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Non-Equilibrium Flow of a Polyatomic Gas through a Normal Shock Wave

By

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The vibrationally relaxing flow of a polyatomic gas through a normal shock wave is examined under the assumptions that the excitation of the vibrational modes takes place in "parallel", that the relaxation frequencies are constant, and that the energy equation can be replaced by the Bethe-Teller relation.

1. Introduction

When a gas is disturbed from a state of equilibrium, as in the passage through a shock wave, the redistribution of energy among the various degrees of freedom is not instantaneous; a certain finite time, the so-called relaxation time, is required for any particular mode to attain its new equilibrium state. The translational and rotational degrees of freedom usually adjust themselves comparatively quickly as compared with vibration, dissociation, etc., and consequently when discussing non-equilibrium effects due to, e.g., vibrational relaxation translation and rotation can very conveniently be regarded as being in a local state of equilibrium. Here we shall be concerned only with vibrational relaxation and it will be assumed that the amount of dissociation, etc., is negligible.

It is usual when studying vibrational relaxation phenomena to assume that the rate of change of the vibrational energy is proportional to the departure of the vibrational energy from its local equilibrium value. This linear rate equation can be shown to be valid for a system of harmonic oscillators when only a small fraction of the oscillators are excited; it is doubtful whether the equation holds for large departures from equilibrium. Moreover, such an equation cannot, in general, govern the excitation of the total vibrational energy in a polyatomic gas which has more than one vibrational mode, since it will, in general, be impossible to characterize the relaxation process by a single relaxation frequency. However, a set of equations of this form may hold for the individual vibrational energies in the various modes. The transfer of energy from the active modes (translation and rotation, which are assumed here to be fully excited) to the vibrational modes can take place in several ways (see Herzfeld and Litovitz (1959)), e.g., each vibrational mode may feed from the active modes but remain independent of the other vibrational modes in the sense that it does not exchange energy directly

with/

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with them. This process is termed excitation in "parallel". An alternative method of approach to equilibrium is a "series" type excitation in which one vibrational mode feeds from the active modes, the other vibrational modes then feed from this one. In a complex molecule both types of excitation will occur.

In this report the non-equilibrium flow of a vibrationally relaxing polyatomic gas through a normal shock wave is analysed for the case when the excitation of the vibrational modes takes place in "parallel". It is assumed that the relaxation is governed by a set of equations of the form

$$\frac{d\sigma_i}{dt} = \omega_i(\bar{\sigma}_i - \sigma_i) \quad \dots(1)$$

where t is the time, σ_i is the vibrational energy in the i^{th} mode, and $\bar{\sigma}_i$ is its local equilibrium value corresponding to the translational temperature T . ω_i is the relaxation frequency for the i^{th} mode and in general is a function of both the temperature and the density, but here it will be assumed constant. This latter assumption, and indeed the form of the rate equation itself, will probably not be valid for strong shock waves (in which there are large temperature changes and large departures from equilibrium).

Vibrational relaxation in normal shock waves in a diatomic gas, for which there is only one rate equation, has been analysed in detail by Johannesen (1961) and by Blythe (1961a), who assumed that the relaxation equation was of the form (1). The first of these papers describes a general approach to the problem while the latter discusses the various approximations that have been used in analysing vibrational relaxation regions in normal shock waves. The structure of such shock waves can be split into two parts (for waves above a certain minimum Mach number) (see Johannesen (1961)), firstly a diffusion resisted part within which translation and rotation are assumed to attain a local state of equilibrium, this part is followed by the relaxation region within which the lagging mode adjusts to its new equilibrium state. The width of the diffusion resisted part of the wave is usually assumed to be negligibly thin compared with the width of the relaxation region. The same picture applies to the present problem save that the structure of the relaxation region can no longer be characterized by a single relaxation frequency.

