ where A' is the local cross-sectional area at any station x', p is the pressure, γ_α is the ratio of the specific heats neglecting vibration, and m is the Mach number based on the frozen speed of sound $\sqrt{(\gamma_\alpha RT')}$. Note that the above equations are equivalent to those governing the quasi-one-dimensional flow, with heating, of a perfect gas (Johannesen 1961).

Under the assumption that $\sigma \ll 1$, the energy equation (6) becomes to a first approximation

$$T + \tfrac{1}{2}(\gamma_\alpha - 1) m_r^2 u^2 = 1 + \tfrac{1}{2}(\gamma_\alpha - 1) m_r^2. \tag{8}$$

(This result would also be true if $\sigma_r - \sigma$ was small everywhere compared with $T + \frac{1}{2}(\gamma_\alpha - 1) m_r^2 u^2$.) This equation, together with equations (4), (5) and (7), governs the isentropic quasi-one-dimensional flow of a perfect gas. The solution to this set of equations is well known (see, for example, Shapiro 1953) and can be written

$$u = \frac{m_r}{m}\left[\frac{1+\frac{1}{2}(\gamma_\alpha - 1)m_r^2}{1+\frac{1}{2}(\gamma_\alpha - 1)m^2}\right]^{\frac{1}{2}}, \tag{9}$$

$$\rho = \left[\frac{1+\frac{1}{2}(\gamma_\alpha - 1)m_r^2}{1+\frac{1}{2}(\gamma_\alpha - 1)m^2}\right]^{1/(\gamma_\alpha - 1)}, \tag{10}$$

$$T = \frac{1+\frac{1}{2}(\gamma_\alpha - 1)m_r^2}{1+\frac{1}{2}(\gamma_\alpha - 1)m^2}, \tag{11}$$

$$A = \frac{m_r}{m}\left[\frac{1+\frac{1}{2}(\gamma_\alpha - 1)m^2}{1+\frac{1}{2}(\gamma_\alpha - 1)m_r^2}\right]^{(\gamma_\alpha+1)/[2(\gamma_\alpha-1)]} \tag{12}$$

In order to compute the first approximation to the vibrational energy distribution these expressions for ρ, T, etc., are substituted into (2) and the resulting first-order linear differential equation integrated. This type of approximation scheme has been carried out numerically by Stollery & Smith (1962) for a particular nozzle geometry. Their results show that the vibrational energy follows the equilibrium distribution fairly closely at first but eventually breaks away and rapidly approaches some final asymptotic (non-zero) value. This picture is in qualitative agreement with the results of the numerical solutions obtained by Bray (1959), Freeman (1959), and Hall & Russo (1959) for dissociation. In the next section it will be shown that this type of behaviour can be deduced analytically from the rate equation and furthermore that an analytical solution for the vibrational energy distribution can be obtained.

3. Vibrational energy distribution

3.1. *Integration of the rate equation*

It is more convenient to solve equation (2) for the departure from equilibrium $\epsilon = \sigma - \bar{\sigma}$ rather than for σ. To this approximation, ρ, T, u, and $\bar{\sigma}$ are known functions of m, and equation (2) is re-written

$$\frac{d\epsilon}{dm} + \Lambda F(m)\,\epsilon = -\frac{d\bar{\sigma}}{dm}, \tag{13}$$

where
$$F(m) = \frac{\rho(m)\,T^s(m)}{u(m)}\frac{dx}{dm},$$

and u, ρ, and T are given by equations (9), (10) and (11). $F(m)$ is a known function of m for a given nozzle shape $A(x)$, since dx/dm can be determined from (12). It will be assumed that at some initial station denoted by the suffix o (which may or may not coincide with the station r) the flow is in equilibrium, i.e. $\epsilon = 0$ at $m = m_0$. Hence, from equation (13)

$$\epsilon = \int_{m_0}^{m}\left(-\frac{d\bar{\sigma}}{dv}\right)\left\{\exp\int_{m}^{v}\Lambda F(w)\,dw\right\}dv, \tag{14}$$

where v, w are dummy variables. Using (3*b*) for $\bar{\sigma}$ gives

$$\epsilon = \exp\left\{-\Lambda\int^{m} F(w)\,dw\right\}\int_{m_0}^{m} g(v)\exp\left[-\theta f(v)\right]dv, \tag{15}$$

where $$g(v) = -\left(\frac{\theta}{T}\right)^2\frac{dT}{dv} \quad\text{and}\quad f(v) = \frac{1}{T}-\frac{\Lambda}{\theta}\int^{v} F(w)\,dw.$$

