FREQUENCY SPECTRA OF ISOTOPICALLY SUBSTITUTED DIATOMIC CHAIN

FREQUENCY SPECTRUM OF A DIATOMIC LINEAR CHAIN WITH RANDOM ISOTOPIC IMPURITIES

By

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SCOPE AND CONTENTS: The frequency spectrum of a diatomic linear chain with randomly placed isotopic impurities is calculated using a Green's function formalism. The calculation follows a method devised by Langer, and yields the density of states exactly to first order in the concentration of impurities. It is found that polarisation mixing causes no problem and the results are analogous to those of Langer for the monatomic chain. Results are presented for various ratios of impurity mass to replaced mass, for which impurity bands are found above the optical band and in the gap between the accoustic and optical bands. A self consistent calculation is also discussed.

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CONTENTS

INTRODUCTION

The problem of calculating vibrational properties of lattices with randomly distributed impurities has been under continued investigation. Earlier work on monatomic lattices with defects and disordered diatomic lattices has been reviewed by Maradudin et al. (1958). Domb et al. (1959) have obtained results for the vibration frequency spectrum of disordered linear chains, using the moment trace method developed by Montroll (1942 and 1943), and the theory of random walks. This method seems to depend on the practicability of calculating even moments of the vibrational spectrum greater than the 20th.

Machine calculations by Dean and Bacon (1965) have shown that the structure of the vibrational spectrum is much more complicated than other calculations have indicated it to be. This is especially true in the case of light impurities, due to the interactions of clusters of defects.

Langer (1961) applied a Green's function formalism to the problem of a one-dimensional, monatomic chain containing substitutional isotopic impurities; that is, atoms differing from the host atoms only in their mass. He was able to find the density of vibrational states in the system, averaged over configurations of impurities, exactly, to the lowest order in the concentration of impurities. Hin-Chiu Poon and Bienenstock (1966) have shown that the analogous problem of a lattice with changed force constants randomly distributed can be reduced mathematically to give a solution corresponding to that of Langer's for isotopic impurities. Using the isotopic impurity model, Davies and Langer (1963) carried out a self consistent approximation by calculating the self energy of the defect with the configuration averaged Green's function in place of the Green's function of the perfect chain. The result was a broader impurity band with no structure.

This work was extended by Elliott and Taylor (1964) to the case of three dimensional crystals. Factors of higher order than the first in concentration were introduced, improving the position of the impurity band, but still not reproducing the spikey structure expected physically in the vibrational spectrum for light impurities. Langer (1961) has indicated that certain higher order concentration terms will give more structure to the impurity band.

The problem of impurities in diatomic crystals introduces the possibility of localized modes or impurity bands in the forbidden gap between the optical and acoustic bands. Mazur, Montroll and Potts (1956) have discussed the effect of a single isotopic mass defect in an alternating diatomic linear chain and have found the conditions under which localized modes will appear in the forbidden gap and above the optical band. Bjork (1957) has considered the same model but extended the calculation to include the effects of force constant changes.

In this paper we consider a diatomic linear chain with substitutional isotopic impurities. In section 2, we introduce the model and find the Green's function and density of states of the unperturbed chain. Following Langer's (1961) calculation, in section 3 we apply a Green's function formalism to find the change in the density of vibrational states to the first order in concentration by averaging over configurations. Section 4 contains the calculated results and a discussion of this approximation for the density of vibrational states.

CHAPTER I

THE FORMULATION OF THE PROBLEM

We consider a long chain of 2N atoms with alternating masses m_1 and m_2. Into this chain we introduce a small concentration of impurities of mass M on m_1 sites only, the probability of an M atom being on an m_1 site being q. The atoms are taken to interact by nearest neighbour harmonic forces with stiffness constant γ. The equation of motion of the perfect lattice is given in matrix form by

[1] $$(\underset{\sim}{A} - \omega^2 \underset{\sim}{I})\underset{\sim}{V} = 0$$

where $\underset{\sim}{I}$ is the unit matrix and $\underset{\sim}{A}$ is the dynamical matrix, whose non-zero elements are

[2] $$A^{\ell\ell}_{\kappa\kappa} = \frac{2\gamma}{m_\kappa}$$
$$A^{\ell\ell}_{12} = A^{\ell\ell}_{21} = A^{\ell-1,\ell}_{21} = A^{\ell,\ell+1}_{21} = -\frac{\gamma}{(m_1\ m_2)^{\frac{1}{2}}}$$

Here the index $\ell(\ell=1,N)$ numbers the unit cells of the chain, and $\kappa(\kappa=1,2)$ numbers the masses within the unit cell. The vector $\underset{\sim}{v}$ is the column matrix of reduced displacements,

[3] $$V(\ell,\kappa) = \sqrt{m_\kappa}\ \ x(\ell,\kappa)$$

where $x(\ell,\kappa)$ is the real displacement of the ℓ,κth atom.

Since in the perturbed case only a substitutional mass change is being considered, the perturbed eqution of motion becomes

[4] $$[\underset{\sim}{A} - \omega^2(\underset{\sim}{I} - \underset{\sim}{\Lambda})]\underset{\sim}{V} = 0$$

where $\underset{\sim}{\Lambda}$ is, in the space representation, a 2Nx2N diagonal matrix with elements

[5] $$\Lambda^{\ell\ell'}_{\kappa\kappa'} = (1 - \frac{m_{\ell\kappa}}{m_\kappa})\ \delta_{\ell\ell'}\ \delta_{\kappa\kappa'}$$

Only a small fraction q/2 of the diagonal elements will be non-zero; those for which $m_{\ell\kappa}$ is an impurity.

The Green's functions of these systems are defined as follows:

For the perfect chain

[6] $$\underset{\sim}{G}^o \equiv (\underset{\sim}{A} - \omega^2\ \underset{\sim}{I})^{-1}$$

For the perturbed chain

[7] $$\underset{\sim}{G} \equiv [\underset{\sim}{A} - \omega^2(\underset{\sim}{I} - \underset{\sim}{\Lambda})]^{-1}$$

From these two equations we obtain the Dyson equation for the perturbed Green's function

[8] $$\begin{aligned}\underset{\sim}{G} &= \underset{\sim}{G}^o - \underset{\sim}{G}^o\omega^2\underset{\sim}{\Lambda}\underset{\sim}{G} \\ &= \underset{\sim}{G}^o - \underset{\sim}{G}^o\omega^2\underset{\sim}{\Lambda}\underset{\sim}{G}^o + \underset{\sim}{G}^o\omega^2\underset{\sim}{\Lambda}\underset{\sim}{G}^o\omega^2\underset{\sim}{\Lambda}\underset{\sim}{G}^o - \ldots\end{aligned}$$

Maradudin (1962) shows that the density of vibrational states $g(\omega)$ of the perturbed chain is given by

$$[9] \qquad g(\omega) = \frac{2\omega}{\pi} \, \mathrm{Im} \lim_{\delta \to 0^+} \frac{1}{2N} \, \mathrm{Tr} \, \underset{\sim}{G}(\omega^2 + i\delta)$$

The density of states $g^o(\omega)$ of the unperturbed chain is related in the same way to the trace of $G^o(\omega^2)$.

The equation of motion [1] can be solved by the introduction of a transformation to the normal coordinates of the perfect lattice $v(k,j)$, where k is the wave vector of the mode and j the branch, such that

$$[10] \qquad V(\ell,\kappa) = \frac{1}{\sqrt{N}} \sum_{kj} \varepsilon_{\kappa}^{j}(k) \, e^{ik\ell} \, V(kj)$$

k has values $\frac{S2\pi}{N}$, $-N/2<S<N/2$ (using cyclical boundary conditions). The quantity $\varepsilon_{\kappa}^{j}(k)$ is a "polarisation vector" and is related to the reduced displacement of the κth atom in the jth branch of the mode of wave vector k. The frequencies of the normal modes of vibration of the chain, or equivalently the eigenfrequencies of the dynamical matrix, are

$$[11] \qquad \omega_{jk}^2 = \gamma \left\{\frac{1}{m_1}+\frac{1}{m_2}+(-1)^j\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2+\frac{2}{m_1 m_2}(\cos k-1)\right]^{\frac{1}{2}}\right\}$$

These frequencies form two bands, the acoustic and optical corresponding to $j = 1$ or 2 respectively. The polarization vectors are normalized to unity and their magnitudes are given by

$$[12] \qquad |\varepsilon_1^j(k)|^2 = \frac{\omega_{jk}^2 - \frac{2\gamma}{m_2}}{2\omega_{jk}^2 - 2\gamma\left[\frac{1}{m_1} + \frac{1}{m_2}\right]}$$

and $$\left|\varepsilon_2^j(k)\right|^2 = \frac{\left(\omega_{jk}^2 - \frac{2\gamma}{m_1}\right)}{2\omega_{jk}^2 - 2\gamma\left[\frac{1}{m_1} + \frac{1}{m_2}\right]}$$

In this representation, the Green's function $\underset{\sim}{G}^{O}$ is diagonal, and has the elements

$$[13] \qquad G^{o\,jj'}_{kk'}(\omega^2) = \delta_{kk'}\,\delta_{jj'}\,\frac{1}{\omega_{jk}^2 - \omega^2}$$

The density of vibrational states for the perfect diatomic crystal can be calculated from equation [9] and the above expression for $\underset{\sim}{G}^{O}$. The result is

$$[14] \qquad g^{o}(\omega) = \frac{2\omega}{2N\pi}\ \mathrm{Im} \sum_{k} \left(\frac{1}{\omega_{1k}^2 - \omega^2} + \frac{1}{\omega_{2k}^2 - \omega^2}\right)$$

The calculation of this summation in integral form can be found in Appendix I with the result.

$$[15] \qquad g^{o}(\omega) = \frac{\omega}{\pi}\,\frac{m_1}{2\gamma}\,\frac{\left|R + 1 - 2R\beta\right|}{\left|\left((\beta-1)(R\beta-1)-1\right)(R\beta-1)(\beta-1)\right|^{1/2}}$$

for regions $0 < \beta < 1, \quad 1/R < \beta < 1 + 1/R \quad$ if $m_1 > m_2$

$0 < \beta < 1/R, \quad 1 < \beta < 1 + 1/R \quad$ if $m_1 < m_2$

where $\beta = \frac{m_1\omega^2}{2\gamma}, \qquad R = \frac{m_2}{m_1}$

Fig. 1 shows the dispersion curve and the density of states of a perfect diatomic chain for the case when $m_1 > m_2$ $(R<1)$. Further details on the diatomic chain can be found in a review article by Ludwig (1966).