It will be assumed that the energy equation can be replaced by the Bethe-Teller relation

$$\frac{d\bar{\sigma}}{d\sigma} = -\mu \quad \dots(2)$$

where $\sigma = \sum_i \sigma_i$, $\bar{\sigma} = \sum_i \bar{\sigma}_i$, and μ is a constant. Under the above assumptions the problem is greatly simplified; in fact (1) and (2) form a linear set of equations with constant coefficients for (in particular) $\epsilon_i = \bar{\sigma}_i - \sigma_i$, provided further that the vibrational specific heats are assumed constant. However, it was pointed out by Blythe (1961a) that (2) is not valid for weak waves and thus the solution derived here has only a limited range of applicability (since we cannot expect the assumption of constant ω_i to be applicable in very strong shocks).

It should be noted that the solution obtained within is applicable to any one-dimensional flow, with a given initial departure from equilibrium, provided the Bethe-Teller relation holds (together of course with all the other assumptions). The n -mode case is solved § 2, and a numerical example for the special case $n = 2$ is given in § 3.

2. Solution for n-Mode Case

From equations (1) and (2) it can easily be shown that

$$\frac{d\varepsilon_i}{dt} + \omega_i \varepsilon_i = k_i \frac{d\varepsilon}{dt} \quad \dots(3)$$

where $\varepsilon_i = \bar{\sigma}_i - \sigma_i$, $\varepsilon = \bar{\sigma} - \sigma$, and $k_i = \frac{\mu}{1 + \mu} \frac{c_{vib_i}}{c_{vib}}$. c_{vib_i} is the vibrational specific heat for the i^{th} mode, and c_{vib} is the total vibrational specific heat ($= \sum_i c_{vib_i}$). The c_{vib_i} , and hence the k_i , are assumed constant. The time t is measured from the downstream end of the diffusion resisted part of the wave which is assumed to be negligibly thin as compared with the width of the relaxation region. The conditions at $t = 0$ are computed from the transition across the diffusion resisted part of the wave, within which translation and rotation are assumed to attain local equilibrium; these boundary conditions for equations (3) are written

$$\varepsilon_i = \varepsilon_{ia} \text{ at } t = 0. \quad \dots(4)$$

The initial value problem defined by equations (3) and (4) can be solved in the usual way. The Laplace transform E_i is defined by

$$E_i = \int_0^{\infty} p \exp(-pt) \varepsilon_i dt$$

and the transformed equations are

$$(p + \omega_i)E_i - p\varepsilon_{ia} = k_i p(E - \varepsilon_a) \quad \dots(5)$$

where

$$E = \sum_i E_i \text{ and } \varepsilon_a = \sum_i \varepsilon_{ia}.$$

This set of equations for the E_i 's can easily be solved. However, it is more convenient to obtain the solution first of all for E . It is apparent from equation (5) that

$$E = \frac{p \sum_i \frac{\varepsilon_{ia} - k_i \varepsilon_a}{p + \omega_i}}{1 - p \sum_i \frac{k_i}{p + \omega_i}} = p \sum_j \frac{A_j}{p + \lambda_j} \quad \dots(6)$$

(note that E is not singular at $p = -\omega_i$, i.e., $\lambda_j \neq \omega_i$) where the λ_j 's are the roots of

$$\sum_i \frac{k_i \lambda}{\lambda - \omega_i} = 1 \quad \dots(7)$$

and the A_j 's are given by (provided the λ_j are distinct)

$$A_j /$$

$$A_j = \frac{\sum_i \frac{\epsilon_{ia} - k_i \epsilon_a}{\lambda_j - \omega_i}}{\sum_i \frac{k_i \omega_i}{(\lambda_j - \omega_i)^2}} \quad \dots(8)$$

It follows that ϵ is given by

$$\epsilon = \sum_j A_j \exp\{-\lambda_j t\}. \quad \dots(9)$$

A sketch of the function $f(\lambda) = 1 - \sum_i \frac{k_i \lambda}{\lambda - \omega_i}$ is given in Fig.1

for the case when all the ω_i are distinct, and in this case it can be shown that $f(\lambda) = 0$ has n real, distinct, positive roots. When all the ω_i are not distinct, say s of them have a common value ω , then $f(\lambda) = 0$ has only $n+1-s$ roots (with $\lambda \neq \omega, \omega_i$), and correspondingly only $n-s+1$ coefficients A_j exist.

