Fröhlich's model of nonthermal excitations in biological systems

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A model of an open system of oscillators which transmit energy from a source to a bath predicts nonthermal excitation of a single mode at sufficiently high energy flux. A nonlinear interaction between the oscillators and the bath produces this far-from-equilibrium steady state by channeling through a single mode energy which may be introduced diffusely into the system. The steady state is stable against fluctuations, and relaxation to the steady state is dominated by a single rate characteristic of the collective nature of the excitation. As predicted by Fröhlich, the model is in qualitative agreement with phenomena observed in metabolizing cells.

I. INTRODUCTION

For many years there has been interest in the possibility of existence of nonthermal excitations of modes of oscillation of biological systems. It was observed by Fröhlich[1] that in living systems there may be instances of anomalous excitation of certain modes in the presence of an otherwise thermalized spectrum of modes. He suggested that the appearance of these modes was due to the flow of energy in the system, usually due to metabolism in the system. Since the scale of lengths involved suggested that dielectric oscillations with frequencies of $10^{11}-10^{12}$ Hz were involved, there might be, he further suggested, the possibility of coupling to these modes with microwave radiation of millimeter wavelength. He also pointed out that such excitations might lead to strong forces between elements of the system, forces which might influence the progress of life processes in critical ways.[2] Phenomena have been observed which may provide support for the existence of both the direct interaction and the indirect effects.

Raman-scattering experiments by Webb *et al.*[3] on *Escherichia coli* cultures indicate that if and only if the cells are metabolizing, Stokes and anti-Stokes lines with frequencies in the range predicted by Fröhlich have nearly equal intensities, evidence of a highly excited mode. A similar effect was observed by Drissler and McFarlane[4] on living cells of *Chlorella pyrenoidosa.* However in that instance it was realized that at least part of the effect could be attributed to a resonance with a carotenoid absorbtion band. Further study by Kinoshita *et al.*[5] suggests that this resonance may be sufficient to account for the entire effect in *Chlorella,* but the issue may still be open to further interpretation.

The effect on growth of yeast cultures of irradiation with a spectrum of millimeter microwaves has been studied by Grundler and Kielmann.[6,7] They found that strongly frequency-dependent enhancement and suppression of the growth rate of irradiated cells occurred even though the intensity of the radiation was well below that necessary to cause significant alteration of the temperature of the cultures. Several resonances were observed. Cooper and Theimer[8,9] have drawn attention to the possibility that the nonthermal excitations may be directly related to a ferroelectric state in the cell at the time of reproduction. They have also suggested that such a state may be characteristic of cancerous malignancies. This suggestion has some support in an observation by Webb *et al.*[10] of Stokes lines from mammary tissue. Lines observed as single resonances in normal tissue were found to be split into doublets in cancerous tissue. As further evidence of such a ferroelectric condition, Pohl[11] studied the attraction of yeast cells on a suspended powder of $BaTiO_3$ and concluded that there was some evidence for the existence for a long-range dispersion force. Studies of the formation of rouleaux in mixtures of mammalian erythrocytes have been conducted by Rowlands *et al.*[12–14] and indicate that in mixtures of like cells a long-range force of the type predicted by Fröhlich[2] influences the rate of rouleaux formation.

Early experiments by Smolyanskaya and Vilenskaya[15] studied the rate of production to colicin in *E. coli* bacteria irradiated with millimeter microwaves. In addition to a strongly frequency-dependent effect on the induction coefficient to colicin synthesis, they observed that the time required for onset of the effect was greater at low temperatures (20 °C) than at higher ones (37 °C), and that once begun, the strength of the effect was independent of the microwave flux density. Fröhlich[16] has explained this as indicating that a threshold power level is required to induce the state of nonthermal excitation, but that once initiated, the consequent processes are unaffected by the incident power level. A spectrum of resonances was observed.

Much more extensive reviews of the experimental work have been presented by Jaggard,[17] by Fröhlich,[18,19] and by Webb.[20] It does appear that excitations of some kind have been observed in the frequency range predicted by Fröhlich. Since thermal excitations of those frequencies would be lost in noise at temperatures characteristic of living systems, it is appropriate to give careful attention to an understanding of features of a model which Fröhlich has proposed[21,22] for the purpose of illustrating how such anomalous excitation may arise. Both Fröhlich's original model and the more general form predict the existence of a high level of excitation of a single mode of oscillation in the presence of sufficiently high energy flux. It is one of the main points of this paper that explicit solutions of a rate equation exist in a far-from-equilibrium regime which appears to correspond to the circumstances of the observed excitations. As discussed briefly elsewhere,[23,24] the solutions which correspond to the excitations occur over a much broader range of rate parameters than was anticipated earlier. The qualitative features of the excitation thus described are consistent throughout the parameter range with the qualitative characteristic of the experiments, including the possibility that the frequency of the excitation may vary as essential parameters are altered. It is important to understand these variations in order that information which the experimental results may yield about the underlying processes can be more fully explored.

In Sec. II, the establishment of the rate equation will be outlined. An exact solution of a special case of the steady-state rate equation will be explored in Sec. III to illustrate essential aspects of the manner in which even a simple dissipative system can exhibit preferential excitation of some single mode in a far-from-equilibrium steady state. Detailed asymptotic solutions of the general steady-state rate equation are developed in Sec. IV and then are applied in Sec. V to study the stability of the nonthermal excitations and the relaxation to the steady state at high energy flux. In Sec. IV present conclusions and some open questions are discussed.

II. THE RATE EQUATION

The model that Fröhlich proposed[22] was based on an idealized system of oscillators, which were driven by an external energy source and which could transfer energy to and from a heat bath. The unique feature of the model was the manner in which the oscillator system could interact with the heat bath. In addition to a simple one-to-one exchange of energy between one of the oscillators and a heat-bath mode, Fröhlich assumed the possibility that any two of the oscillators could transfer energy simultaneously to a heat-bath mode in such a manner that one oscillator would be further excited while the other was being relaxed with the heat bath providing or accepting the amount of energy needed for conservation of energy in the two-one interaction. Such a process then leads one to expect that in a net transfer of energy to the heat bath, the oscillator of low frequency in the two-one interaction would be stimulated. Fröhlich was able to show qualitatively that, in fact, at sufficiently high rates of energy transfer, only one oscillator in the system, that of lowest frequency, would be excited. Later, Lifshits[25,26] pointed out that a second two-one interaction might be included, an interaction in which two of the oscillators are both either excited or relaxed while the heat bath again responds to accommodate the energy change. The process proposed by Lifshits competes with that proposed by Fröhlich, and if sufficiently strong might overcome it. Fröhlich[27] responded that the magnitude of the Lifshits terms would be unlikely to be of concern, an argument which he further buttressed[19] with an appraisal of constraints which conservation of both energy and momentum would require.

Fröhlich had postulated the rate equation[21] and had not analyzed further the origin of the various terms. Such an analysis has been presented by Wu and Austin[28–30] in discussions of the derivation of the rate equation from a Hamiltonian which incorporated the essential features of the Fröhlich model. It is however still not clear what limitations are necessary for the validity of the rate equation. Wu and Austin[31] have argued that the rate equation is, in fact, exact in essentially the Fröhlich form with the addition of Lifshits-type terms. However their analysis, based on a diagrammatic Green's function approach, is brief and requires acceptance of an assertion that the rate coefficients accommodate through renormalization the affects of high-order terms. This is in contradiction to a number of studies of derivation of rate equations, such as those by Zwanzig *et al.*,[32–34] wherein quantum correlation effects produce qualitative as well as quantitative changes when higher-order terms are considered. It also was not made clear by Wu and Austin how in an exact treatment the invariance of the dynamical equations under time reversal goes into the irreversible character of the rate equation. The essential features of derivation of an approximate rate equation equivalent to Fröhlich's will only be outlined in order not to deviate too far from the principal topic of this paper, the solutions of the rate equation. A more complete treatment of the rate equations will be presented separately.

As Fröhlich has discussed,[19] the root of the problem arises in consideration of the effects of a strong polarization field on a system which can deform in response to the field. Thus, Fröhlich argues, polarization of a material $\vec{P}$ produces an electric self-energy proportional to P^2. This in turn leads to elastic deformation, represented by div$\vec{A}$, where $\vec{A}$ is the elastic field. The net interaction of polarization field and elastic deformation is proportional to P^2div$\vec{A}$. (He also has stipulated that terms of higher order in P^2 are needed to assure ultimate mechanical stability, but such terms will not be considered here.) If one assumes that $\vec{P}$ and $\vec{A}$ may be represented as a superposition of contribution of various modes of oscillation, replacement of the oscillator amplitudes by combinations of simple harmonic oscillator raising and lowering operators gives essentially the Fröhlich-Lifshits interaction. Both types of terms follow from the P^2div$\vec{A}$ interaction. The magnitudes of the coefficients depend then on the resolution of $\vec{P}$ and of $\vec{A}$ into components, but the presence of div$\vec{A}$ rather than $\vec{A}$ suggests that low-wavelength elastic modes may have preferential weighting. The elastic phonons play the part of the heat bath. Adding terms to represent an energy source thus leads to a Hamiltonian