For θf large, except perhaps in isolated regions where f is a minimum, this integral is of the steepest-descents type (Jeffreys & Jeffreys 1946, p. 472). The maximum contribution to the integral will come from the neighbourhood of $f' = 0$ (the saddle point). Upstream of this region the integrand and the integral are relatively small. In the region of the saddle point both the integrand and the integral increase rapidly. Downstream of this region the integrand decreases and the integral tends to some constant (non-zero) value. These statements will be expressed more rigorously below when a particular case is considered in detail. However, this behaviour is precisely what has been found in the numerical solutions and the condition $f' = 0$ corresponds to the onset of the freezing, or breaking away from the equilibrium distribution, that is observed in these solutions.

The condition $f' = 0$ is satisfied at the point where

$$\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{dm} = -\Lambda F(m), \tag{16}$$

which is the same type of criterion as that derived by Bray (1959) by qualitative arguments for the position of freezing for dissociational relaxation in a nozzle. Note that (16) is a general result for a rate equation of the form (1) provided $F(m)$ is modified according to the temperature dependence used for $\Omega'(T')$.

A criterion equivalent to that proposed by Stollery and Smith (1961) is given by

$$\left(\frac{d\bar{\sigma}}{dm}\right)^{-1}\frac{d^2\bar{\sigma}}{dm^2} = -\Lambda F(m).$$

It is easily shown that this equation reduces to (16) for $\theta \gg 1$. It is interesting to note that this criterion is satisfied at the position where the integrand as a whole has a maximum with respect to m. For the precise criteria of Bray and of Stollery & Smith the reader is referred to the respective papers by these authors.

3.2. *Application of steepest-descents technique to the special case of hypersonic flow through a conical nozzle*

This case is one which is readily amenable to an analytical treatment, and the study of such a case has the advantage that the ideas outlined above can be reiterated in a more rigorous, but nevertheless simple, fashion.

For $x < 0$ the gas is assumed to be in thermodynamic equilibrium and to be flowing at hypersonic speed along a constant area channel. For $x \geqslant 0$ the gas is expanded through a conical nozzle for which the cross-sectional area ratio is given by

$$A = (1+x)^2 \quad (x \geqslant 0). \tag{17}$$

The station r is in this case identified with the station o (both being defined by $x = 0$), and use of equation (17) and the limiting form of equations (9)–(12) for $m, m_r \gg 1$ gives

$$g(m) = 2\theta^2 \frac{m}{m_r^2}; \quad f(m) = \left(\frac{m}{m_r}\right)^2 + \frac{\Lambda}{\theta n(\gamma_\alpha - 1)(m/m_r)^n},$$

where $n = (\gamma_\alpha - 1)^{-1} + 2s$. Denoting m/m_r by z, equation (15) becomes

$$\epsilon = 2\theta^2 \left\{\exp \frac{\Lambda}{(\gamma_\alpha - 1) n z^n}\right\} \int_1^z y \exp\left\{-\left[\theta y^2 + \frac{\Lambda}{(\gamma_\alpha - 1) n y^n}\right]\right\} dy, \tag{18}$$

where y is a dummy variable.

The saddle point or freezing point is given from equation (16) by

$$z_s = \left[\frac{\Lambda}{2(\gamma_\alpha - 1)\theta}\right]^{1/(n+2)} = \Phi \quad \text{(say)}. \tag{19}$$

A new variable ξ is defined by $\xi = z/\Phi$, and equation (18) becomes

$$\epsilon = \left\{2\theta N^2 \exp \frac{2N^2}{n\xi^n}\right\} \int_{\Phi^{-1}}^{\xi} \psi \exp\left[-N^2\left(\psi^2 + \frac{2}{n\psi^n}\right)\right] \mathrm{d}\psi, \tag{20}$$

where $N = \theta^{\frac{1}{2}}\Phi$, and ψ is a dummy variable. The integral is now typical of those evaluated by the method of steepest descents provided that $N^2 \gg 1$ and that the saddle point occurs within the range of integration. In order for this latter condition to hold, Φ must be greater than unity, in which case $N \gg 1$ (since $\theta \gg 1$), and furthermore, from equation (19), Λ is at least of order θ. When $\Phi < 1$, the stationary point (freezing point) no longer occurs in the physical flow (since $m \geqslant m_r$ everywhere). This case corresponds to near-frozen flow (Λ small) when the vibrational energy distribution never follows the equilibrium curve.