Returning to equation (5) it is found that

$$E_i = \frac{\left\{ \epsilon_{ia} - k_i \epsilon_a - \sum_j' \frac{k_i \omega_i A_j}{\lambda_j - \omega_i} \right\}^p}{p + \omega_i} + \sum_j' \frac{k_i \lambda_j \cdot A_j^p}{(\lambda_j - \omega_i)(p + \lambda_j)}. \quad \dots(10)$$

From equation (6) it can be seen that

$$\frac{\epsilon_{ia} - k_i \epsilon_a}{k_i \omega_i} = \sum_j' \frac{A_j}{\lambda_j - \omega_i}$$

(consider the limiting process $p + \omega_i \rightarrow 0$), provided the ω_i are distinct. Hence the coefficient of $p/p + \omega_i$ in equation (10) is zero in this case. If, however, there are s ω_i 's the same ($= \omega$), and for convenience it will be assumed that these correspond to the modes numbered $n+1-s$ to n , then

$$\frac{\sum_{i=n-s+1}^n \{\epsilon_{ia} - k_i \epsilon_a\}}{\omega \sum_{i=n-s+1}^n k_i} = \sum_j' \frac{A_j}{\lambda_j - \omega}$$

and the coefficient of $\frac{p}{p + \omega}$ in (10) is $\epsilon_{ia} - \frac{k_i}{\sum_{i=n-s+1}^n k_i} \cdot \sum_{i=n-s+1}^n \epsilon_{ia}$.

Thus/

Thus
$$\epsilon_i = \sum_j a_{ij} \exp\{-\lambda_j t\} + b_i \exp\{-\omega_i t\} \quad \dots(11)$$

where

$$a_{ij} = \frac{k_i \lambda_j}{\lambda_j - \omega_i} A_j, \quad j \leq n-s+1 \quad \dots(12)$$

$$\left. \begin{aligned} b_i &= 0, & i &\leq n-s \\ &= \epsilon_{ia} - \frac{k_i}{\sum_{i=n-s+1}^n k_i} \sum_{i=n-s+1}^n \epsilon_{ia}, & i &\geq n-s+1 \end{aligned} \right\} \dots(13)$$

and s is the number of repeated ω_i 's. Note that if for $i \geq n-s+1$ all the modes are identical (i.e., all the k_i 's are equal, etc.) then $b_i = 0$ for all i .

3. The Case $n = 2$

Suppose that in a three mode gas (non-linear triatomic molecule) one relaxation frequency is very much greater than the other two, then this mode can be regarded as an active mode and the gas treated as having only two lagging vibrational modes (strictly no gas exists which has only two vibrational modes*). This case is, of course, the easiest to examine, apart from the trivial case $n = 1$, and in particular an explicit expression for the λ_j 's can be obtained, i.e.,

$$2\lambda = (1+\mu) \left\{ (1-k_2)\omega_1 + (1-k_1)\omega_2 \pm \sqrt{[(1-k_2)\omega_1 + (1-k_1)\omega_2]^2 - \frac{4}{1+\mu} \omega_1 \omega_2} \right\}. \quad \dots(14)$$