CHAPTER II

THE FIRST ORDER APPROXIMATION

It is convenient to work in the j,k, representation since the Green's function for the perfect chain is then diagonal. In this representation the elements of the perturbing matrix $\underset{\sim}{\Lambda}$ are

$$\begin{aligned} \Lambda^{jj'}_{kk'} &= \frac{1}{N} \sum_{\ell\kappa} e^{-i\ell(k-k')} \varepsilon^{j*}_{\kappa}(k)\left(1-\frac{m_{\ell\kappa}}{m_{\kappa}}\right)\varepsilon^{j'}_{\kappa}(k') \\ &= \frac{1}{N} \sum_{\ell} e^{-i\ell(k-k')} \varepsilon^{j*}_{1}(k)\left(1-\frac{m_{\ell 1}}{m_{1}}\right)\varepsilon^{j'}_{1}(k) \end{aligned} \qquad [16]$$

The polarization vectors refer only to atom 1 because all elements of the sum corresponding to $\kappa = 2$ are zero. Using the expression in equation [8] for the Dyson expansion, an element of the Green's function becomes

$$\begin{aligned} G^{jj'}_{kk'} &= G^{oj}_{k}\,\delta_{jj'}\,\delta_{kk'} - G^{oj}_{k}\,\omega^2\Lambda^{jj'}_{kk'}\,G^{oj'}_{k'} \\ &\quad + G^{oj}_{k}\,\omega^2\,\Lambda^{jj_1}_{kk_1}\,G^{oj_1}_{k_1}\,\omega^2\,\Lambda^{j_1j'}_{k_1k'}\,G^{oj'}_{k'} - \ldots . \end{aligned} \qquad [17]$$

The exact configuration of impurities in the lattice is unknown and so, following Langer's (1961) treatment, we average over all configurations of impurities. The averaging procedure has been described in detail by Langer (1961). The results for the first two terms of the perturbed Green's function are

[18]

$$\left\langle (\omega^2 \Lambda)^{jj'}_{kk'} \right\rangle = \frac{1}{N} \left\langle \sum_{\ell} \varepsilon_1^{j*}(k)\, e^{-i(k-k')\ell}\, \varepsilon_1^{j'}(k) \left(1 - \frac{m_{\ell 1}}{m_1}\right) \right\rangle$$

$$= \omega^2 q \lambda\, \varepsilon_1^{j*}(k)\, \varepsilon_1^{j'}(k)\, \delta_{kk'}$$

[19]

$$\left\langle (\omega^2 \Lambda G^{\circ} \omega^2 \Lambda) \right\rangle = \frac{1}{N^2} \sum_{k_1 j_1} \left\langle \sum_{\ell_1} \omega^2 \varepsilon_1^{j*}(k)\, e^{-i(k-k_1)\ell_1}\, \varepsilon_1^{j_1}(k_1)\, G^{\circ j_1}_{k_1} \right.$$

$$\left. \times \sum_{\ell_2} \omega^2 \varepsilon_1^{j_1}(k')\, \varepsilon_1^{j'}(k')\, e^{-i(k_1-k')\ell_2} \left(1 - \frac{m_{\ell_1 1}}{m_1}\right)\left(1 - \frac{m_{\ell_2 1}}{m_1}\right) \right\rangle$$

$$= \lambda^2 (q - q^2) \frac{\delta_{kk'}}{N} \omega^2 \varepsilon_1^{j*}(k)\, \varepsilon_1^{j'}(k) \sum_{k_1 j_1} \frac{\left|\varepsilon_1^{j_1}(k)\right|^2}{(\omega_{j_1}{}^2 k_1 - \omega^2)}$$

$$+ \omega^4 \lambda^2 q^2 \delta_{kk_1} \delta_{k_1 k'}\, \varepsilon_1^{j*}(k)\, \varepsilon_1^{j'}(k) \sum_{j_1} \frac{\left|\varepsilon_1^{j_1}(k)\right|^2}{(\omega^2_{j_1 k} - \omega^2)}$$

Where $\lambda = (1 - \frac{M}{m_1})$ and is positive and less than 1 for a light impurity, and negative for a heavy impurity, and the brackets <> denote configuration average.

The result of the configurational average is to make all the terms diagonal in k. This is understandable since the change due to defects is averaged over the crystal, restoring translational symmetry. However, these terms are not diagonal in j, which indicates mixing of the branches. It is convenient to represent these terms by diagrams. In Figure 2 the straight horizontal line represents the phonon of wave vector k and frequency ω whose propagation is described by $G_k^{oj}(\omega^2)$. The vertical dotted line represents the interaction of the phonon with an impurity and the double horizontal line represents the configuration averaged Green's function $\langle G_{kk'}^{jj'} \rangle$, of the perturbed lattice.

Figures 2a), 2b) and 2c) represent the first, second and third terms in the Dyson expansion, respectively. The graphs consist of one-phonon lines connected by self energy parts. We define a proper self energy part as represented by the diagram which cannot be broken into two parts by simply cutting the phonon line once. For example 2b(i) is a proper self energy part whereas 2b(ii) is not since it can be split into two diagrams like 2a). The proper self energy parts are always diagonal in k but not in j.

The proper self energy can be represented by a matrix diagonal in k and elements $M_k^{jj'}$ given by figure 3.

Since we are working with very small concentrations of defects, we further approximate the self energy function by considering only those diagrams which are of the first order in concentration, (that is those diagrams with interactions with only one impurity) and omitting higher concentration corrections to these diagrams due to restricted summations in higher order diagrams (interactions with more than one impurity.) The expression for the self energy $M_k^{jj'}(\omega^2)$ becomes

$$M_K^{jj'}(\omega^2) = \omega^2 q \lambda\, \mathcal{E}_1^{j*}(K)\, \mathcal{E}_1^{j'}(K) \times$$

$$[20] \quad \times \left[1 - \omega^2 \frac{\lambda}{N} \sum_{j_1 K_1} \frac{|\mathcal{E}_1^{j_1}(K)|^2}{(\omega_{j_1 K_1}^2 - \omega^2)} + \left[\frac{\omega^2 \lambda}{N} \sum_{K_1 j_1} \frac{|\mathcal{E}_1^{j_1}(K)|^2}{(\omega_{j_1 K_1}^2 - \omega^2)} \right]^2 - \cdots \right]$$

$$= \frac{\omega^2 q \lambda\, \mathcal{E}_1^{j*}(K)\, \mathcal{E}_1^{j'}(K)}{\left[1 + \frac{\omega^2 \lambda}{N} \sum_{K_1 j_1} \frac{|\mathcal{E}_1^{j_1}(K)|^2}{(\omega_{j_1 K_1}^2 - \omega^2)} \right]}$$

The poles of the self energy function are given by the poles of equation [20]

$$[21] \quad \frac{\omega^2}{N} \sum_{j_1 K_1} \frac{|\mathcal{E}_1^{j}(K)|^2}{(\omega_{jK}^2 - \omega^2)} = -\frac{1}{\lambda}$$

The solutions of this equation are frequencies of vibration of the diatomic linear chain with only one mass defect (Mazur et al. 1956), and can be found with the aid of diagram 4. In both parts of the diagram the infinities of the sum occur at the eigenfrequencies of the unperturbed lattice $\omega^2 = \omega_{jk}^{\ 2}$. The solutions of equation (21) occur between these infinities. (The perturbed chain also has a normal mode exactly at the frequency $\frac{2\gamma}{m_2}$; the frequency of this mode is unchanged by the impurity, since in this mode the mass m_1 does not move.) In diagram 4a) when $m_2 > m_1$ it can be seen that for a heavy impurity there is a pole in the self energy function in the forbidden gap, whereas for a light impurity a pole occurs above the optical band. When $m_1 > m_2$ (fig. 4(b)), there are no poles out of the bands for a heavy impurity, but for a light impurity there are two poles which move up out of the bands, one into the forbidden gap and the other above the optical band.