In general, the only significant contributions to the integral will come from a region of order N^{-1} in thickness in the neighbourhood of the saddle point or freezing point. Within this region the integral increases sharply and there is a relatively large departure from equilibrium. The structure of this rapid transition region or boundary-layer region is analysed below.

A new variable η is defined by

$$\eta = \operatorname{sgn}(\psi - 1)\,[2\{(q(\psi) - q(1)\}]^{\frac{1}{2}},$$

where $q(\psi) = \psi^2 + 2/n\psi^n$ and $\psi = 1$ is the saddle point. In terms of η, the usual steepest-descents variable, equation (20) becomes

$$\epsilon = \left\{2\theta N^2 \exp\left(\frac{2}{n\xi^n} - q(1)\right)\right\} \int_{B(\Phi^{-1})}^{B(\xi)} \psi \frac{d\psi}{d\eta} \exp\left(-\tfrac{1}{2}N^2\eta^2\right) d\eta,$$

where $$B(\xi) = \operatorname{sgn}(\xi - 1)\,[2\{q(\xi) - q(1)\}]^{\frac{1}{2}}.$$

Near the saddle point $\frac{1}{2}\eta^2$ can be expanded in the form

$$\tfrac{1}{2}\eta^2 = \tfrac{1}{2}(\psi - 1)^2 q''(1) + \ldots,$$

and this series can be inverted to obtain

$$\psi - 1 = \frac{1}{[q''(1)]^{\frac{1}{2}}}\eta - \frac{q'''(1)}{6[q''(1)]^2}\eta^2 + \ldots,$$

and hence
$$\psi\frac{d\psi}{d\eta} = \frac{1}{[q''(1)]^{\frac{1}{2}}} + \frac{\eta}{q''(1)}\left[1 - \frac{q'''(1)}{3q''(1)}\right] + \dots$$
$$= \sum_{r=0} a_r \eta^r \quad \text{(say).}$$

The function
$$L(\eta) = \frac{1}{\eta}\left(\psi\frac{d\psi}{d\eta} - a_0\right)$$

is continuous through the saddle point and bounded. As $\eta \to \infty$, $L \to 0$; as $\eta \to B(\Phi^{-1})$ then provided Φ is at least $O(1)$, the function $L[B\Phi^{-1})]$ is at most $O(1)$. Let

$$I = \int_{B(\Phi^{-1})}^{B(\xi)} \psi\frac{d\psi}{d\eta}\exp(-\tfrac{1}{2}N^2\eta^2)\,d\eta$$
$$= \int_{B(\Phi^{-1})}^{B(\xi)} a_0\exp(-\tfrac{1}{2}N^2\eta^2)\,d\eta + \int_{B(\Phi^{-1})}^{B(\xi)} \frac{1}{\eta}\left(\psi\frac{d\psi}{d\eta} - a_0\right)\eta\exp(-\tfrac{1}{2}N^2\eta^2)\,d\eta$$
$$= \left[\frac{a_0}{N}E(N\eta) - \frac{1}{N^2}\frac{1}{\eta}\left(\psi\frac{d\psi}{d\eta} - a_0\right)\exp(-\tfrac{1}{2}N^2\eta^2) + O\left(\frac{1}{N^3}E(N\eta)\right)\right]_{B(\Phi^{-1})}^{B(\xi)}$$

where
$$E(N\eta) = \int_{-\infty}^{N\eta}\exp(-\tfrac{1}{2}t^2)\,dt = \left(\frac{\pi}{2}\right)^{\frac{1}{2}}\left[1 + \operatorname{erf}\left(\frac{N\eta}{\sqrt{2}}\right)\right].$$

Upstream of the boundary-layer region the first two terms in the above expression for I are of the same order of magnitude. It will be shown later (§ 3.3) that in this region the solution does reduce to the near-equilibrium solution expected there. Within the boundary-layer region (and downstream of it) the first term dominates and represents the rapid departure from equilibrium which occurs there. Downstream of this region the error term is of a greater order of magnitude than the second term. Neglecting the error term in the above expression and using equation (20) gives

$$\epsilon = \{2a_0\theta N\exp[-N^2q(1)]\}\{E[NB(\xi)] - E[NB(\Phi^{-1})]\}\exp(2N^2/n\xi^n)$$
$$-2\theta L[B(\xi)]\exp(-N^2\xi^2) + 2\theta L[B(\Phi^{-1})]\exp[-N^2q(\Phi^{-1})]\exp(2N^2/n\xi^n). \tag{21}$$