Firstly we note that for $\omega_1 = \omega_2 = \omega$, the two roots are $(1+\mu)\omega, \omega$. The latter root is not permissible since $\lambda_j = \omega_i$ was excluded from the analysis (although terms $b_i \exp - \omega t$ will occur). Reconsider equation (7): as already noted if there are s equal ω_i 's then this equation has only $n-s+1$ roots. However, in practice one does not solve (7) but the equivalent polynomial expression

$$\prod_k (\lambda - \omega_k) = \lambda \sum_i k_i \prod_{k \neq i} (\lambda - \omega_k)$$

which has n distinct roots provided all the ω_i 's are distinct, but if there are s equal ω_i 's ($= \omega$) then

$$(\lambda - \omega)^s /$$

*A linear molecule has $3a - 5$ vibrational modes, and a non-linear molecule $3a - 6$, where a is the number of atoms.

$$(\lambda - \omega)^s \prod_k^{n-s+1} (\lambda - \omega_k) = \lambda(\lambda - \omega)^{s-1} \sum_i k_i \prod_{k \neq i}^{n-s+1} (\lambda - \omega_k)$$

which has $s-1$ roots $\lambda = \omega$ and a further $n-s+1$ distinct roots. (However, (6) cannot have a partial fraction of the form $\frac{pA}{p + \omega}$, and the roots $\lambda = \omega$ are excluded.) Returning to equation (14) it is now obvious why the root $\lambda = \omega$ occurs when $\omega_1 = \omega_2$.

For convenience we shall take $\omega_1 > \omega_2$ and define λ_1 as the larger of the two roots. Consequently $\lambda_1 > \omega_1 > \lambda_2 > \omega_2$. It is apparent from (12) that a_{11}, a_{12} have the same sign as A_1, a_{12} is of opposite sign to A_2 , and a_{22} has the same sign as A_2 . (In general if we specify $\omega_1 > \omega_2 \dots > \omega_n$ and enumerate the λ_j 's similarly, a_{ij} and A_j will have the same sign for $i \geq j$, and will be of opposite sign for $i < j$.) It can be shown from equations (8) and (14), after a little manipulation, that $A_1 > 0$. On the other hand $A_2 > 0$ if

$$\frac{\omega_1 - \lambda_2}{\omega_1 - \omega_2} > (1 + \mu) \left(\frac{\epsilon_{1a}}{\epsilon_a} - k_1 \right)$$

from which it can be shown that $A_2 > 0$ for all $\omega_2 < \omega_1$ if

$$\frac{c_{vib_1}}{c_{vib}} > \frac{\epsilon_{1a}}{\epsilon_a}.$$

It is worth noting that the relaxation frequencies (for parallel excitation) will depend strongly on the vibrational frequencies ν_i , i.e., $\nu_1 < \nu_2$ implies $\omega_1 > \omega_2$ (Herzfeld and Litovitz (1959, p.91)). Hence $\omega_1 > \omega_2$ implies $\bar{\sigma}_1 > \bar{\sigma}_2$ etc.*, but specifying $\epsilon_{1a} > \epsilon_{2a}$ is not sufficient to satisfy the above inequality. It appears that it is, in fact, possible for A_2 to be negative, though for ω_2/ω_1 sufficiently less than unity A_2 is positive (see e.g. the numerical example given below). If A_2 is negative this implies that the total vibrational energy and also the energy in the slower mode 2 will overshoot their equilibrium values; if A_2 is positive there will be an overshoot only in the fast mode 1. Physically, it seems hard to conceive the slower mode overshooting and for this reason it might be expected that in practice the relative magnitude of $\omega_2/\omega_1, \epsilon_{2a}/\epsilon_{1a}$ may be such that $A_2 > 0$. By analogy we might expect that in the general n -mode case the slowest mode would not overshoot, i.e., $a_{nj} > 0$, and hence $A_j > 0$ so that the total vibrational energy would not overshoot, although there would be overshoots of varying magnitude in each of the individual modes except the n th. (However, it should be borne in mind that theoretically, it is possible in general for there to be an overshoot in the slowest mode.)