By resummation of the diagrams we can rewrite equation [5] for the Green's function of the perturbed lattice as

$$[22] \qquad \langle \underset{\sim}{G} \rangle = \underset{\sim}{G}^{\circ} + \underset{\sim}{G}^{\circ} \underset{\sim}{M} \langle \underset{\sim}{G} \rangle$$

Since the Green's function <G> and the self energy M are both diagonal in k but not in j then this equation reduces to the solution of a 2x2 matrix equation. The diagonal elements of <G> are

$$[23] \qquad \left\langle G(\omega^2)\right\rangle_k^{11} = \frac{\omega_{2k}^2 - \omega^2\left(1 - q\lambda\left|\varepsilon_1^2(k)\right|^2 B(\omega^2)\right)}{(\omega_{1k}^2 - \omega^2)(\omega_{2k}^2 - \omega^2) + q\lambda\omega^2 B(\omega^2)\left(\frac{2\gamma}{m_2} - \omega^2\right)}$$

$$\left\langle G(\omega^2)\right\rangle_k^{22} = \frac{\omega_{1k}^2 - \omega^2\left(1 - q\lambda\left|\varepsilon_1^1(k)\right|^2 B(\omega^2)\right)}{(\omega_{1k}^2 - \omega^2)(\omega_{2k}^2 - \omega^2) + q\lambda\omega^2 B(\omega^2)\left(\frac{2\gamma}{m_2} - \omega^2\right)}$$

$B(\omega^2)$ is related to the self energy by

$$[24] \qquad M_k^{jj'}(\omega^2) = +q\lambda\,\varepsilon_1^{j*}(k)\,\varepsilon_1^{j'}(k)\,\omega^2\,B(\omega^2)$$

Note that $B(\omega^2)$ contains the poles of the self energy function and determines the poles of the Green's function. The denominators of $\left\langle G(\omega^2)\right\rangle_k^{11}$ and $\left\langle G(\omega^2)\right\rangle_k^{22}$ are both the same and therefore both have the same poles. Fig. 5 illustrates the positions of the zeros of the denominator of some element $\left\langle G(\omega^2)\right\rangle_k^{jj'}$ of the Green's function for the case of light impurities replacing the heavier mass. The vertical straight lines represent the poles of the self energy function. The zeros of $B(\omega^2)$ occur at eigenfrequencies of the unperturbed lattice. The poles of the Green's function element $\left\langle G\right\rangle_k^{jj}$ occur at the two unperturbed poles ω_{1k}^2 and ω_{2k}^2

and at frequencies displaced by a factor q/N from the poles of the self energy function. Since in this case the pole of the Green's function associated with the local mode occurs above the local mode frequency, it is to be expected that the impurity bands of light impurities in the heavy sublattice will occur above the local mode frequencies arising in the single defect problem. Similar investigations in the case where the lighter mass is replaced will show that the impurity band for heavy impurities appears below the local mode frequency in the forbidden gap, and for light impurities above the local mode above the optical band.

In order to find the density of vibrational states the factor $B(\omega^2)$ in the self energy expression must be evaluated. The summation over k and j in the denominator of $B(\omega^2)$ is evaluated in the integral limit in analogy with the method of calculating the density of states function of the unperturbed lattice (see Appendix 1) with the result.

$$[25] \quad \frac{1}{N} \sum_{kj} \frac{\left|\varepsilon_1^j(k)\right|^2}{(\omega_{jk}^2 - \omega^2)} = \frac{1}{N} \sum_{k} \frac{m_1}{2\gamma} \frac{(1 - R\beta)}{(\beta-1)(R\beta-1) - \frac{1}{2}(\cos k+1)}$$

$$\underset{N \to \infty}{=} \quad \frac{m_1}{2\gamma} \quad \frac{(1 - R\beta)}{\left[((\beta-1)(R\beta-1)-1)(\beta-1)(R\beta-1)\right]^{1/2}}$$

The expression for $B(\omega^2)$ is then

$$[26] \qquad B(\omega^2) = 1 \Big/ \left[1 - \frac{\lambda \beta (R\beta - 1)}{\left[((\beta-1)(R\beta-1)-1)(\beta-1)(R\beta-1)\right]^{1/2}} \right]$$

The possible local mode frequencies of the single defect problem are given outside the bands by the zeros of the denominator of $B(\omega^2)$:

$$[27] \qquad \beta = \frac{1 - \lambda^2 + 2R \pm \left((1-\lambda^2)^2 + 4R^2\lambda^2\right)^{1/2}}{2R(1-\lambda^2)}$$

However, the occurrence of these modes depends physically on whether elements of the lighter or heavier sublattice are replaced by a light or heavy impurity relative to this sublattice. Table I indicates the occurrence of local modes for the four possible configurations of masses.

It is interesting to note that since the square root in the denominator of $B(\omega^2)$ becomes imaginary in the bands there are no inband solutions of equation [27]. Therefore this theory does not show any inband impurity resonances.

Having now established an analytic form for the self energy function we can procede to calculate the density of states of the imperfect crystal to lowest order in impurity concentration.

Using equation [23] for the Green's function and [24] for the self energy function, the density of states from equation [9] becomes in the integral limit [appendix 1]

$$[28] \qquad g(\omega) = \frac{\omega}{\pi}\,\frac{m_1}{2\gamma}\,\left(\frac{R+1-R\beta(2-C)}{(((\beta(1-C)-1)(R\beta-1)-1)(\beta(1-C)-1)(R\beta-1))}\right)^{1/2}$$

where $C = C(\omega^2) = q\lambda B(\omega^2)$

Within the bands of the perfect lattice the factor inside the square root will have a real negative part and a small complex part (of order concentration) due to $C(\omega^2)$. This means that the density of states within the band will differ little from the density of states of the perfect crystal.

Outside of the bands, C is real and the expression within the square root will be real and positive except for very small regions near the possible local mode frequencies where C becomes very large and the argument of the square root may become negative. In this case there will be a contribution to $g(\omega)$. There will be an impurity band in the density of states spectrum whenever

$$[29] \qquad 0 < (\beta(1-C)-1)(R\beta-1) < 1$$

The density of states spectrum has been computed from equation [28] and is plotted in Fig. 6 for various ratios of host crystal masses and impurity mass parameter λ .

CHAPTER III

RESULTS AND DISCUSSION

Expression [28] for the density of states of the perturbed chain is exact to first order in the concentration of impurities. The mixing of polarization branches by the perturbation has caused no difficulty in the evaluation of an analytic expression for the Green's function or the density of states. The density of states spectra plotted in figure 6 are therefore essentially exact. The bands are narrow and sharp and appear above the appropriate local mode frequencies for light impurities (6(a) and (c)) and below this frequency for heavy impurities. There is very little change in the unperturbed bands and, as has been indicated in section 3 in the discussion of the poles of the Green's function, there is no possibility of inband resonances in this model.

Further corrections to the first order result due to restricted summations of higher order diagrams have been discussed by Langer (1961). Elliott and Taylor (1964) have argued that all such corrections coming from all the diagrams included in the final expansion of the Green's function should be included. These corrections have the effect of centering the impurity bands over the local mode frequencies. Leith and Goodman (1966), have calculated the exact concentration polynomials associated with each first order diagram, and find the impurity band slightly displaced from the pole at the one defect problem in agreement with Langer (1961). Since both predictions require retention of selected higher order effects, it is difficult to decide between them in a theory based on resummation.

Langer (1961) has also discussed the effect of higher order diagrams on the perturbed Green's function. Their addition would cause the density of states spectrum to show spikey behaviour, in the case of light impurities. This is also expected on the basis of Dean's (1960) numerical results. For small concentrations of impurities these other peaks would be negligable since the area under a peak arising from an n^{th} order term is of the order of q^n. However their inclusion reduces the strength of the singularities found in the first order results. Since these terms are difficult to evaluate Davies and Langer (1964) have attempted to approximate this effect by formulating a self consistent approach to the problem. Since similar concentration effects are expected for the diatomic chain we have also carried out an analogous self consistent calculation by substituting the configuration averaged self consistent Green's function instead of the perfect Green's function into the expression for the self energy part. The two resulting equations to be solved self consistently can be reduced mathematically to the solution of a quartic equation, which can be solved numerically to give the self consistent density of states. The result of this calculation for the case of light impurities substituted into the heavy sublattice is shown in diagram 7. The impurity bands are now much broader than the narrow bands of the first order approximation. They are located over the local mode frequencies and are smooth with no singularities. The band edges at the top of the accoustic and optical bands have moved down in frequency which causes the singularities at these points to disappear. The density of states function goes to zero with infinite slope at the new band edges. These results are in all respects analogous to those found by Davies and Langer (1963) for the perturbed monatomic chain.

However the physical significance of the self consistent approximation for the case of light impurities has been called into question by Elliott and Taylor (1964). The quantitative discrepancy between the results of the self-consistent approximation and the numerical results of Dean (1961) also supports their view. For this reason, while it may be valuable to know that the self consistent approximation can be carried through in the diatomic chain, the details of this calculation are not presented in the main body of this thesis, but are further discussed in Appendix II. All numerical calculations were carried out on the IBM 7040 computor at McMaster and the program used is shown in Appendix III.

APPENDIX I

Throughout this paper we need to evaluate summations of the form

$$[\mathrm{A1}] \qquad I = \frac{1}{N} \sum_k \frac{1}{(\beta(1-X)-1)(R\beta-1)-\frac{1}{2}(\cos k+1)}$$

where $\beta = \frac{M_1\omega^2}{2}$, $R = \frac{M_2}{M_1}$ and X is generally zero (for evaluation of the unperturbed density of states) or small and of the order of concentration of impurities as in the evaluation of the perturbed density of states. The sum runs over the wave vectors $k = \frac{2\pi S}{N}$, $-N/2<S<N/2$, of the lattice with periodic boundary conditions.