When the freezing point lies within the nozzle (i.e. $\Phi > 1$), $B(\Phi^{-1}) < 0$, $|NB(\Phi^{-1})| \gg 1$, and $E[NB(\Phi^{-1})]$ can be expanded in the form

$$E[NB(\Phi^{-1})] = -\frac{1}{NB(\Phi^{-1})}\exp[-\tfrac{1}{2}N^2B^2(\Phi^{-1})] + O\left(\frac{1}{N^2B^2(\Phi^{-1})}\exp[-\tfrac{1}{2}N^2B^2(\Phi^{-1})]\right).$$

Using this expression, equation (21) simplifies slightly to

$$\epsilon = \{2a_0\theta N\exp[-N^2q(1)]\}E[NB(\xi)]\exp(2N^2/n\xi^n)$$
$$-2\theta L[B(\xi)]\exp(-N^2\xi^2) + 2\theta\left(\frac{\psi}{\eta}\frac{d\psi}{d\eta}\right)_{\psi=\Phi^{-1}}\exp[-N^2q(\Phi^{-1})]\exp(2N^2/n\xi^n). \tag{22}$$

The full expressions (either (21) or (22)) are only justifiable upstream of the boundary-layer region.† Downstream of this region both the second and third terms are exponentially smaller than the error terms omitted from the above

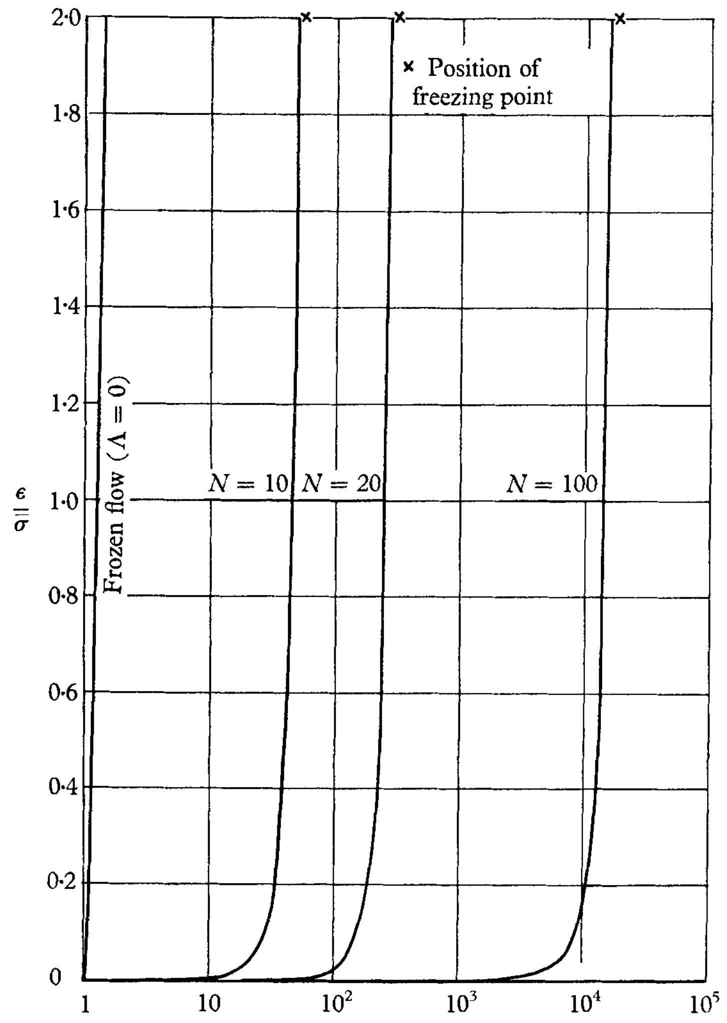

FIGURE 2. Relative departure from equilibrium as a function of x for various values of N.

equations, (the $\bar{\sigma}$ term contained in ϵ on the left-hand side is also exponentially smaller than the error terms). Within and downstream of the boundary-layer region, equation (22) can be written

$$\sigma = 2a_0\theta N \exp\{-N^2q(1)\}\{E[NB(\xi)]\exp(2N^2/n\xi^n)\}\{1+O(N^{-1})\}. \tag{23}$$

Downstream of the 'boundary-layer' region the error term is $O(N^{-2})$.