In Figs.2 and 3 some of the results of a numerical calculation are shown for $n = 2$. The characteristic temperatures of vibration were taken as 1000°K and 1500°K. The shock considered was such that the final equilibrium temperature was 2000°K with the initial temperature ahead of the

shock/

*In particular $\omega_1 = \omega_2$ really implies $\bar{\sigma}_1 = \bar{\sigma}_2$ etc., and in general from equation (13) it is apparent that if this is so $b_i = 0$ for all i . One can in this case regard the $(n+1-s)$ th mode as being a weighted mode comprised of the s similar modes.

shock wave equal to 300°K. This corresponds to a shock Mach number $m_s \approx 6.50$, where m_s is the Mach number based on the active (frozen) speed of sound. The equilibrium properties were calculated assuming that each of the modes could be regarded as a system of simple harmonic oscillators. μ was calculated by fitting the integrated form of equation (2) to the

conditions at $t = 0$ and at equilibrium (i.e., $\mu = \frac{\bar{\sigma}_a - \bar{\sigma}_e}{\bar{\sigma}_e - \bar{\sigma}_s}$, where the

suffix s denotes conditions ahead of the wave, and the suffix e the final equilibrium conditions far downstream of the wave). The constant values of c_{vib_i} in the relaxation region were defined by $\frac{1}{2}(c_{vib_{ia}} + c_{vib_{ie}})$.

For $\omega_1 = \omega_2$ ϵ has only a single exponential dependence (only one λ_j exists), and both ϵ_1 (which has a double exponential dependence) decrease monotonically to zero: on the other hand, ϵ_2 does have a minimum value (i.e., an overshoot). The magnitude of this minimum is very small and occurs at $\omega_1 t > 6.5$. For $1 > \frac{\omega_2}{\omega_1} > 0.977$ both ϵ_2 and ϵ_1 overshoot, and for $0.977 > \frac{\omega_2}{\omega_1}$ ϵ_1 overshoots. The magnitude of these minima (overshoots) is again very small and they occur outside the time scale of the figures. Note that for a fixed ω_1 the manner in which the first mode approaches equilibrium is affected very little by the magnitude of ω_2 (see Fig.2), and of course vice-versa.

4. Concluding Remarks

The solution given here determines ϵ and the ϵ_i as functions of t . From e.g. (2) the variation of the temperature T with t can easily be found. To derive the dependence of the density, etc., on t , or the more useful variation with x , one can use either the usual continuity and momentum equations together with the equation of state, or some of the approximations outlined in Blythe (1961a).

The simplicity of the solution obtained above arises from the assumption that the Bethe-Teller relation is valid, and the assumptions that ω_i and c_{vib_i} are constants in the relaxation region. If the first of these assumptions is relaxed then it is easily shown that

$$\frac{d\epsilon_i}{dt} + \omega_i \epsilon_i = \frac{c_{vib_i}}{c_p} \left(\frac{d\epsilon}{dt} - v \frac{dv}{dt} \right)$$

where v is the velocity relative to the shock wave. It can be seen that the modifications to (3) are the introduction of a non-linear term

$v \frac{dv}{dt}$ on the right-hand side, and a slight change in the constant k_i

(if constant enthalpy had been used as the modified energy relation then k_i in (3) would have been c_{vib_i}/c_p). The non-linear term arises as the

direct consequence of including the kinetic energy term in the energy equation. While the solution of this set of equations is beyond the scope of the present paper it is of interest to note that a non-linear

integro-differential/

integro-differential equation for v or for ϵ can be derived, assuming constant ω_i and c_{vib_i} , (the usual conservation equations together with the equation of state can be linked to give a relation between v and ϵ). It can be shown that the corresponding integro-differential equation for ϵ in the linear case has the solution already obtained here. In the non-linear case the integro-differential equation admits of solutions of the type found in the corresponding one-mode case, but the general solution has not been found.