In the limit as $N \to \infty$ the summation becomes

$$[\mathrm{A2}] \qquad I = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{dk}{(\beta(1+x)-1(R\beta-1)-\frac{1}{2}(\cos k+1)}$$

with the transformation $z = e^{ik}$ the integral becomes

$$[\mathrm{A3}] \qquad \begin{aligned} I &= \frac{1}{2\pi} \oint_{\substack{\text{unit}\\ \text{circle}}} \frac{dz \qquad 4}{-i\left[z^2-2z(2a_1a_2-1)+1\right]} \\ &= \frac{1}{2\pi} \oint \frac{dz \qquad 4}{-i \quad (z-b_+)(z-b_-)} \end{aligned}$$

where $a_1 = (\beta(1-x)-1)$ and $a_2 = (R\beta-1)$

$$b_\pm = (2a_1a_2-1) \pm (4a_1a_2(a_1a_2-1))^{\frac{1}{2}}$$

If both poles are inside the unit circle then the integral is zero, since the residues are equal and opposite. However at high frequencies ($\beta \rightarrow \infty$) X is real and small, or zero, and the root b_- is within the unit circle and b_+ is outside. The quantity I becomes

A4 $$I = \frac{1}{(a_1 a_2 (a_1 a_2 - 1))^{\frac{1}{2}}}$$

The same expression can be shown by analytic continuation to hold for all frequencies in the upper half of the complex β plane.

APPENDIX II

THE SELF CONSISTENT APPROXIMATION

Analytic self consistency requires that both the exact Green's function $\underset{\sim}{G}$ and the self energy part $\underset{\sim}{M}$ should have branch cuts along the real frequency axis coinciding with bands of the density of states function. This can be achieved by substituting the exact averaged Green's function $\underset{\sim}{G}^{SC}$ into the self energy expression (given diagramatically in Figure 3) in the place of the unperturbed Green's function $\underset{\sim}{G}^{o}$. In making this substitution all nested self energy diagrams have been added to the Green's function approximation.

The configuration averaged self consistent Green's function $\underset{\sim}{G}^{SC}$ is taken to be related to the self energy function $\underset{\sim}{M}^{SC}$ by

$$[A5] \qquad \underset{\sim}{G}^{SC} = \underset{\sim}{G}^{o} + \underset{\sim}{G}^{o}\underset{\sim}{M}^{SC}\;\underset{\sim}{G}^{SC}$$

and the elements of the self energy function become

$$[A6] \qquad M^{SCjj'}_{kk'} = \frac{-q\lambda\omega^{2}\varepsilon_{1}^{j*}(k)\,\varepsilon_{1}^{j'}(k)\,\delta_{kk'}}{1+\frac{\omega^{2}\lambda}{N}\displaystyle\sum_{j_1,k_1,j_2}\varepsilon_{1}^{j_1}(k)\,\langle G^{SC}\rangle_{k}^{j_1 j_2}\,\varepsilon_{1}^{j_2 *}(k)}$$

These two above equations are to be solved self-consistently. The summation in the denominator of the self energy expression becomes

$$[A7]\ \sum_{j_1 j_2 k} \mathcal{E}_1^{j_1}(k)\langle G^{sc}\rangle_k^{j_1 j_2}\mathcal{E}_1^{j_2}(k) = \frac{m_1}{2\gamma}\sum_k \frac{-(R\beta-1)}{(R\beta-1)(\beta(1-F)-1)-\frac{1}{2}(\cos k+1)}$$

where $F(=F(\omega^2))$ is related to the self energy expression by

In general we know that $F(\omega^2)$ may be a complex quantity with branch cuts along the real ω axis, since it contains the poles of the self energy function. We can evaluate the summation at high frequencies when $F(\omega^2)$ is small and real and then analytically continue the results to lower frequencies in the upper complex frequency plane ($\omega^2=\omega^2+i\delta$)(see Appendix 1). The result for the summation is such that $F(\omega^2)$ becomes

$$[A8]\ F(\omega^2) = q\lambda\Big/\left\{1-\frac{\lambda\beta(R\beta-1)}{\left[(\beta(1-F)-1)(R\beta-1)((\beta(1-F)-1)(R\beta-1)-1)\right]^{1/2}}\right\}$$

We now define a quantity $\eta(\beta)$ by the equation

$$[A9] \quad \eta(\beta) = 1/\left[(\beta(1-F)-1)(R\beta-1)((\beta(1-F)-1)(R\beta-1)-1)\right]^{1/2}$$

There are now two equations for $F(\omega^2)$ in terms of $\eta(\beta)$. The first comes from the definition itself

$$[A10] \quad F(\omega^2) = 1 - \frac{1}{2\beta(R\beta-1)}\left[(2R\beta-1) \pm (1+4/\eta^2)^{1/2}\right]$$

The second from the substitution of $\eta(\beta)$ from equation [A9] into equation [A8] to give

$$[A11] \quad F(\omega^2) = q\lambda/(1-\lambda\beta(R\beta-1)\eta)$$

By equating these two expressions for $F(\omega^2)$ the following quartic equation for $\eta(\beta)$ is obtained

$$[A12] \quad f(\eta) = 0 = (1-c\eta)^2(\eta^2 d-1) + qc\eta^2[qc-g+c\eta g]$$

where $c = \lambda\beta(R\beta-1)$
$d = (\beta-1)(R\beta-1)\beta(R\beta-R-1)$
$g = 2(\beta-1)(R\beta-1)-1, \quad g^2-1 = 4d$

The roots of this equation define $F(\omega^2)$ at any given frequency. Since the self consistent density of states function can be written in a form analogous to equation [28] for the density of states in the first order approximation, with C replaced by F, the self consistent density of states function in terms of $\eta\ (=R(\eta)+\mathcal{I}(\eta))$ becomes

$$[\text{A13}]\quad g^{sc}(\omega) = \frac{m_1}{2\gamma}\,\frac{2\omega}{\pi}\left[2R\beta - R - 1 - \frac{R\beta q\lambda}{(1-cR(\eta))^2 + c^2\,\mathcal{I}(\eta)^2}\right]\mathcal{I}(\eta)$$

In the limit of no impurities (q=0) the roots of $f(\eta)$, $1/c$, $1/c$, $\pm\ 1/\sqrt{d}$. The first two of these roots are spurious since λ does not exist in this limit and either of the latter two roots substituted into equation [A13] for $g^{SC}(\omega)$ will give the density of states of the perfect chain (see equation [15]).

Figure 8 is a plot of $f(\eta)$ against η for various frequencies. The roots A and B occur near $\pm\ 1/d^{1/2}$ respectively and C_1 and C_2 near $1/c$. When there are four real roots as in fig. 8(a) there is no contribution to the density of states, and therefore these frequencies do not lie in a band. For a small region near possible local mode frequencies the roots B, C_1 and C_2 become very close and two of them become complex (fig. 8(b)). The vibrational spectrum has an impurity band at these frequencies.

The optical and accoustic bands in the density of states function occur at the frequencies when A and B are complex. It is interesting to note the behaviour of $f(\eta)$ near the unperturbed band edges. When q = 0 the roots

A and B go to infinity and become complex at these band edges, however when there is a small concentration of impurities the q-dependent part of $f(\eta)$ dominates and prevents A and B from becoming complex for a very small region of frequencies near the unperturbed band edges; thus causing the band edges to move (fig. 8(c)).

We can investigate the behaviour of $f(\eta)$ at the former band edges $\beta = 1$ and $\beta = 1 + 1/R$ by assuming that as A and B tend to infinity the roots c_1 and c_2 remain practically constant and we can therefore factor them out of $f(\eta)$. (At the other band edges $\beta = 0$ and $\beta = 1/R$ the roots C_1 and C_2 also tend to infinity and we cannot follow this procedure.) The resulting polinomial after factorisation is

$$[A14]. \quad d\eta^2 + qg\eta + q^2 + \frac{qg}{c} - 1 \cong 0$$

The roots of this equation are

$$[A15] \quad \eta = \left[-qc \pm \sqrt{q^2 - \frac{4dgq}{c} + 4d}\,\right] / 2d$$

These roots are equal when

$$[A16] \quad d = \frac{q^2}{4\left(\frac{qg}{c} - 1\right)} \approx -\frac{q^2}{4}\left(1 + \frac{qg}{c}\right)$$

This implies that the top edge of the optical band moves down by an amount

$$[A17] \quad \Delta\beta = \frac{-q^2}{4\,(R+1 - q/\lambda)}$$

if $m_1 > m_2$ the top of the accoustic band also moves by an amount

$$[A18] \quad \Delta\beta = \frac{q^2}{(q/\lambda + R - 1)}$$

If $m_2 > m_1$ the bottom of the optical band moves up by the same amount.

The other band edges do not move. For example if $m_1 > m_2$ the bottom of the optical band does not move. The behaviour of $g^{SC}(\omega)$ at such band edges does not change. This is expected since these correspond to movement of the mass which has not been replaced. However at the band edges which move $g^{SC}(\omega)$ becomes zero with infinite slope as discussed in section 4.