$$H=\sum_\alpha E_\alpha A_\alpha^\dagger A_\alpha+\sum_i \omega_i a_i^\dagger a_i+\sum_r \Omega_r b_r^\dagger b_r + \left[\sum_{\alpha,r} p_{\alpha i}A_\alpha^\dagger a_i+\sum_{i,r}\xi_{ir}a_i^\dagger b_r+\sum_{i,j,r}(\zeta_{ijr}a_i^\dagger a_j+\sigma_{ijr}a_i^\dagger a_j^\dagger)b_r+\text{H.c.}\right], \tag{2.1}$$

where $A_\alpha^\dagger, A_\alpha$ are creation and annihilation operators for modes of the energy source (either metabolic processes or external sources such as microwave radiation) of frequency $E_\alpha(\hbar=1)$; $a_i^\dagger, a_i$ are creation and annihilation operators for oscillators of frequency ω_i, and $b_r^\dagger, b_r$ creation and annihilation operators for bath modes of frequency Ω_r. The open system of oscillators will be assumed to involve a finite number A of nondegenerate modes. The ω_i will be enumerated so that $i\le j$ implies $\omega_i\le\omega_j$. The coupling factors are rationalized in the manner discussed above, but no particular functional form will be assumed here other than that both the Fröhlich two-one interaction strength ζ_{ijr} and the Lifshits two-one interaction strength σ_{ijr} will be assumed symmetrical in the oscillator indices, consistent with their common origin in the P^2 term. To avoid self-excitation processes, it is assumed that ζ_{iir} and σ_{iir} vanish. All oscillators will be assumed to satisfy the usual commutation rules, although, as Wu and Austin have noted,[30] the formalism carries through equally well if the bath modes satisfy anticommutation rules instead. This would suggest, however, that the open system of oscillators couples to a bath of fermions, such as conduction electrons in a metal, a situation which does not seem appropriate here.

Beginning with the Hamiltonian (2.1), one seeks to derive rate equations for the expectation values of the occupation numbers of the oscillators in the open systems,

$$n_i=\text{Tr}(\rho a_i^\dagger a_i)\ , \tag{2.2}$$

where ρ represents the density matrix for the source-system-bath complex. Expansion of the density matrix through second order in the interaction terms then leads to a rate equation

$$\dot n_i=s_i+\Phi_i(n_i+1-n_ie^{\beta\omega_i}) + \sum_j{}'\{\Lambda_{ij}[(n_i+1)n_j-n_i(n_j+1)e^{\beta(\omega_i-\omega_j)}]+\Gamma_{ij}[(n_i+1)(n_j+1)-n_in_je^{\beta(\omega_i+\omega_j)}]\}\ , \tag{2.3}$$

where the primed sum has no term $j=i$. Here

$$s_i=\pi\sum_\alpha |p_{\alpha i}|^2N_\alpha\delta(E_\alpha-\omega_i)\ , \tag{2.4}$$

where N_α is the occupation number of source mode α, assuming $N_\alpha\gg1$, and s_i indicates the excitation rate of oscillator mode Ai by the energy source or "pump." The condition on N_α assures energy flow only from the source to the system. The time scale is long enough to replace time integrals in the perturbation expansion by delta functions, which assures energy conservation. In the system-bath interaction terms,

$$\Phi_i \equiv \pi \sum_r |\xi_{ir}|^2 \delta(\omega_i - \Omega_r) \frac{1}{e^{\beta\omega_i} - 1} \tag{2.5}$$

represents the excitation rate of oscillator i through interaction with the bath. The latter is assumed in thermal equilibrium at temperature T ($\beta = 1/k_B T$). The Lifshits contribution is represented by terms of coefficients

$$\Gamma_{ij} = \Gamma_{ji} \equiv 4\pi \sum_r |\sigma_{ijr}|^2 \delta(\omega_i + \omega_j - \Omega_r) \frac{1}{e^{\beta(\omega_i + \omega_j)} - 1} , \tag{2.6}$$

while the Fröhlich terms are represented by terms with coefficients

$$\Lambda_{ij} \equiv \pi \sum_r |\zeta_{ijr}|^2 \times \begin{cases} \delta(\omega_j - \omega_i - \Omega_r) \dfrac{1}{1 - e^{-\beta(\omega_j - \omega_i)}}, & j > i \\ \delta(\omega_i - \omega_j - \Omega_r) \dfrac{1}{e^{\beta(\omega_i - \omega_j)} - 1}, & i > j . \end{cases} \tag{2.7}$$

The Λ_{ij} are not symmetrical in the oscillator indices, but rather they satisfy a balance condition which follows from (2.7),

$$\Lambda_{ij} e^{-\beta\omega_j} = \Lambda_{ji} e^{-\beta\omega_i} . \tag{2.8}$$

All of the coefficients s_i, Φ_i, Γ_{ij}, and Λ_{ij} are manifestly positive. Also, Λ_{ii} and Γ_{ii} vanish. The assumption $N_\alpha \gg 1$ [used in (2.4)] and the appearance of the thermal weighting factors in (2.5)–(2.7) represent a decoupling of the portions of the density function related to the source and bath from that representing the system of oscillators. The irreversibility of the rate equation (2.3) is attributable to these approximations.

More detailed information about the coupling factors ζ_{ijr} and σ_{ijr} would require more detailed specification of the model. However, if these factors are of the same order of magnitude, then

$$\Gamma_{ij} \sim \frac{|e^{\beta(\omega_i - \omega_j)} - 1|}{e^{\beta(\omega_i + \omega_j)} - 1} \Lambda_{ij} < \Lambda_{ij} . \tag{2.9}$$

In the papers by Fröhlich and by Wu and Austin, it has been assumed that the ζ_{ijr} and σ_{ijr} are generally independent of the oscillator indices and further that the oscillator spectrum is a narrow band, $\Delta\omega \ll \omega_{\text{av}}$. If $T \sim 25\,^\circ\text{C}$ and $\omega_{\text{av}} \sim 10^{11}$ Hz, then $\beta\omega \sim 10^{-2}$ and (2.9) becomes, with the narrow-band assumption,

$$\Gamma_{ij} \sim \frac{|\omega_i - \omega_j|}{\omega_i + \omega_j} \Lambda_{ij} \ll \Lambda_{ij} . \tag{2.10}$$

It is not clear, however, that the ζ and σ coefficients will always lead to (2.10). It will be shown in Sec. III that solutions of the rate equations (2.3) exist for a wide range of values of Λ_{ij} and Γ_{ij} but that throughout the range the solutions have the characteristics of the nonthermal excitations.

It will be useful to use the notation

$$\epsilon_i = \Phi_i (e^{\beta\omega_i} - 1) , \tag{2.11}$$

$$\gamma_{ij} = \Gamma_{ij} (e^{\beta(\omega_i + \omega_j)} - 1) = \gamma_{ji} , \tag{2.12}$$

and

$$\lambda_{ij} = \Lambda_{ij} (e^{\beta(\omega_i - \omega_j)} - 1) = -\lambda_{ji} . \tag{2.13}$$

Note that λ_{ij} is positive if $i > j$. The comparison of magnitudes of γ_{ij} and λ_{ij} is in fact more important in characterizing the solutions of the rate equations than comparison of magnitudes of Γ_{ij} and Λ_{ij}. One may in fact have $\Gamma_{ij} < \Lambda_{ij}$, while $\gamma_{ij} > \lambda_{ij}$.

It is also useful to define a total pump rate S,

$$S = \sum_i s_i , \tag{2.14}$$

and write

$$s_i = \alpha_i S, \quad \sum_i \alpha_i = 1 . \tag{2.15}$$

An important sum rule involving S follows by summing the rate equation over the oscillator indices. The total excitation rate $\dot{N}$ is

$$\dot{N} = \sum_i \dot{n}_i = S + \sum_i (\Phi_i - \epsilon_i n_i) + \sum_{i,j}{}' [\Gamma_{ij}(n_i + n_j + 1) - \gamma_{ij} n_i n_j] . \tag{2.16}$$

As a consequence of the balance condition (2.8), the Fröhlich terms in the rate equation do not contribute to the total excitation rate of the system. Such terms contribute overall only to transfers of energy within the open system.

In the steady state, all the $\dot{n}_i$ vanish and the sum rule then requires that at most one n_i be proportional to S for large S. In Sec. III it will be shown if there are only two oscillators, either can be linear in S, depending on the parameters, except for a special case where both vary as $S^{1/2}$ at large S. Thus Fröhlich nonthermal excitation is expected for sufficiently large S except in this special case. In Sec. IV, it is shown that the linear dependence of one and only one of the n_i on large S follows as an asymptotic result for any finite number of oscillators in the system.

III. EXACT SOLUTION FOR TWO OSCILLATORS

In an experimental situation, one would expect the set of oscillators to contain a large number of modes, and indeed the model was treated in that way by Fröhlich.[21] However, the rate equations for a system of only two oscillators can be solved exactly for the steady-state excitation numbers, and so it is possible to examine in detail how these excitation numbers depend on S, on the transfer rates Φ_i, Γ_{ij}, and Λ_{ij}, and on the pump coefficients $\{\alpha_i\}$. Some of the features of the two-oscillator problem carry over to the more general problem, and so the insight gained in the simple case improves understanding of the more general and more realisitic case.