In figure 2 the relative departure from equilibrium $\epsilon/\bar{\sigma}$ is plotted as a function of x for various values of N. Note that this function approaches infinity for large x

† In fact the full expression (21) is justifiable wherever $|NB(\xi)| \gg 1$ which includes the case when the 'freezing' point does not occur in the nozzle, i.e. near-frozen flow (see § 3.3).

for all finite N. A common feature of all the curves (apart from that for 'frozen' flow) is that $\epsilon/\bar{\sigma}$ remains effectively zero until the freezing point is approached where there is a rapid increase in the departure from equilibrium.

Although the solution given here is for a particular temperature dependence of the relaxation frequency and a specific nozzle shape, i.e. particular $F(m)$, the results are applicable to a general temperature dependence and nozzle shape, i.e. general $F(m)$, provided q and N are suitably reinterpreted. Scaling with respect to the values at the freezing point gives, in the general case

$$N^2 = \tfrac{1}{2}\Lambda F_s \Phi' = -\frac{1}{2}\left(\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{dm}\right)_s \Phi',$$

and

$$q(\xi) = 2\int^{\xi}\left[\left\{\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{d\psi}\bigg/\left(\frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{d\psi}\right)_s\right\} - \frac{F}{F_s}\right]d\psi.$$

Here the suffix s denotes conditions at the freezing point (saddle point) and $\Phi' = m_s$ is the solution of (16) for m. Note that it is not always possible to write down Φ' as an explicit function of Λ and θ.

3.3. *Solution away from the 'freezing' point*

Upstream of the boundary-layer region it is expected that some suitable near-equilibrium solution should be applicable. Alternatively if the freezing point does not lie in the nozzle a near-frozen solution may be valid. These solutions can be obtained by a straightforward expansion of the integral in equation (18). This equation can be written

$$\epsilon = 2\theta^2 \exp\left\{\frac{\Lambda}{(\gamma_\alpha - 1)\, nz^n}\right\}\int_{f_1(1)}^{f_1(z)} \frac{y}{f_1'(y)} \exp\{-\theta f_1(y)\}\, df_1,$$

where $f_1(y) = f(ym_r) = y^2 + \Lambda/y^n n\theta(\gamma_\alpha - 1)$. Assuming that the point defined by $f_1'(y) = 0$ does not lie within the range of integration, integration by parts gives

$$\epsilon = 2\theta^2 \exp\left\{\frac{\Lambda}{(\gamma_\alpha - 1)\, nz^n}\right\}\left[\frac{-y}{f_1'(y)}\frac{\exp\{-\theta f(y)\}}{\theta}\right]_{f_1(1)}^{f_1(z)}\left\{1 + O\left(\frac{1}{\theta f_1'(z)^2}\right)\right\}. \quad (24)$$

The condition $\theta f_1'(z)^2 \gg 1$ is equivalent to $N^2 q'(\xi)^2 \gg 1$ which implies that the flow never passes through the freezing point. This does not necessarily mean that the analysis is valid only upstream of the boundary-layer region since in some cases the freezing point does not lie in the nozzle, though the above condition may be valid (the error term is then $O(1/\theta)$). Expanding (24) and neglecting smaller order terms gives

$$\epsilon = 2\theta \exp\left\{\frac{\Lambda}{(\gamma_\alpha - 1)\, nz^n}\right\}\left[\left\{2 - \frac{\Lambda}{\theta(\gamma_\alpha - 1)}\right\}^{-1} \exp\left\{-\left(\theta + \frac{\Lambda}{(\gamma_\alpha - 1)\, n}\right)\right\}\right.$$
$$\left. - \left\{2 - \frac{\Lambda}{\theta(\gamma_\alpha - 1)\, z^{n+2}}\right\}^{-1} \exp\left\{-\left(\theta z^2 + \frac{\Lambda}{(\gamma_\alpha - 1)\, nz^n}\right)\right\}\right]. \quad (25)$$

Note that equation (21) reduces to equation (25) when $|NB(\xi)| \gg 1$ which is again equivalent to conditions holding either upstream of the boundary-layer region or when the freezing point does not lie in the nozzle. The solution (21) can be regarded as rendering (25), which has a singularity at the freezing point, uniformly valid throughout the whole flow region.