APPENDIX III

TO FIND THE DENSITY OF STATES OF A DIATOMIC LINEAR ..AIN

```
       DIMENSION R1(5),R2(5),RE(A1(4),RE(A2(4),IE(A1(4),I  A2(4)
      COMPLEX CDENS,G1,G2,F1,F2,D11,D12,D31,D32,D41,D42,DXXQ1,D4SQ2,CDEN
     1S1,CDENS2,ETA1,ETA2,SELFN1,CDNSC1,SELFN2,CDNSC2,Y
      REAL L2,L21,LMDA,IETA1,IETA2
      Q=0.05
      Q1=1.0-Q
      Q2=Q*Q
      Q12=Q1*Q1
    1 READ(5,100)R,LMDA
      R1=R+1.0
      R1R=R1/R
      R1L=1.0/R+1.0/(1.0-LMDA)
      QL=Q*LMDA
      L2=LMDA**2
      L21=1.0-L2
      Z=2.0*R*L21
      Z1=2.0*R+L21
      Z2=4.0*L2*R**2.0+L21**2.0
      Z3=SQRT(Z2)
      WPOLE1=(Z1-Z3)/Z
      WPOLE2=(Z1+Z3)/Z
      WRITE(6,103)WPOLE1,WPOLE2,LMDA,R ,Q
      WRITE(6,104)
      W1=0.01
    2 W2=R*W1
      A1=W1-1.0
      A2=W2-1.0
      A3=A1*A2
      A4=A3*(A3-1.0)
      Y=CMPLX(A4,0.0)
      SQW1=SQRT(W1)
      CDENS=SQW1*(R*A1+A2)/CSQRT(Y)
      AIDENS=AIMAG(CDENS)
      DENS=ABS(AIDENS)
      C=LMDA*W1*A2
      C2=C*C
      IF(A4.LT.0.0)GOTO12
      SQA4=SQRT(A4)
      GWIC1=C/SQA4
      GWIC2=Q1*C/SQA4
      IF(A1.LT.0.0.OR.A2.LT.0.0)GO TO 13
      GW1=1.0-GWIC1
      GW2=1.0-GWIC2
   16 G1=CMPLX(QL/GW1,0.0)
      G2=CMPLX(QL/GW2,0.0)
      GO TO 20
   13 GW1=1.0+GWIC1
       GW2=1.0+GWIC2
```

```
      GO TO 16
   12 SQMA4=SQRT(-A4)
      GWIC1=C/SQMA4
      GWIC2=Q1*C/SQMA4
      IF(A1.LT.0.0.AND.A2.LT.0.0)GO TO 14
      F1=CMPLX(1.0,GWIC1)
      F2=CMPLX(1.0,GWIC2)
      GO TO 17
   14 F1=CMPLX(1.0,-GWIC1)
      F2=CMPLX(1.0,-GWIC2)
   17 G1=QL/F1
      G2=QL/F2
   20 D11=W1*(1.0-G1)-1.0
      D12=W1*(1.0-G2)-1.0
      D2=A2
      D31=D11*D2
      D32=D12*D2
      D41=D31*(D31-1.0)
      D42=D32*(D32-1.0)
      D4SQ1=CSQRT(D41)
      D4SQ2=CSQRT(D42)
      CDENS1=SQW1*(R*D11+D2)/D4SQ1
      CDENS2=SQW1*(R*D12+D2)/D4SQ2
      DENS1=ABS(AIMAG(CDENS1))
      DENS2=(AIMAG(CDENS2))
      DIFF1P=DENS1-DENS
      DIFF2P=DENS2-DENS
      WRITE(6,105)W1,DENS,DENS1,DENS2,DIFF1P,DIFF2P
      D=2.0*A3-1.0
      QC2D=Q*C2*D
      B1(1)=C2*A4
      B1(2)=-2.0*C*A4+QC2D
      B1(3)=A4-C2-Q*C*D+Q2*C2
      B1(4)=2.0*C
      B1(5)=-1.0
      CALL BAIRST(B1,RETA1,IETA1,4)
      DO 40 J=1,3,2
      ETA1=CMPLX(RETA1(J),IETA1(J))
      SELFN1=QL/(1.0-C*ETA1)
      CDNSC1=SQW1*(R*(W1*(1.0-SELFN1)-1.0)+A2)*ETA1
      DENSC1=ABS(AIMAG(CDNSC1))
      DIFSCP=DENSC1-DENS
      WRITE(6,106)DENSC1,DIFSCP
   40 CONTINUE
      B2(1)=A4*Q12*C2
      B2(2)=-2.0*Q1*C*A4+QC2D*Q1
      B2(3)=A4-Q12*C2-Q*C*D+Q2*C2
      B2(4)=2.0*Q1*C
      B2(5)=-1.0
      CALL BAIRST(B2,RETA2,IETA2,4)
      DO 41 K=1,3,2
      ETA2=CMPLX(RETA2(K),IETA2(K))
      SELFN2=QL/(1.0-Q1*C*ETA2)
```

```
      CDNSC2=SQW1*(R*(W1*(1.0-SELFN2)-1.0)+A2)*F↑A2
      DENSC2=ABS(AIMAG(CDNSC2))
      DFSCP2=DENSC2-DENS
      WRITE(6,107)DENSC2,DFSCP2
   41 CONTINUE
      IF(W1.GT.R1L)STOP
      W1=W1+0.04
      GO TO 2
  100 FORMAT(3F10.0)
  103 FORMAT(1H1,1X,7HWPOLE1=,F10.4,3X,7HWPOLE2=,F10.4,3X((HLMDA=,F10.4,13X,2HR=
     113X,2HR=,F10.3,13X,2HQ=,F10.3 )
  104 FORMAT(1H0,4X,2HW1,5X,8HDENS PER,6X,7HSCDENS1,6X,6HMMENS1,6X,7HSCDENS2,6X,
     1ENS2,6X,8HL+TDENS2,4X,9HDIFFSC1-P,4X,8HDIFFL1-P,5X,IIDIFFLC2-P,4X,
     29HDIFFLT2-P)
  105 FORMAT(1X,F7.3,E13.4,4(13X,E13.4))
  106 FORMAT(21X,E13.4,39X,F13.4)
  107 FORMAT(47X,E13.4,39X,E13.4)
      END


  0.60      0.25
```

Table I. Occurrence of Local Modes and Impurity Bands

	$m_1 > m_2 (R < 1)$	$m_2 > m_1 (R > 1)$
$\lambda > 0$	Forbidden Gap Above Optical Band	Above optical band
$\lambda < 0$	none	Forbidden Gap

LEGENDS

Fig. 1. Plot of the dispersion curve and the frequency spectrum of a perfect diatomic linear chain with nearest neighbour interactions and $m_2/m_1 = 3/5$ (=R as defined in equation [15]).

Fig. 2. Graphs occuring in the first three terms of the Dyson expansion for the Green's function $\underset{\sim}{G}(\omega^2)$.

Fig. 3. Graphs which contribute to the self energy function $\underset{\sim}{M}(\omega^2)$.

Fig. 4. Schematic plot showing the determination of the poles of the self energy function as given by the solutions of equation [20]. The poles occur at the intersection of the solid curves with the dashed horizontal lines; the upper line for heavy impurities and the lower for light impurities.

Fig. 5. Schematic plot showing the determination of the poles of the perturbed Green's function $\langle G(\omega^2)\rangle k$. The poles occur at the intersection of the line $(\omega_{k1}^2-\omega^2)(\omega_{k2}^2-\omega^2)$ with the vertical lines.

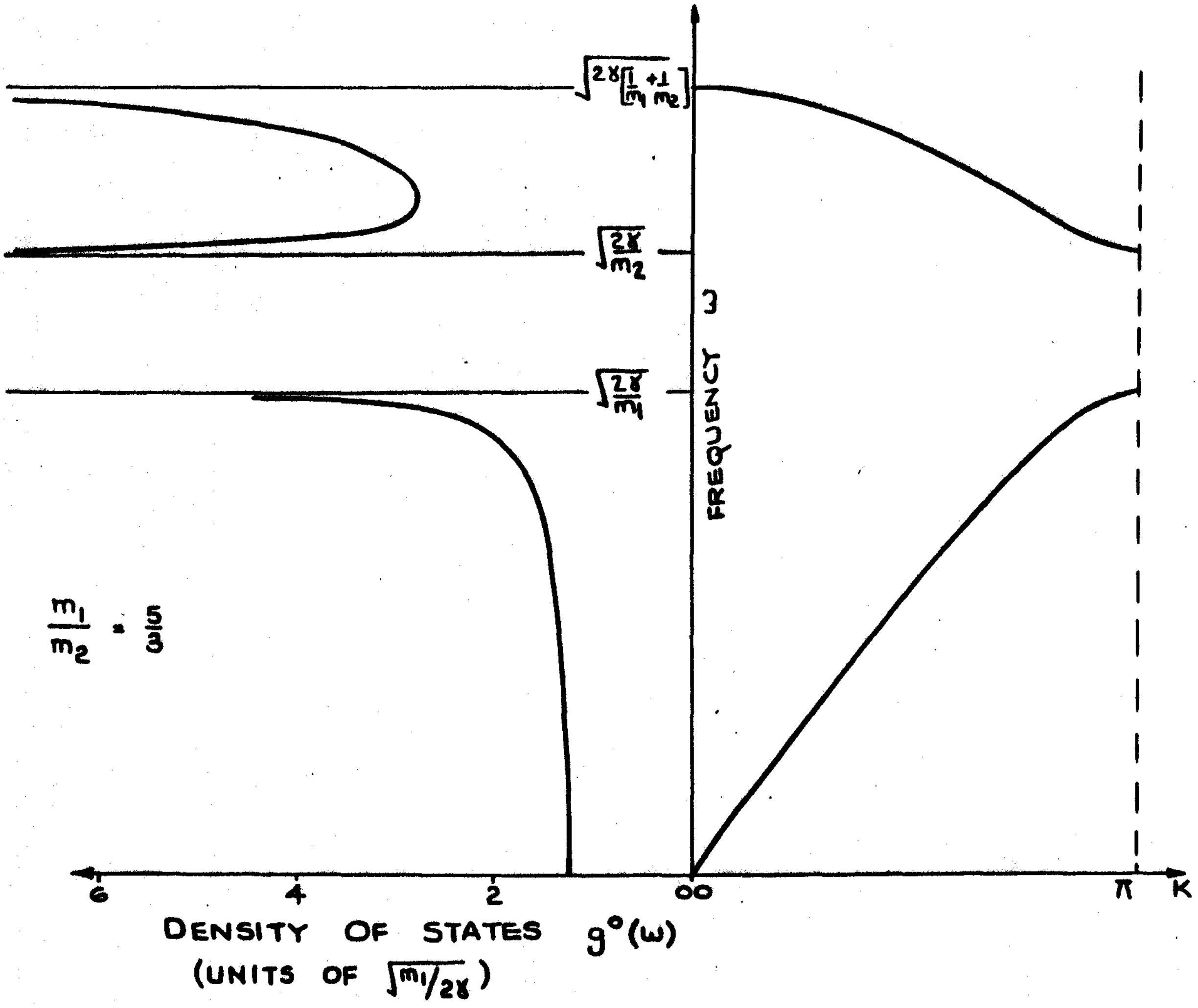
Fig. 6. The density of states function $g(\omega)$ for a diatomic chain with impurities as given by equation [28] for different mass ratios and $q = 1/20$. (a) The heavy mass replaced by light impurities. (b) The heavy mass replaced by heavier impurities. (c) The light mass replaced by lighter impurities. (d) The light mass replaced by heavy impurities.