For two oscillators, the rate equations (2.3) become

$$\dot{n}_1=\alpha_1 S+\Phi_1-\epsilon_1 n_1+\Lambda_{12}(n_2-n_1 e^{\beta(\omega_1-\omega_2)})-\lambda_{12}n_1 n_2+\Gamma_{12}(n_1+n_2+1)-\gamma_{12}n_1 n_2 \quad (3.1)$$

and

$$\dot{n}_2=\alpha_2 S+\Phi_2-\epsilon_2 n_2+\Lambda_{21}(n_1-n_2 e^{\beta(\omega_2-\omega_2)})-\lambda_{21}n_1 n_2+\Gamma_{21}(n_1+n_2+1)-\gamma_{21}n_1 n_2 \ . \quad (3.2)$$

For the steady state $\dot{n}_1=\dot{n}_2=0$ one has a pair of equations bilinear in n_1 and n_2. Elimination of either variable leaves a quadratic in the other,

$$A_1 n_1^2+B_1 n_1-C_{1=0} \ , \quad (3.3)$$

where

$$A_1=(\epsilon_1+\Lambda_{21}-\Gamma_{21})(\gamma_{21}+\lambda_{21})+(\Lambda_{21}+\Gamma_{21})(\gamma_{21}-\lambda_{21})=\epsilon_1(\gamma_{21}+\lambda_{21})+2(\Lambda_{21}\gamma_{21}-\Gamma_{21}\lambda_{21}) \ , \quad (3.4)$$

$$B_1=(\epsilon_1+\Lambda_{21}-\Gamma_{21})(\epsilon_2+\Lambda_{12}-\Gamma_{12})-(\Lambda_{12}+\Gamma_{12})(\Lambda_{21}+\Gamma_{21})+(\Phi_2+\Gamma_{21})(\gamma_{21}-\lambda_{21})$$
$$-(\Phi_1+\Gamma_{12})(\gamma_{21}+\lambda_{21})-[\lambda_{21}+(\alpha_1-\alpha_2)\gamma_{21}]S \ , \quad (3.5)$$

and

$$C_1=(\Phi_2+\Gamma_{21})(\Lambda_{12}+\Gamma_{12})+(\epsilon_2+\Lambda_{12}-\Gamma_{12})(\Phi_1+\Gamma_{12})+[\alpha_1\epsilon_2+\Lambda_{12}-(\alpha_1-\alpha_2)\Gamma_{12}]S \ . \quad (3.6)$$

A similar equation for n_2 is obtained and amounts to interchanging indices 1 and 2 where appearing. Note that A_1 can usually be expected to be positive, but A_2 can be negative. The sum rule (2.16) becomes, for two oscillators in the steady state,

$$S+\Phi_1+\Phi_2+2\Gamma_{12}=(\epsilon_1-2\Gamma_{12})n_1+(\epsilon_2-2\Gamma_{21})n_2+2\gamma_{12}n_1 n_2 \ . \quad (3.7)$$

After considerable algebra, one verifies that this equation is satisfied by the exact n_1,n_2:

$$n_i=[-B_i+(B_i^2+4A_iC_i)^{1/2}]/(2A_i) \ . \quad (3.8)$$

Moreover, the quantity $B_1^2+4A_1C_1$ equals $B_2^2+4A_2C_2$ for all values of S. Further algebra verifies that for $S=0$, (3.8) reduces to $(e^{\beta\omega_i}-1)^{-1}$ as expected. The roots with negative radical are not of physical interest since n_i must be positive.

Analysis of these formal results is made quite a bit more difficult by the fact that the various coefficients can be either sign, depending on the value of the parameters. Thus the result in (3.8) is acceptable physically ($n_i>0$) for either sign of A_i if $C_i>0$. While this seems plausible, there is no proof that it is assured. In order to examine these equations more closely, it is necessary to make some estimates of the magnitudes of the parameters. Asymptotic properties can then be derived. The solutions which correspond to these parameter choices can also be displayed graphically as functions of S. In keeping with Fröhlich's original suggestion, it will be assumed that $\beta\omega_i\sim 10^{-2}$, consistent with the temperature range of living systems and a frequency range of $10^{11}-10^{12}$ Hz. One does not expect the oscillator frequencies to vary too widely; so it seems reasonable to specialize here to $\omega_2\sim 1.1\omega_1$ corresponding to Fröhlich's narrow-band assumption. This is not crucial but implies here that $\Lambda_{12}\sim\Lambda_{21}$ and

$\lambda_{21} \sim 10^{-3}\Lambda_{21}$. Since the coordination of events to produce simple interactions is more probable than that needed to support more complicated interactions, it appears plausible that the one-one transfer rates Φ_i may be rapid than the two-one processes. So, it is estimated that if the Φ_i are about 1 on a suitable scale, the Λ_{ij} factors are about 0.1. Then the ϵ_i will be about 10^{-2} and the $\lambda_{21} \sim 10^{-4}$. It is convenient to estimate relative strengths of the Fröhlich and Lifshits terms through λ_{21} and γ_{21}. If $\gamma_{21} = 0.1\lambda_{21} \sim 10^{-5}$, $\Gamma_{21} \sim 10^{-3}$. If $\gamma_{21} = 10\lambda_{21} \sim 10^{-3}$, $\Gamma_{21} \sim 0.1 \sim \Lambda_{21}$. For either of these cases, both coefficients C_i are positive. For the C_i to become negative, Γ_{21} would need to be much larger than would be expected here.

The coefficients A_i are also positive in this range, but for much smaller values of γ_{21}, A_2 can be negative. Then

$$\Delta = \lambda_{21} + (\alpha - \alpha_2)\gamma_{21} > 0 ,$$

and $B_1 < 0$, $B_2 > 0$. The excitation numbers n_i are then given as follows:

$$A_1 n_1^2 - |B_1| n_1 - C_1 = 0 ,$$

$$n_1 = \frac{|B_1|}{A_1} + \frac{C_1}{A_1 n_1} \sim -\frac{B_1}{A_1} = \frac{\Delta}{A_1} S ; \tag{3.9}$$

$$A_2 n_2^2 + B_2 n_2 - C_2 = 0 ,$$

$$n_2 = \frac{C_2}{B_2} - \frac{A_2 n_2^2}{B_2} \cong \frac{C_2}{B_2}$$

$$\cong \frac{\alpha_2\epsilon_1 + \Lambda_{21} + (\alpha_1 - \alpha_2)\Gamma_{12}}{\Delta} . \tag{3.10}$$

The other solution for n_2 for $A_2 < 0$ is not compatible in the sum rule with the only physically acceptable solution for n_1.

If rather than $\gamma_{21} = 10^{-1}\lambda_{21}$, one takes $\gamma_{21} = 10\lambda_{21} \sim 10^{-3}$, then $\Gamma_{12} \sim 10^{-1} \sim \Lambda_{12}$. The C_i are still positive. The sign of Δ varies with the α_i such that Δ is greater or less than zero as α_2 is greater or less than $\frac{1}{2}(1 + \lambda_{ij}/\gamma_{ij})$. Consider now the asymptotic behavior of the n_i. For $\Delta > 0$, (3.9) and (3.10) follow again as the asymptotic solutions. If α_2 and γ_{21} are great enough that $\Delta < 0$,

$$n_1 \cong \frac{C_1}{B_1} \simeq \frac{\alpha_1\epsilon_2 + \Lambda_{12} - (\alpha_1 - \alpha_2)\Gamma_{12}}{(\alpha_2 - \alpha_1)\gamma_{21} - \lambda_{21}} , \tag{3.11}$$

$$n_2 \cong -\frac{B_2}{A_2}$$

$$\cong \frac{[(\alpha_2 - \alpha_1)\gamma_{21} - \lambda_{21}]S}{\epsilon_2(\gamma_{21} - \lambda_{21}) + 2(\Lambda_{12}\gamma_{21} + \Gamma_{12}\lambda_{21})} . \tag{3.12}$$

Recall that Δ can be negative only if γ_{21} exceeds λ_{21} sufficiently, so the denominators in both (3.11) and (3.12) will be positive.

In the Fröhlich limit, Γ_{12} vanishes and

$$n_1 \cong S/\epsilon , \tag{3.13}$$

$$n_2 \cong \left[1 + \frac{\alpha_2\epsilon_1}{\Lambda_{21}} \right] \frac{1}{e^{\beta(\omega_2 - \omega_1)} - 1} . \tag{3.14}$$

It seems unlikely to occur in view of the previous estimates of the Γ_{ij} and Λ_{ij}, but, for completeness consider a limit in which the Lifshits γ_{21} dominates and λ_{21} is negligible. Then, for $\alpha_1 > \alpha_2$,

$$n_1 \cong (\alpha_1 - \alpha_2)S/\epsilon_1 , \tag{3.15}$$

$$n_2 \cong \left[1 + \frac{\alpha_2\epsilon_1}{(\alpha_1 - \alpha_2)\Gamma_{12}} \right] \frac{1}{e^{\beta(\omega_1 + \omega_2)} - 1} . \tag{3.16}$$

When $\alpha_2 > \alpha_1$, n_2 is linear in S. The corresponding expressions are obtained by interchanging indices 1 and 2 in (3.15) and (3.16). A nonthermal excitation is thus predicted throughout the entire range of the parameters γ_{21} and λ_{21}, provided only that the energy pump rate S is sufficiently great.