In the case which corresponds to conditions upstream of the boundary-layer region,

$$\frac{\Lambda}{\theta(\gamma_\alpha - 1)\, z^{n+2}} \gg 2,$$

(this condition implies that Λ is very large) and equations (25) or (21) reduce to

$$\epsilon = \frac{2\theta^2(\gamma_\alpha - 1)\, e^{-\theta}}{\Lambda}\left[z^{n+2}\exp\{-\theta(z^2-1)\} - \exp\left\{-\frac{\Lambda}{(\gamma_\alpha - 1)\, n}\left(1 - \frac{1}{z^n}\right)\right\}\right]. \quad (26)$$

In order to retain the correct behaviour near $z = 1$ (see appendix) both terms inside the square bracket must be retained, but for z sufficiently greater than unity (in fact outside a region near $z = 1$ whose thickness is $O(1/\Lambda)$) the first term dominates and

$$\epsilon = \frac{2\theta^2(\gamma_\alpha - 1)}{\Lambda} z^{n+2}\exp(-\theta z^2),$$

or alternatively

$$\epsilon = \frac{1}{\Lambda F}\left(-\frac{d\sigma}{dm}\right), \quad (27)$$

which is the usual near-equilibrium solution obtained by a formal expansion in powers of $1/\Lambda$ (see appendix). Note again that since (21) reduces to (25) upstream of the boundary-layer region these conclusions can be deduced from (21) which is also valid within the boundary-layer region.

In the limiting case when the freezing point does not occur in the nozzle,

$$\frac{\Lambda}{(\gamma_\alpha - 1)\,\theta} \ll 2,$$

and this corresponds to near-frozen flow. Either equation (25) or equation (21) reduces to

$$\epsilon = \theta e^{-\theta}\left[\exp\left\{-\frac{\Lambda}{(\gamma_\alpha - 1)\, n}\left(1 - \frac{1}{z^n}\right)\right\} - \exp\{-\theta(z^2-1)\}\right]. \quad (28)$$

In this case, away from $z = 1$, the first term inside the square brackets dominates and for $\Lambda \ll 1$ an expansion in powers of Λ can be inferred. To obtain the correct behaviour near $z = 1$ both terms must be retained and for $\Lambda \ll 1$

$$\epsilon = \overline{\sigma}_r - \overline{\sigma} - \frac{\Lambda}{n(\gamma_\alpha - 1)}\left(1 - \frac{1}{z^n}\right)\overline{\sigma}_r,$$

or

$$\sigma = \overline{\sigma}_r\left\{1 - \frac{\Lambda}{(\gamma_\alpha - 1)\, n}\left(1 - \frac{1}{z^n}\right)\right\}, \quad (29)$$

which is the usual near-frozen flow solution (see appendix).

3.3. *Asymptotic solution*

As $x, z \to \infty$, $\overline{\sigma} \to 0$ exponentially fast and for large z the rate equation takes the form

$$\frac{d\sigma}{dm} = -\Lambda F \sigma,$$

which on integration gives (in terms of the variable ξ)

$$\sigma = C\exp(2N^2/n\xi^n). \tag{30}$$

The constant C is equal to the final asymptotic frozen value far downstream. We wish to determine this constant in terms of the conditions at the freezing point. In general from equation (20) it is seen that

$$C = 2\theta N^2 \int_{\Phi^{-1}}^{\infty} \psi \exp\left\{-N^2\left(\psi^2 + \frac{2}{n\psi^n}\right)\right\} d\psi.$$