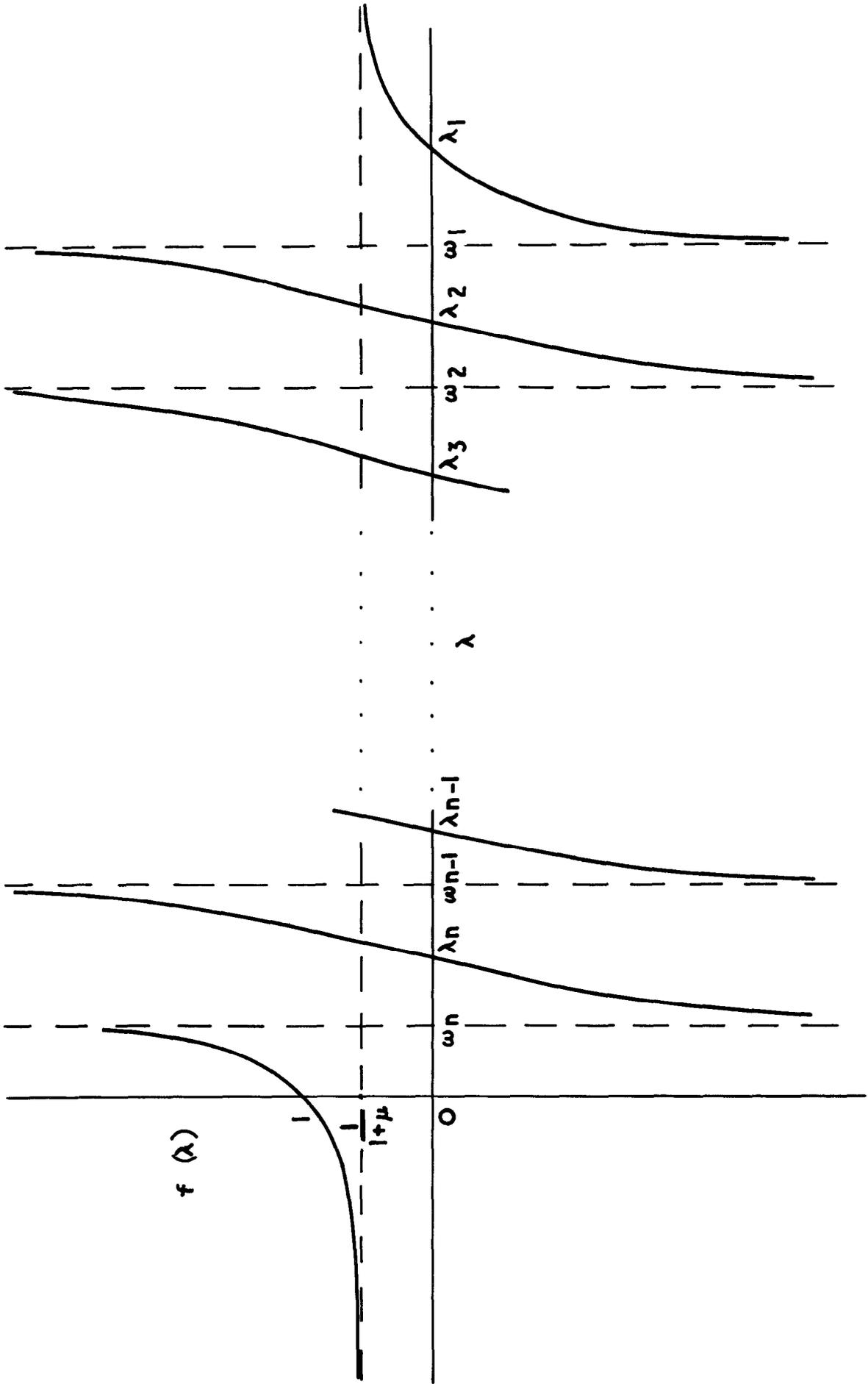
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FIG. 1.