An interesting special case occurs when Δ vanishes, for then the only dependence of the n_i on S is through the C_i,

$$\Delta = 0 \Longrightarrow n_i = (C_i/A_i)^{1/2} \tag{3.17}$$

or

$$n_1 \cong \left[\frac{[\alpha_1\epsilon_2 + \Lambda_{12} - (\alpha_1 - \alpha_2)\Gamma_{12}]S}{\epsilon_1(\gamma_{21} + \lambda_{21}) + 2(\Lambda_{21}\gamma_{21} - \Gamma_{21}\lambda_{21})} \right]^{1/2} \tag{3.18}$$

and

$$n_2 \cong \left[\frac{[\alpha_2\epsilon_1 + \Lambda_{21} + (\alpha_1 - \alpha_2)\Gamma_{21}]S}{\epsilon_2(\gamma_{21} - \lambda_{21}) + 2(\Lambda_{12}\gamma_{21} + \Gamma_{21}\lambda_{21})} \right]^{1/2} . \tag{3.19}$$

In the Lifshits limit, $\Delta = 0$ requires $\alpha_1 = \alpha_2 = 0.5$ and

$$n_1 \cong \left[\frac{\epsilon_2 S}{2\epsilon_1\gamma_{21}} \right]^{1/2} \cong \frac{\epsilon_2}{\epsilon_1} n_2 . \tag{3.20}$$

In order to illustrate better the behavior of n_1 and n_2 as functions of S, calculations of these quantities have been performed using parameters in the range discussed above. In particular, for $\beta\omega_1 = 0.01$, $\beta\omega_2 = 0.011$, and $\Lambda_{12} = 0.1$, n_1 and n_2 were calculated for several values of $\alpha_1 (= 1 - \alpha_2)$ and S for $\gamma_{21} = 0.1\lambda_{21}$ and for $\gamma_{21} = 10\lambda_{21}$. The results of the first calculation set are shown in Figs. 1(a) and 1(b). It is apparent that after a period of increase with increasing S a threshold region is reached. Further increase of S then results in values of n_1 and n_2 which

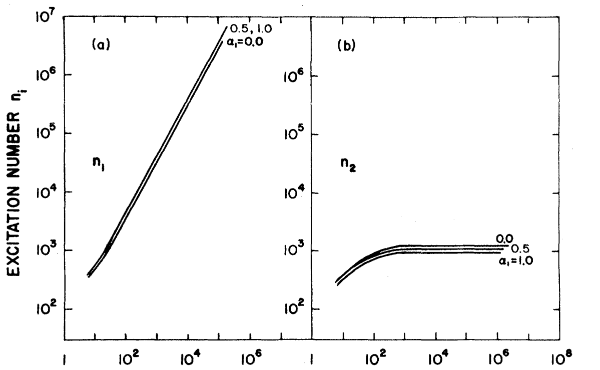

FIG. 1. n_i vs S for $\lambda_{21}=10\gamma_{21}=10^{-4}$. Here and elsewhere the (a) figure shows n_1 calculated from the exact (3.8) and the (b) figure the corresponding n_2. The values of other parameters are as stipulated in the text. Dependence of n_i at large S is consistent with (3.11) and (3.12). Displacement of points on the n_1 curve for the α_1 above 0.0 is within the width of the line for large S. [An expression more accurate than (3.11) indicates displacement of the various n_1 curves independent of S.]

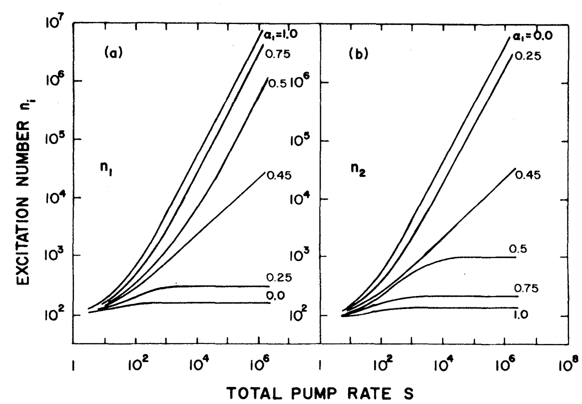

FIG. 2. n_i vs S for $\gamma_{21}=10\lambda_{21}=10^{-3}$. All n_1 for $\alpha_1>0.45$ ($\alpha_2<0.55$) are linear in S at large S, whereas all n_2 for $\alpha_1<0.45$ ($\alpha_2<0.55$) are linear in S at large S. Asymptotic $S^{1/2}$ dependence of the crossover case $\alpha_1=0.45$ ($\alpha_2=0.55$) is shown. For small α_1 (large α_2) comparison is to the asymptotic (3.15) and (3.16).

behave according to Eqs. (3.9) and (3.10). Only n_1 increases with S beyond the threshold value, regardless of the relative rates, α_1,α_2, at which energy is provided to either oscillator by the pump. Even if *all* the energy goes into the oscillator of higher frequency, the oscillator of lower frequency is preferentially excited as a consequence of the energy flow as long as the quantity Δ is positive. As shown in Figs. 2(a) and 2(b) for the calculation with $\gamma_{21}=10\lambda_{21}$ this remains so even when γ_{21} exceeds λ_{21} as long as Δ is positive. However, when α_2 is large enough, i.e., large enough a fraction of the energy put into the system goes into the oscillator of higher frequency, there is a qualitative change. Then for $\gamma_{21}>\lambda_{21}$ and for any α_1 small enough that Δ is negative, the oscillator of higher frequency is preferentially excited when S exceeds the threshold range, and the oscillator of lower frequency saturates in accord with Eqs. (3.11) and (3.12). It is apparent from the figures that as an oscillator is more strongly driven, the threshold value of S decreases. (No useful analytical specification of the threshold value has been found.)

In Figs. 2(a) and 2(b), the $S^{1/2}$ dependence of n_1 and n_2 at the transition value of α_2, 0.55 in this case, is apparent from the slope on the log-log plot. It may be that the relative values of α_1 and α_2 can be adjusted by changing the intensity of incident microwave radiation. If so it would be interesting if the transition from positive Δ to negative Δ could be observed experimentally. In view of the idealized nature of this two-oscillator case, such an observation may not be practical. In Sec. IV, where asymptotic solutions of the steady-state rate equation are discussed for an arbitrary number of oscillator modes, the possibility of similar transitions will be discussed.

In summary, it has been shown that if a pair of oscillators can receive energy from a source and transmit the energy to a heat bath via a form of bilinear interaction, at low energy-flux rates the occupation numbers resemble the equilibrium (zero-flux) values. In contrast to this near-equilibrium behavior, when a threshold flux rate is exceeded, a far-from-equilibrium steady state is observed in which nonthermal excitation of the oscillators occurs. It depends on both the relative transfer rates due to the Fröhlich and Lifshits processes and the relative rates at which the sources drive the oscillators which of the oscillators will be preferentially excited, but except for a special transition case, one or the other will become dominant. These qualitative characteristics also follow from the rate equation (2.3) for the steady-state excitation of a larger number of oscillators.

IV. ASYMPTOTIC SOLUTIONS FOR Z OSCILLATORS

The fortunate situation which permits exact solution of the steady-state rate equation for two oscillators does not extend to the next simpler case of three oscillators. For $Z=3$, elimination of variables in the rate equations leads to seventh-order polynomials which do not appear to be tractable. The order of the resolvant polynomial grows prodigiously with the number Z of oscillators. Hence it is necessary to benefit from the information gained from the $Z=2$ solutions and from inspection of the sum rule (2.16) in order to go on.

In the steady state, $\dot{N}$ vanishes and (2.16) can be rewritten

$$S+\sum_i \Phi_i+\sum_{i,j}{}'\Gamma_{ij}=\sum_i\left[\epsilon_i-2\sum_j{}'\Gamma_{ij}\right]n_i+\sum_{i,j}{}'\gamma_{ij}n_in_j\ . \tag{4.1}$$

It is compatible with (4.1) that one of the n_i will be linear in S for sufficiently large S, while the remaining n_j are of order S^0. The steady-state rate equation can be put in the form

$$\alpha_iS+\Phi_i+\sum_j{}'[\Lambda_{ij}n_j+\Gamma_{ij}(n_j+1)]=n_i\left[\epsilon_i+\sum_j{}'[\Lambda_{ji}-\Gamma_{ji}+n_j(\lambda_{ij}+\gamma_{ij})]\right]\ . \tag{4.2}$$