The dotted lines indicate local mode frequencies.

Fig. 7. The self consistent density of states for a diatomic linear chain with light impurities; for mass ratios $m_1/m_2 = 5/3$, $M/m_1 = 3/4$ and $q = 1/20$. The arrows indicate local mode frequencies.

Fig. 8. Schematic plot showing the roots of the quartic $f(\eta)$ given in equation [A12]. (a) out of band frequencies (b) frequencies within impurity bands (c) frequencies near band edges.

FIG 1



$\sqrt{2\gamma\left[\frac{1}{m_1}+\frac{1}{m_2}\right]}$
$\sqrt{\frac{2\gamma}{m_2}}$
$\sqrt{\frac{2\gamma}{m_1}}$
FREQUENCY ω
$\frac{m_1}{m_2} = \frac{5}{3}$
6
4
2
0
0
π
K
DENSITY OF STATES g°(ω)
(UNITS OF $\sqrt{m_1/2\gamma}$)

FIG 2

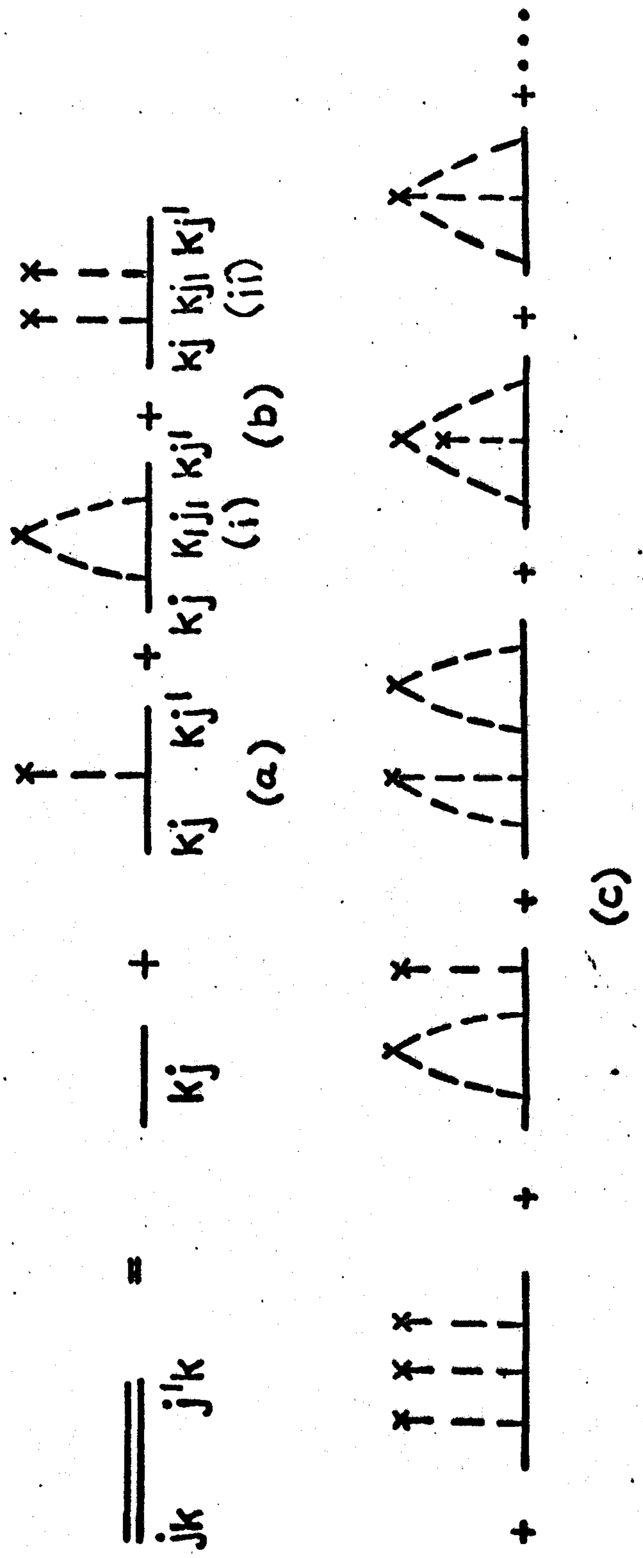
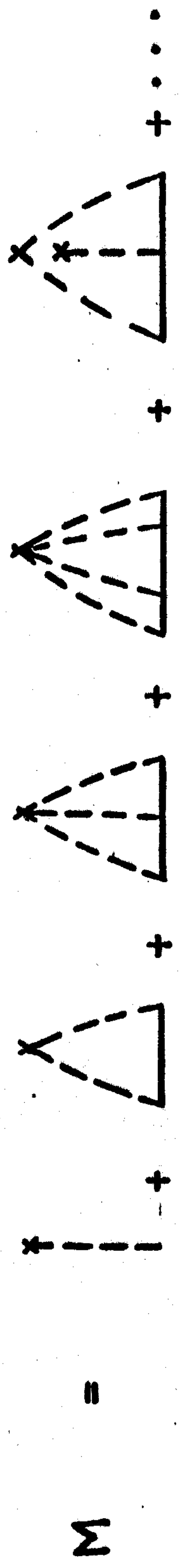