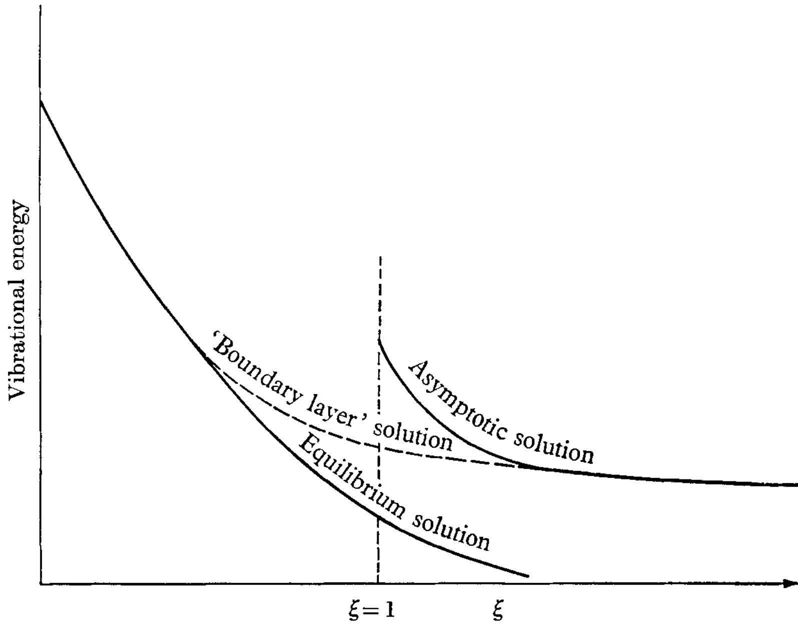

FIGURE 3. Various solution regimes (schematic).

Applying the steepest-descents analysis, assuming that the freezing point lies in the nozzle (so that $\Phi > 1$), gives

$$C = 2(2\pi)^{\frac{1}{2}} a_0 \theta N \exp\{-N^2 q(1)\}\{1 + O(N^{-2})\}. \tag{31}$$

This can be re-expressed in terms of the equilibrium conditions at the freezing point in either of the forms

$$C = 2\surd(2\pi)\, a_0 N\bar{\sigma}_s \exp(-2N^2/n)\{1 + O(N^{-2})\}, \tag{32a}$$

or

$$C = \left(\frac{2\pi}{\theta}\right)^{\frac{1}{2}} a_0 \left(-\frac{d\bar{\sigma}}{dz}\right)_s \exp(-2N^2/n)\{1 + O(N^{-2})\}. \tag{32b}$$

Alternatively the constant can be expressed in terms of the actual value of the vibrational energy at the freezing point (rather than its equilibrium value there), i.e.

$$C = 2\sigma_s \exp(-2N^2/n)\{1 + O(N^{-2})\}. \tag{32c}$$

It is apparent that in order to obtain the correct asymptotic solution from equation (30) a boundary condition of the form $\sigma = O(\bar{\sigma}_s)$ at the freezing point is not applicable, the correct boundary condition being of the form $\sigma = O(N\bar{\sigma}_s)$; that is to say the asymptotic solution cannot be matched directly to the equilibrium solution at the freezing point (see figure 3). Moreover, the final frozen value is also not $O(\bar{\sigma}_s)$ but $O(\bar{\sigma}_s N \exp\{-2N^2/n\})$. The discrepancy between these results and the matching procedure used by Bray (1959) is discussed in the next section.

4. Concluding remarks

The criterion for the onset of freezing was found to be of the same form (equation (16)) as that derived by Bray (1959) from qualitative arguments for the dissociation case. It was shown that it is not correct to match the asymptotic solution directly to the equilibrium solution at the freezing point; the final frozen value was found to be $O(\bar{\sigma}_s N \exp\{-2N^2/n\})$. These latter results are not in agreement with the assumption, made by Bray for dissociation, that the asymptotic solution can be correctly represented by the equilibrium value at the freezing point (see figure 1), though Bray did find that for dissociation there was reasonable agreement between his exact numerical solution and his approximate solution insofar as the final frozen value was concerned. However, because of fundamental differences in the asymptotic forms of the rate equations for vibration and dissociation the final frozen values in the respective cases will probably be of different orders of magnitude and the two cases are not directly comparable. For vibrational relaxation the asymptotic form of the rate equation is, as already pointed out above $d\sigma/dm = -\Lambda F\sigma$, and the solution of this equation decays exponentially to the final frozen value. For dissociation the equivalent form is $d\alpha/dm = -\Lambda F\alpha^2$, where α is the dissociation fraction. This equation has a solution of the form

$$\frac{1}{\alpha} = \text{const.} - \int_m^\infty \Lambda F\, dm.$$

The manner of approach to the final frozen value is not so severe as in the vibrational case. Before the question regarding the final frozen value in this case can be answered a detailed investigation of the full rate equation for dissociation is necessary. Under similar assumptions to those used above (i.e. $\alpha \ll 1$) this rate equation has the form

$$\frac{d\alpha}{dm} = \Lambda F(m)\,(\bar{\alpha}^2(m) - \alpha^2).$$

As pointed out by Freeman (1959) this equation is a Ricatti equation and by a suitable transformation can be reduced to a second-order linear equation with known coefficients.