Trial solutions of the form

$$n_i=c_{i,1}S+\sum_{t=0}^{\infty}c_{i,-t}S^{-1},\quad \text{for some select } i \tag{4.3}$$

and

$$n_j=\sum_{t=0}^{\infty}c_{j,-t}S^{-t},\quad \text{for all } j\neq i \tag{4.4}$$

are substituted into (4.2), and coefficients of given powers of S are isolated to obtain the following set of equations. From (4.2) for n_i,

$$S:\ \alpha_i=c_{i,1}\left[\epsilon_i+\sum_j{}'[\Lambda_{ji}-\Gamma_{ji}+c_{j,0}(\lambda_{ij}+\gamma_{ij})]\right]\ , \tag{4.5}$$

$$S^0:\ \Phi_i+\sum_j{}'[c_{j,0}(\Lambda_{ij}+\Gamma_{ij})+\Gamma_{ij}]=c_{i,1}\sum_j{}'(\lambda_{ij}+\gamma_{ij})c_{j,-1}+c_{i,0}\left[\epsilon_i+\sum_j{}'[\Lambda_{ji}-\Gamma_{ji}+c_{j,0}(\lambda_{ij}+\gamma_{ij})]\right]\ , \tag{4.6}$$

$$S^{-n}:\ \sum_j{}'(\Lambda_{ij}+\Gamma_{ij})c_{j,n}=c_{i,1}\sum_j{}'(\lambda_{ij}+\gamma_{ij})c_{j,-(n+1)}+c_{i,-n}\left[\epsilon_i+\sum_j{}'(\Lambda_{ji}-\Gamma_{ji})\right]+\sum_j{}'(\lambda_{ij}+\gamma_{ij})\sum_{r=0}^{n}c_{i,-r}c_{j,-(n-r)}\ , \tag{4.7}$$

and from (4.2) for n_j,

$$S:\ \alpha_j+(\Lambda_{ji}+\Gamma_{ji})c_{i,1}=c_{j,0}c_{i,1}(\lambda_{ji}+\gamma_{ji})\ , \tag{4.8}$$

$$S^0:\ \Phi_j+\sum_k{}'\Gamma_{jk}+\sum_k{}'(\Lambda_{jk}+\Gamma_{jk})c_{k,0}=c_{j,0}\left[\epsilon_j+\sum_k{}'(\Lambda_{kj}-\Gamma_{kj})\right]+c_{i,1}c_{j,-1}(\lambda_{ji}+\gamma_{ji})+c_{j,0}\sum_k{}'(\lambda_{jk}+\gamma_{jk})c_{k,0}\ , \tag{4.9}$$

$$S^{-n}:\ \sum_k{}'(\Lambda_{jk}+\Gamma_{jk})c_{k,-n}=c_{i,1}c_{j,-(n+1)}(\lambda_{ji}+\gamma_{ji})+c_{j,-n}\left[\epsilon_j+\sum_k{}'(\Lambda_{kj}-\Gamma_{kj})\right]+\sum_k{}'(\lambda_{jk}+\gamma_{jk})\sum_{r=0}^{n}c_{j,-r}c_{k,-(n-r)}\ . \tag{4.10}$$

From (4.8), the product $c_{i,1}c_{j,0}$ depends linearly only on $c_{i,1}$, so substitution into (4.5) then gives a simple equation for $c_{i,1}$,

$$\alpha_i-\sum_j{}'\alpha_j\frac{\lambda_{ij}+\gamma_{ij}}{\lambda_{ji}+\gamma_{ji}}=c_{i,1}\left[\epsilon_i+\sum_j{}'\left[\Lambda_{ji}-\Gamma_{ji}+(\Lambda_{ji}+\Gamma_{ji})\frac{\lambda_{ij}+\gamma_{ij}}{\lambda_{ji}+\gamma_{ji}}\right]\right]\ , \tag{4.11}$$

which can be rewritten

$$c_{i,1}\left[\epsilon_i+4\sinh(\beta\omega_i)\sum_k{}'\frac{\Lambda_{ki}\Gamma_{ki}e^{\beta\omega k}}{\lambda_{ki}+\gamma_{ki}}\right]=\alpha_i+\sum_k{}'\alpha_k\frac{\lambda_{ki}-\gamma_{ki}}{\lambda_{ki}+\gamma_{ki}}\ . \quad (4.12)$$

From (4.8) with $c_{i,1}$ now known,

$$c_{j,0}=\frac{(\Lambda_{ji}+\Gamma_{ji})+\alpha_j/c_{i,1}}{\lambda_{ji}+\gamma_{ji}}\ . \quad (4.13)$$

Similarly, from (4.9), the products $c_{i,1}c_{j,-1}$ are functions of the $c_{j,0}$ and the unknown $c_{i,0}$. Substitution into (4.6) then gives a linear equation in $c_{i,0}$ in terms of the known $c_{i,1}$ and $c_{j,0}$. Thus if the coefficient of $c_{i,0}$ is nonzero, $c_{i,0}$ is known. The $c_{j,-1}$ then follow from (4.9). When $c_{i,-(n-1)}$ and $c_{j,-n}$ are known for all $n\le N$, the products $c_{i,+1}c_{j,-(N+1)}$ can be eliminated between (4.10) and (4.7) to give an equation linear in $c_{i,-N}$. Solution of this equation permits solution of (4.7) for $c_{j,-(N+1)}$. Thus by induction, the entire set of coefficients for the trial solution follows, provided no vanishing coefficients appear in the chain. For the asymptotic solution, it suffices to concentrate on (4.12) and (4.13).

In Fröhlich's limiting case,[22] all Γ_{ij}, and hence all γ_{ij}, vanish. Then $c_{i,1}$ and $c_{j,0}$ are very simple,

$$c_{i,1}=1/\epsilon_i\ ,$$

$$c_{j,0}=\left[1+\frac{\alpha_j\epsilon_i}{\Lambda_{ji}}\right]\frac{1}{e^{\beta(\omega_j-\omega_i)}-1}\ ,$$

$$\text{for all }\Gamma_{ij}=0\ . \quad (4.15)$$

Some of the $c_{j,0}$ will be less than zero if i exceeds 1. Physically, the only acceptable solutions are those for all $n_i,n_j>0$. Hence in the Fröhlich limit, the only mode of oscillation in which a nonthermal excitation is predicted is that in which the frequency is least, ω_1. Since $c_{i,1}$ does not involve α_1 in a singular manner, the $c_{j,0}$ also will be regular in α_1. Therefore in the Fröhlich limit, the oscillator of least frequency will be preferentially excited for sufficiently large pump rate S, regardless of the manner in which the energy is put into the system of oscillators even when α_1 vanishes. One can see from (4.12) and (4.13), that this will not always be the case. If for all pairs $j>i$, λ_{ji} exceeds γ_{ji}, there is no complication, and for any set of pump coefficients $\{\alpha_i\}$, $c_{i,1}$ is well defined and positive. Further, that λ_{ji} exceeds γ_{ji} for j greater than i implies that $\lambda_{ij}+\gamma_{ij}$ is negative for the same pair i and j. Thus if i exceeds 1, some of the $c_{j,0}$ will be negative. However, if for some $j>i$, γ_{ji} exceeds λ_{ji}, an increase of the pump coefficient α_j (accompanied by corresponding diminishment of the other α_k to maintain their sum equal to 1) can cause the right-hand side of (4.12) to become negative except for $c_{j,1}$. Thus as in the case for $Z=2$, multiple excitations may occur for general Z when some $\gamma_{ji}>\lambda_{ji}$. The present model is not sufficiently specific to establish more completely when this will happen or what particular combinations of the α_i and the γ_{ji},λ_{ji} might produce crossover from nonthermal excitation of one mode to that of another. Later in this section a specific mechanism will be assumed to illustrate this point more completely.

In the simple case of two oscillators, the availability of exact solutions makes it possible to discuss explicitly the crossover case, where both oscillators are strongly nonthermally excited. Such a situation, where a pair or more of the n_i are proportional to $S^{1/2}$, is not in obvious conflict with either the sum rule (4.1) or the rate equation (4.2). In the exact case $Z=2$,

$$n_i=(a_iS+b_i)^{1/2}\sim S^{1/2}\sum_{t=0}^{\infty}d_{i,-t}S^{-t}\ , \quad (4.16)$$

where a_i and b_i are constants from the A_i and C_i of (3.4) and (3.6). Substitution of this form into (4.1) and (4.2) leads to algebra of such complexity that it appears intractable for $Z>3$. Even for $Z=3$ the restrictions on the coefficients α_i, Φ_i, Λ_{ij}, and Γ_{ij} comparable to the crossover condition for two oscillators, $\Delta=0$, are not suitable for useful analysis. Thus it cannot be stated with confidence that the conditions on the coefficients suitable for causing crossover from nonthermal excitation of one mode of oscillation to similar excitation of another can be described in as simple a manner as given in (4.16). The high order of the resolvant polynomials also suggests more complicated functional forms are involved when $Z>2$.

In Fröhlich's original discussion of this type of model, the realization that a nonthermal excitation should occur was achieved in a different way from that described above. It is of interest to review that approach here in order to compare the two. To begin, the steady-state rate equation is put in the form

$$\alpha_iS+F_{1i}(\{n_j\})=n_i[F_{2i}(\{n_j\})e^{\beta\omega_i}-F_{1i}(\{n_j\})]\ , \quad (4.17)$$

wherein the F_{ji}, functionals of the $\{n_j,j\neq i\}$, are defined as

$$F_{1i}(\{n_j\})=\Phi_i+\sum_j{}'[\Lambda_{ij}n_j+\Gamma_{ij}(n_j+1)] \quad (4.18)$$

and

$$F_{2i}(\{n_j\})=\Phi_i+\sum_j{}'[\Lambda_{ij}e^{-\beta\omega_j}(n_j+1)+\Gamma_{ij}e^{\beta\omega_i}n_j] . \quad (4.19)$$

A formal solution of (4.17) gives an implicit equation

$$n_i=\left[1+\frac{\alpha_i S}{F_{1i}}\right]\frac{1}{e^{\beta(\omega_i-\mu_i)}-1} , \quad (4.20)$$

where a new quantity μ_i is introduced by the definition

$$e^{\beta\mu_i}\equiv\frac{F_{1i}}{F_{2i}}=1+\frac{1}{F_{2i}}\sum_j{}'(\Lambda_{ij}e^{-\beta\omega_j}-\Gamma_{ij})\times[n_je^{\beta\omega_j}-(n_j+1)] , \quad (4.21)$$

a definition successful since both F_{2i} and F_{1i} are positive. For zero S, n_j+1 equals $n_je^{\beta\omega_j}$ and μ_i is zero. If S is nonzero, n_j exceeds by a quantity δ_j the value n_{j0} of n_j for zero S. Then

$$n_je^{\beta\omega_j}-(n_j+1)=n_{j0}e^{\beta\omega_j}-(n_{j0}+1)+\delta_j(e^{\beta\omega_j}-1)>0 . \quad (4.22)$$