FIG 3



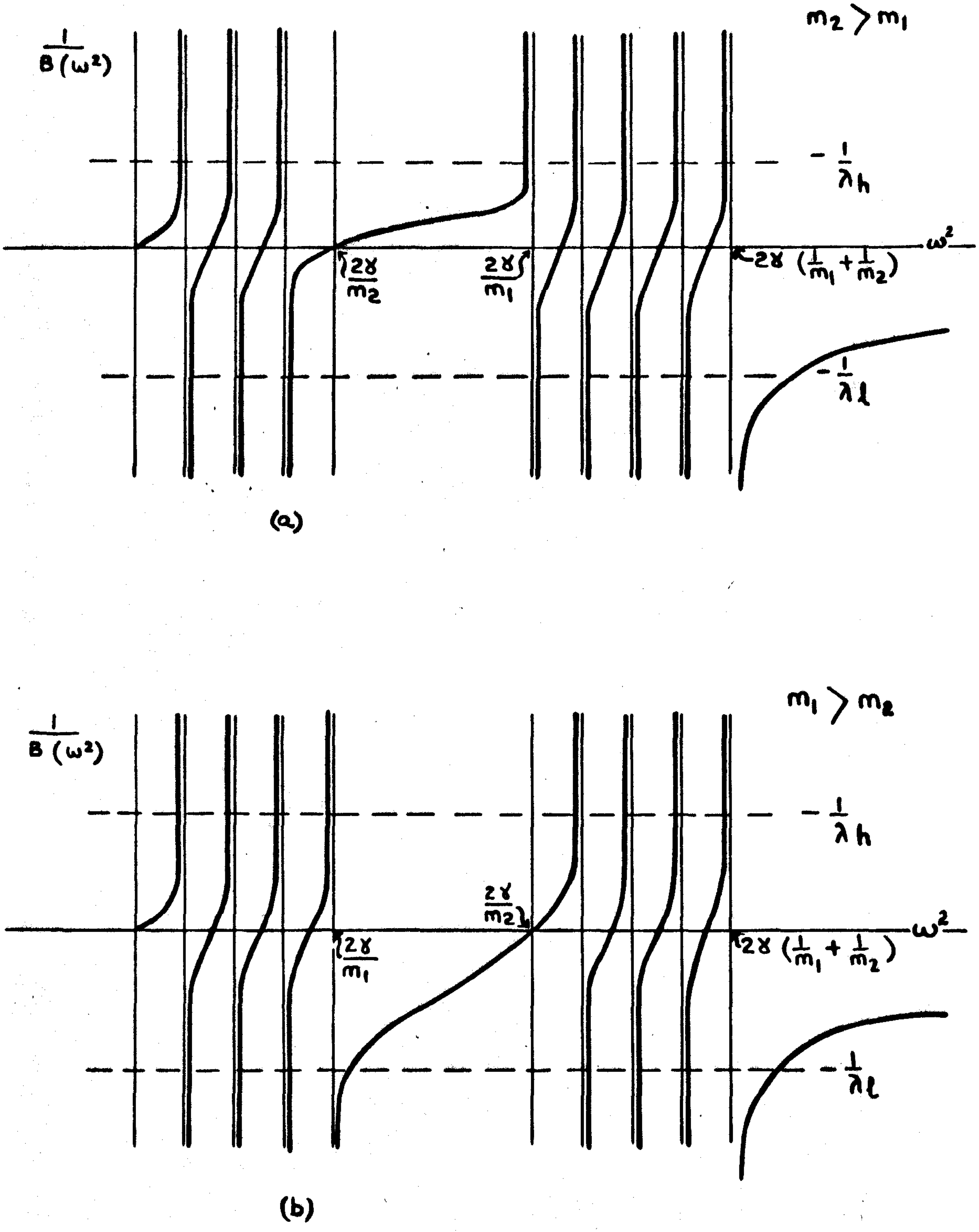

$m_2 > m_1$
$\frac{1}{B(\omega^2)}$
$-\frac{1}{\lambda_h}$
ω^2
$\frac{2\gamma}{m_2}$
$\frac{2\gamma}{m_1}$
$2\gamma\left(\frac{1}{m_1}+\frac{1}{m_2}\right)$
$-\frac{1}{\lambda_l}$
(a)
$m_1 > m_2$
$\frac{1}{B(\omega^2)}$
$-\frac{1}{\lambda_h}$
$\frac{2\gamma}{m_2}$
ω^2
$\frac{2\gamma}{m_1}$
$2\gamma\left(\frac{1}{m_1}+\frac{1}{m_2}\right)$
$-\frac{1}{\lambda_l}$
(b)

FIG 4

FIG 5

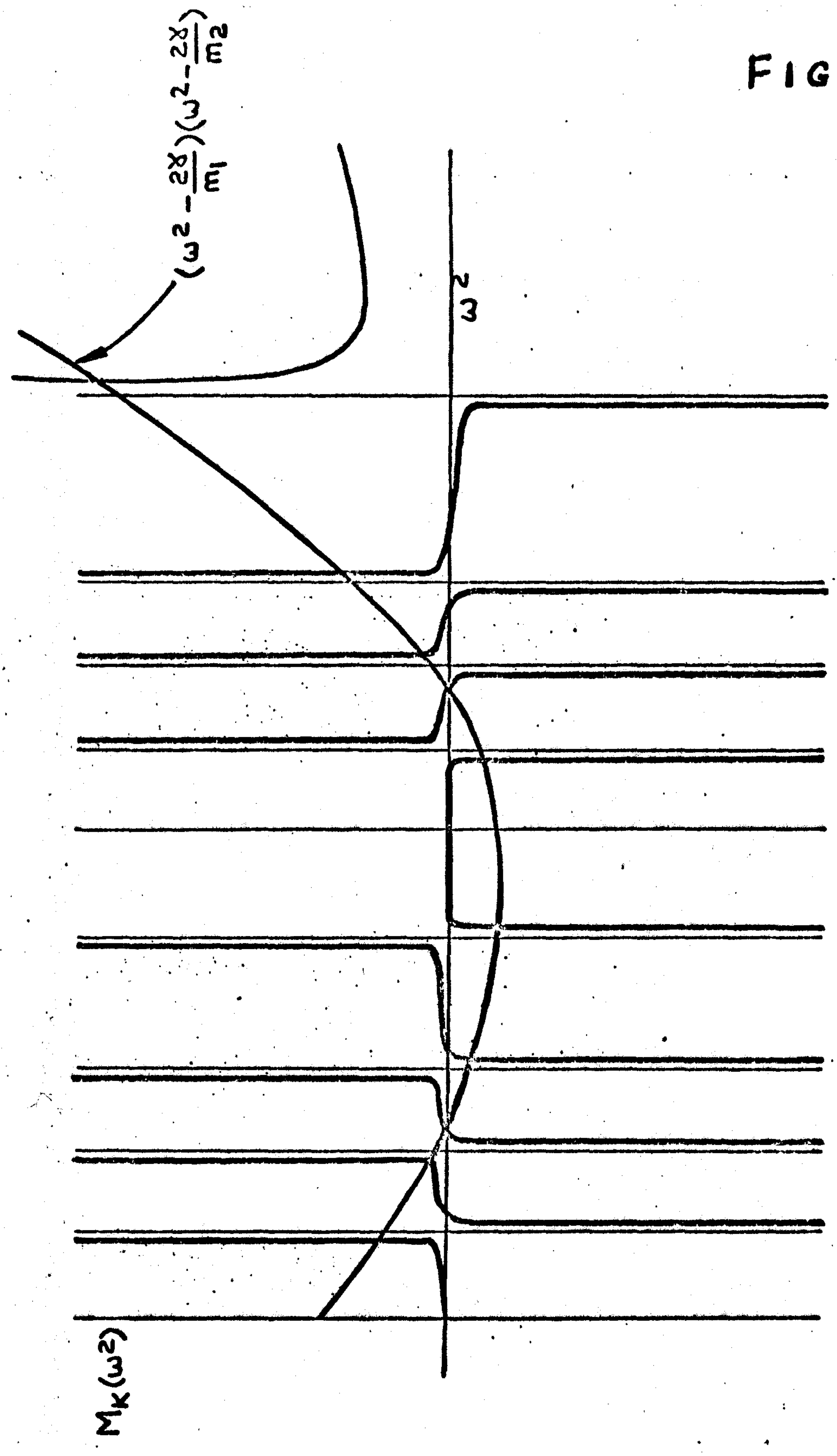

$(\omega^2-\frac{2\gamma}{m_1})(\omega^2-\frac{2\gamma}{m_2})$
ω^2
$M_K(\omega^2)$