An alternative approach to obtain conditions near the freezing point can be made via the differential equation for $\epsilon/\bar{\sigma}$. This equation can be written (in the linear case) as

$$\frac{d(\epsilon/\bar{\sigma})}{dm} + \left(\Lambda F(m) + \frac{1}{\bar{\sigma}}\frac{d\bar{\sigma}}{dm}\right)\left(\frac{\epsilon}{\bar{\sigma}}\right) = -\frac{1}{\sigma}\frac{d\bar{\sigma}}{dm},$$

and it can be seen that the coefficient of $\epsilon/\bar{\sigma}$ vanishes at the freezing point. The behaviour in the region of the freezing point can be deduced by considering the behaviour of this equation in the vicinity of this zero and the asymptotic solution can be derived by application of a suitable limiting procedure. This approach is of course equivalent to the steepest-descents analysis in the linear case, but it is hoped that such an approach, applied to the non-linear case, will yield some useful information on the correct form of the asymptotic solution.

In general the sonic point does not occur at the physical throat in a relaxing flow. In so far as the present approximation is concerned the sonic point is fixed at the throat since the basic flow is taken to be that corresponding to $\sigma = 0$. Higher approximations to the theory, i.e. the perturbation to the flow field, have been considered by Freeman (1962) who has derived the variation with Λ of the position of the sonic throat and also the dependence of the mass flow on the rate parameter.

The author is indebted to Dr N. C. Freeman for many helpful discussions.

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Appendix. Near-equilibrium and near-frozen solutions

Near-equilibrium and near-frozen one-dimensional flows have been treated extensively by Bloom & Ting (1960). A near-equilibrium solution can be formally derived by seeking a solution of the form ($\Lambda \gg 1$)

$$\epsilon = \frac{\epsilon_1}{\Lambda} + \frac{\epsilon_2}{\Lambda^2} + \dots.$$

Substitution into equation (13) gives

$$\epsilon = \frac{1}{\Lambda F}\left(-\frac{d\bar{\sigma}}{dm}\right) + \dots,$$

which is in agreement with the expression (27) derived in the main text. However, this solution cannot remain valid up to and including $m = m_r$ since at this point $d\sigma/dm = 0$ but $d\bar{\sigma}/dm$ is finite. The correct behaviour there can be deduced from (13) by solving this equation for m near to m_r. This solution can be written

$$\epsilon = \frac{1}{\Lambda F_r}\left(-\frac{d\bar{\sigma}}{dm}\right)_r [1 - \exp\{-\Lambda F_r(m-m_r)\}].$$

The exponential term is only important in a region near $z = m/m_r = 1$ whose thickness is $O(1/\Lambda)$ (with respect to z). Outside this region the usual approach of seeking a solution in the form of an expansion in powers of $1/\Lambda$ is valid (except near the freezing point).

A near frozen solution can be obtained by an expansion of the form ($\Lambda \ll 1$)

$$\epsilon = \epsilon^0 + \Lambda\epsilon' + \dots,$$

which gives

$$\epsilon^0 = \bar{\sigma}_r - \bar{\sigma},$$

and

$$\epsilon' = -\int_{m_r}^{m} \epsilon_0(v)\, F(v)\, dv = \left[\frac{\bar{\sigma}_r}{(\gamma_\alpha - 1)\, n y^n}\right]_{y=1}^{z} + \theta \int_1^z \frac{\exp(-\theta y^2)}{(\gamma_\alpha - 1)\, n y^n}\, dy,$$

i.e.

$$\epsilon' = -\frac{1}{n(\gamma_\alpha - 1)}\left(1 - \frac{1}{z^n}\right)\bar{\sigma}_r\left[1 + O\left(\frac{1}{\theta}\right)\right].$$

For $\theta \gg 1$ the error term can be neglected and

$$\epsilon = \overline{\sigma}_r - \overline{\sigma} - \frac{\Lambda}{(\gamma_\alpha - 1)\,n}\left(1 - \frac{1}{z^n}\right)\overline{\sigma}_r,$$

or

$$\sigma = \overline{\sigma}_r\left\{1 - \frac{\Lambda}{(\gamma_\alpha - 1)\,n}\left(1 - \frac{1}{z^n}\right)\right\},$$

which is in agreement with equation (29) in the main text.

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