Thus as long as $\Lambda_{ij}e^{-\beta\omega_j}$ exceeds Γ_{ij}, all i and j, the quantity μ_i will be greater than zero for nonzero S. The n_i thus have the form of a modified Bose distribution, with the quantity μ_i identified as a chemical potential. Again from the steady-state sum rule it follows that some n_i will be linear in S while the others, n_j, will be of order S^0. Then asymptotically

$$e^{\beta\mu_j}\sim\frac{\Lambda_{ji}+\Gamma_{ji}}{\Lambda_{ji}e^{-\beta\omega_i}+\Gamma_{ji}e^{\beta\omega_i}} \quad (4.23)$$

from which

$$\mu_j\sim\omega_i+\frac{1}{\beta}\ln\left[1-\frac{\Gamma_{ji}(e^{2\beta\omega_i}-1)}{\Lambda_{ji}+\Gamma_{ji}e^{2\beta\omega_i}}\right]\le\omega_i . \quad (4.24)$$

The equality holds either at absolute zero, a condition not of interest for biological systems, or in the Fröhlich limit in which all Γ_{ij} vanish. From (4.20) and (4.24), it then follows that n_j will be negative for all $j<i$ if i exceeds 1. Hence the physical requirement that all n_i,n_j be positive selects from among the Z mathematical possibilities one physically acceptable one, that $i=1$. As for μ_i, the requirement that

$$n_i\sim c_{i,1}S\sim\frac{\alpha_1 S}{F_{1i}}\frac{1}{e^{\beta(\omega_i-\mu_i)}-1} \quad (4.25)$$

implies

$$\mu_i=\omega_i-\frac{1}{\beta}\ln\left[1+\frac{\alpha_i}{c_{i,1}F_{1i}}\right] . \quad (4.26)$$

This makes more precise the manner in which, as Fröhlich asserted,[21,22] μ_i must approach ω_i in order to give a n_i which is predominant over the other n_j. Since the mathematical description from (4.17)–(4.26) is reminiscent of condensation in an ideal Bose-Einstein gas, it has been asserted by several authors that the nonthermal excitations in biological systems may be manifestations of Bose condensation. One may object that Bose condensation usually refers to a system in thermal equilibrium, not in a far-from-equilibrium steady state. Moreover, Bose condensation is understood as a consequence of a statistical distribution of population of available states, not a consequence of an explicit dynamical mechanism. However, from (4.18) and (4.19), F_{1i} and F_{2i} both reduce to Φ_i if the nonlinear coupling mechanism is absent, and then the μ_i vanish regardless of the value of S. One can go further in assessing the importance of the nonlinear mechanism in this effect. The defining statements of the Γ_{ij} and Λ_{ij} in (2.6) and (2.7) were used to support the argumentation including (2.9) and (2.10) that in general Λ_{ij} is much greater than Γ_{ij}. It is apparent from (2.9) that if the original coupling factors ζ_{ijr} and σ_{ijr} are of the same order of magnitude, then Γ_{ij} will be on the order of $\Lambda_{ij}e^{-2\omega_j}$, sufficient to give a positive μ_i in (4.21). However, it is not mandatory that the coupling factors give this result, and it is interesting to consider the special case where $\Lambda_{ij}e^{-\beta\omega_j}$ equals Γ_{ij} for all pairs of oscillators. Then, from (4.21) the μ_i vanish identically for any pump rate S, and so an anomalous n_j can in no way be associated with Bose condensation. But in this case (4.12) and (4.13) become (with $\Lambda_{ij}e^{-\beta\omega_j}\equiv\Gamma_{ij}$)

$$c_{i,1}\left[\epsilon_i+4\sinh(\beta\omega_i)\sum_k{}'\frac{\Lambda_{ik}}{(e^{\beta\omega_k}-1)(1+e^{-\beta\omega_i})}\right]=\alpha_i-\sum_k{}'\alpha_k\frac{\tanh(\beta\omega_k/2)}{\tanh(\beta\omega_i/2)} , \quad (4.27)$$

$$n_j\sim c_{j,0}=\left[1+\frac{\alpha_j}{c_{i,j}\Lambda_{ji}(1+e^{-\beta\omega_i})}\right]\frac{1}{e^{\beta\omega_j}-1} , \quad j\neq i . \quad (4.28)$$

In (4.28), the unmodified Bose distribution appears explicitly in the n_j. The n_j are postitive for all j regardless of the value of i, provided $c_{i,1}$ is positive. In (4.27), the coefficient of $c_{i,1}$ is positive, and the right-hand side is positive for suitable choice of the pump coefficients $\{\alpha_i\}$, subject to the spectrum of the oscillators. If this positive condition is so for some particular choice of i, then it is equivalent to state that

$$\alpha_i \tanh(\beta\omega_i/2) > \sum_{k\neq i} \alpha_k \tanh(\beta\omega_k/2) . \quad (4.29)$$

For any other index j, it follows that

$$\alpha_j \tanh(\beta\omega_j/2) - \sum_{k\neq j} \alpha_k \tan(\beta\omega_k/2) < -2 \sum_{k\neq i,j} \alpha_k \tanh(\beta\omega_k/2) . \quad (4.30)$$

Consequently, at most one oscillator will be nonthermally excited, in agreement with the sum rule (4.1). But from the sum rule, it is expected that at least one oscillator will have n_i proportional to S. Thus even in the case where Fröhlich's μ_i vanishes identically for any S as a consequence of a particular mechanism, the nonlinear excitation of some one oscillator will occur for sufficiently great value of S. It appears from (4.27) that if the $\{\alpha_i\}$ are varied by changing the intensity of microwave radiation at various frequencies, it may be possible to alter selectively which mode of oscillation undergoes nonthermal excitation. In this connection it is interesting that multiple excitations have been observed in two different sets of experiments, those of Grundler and Kielmann[6,7] and of Smolyanskaya and Vilenskaya.[15] If this similarity of the experiments and the present theory should be found to be more than coincidental, it should help determine better the relative importance of the Fröhlich terms and those suggested by Lifshits.

Since it was convenient to alter parameters in the calculations for two oscillators, the analog of this special case was run, and the results are presented in Fig. 3. It is apparent that qualitatively the behavior of n_1 and n_2 as functions of S are like those shown in Fig. 2, where also $\gamma_{21} > \lambda_{21}$. The different value of α_1 (or α_2) at which the crossover transition occurs reflects the different ratio of γ_{21} to λ_{21}. To carry this a step further, a case was run in which the Fröhlich μ_i might be negative. With Γ_{12} approximately $1.1\Lambda_{12}e^{-\beta\omega_2}$, the data were calculated which were plotted in Fig. 4. It is interesting to note a new feature. Here, when there is driving of only one oscillator, the excitation of the other is less at high pump rates than at lower pump rates. (This suggests that Fröhlich's μ_i is positive even in this case.) The strength of the Lifshits term is such that the high rate of energy transfer causes some deexcitation of the passive oscillator, while the other is strongly driven. When both are driven to some degree, both are excited as usual.

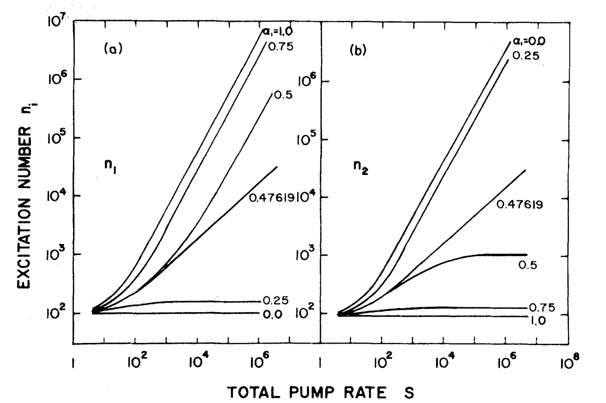

FIG. 3. n_i vs S for $\gamma_{21}=2.10\times10^{-3}$, $\lambda_{21}=10^{-4}$ ($\Gamma_{21}=\Lambda_{21}e^{-\beta\omega_i}$). General qualitative similarity to the curves of Figs. 2(a) and 2(b) is evident. Crossover with asymptotic $S^{1/2}$ dependence occurs here for $\alpha_1=0.476\,19$ ($\alpha_2=0.523\,81$). n_1 for $\alpha_1=0.0$, or n_2 for $\alpha_2=0.0$, is nearly independent of S.