FIG 6

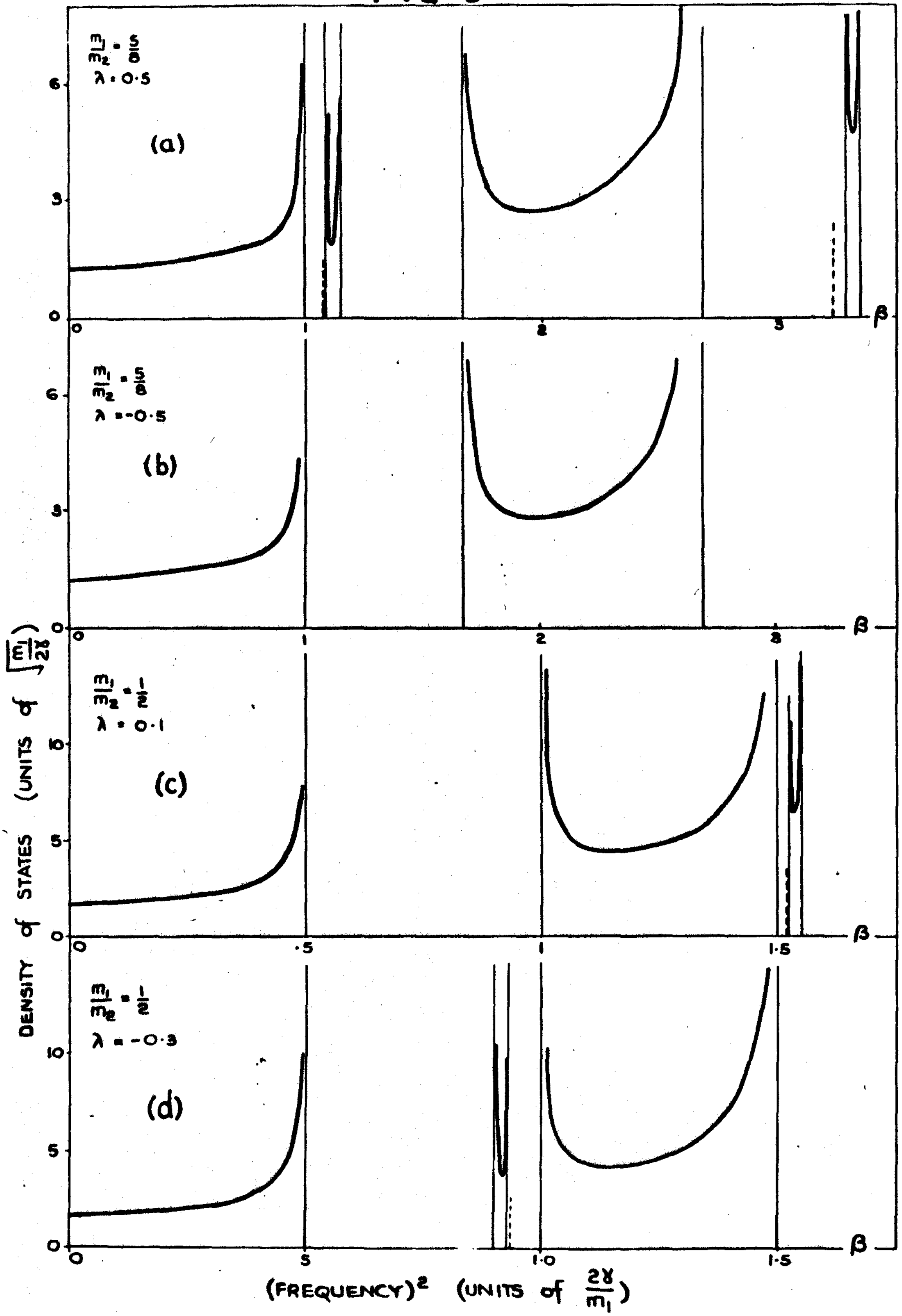
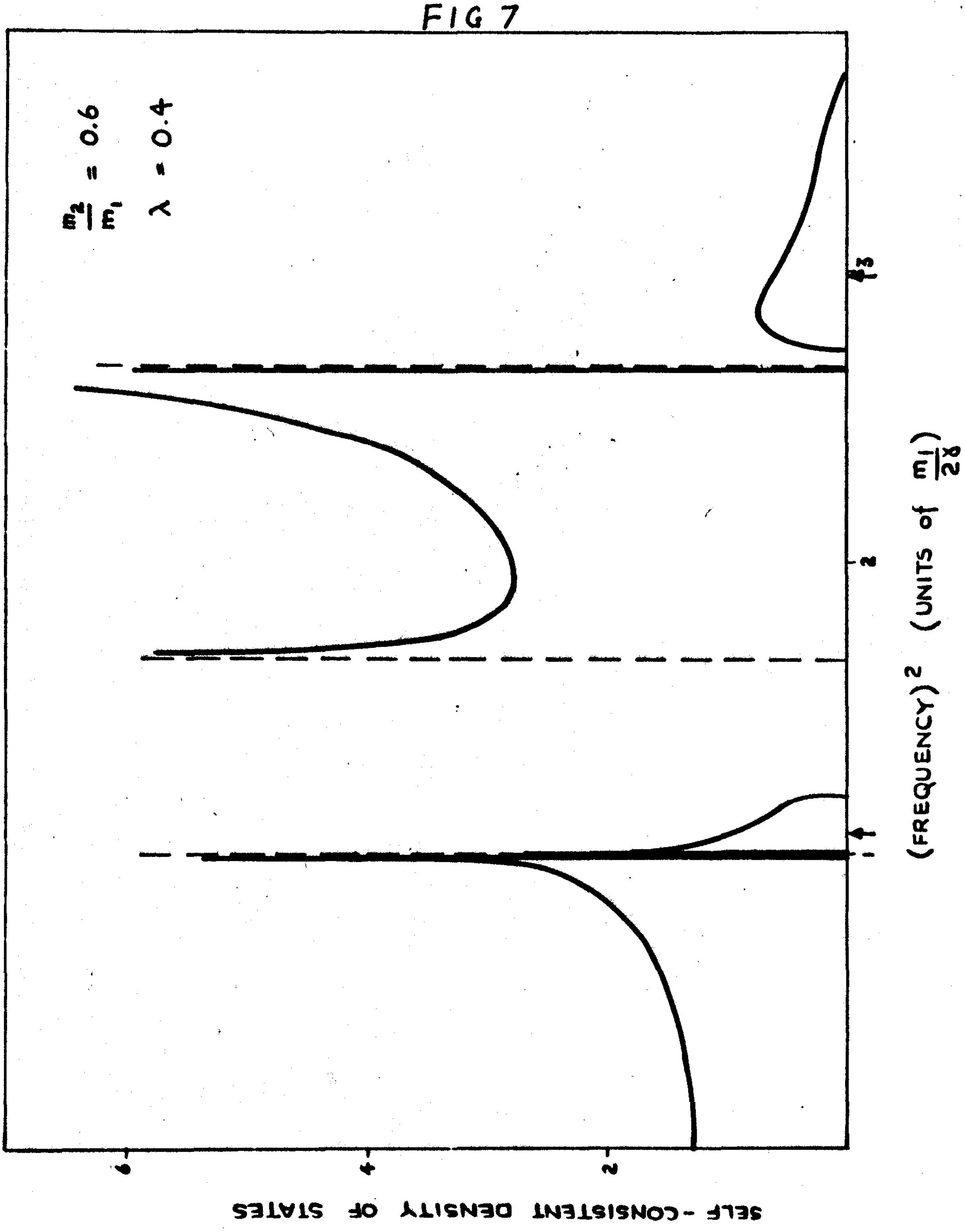

$\frac{m_1}{m_2} = \frac{5}{8}$
$\lambda = 0.5$
(a)
$\frac{m_1}{m_2} = \frac{5}{8}$
$\lambda = -0.5$
(b)
$\frac{m_1}{m_2} = \frac{1}{2}$
$\lambda = 0.1$
(c)
$\frac{m_1}{m_2} = \frac{1}{2}$
$\lambda = -0.3$
(d)
0
3
6
0
3
6
0
5
10
0
5
10
0
1
2
3
0
1
2
3
0
·5
1
1·5
0
·5
1·0
1·5
β
β
β
β
DENSITY of STATES (UNITS of $\sqrt{\frac{m_1}{2\gamma}}$)
(FREQUENCY)^2 (UNITS of $\frac{2\gamma}{m_1}$)

FIG 7


$m_2/m_1 = 0.6$
$\lambda = 0.4$
SELF-CONSISTENT DENSITY OF STATES
6
4
2
2
3
$(\text{FREQUENCY})^2$ (UNITS of $\frac{m_1}{2\gamma}$)

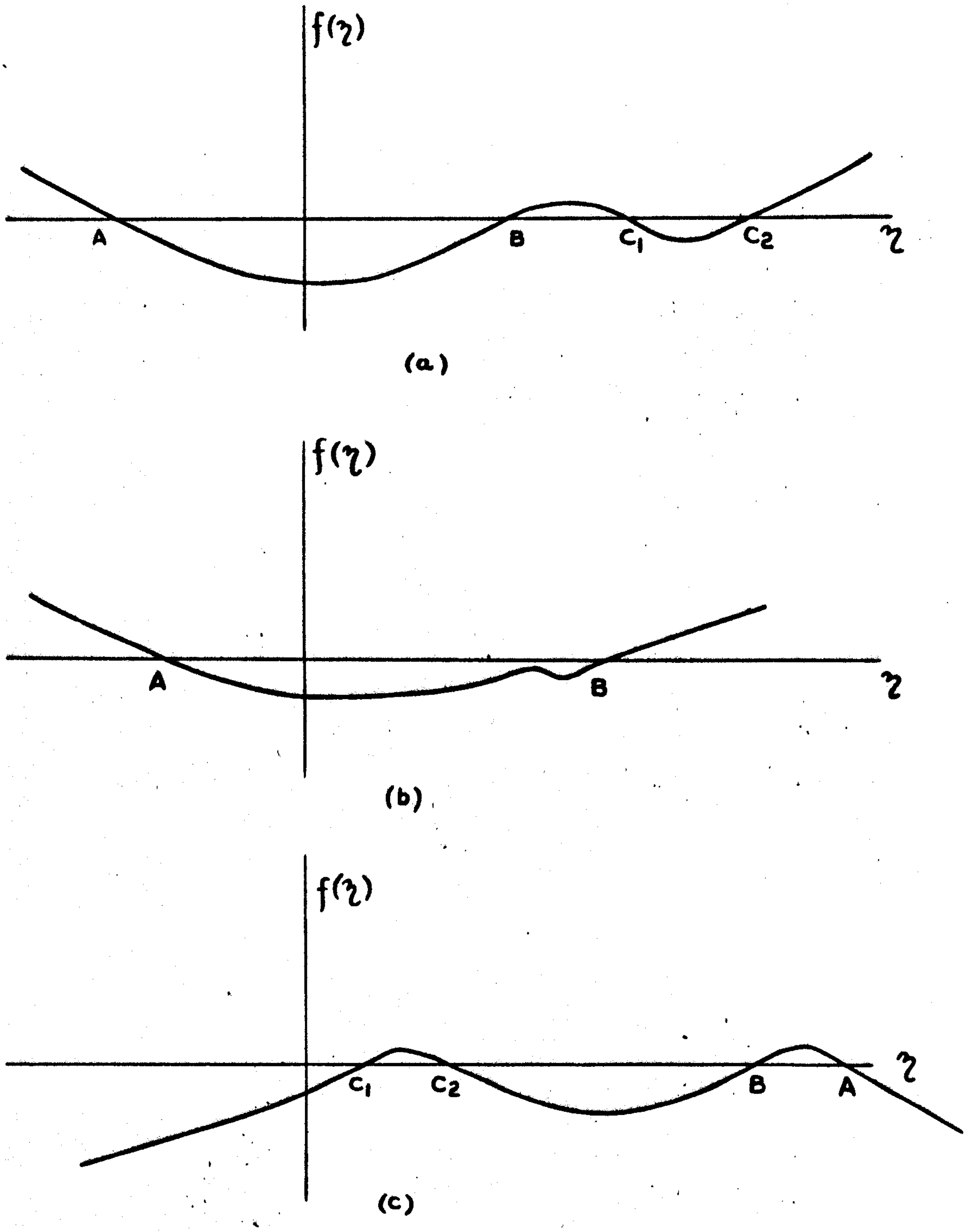


FIG 8

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