The function $f(\lambda)$

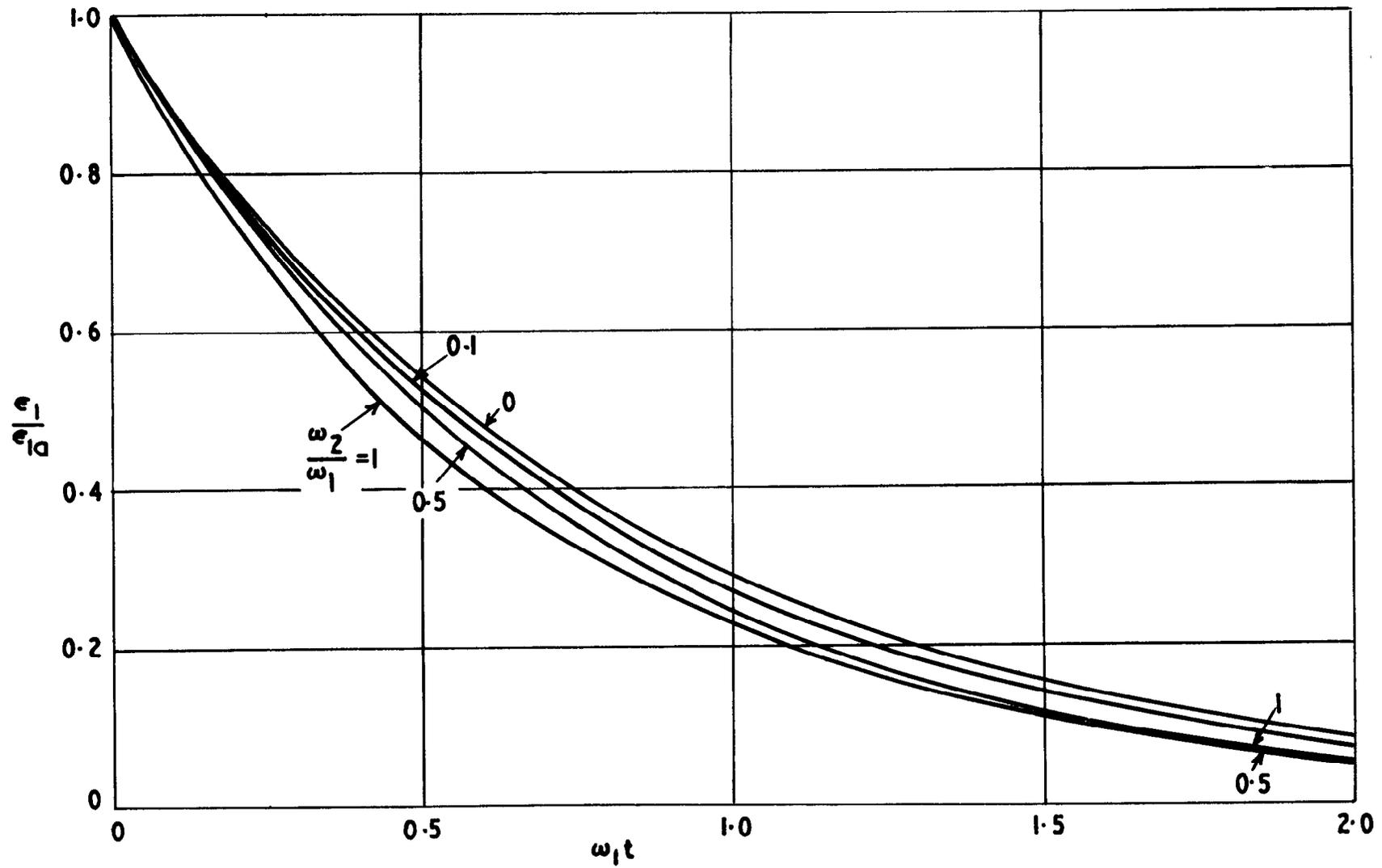
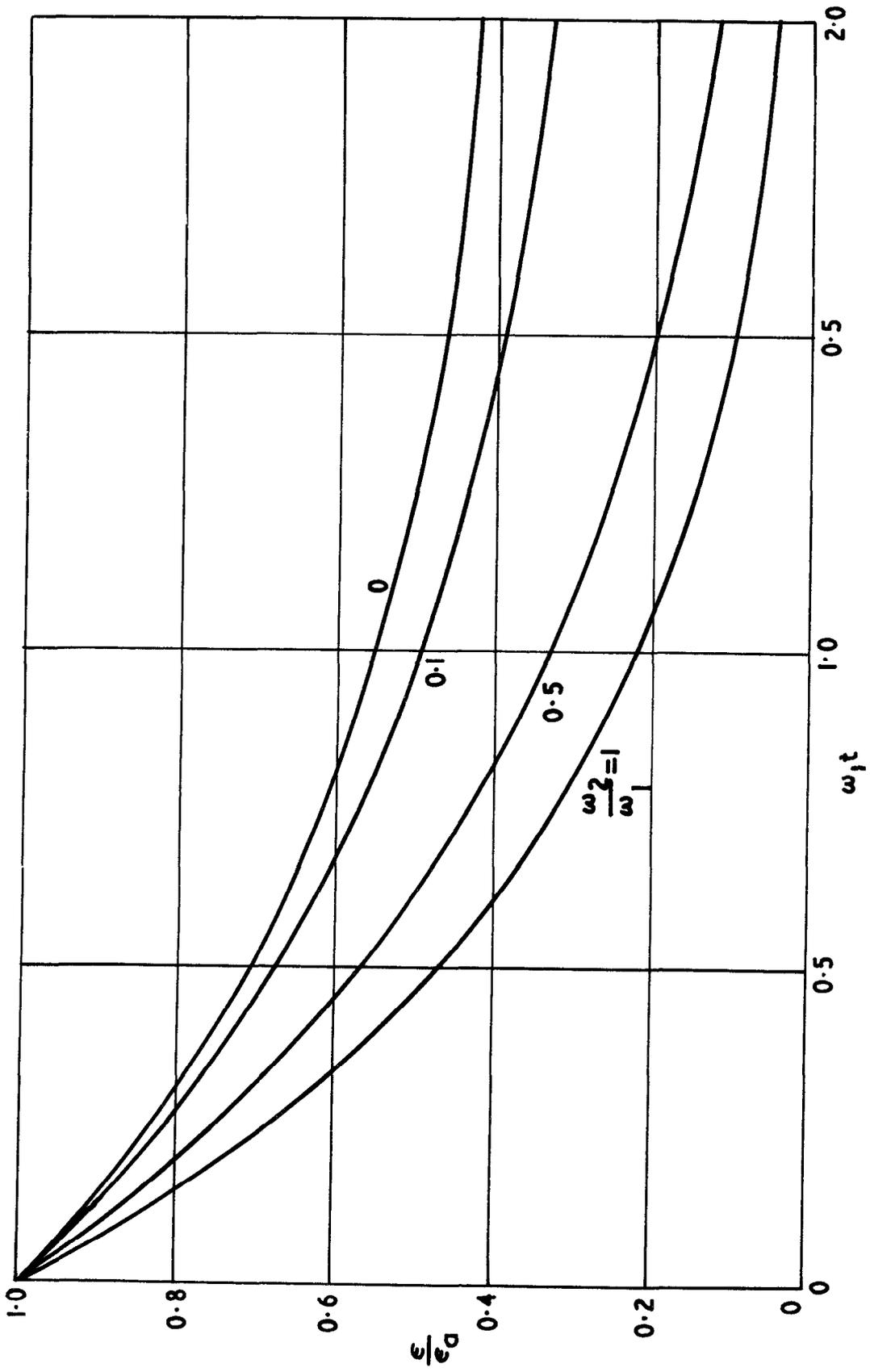


FIG. 2.

Energy defect for mode I as a function of time for various ω_2

FIG. 3.



Total energy defect as a function of time for various ω_2

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