The effect of adding more complicated interaction terms to the rate equation (2.3) has been considered by Moskalenko *et al.*[35] They suggest from analyses of rate equations for phonons in solid-state systems that cubic and quartic interaction terms should be concluded. The result gives counterparts to the present (4.17)–(4.21), differing only in more complicated forms for the $F_{ki}(\{n_j\})$. They conclude from the similarity in form of the equations that the substance of earlier predictions by Fröhlich[22] and others

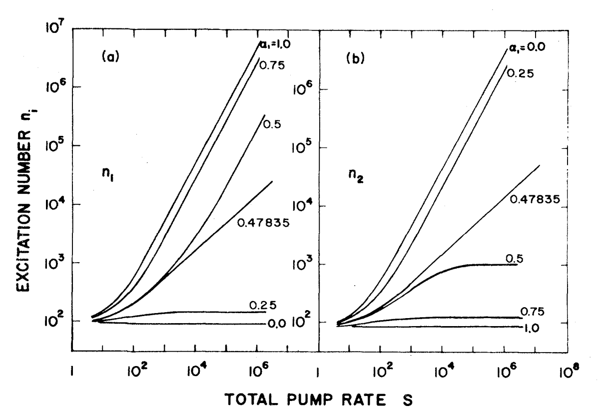

FIG. 4. n_i vs S for $\gamma_{21}=2.31\times10^{-3}$, $\lambda_{21}=10^{-4}$ ($\Gamma_{21}=1.1\Lambda_{21}e^{-\beta\omega_i}$). General qualitative similarity to the curves of Figs. 2(a) and 2(b) is apparent. Crossover from divergent n_1 to n_2 occurs at $\alpha_1=0.478\,35$ ($\alpha_2=0.521\,65$). n_1 for $\alpha_1=0.0$, or n_2 for $\alpha_2=0.0$, decreases with increasing S.

are unchanged. However, Moskalenko's $F_{2i}(\{n_j\})$ is not necessarily positive, and Eq. (4.21) would not yield a valid definition of a function μ_i if the ratio of F_{1i} to F_{2i} were negative. The discussion by Moskalenko *et al.*[36] shows that a certain mathematical form can be achieved but not that the existence of the form is guaranteed. Thus the effect of higher-order interactions on the prediction of nonthermal excitations remains an unresolved question.

The existence of the asymptotic solutions corresponding to the physical nonthermal excitations has thus been demonstrated, both by calculation of exact equations for $Z=2$ and by display of appropriate coefficients for $Z\geq 2$, to occur in a situation where Bose condensation cannot be involved. But such a concept is not needed to understand the phenomena which are predicted. Physically, the nonthermal excitations can be understood straightforwardly as the consequence of a suitable nonlinear mechanism in a situation of energy flow sufficient to result in a far-from-equilibrium steady state of the open system. The nonlinear mechanism, in fact, induces the phase coherence needed for excitation to large amplitude and also makes possible a collective effect in which excitation of one component of the open system affects the excitation of all the other components.

As in the special case of $Z=2$, the general asymptotic solutions show that the nonthermal excitation is predicted for arbitrary Z even when the γ_{ij} are large enough that the λ_{ij} can be neglected. Then for $\gamma_{ij} \gg |\lambda_{ij}|$,

$$n_i \cong (2\alpha_i - 1)S/\epsilon_i \ , \tag{4.31}$$

$$n_j \cong \left[1+\frac{\alpha_j \epsilon_i}{(2\alpha_i-1)\Gamma_{ij}}\right]\frac{1}{e^{\beta(\omega_i+\omega_j)}-1} \ , \quad j\neq i \ . \tag{4.32}$$

This requires that α_i exceed 0.5 (which can happen for at most one mode) in order that both n_i and the n_j be positive. This result, as well as that of Eqs. (4.27) and (4.28), illustrates the importance of both the interactions and the pump coefficients in determining the character of the collective far-from-equilibrium steady state.

V. STABILITY AND RELAXATION TIMES

It is desirable to gain some information about the time dependence of solutions of the rate equation (2.3). However, an exact solution does not appear possible even in the simplest case $Z=2$ because of the nonlinear terms. For this reason, it is necessary to resort to linearization of the equations by considering small variations η_i of the η_i about the steady-state solutions n_{is}. Thus it is assumed that

$$n_j = n_{js} + \eta_j, \quad \eta_j \ll n_{js}, \quad \text{for all } j \ . \tag{5.1}$$

Substitution into (2.3), with recollection that the n_{is} satisfy (4.2), leads upon expansion to linearized equations for the η_j,

$$\dot{\eta}_j = -\left[\epsilon_j + \sum_k{}' [\Lambda_{kj} - \Gamma_{kj} + n_{ks}(\lambda_{jk}+\gamma_{jk})]\right]\eta_j + \sum_k{}' [\Lambda_{jk} + \Gamma_{jk} - n_{js}(\lambda_{jk}+\gamma_{jk})]\eta_k \ . \tag{5.2}$$

In general, the solutions to these equations have the form

$$\eta_j(t) = \sum_{r=1}^{Z} h_{jr} e^{-\lambda_r t} \ , \tag{5.3}$$

where the λ_r are the eigenvalues of the coefficient matrix in (5.2), and the h_{jr} are coefficients determined from specific initial conditions. It should be noted that the relaxation processes represented by the λ_r are characteristic of the system of oscillators, not of the features of individual modes ω_j, for all of the modes contribute to the determination of the eigenvalues.

Let i denote the mode for which n_{is} is linear in S. Then (5.2) becomes

$$\dot{\eta}_1 = -\left[\epsilon_i + \sum_k{}' [\Lambda_{ki} - \Gamma_{ki} + n_{ks}(\lambda_{ik}+\gamma_{ik})]\right]\eta_i - n_{is} \sum_k{}' (\lambda_{ik}+\gamma_{ik})\eta_k \ , \tag{5.4}$$

where on the right-hand side, terms of order S^0 have been neglected where compared with the terms of order S. Substitution of the form (4.13) for the n_{ks}, $k\neq i$, gives the simple equation

$$\dot{\eta}_i = \frac{-\alpha_i}{c_{i,1}}\eta_i - n_{is}\sum_k{}' (\lambda_{ik}+\gamma_{ik})\eta_k \ . \tag{5.5}$$

In a similar manner, (5.2) reduces for $j\neq i$ to

$$\dot{\eta}_j = -\frac{\alpha_j}{c_{i,1}}\eta_i - n_{is}(\lambda_{ji}+\gamma_{ji})\eta_j + \sum_{k\neq i,j} [\Lambda_{jk}+\Gamma_{jk} - n_{js}(\lambda_{jk}+\gamma_{jk})]\eta_k \ . \tag{5.6}$$

Introduction of the exponential time dependence $e^{-\lambda t}$ then gives the following set of equations for the eigenvalues λ_r:

$$0 = \left[\lambda - \frac{\alpha_i}{c_{i,1}}\right]\eta_i + n_{is}\sum_k{}' (\lambda_{ki}-\gamma_{ki})\eta_k \ , \tag{5.7}$$

$$0 = -\frac{\alpha_j}{c_{i,1}}\eta_i + [\lambda - n_{is}(\lambda_{ji}+\gamma_{ji})]\eta_j + \sum_{k\neq i,j} [\Lambda_{jk}+\Gamma_{jk} - n_{js}(\lambda_{jk}+\gamma_{jk})]\eta_k \ , \quad j\neq i \ . \tag{5.8}$$

One can proceed by direct calculation of the determinant of the coefficients of the η_j, but to do so it is necessary to use again the magnitude of S in the various terms. It is also possible to do this more directly by consideration of the presence of S-dependent terms in (5.7) and (5.8).

Assume λ_1 to be of order S^0. Then (5.8) can be written

$$\eta_j \cong \frac{1}{n_{is}(\lambda_{ji}+\gamma_{ji})}\left[-\frac{\alpha_j}{c_{i,1}}\eta_i + \sum_{k\neq i,j}[\Lambda_{jk}+\Gamma_{jk}-n_{js}(\lambda_{jk}+\gamma_{jk})]\eta_k\right] . \quad (5.9)$$

Iteration of (5.9) beginning with the term in η_i shows that the terms in the sum are less than the initial term by a factor S^{-1} and so can be neglected. Substitution of the resulting approximation for the η_j into (5.7) then gives

$$0 \cong \left[\lambda_1 - \frac{\alpha_i}{c_{i,1}} - \frac{1}{c_{i,1}}\sum_k{}' \alpha_k \frac{\lambda_{ki}-\gamma_{ki}}{\lambda_{ki}+\gamma_{ki}}\right]\eta_i . \quad (5.10)$$

It follows, using (4.12), that

$$\lambda_1 \cong \epsilon_i + 4\sinh(\beta\omega_i)\sum_k{}' \frac{\Lambda_{ki}\Gamma_{ki}e^{\beta\omega_k}}{\lambda_{ki}+\gamma_{ki}} . \quad (5.11)$$

For $r\neq 1$, assume

$$\lambda_r \cong n_{is}(\lambda_{ji}+\gamma_{ji})+\theta_r , \quad (5.12)$$

where θ_j, to be determined, is assumed of order S^0. Then from (5.8)

$$0 \cong -\frac{\alpha_j}{c_{i,1}}\eta_i + \theta_r\eta_j + \sum_{l\neq i,j}[\Lambda_{jl}+\Gamma_{jl}-n_{js}(\lambda_{jl}+\gamma_{jl})]\eta_l \quad (5.13)$$

and

$$0 \cong -\frac{\alpha_k}{c_{i,1}}\eta_i + n_{is}(\lambda_{ji}+\gamma_{ji}-\lambda_{ki}-\gamma_{ki})\eta_k + \sum_{l\neq i,k}[\Lambda_{kl}+\Gamma_{kl}-n_{ks}(\lambda_{kl}+\gamma_{kl})]\eta_l , \quad k\neq i,j . \quad (5.14)$$

As in the discussion of (5.8), solution of (5.14) for η_k and iteration beginning with the term in η_i shows that except for the term in η_j the terms in the sum are smaller than the others by a factor of S^{-1} and so can be neglected. Thus one concludes that for k not equal to i or j, η_k is less than either η_i or η_j by a factor of S^{-1}, and so the sum in (5.13) can also be neglected. Then η_j is obtained from (5.13) in terms of η_i and with (5.12), (5.7) becomes to order S

$$0 \cong n_{is}\left[(\lambda_{ji}+\gamma_{ji}) + \frac{1}{\theta_r c_{i,1}}\sum_{k\neq i}\alpha_k(\lambda_{ki}-\gamma_{ki})\right]\eta_i . \quad (5.15)$$

Then

$$\theta_r \cong \frac{-1}{c_{i,1}}\sum_{k\neq j}\alpha_k\frac{\lambda_{ki}-\gamma_{ki}}{\lambda_{ji}+\gamma_{ji}} , \quad (5.16)$$

and so

$$\lambda_r \cong n_{is}(\lambda_{ji}+\gamma_{ji}) - \frac{1}{c_{i,1}}\sum_{k\neq i}\alpha_k\frac{\lambda_{ki}-\gamma_{ki}}{\lambda_{ji}+\gamma_{ji}} , \quad r>1 . \quad (5.17)$$

The λ_1 and the $Z-1$ λ_r are all real. In the event that for $j>i$ all $\lambda_{ji}>\gamma_{ji}$, then the nonlinear excitation will occur for the mode of least frequency ω_1, and all the leading terms for any of the λ_r are positive. Since the λ_r are on the order of S while λ_1 is on the order of S^0, the terms in (5.3) proportional to $\exp(-\lambda_r t)$ will diminish rapidly and leave λ_1 representing the predominant process by which the n_i relax to n_{is}. Moreover, because of the fact that the λ_1,λ_r are positive, the steady state is stable against fluctuation.

It has been shown that when $\gamma_{ji}>\lambda_{ji}$, certain values of the pump coefficients $\{\alpha_i\}$ may lead to a mode other than ω_1 being excited. The comments about the positive character of λ_1 and the λ_r, $r>1$, still apply however, so the ω_1 excitation is also stable against fluctuation when driven, and λ_1 still indicates the most slowly decaying process. Thus the time required for the system to relax to the steady state will be on the order of

$$\tau = \frac{1}{\lambda_1} \cong c_{i,1}\left[\alpha_i + \sum_k{}' \alpha_k\frac{\lambda_{ki}-\gamma_{ki}}{\lambda_{ki}+\gamma_{ki}}\right]^{-1} . \quad (5.18)$$

This rate reflects the collective nature of the nonthermal excitation. As a check of the reasonableness of this result, note that in the Fröhlich limit, $\gamma_{ij}\equiv 0$, and then τ equals $1/\epsilon_1$. This is consistent with the sum rule (2.16), for N depends only on the Φ_i, and the highly excited mode ω_1 will dominate in the sum.

Although it is not possible to make general statements about the crossover from nonlinear excitation of one mode to another, the case $Z=2$ still gives some insight. Then both n_{is} are on the order of $S^{1/2}$, and the condition that Δ vanishes, as in (3.16), can be used to simplify the eigenvalue equations to give

$$0 \cong (\lambda - 2\alpha_1\gamma_{21}n_{2s})\eta_1 - 2\alpha_1\gamma_{21}n_{1s}\eta_2 \quad (5.19)$$

and

$$0 \cong -2\alpha_2\gamma_{21}n_{2s}\eta_1 + (\lambda - 2\alpha_2\gamma_{21}n_{is})\eta_2 \ . \quad (5.20)$$

From this,

$$\lambda_1 = 0, \quad \lambda_2 = 2\gamma_{21}(\alpha_1 n_{2s} + \alpha_2 n_{1s}) \ . \quad (5.21)$$

In this case, the steady state is in neutral equilibrium rather than stable equilibrium against perturbation by fluctuations. This seems plausible, and perhaps the result is typical of the crossover steady states for more complicated systems.

In a laboratory situation, the time required for the steady state to become manifest will depend on several factors, depending in part on the variable which is being observed. In experiments such as those involving Raman scattering, observation of the excited mode is direct, and after suitable threshold S is reached, a relaxation time of the character of the τ in (5.18) should be observed. In experiments where the observation is indirect, the time for cells to reproduce or to congregate may be influenced by the presence of the nonthermally excited state, but those times can be expected to differ from τ. The physical relaxation time thus can have several components of which (5.18) may be only one.

A different estimate of the relaxation time was given by Wu and Austin.[31] They estimated τ by calculating the lifetime of the nonthermally excited state, and found it, in the Fröhlich limit, to depend on the Λ_{ij} coefficients. Such a time scale is appropriate to intrasystem transfers of energy as S is increased. However, when threshold is reached, these intrasystem transfers balance, as (2.16) indicates, and relaxation to the steady state is not affected by them. A time scale depending on the Λ_{ij} may be important, however, in determining the time needed to reach threshold as S is increased.

CONCLUSIONS

Study of the generalized Fröhlich model of nonthermal excitations of a driven open system leads to a better realization that in the steady-state energy coupled into a spectrum of modes of the system may be channeled through a single mode of the system prior to discharge into the bath. This concentration of energy flow occurs as a consequence not of a statistical process, but rather as a consequence of the presence of a suitable nonlinear interaction between the modes of the system and the modes of a heat bath with which the system communicates. In the Fröhlich limit, where only difference modes are excited by the nonlinear interaction, the result is especially simple. Only the system mode of least frequency will be preferentially excited, even though there may be zero energy put into that mode directly from the energy source. In the more general case where sum modes also are excited by the nonlinear interaction, it still follows that in the steady state at most one mode will undergo nonthermal excitation, while the remainder remain in or near the equilibrium distribution of the system. The determination of which one of the modes will be preferentially excited has been shown to depend both on the relative magnitudes of the coupling factors for the terms of the nonlinear interaction, and on the relative amounts of energy put into the various modes. Since the latter may be controlled from an external source, there is the interesting possibility that a particular nonthermal excitation may be stimulated under proper conditions. In any case, a threshold rate of energy flow must be present to produce the preferred excitation.

The analysis of the model presented here succeeds because of the special bilinear nature of the interaction. The method is not well adapted for considering the effect of higher-order interactions. One infers from the stability of the modes against small displacement from the steady state that small cubic or quartic interaction terms are not likely to alter the effect significantly. One expects, however, that large high-order terms will bring about an important change. The prediction of the present model that the nonthermal excitation will increase indefinitely with increasing energy flow would lead one to expect destruction of the system at sufficiently high flux. Fröhlich has pointed out[18,19] that the presence of a term of fourth order in the polarization $\vec{P}$ is to be expected and would ultimately stabilize the excitation. Bilz *et al.*[36] have discussed this point further in the context of interaction between the elastic field and the polarization field in a ferroelectric medium. Further study is needed to understand how such terms translate into contributions to the Hamiltonian (2.1) and the rate equation (2.3) of the present model, and how such contributions may limit the nonthermal excitations. It should be noted that some higher-order terms were considered by Kaiser[37] in a derivation of a Peierls-Boltzmann equation describing the transport of phonons. However, where comparison of his results to the Fröhlich rate equation was made, no extensive use was made of the extra terms and so their possible limiting effect appears still to be determined.

The Fröhlich model is not unique in predicting nonthermal interaction. Bhaumik *et al.*[38] have considered an interaction linear in the bath and oscillator modes but which leads to a form similar to (4.15) or (4.20) upon consideration of perturbation terms of second order in the interaction. An entirely different approach was taken by Fain[39,40] who considered disruption of thermalization of the bath itself as a consequence of intense energy flow.

The Fröhlich model does not attempt to identify the dynamical character of the oscillations in the open system, so it is of interest that other work shows promise in providing information of that type. The propagation of solitons or solitary excitons in the essentially one dimensional structures of α-helical protein molecules has been considered by Davydov.[41] Del Giudice *et al.*[42,43] have discussed qualitative comparisons of features of such excitations with the Raman-scattering observations in *Chlorella pyrenoidosa* reported by Drissler and MacFarlane[4] and with similar observations on *E. coli* by Webb *et al.*[3] and the other systems discussed by Webb.[20] Del Giudice *et al.* have also discussed the relevance of the Fröhlich model as illustrating how diffuse energy flowing in an open system can be channeled into special modes such as the Davydov solitons.[43,44] An extension of the Davydov theory has been made by Scott[45,46] and applied to the Raman-scattering data of Webb *et al.*[3] taken on metabolizing *E. coli.* Scott calculated the energies of two Davydov solitons for α-helix proteins. Without further adjustment of parameters, he found that the frequencies of the Raman lines from *E. coli* could be described nicely as harmonic or sums or differences of the soliton frequencies. A comparison of the oscillations of the Fröhlich model with solitons was also made by Bilz *et al.*[36]

It will be important to develop experimental information adequate to understand both the dynamical mechanism of the nonthermal excitations which have been reported and the interaction mechanisms which produce a concentration of energy in one mode when many modes are driven. In this way there may result new insights into the progress of molecular processes peculiar to the far-from-equilibrium states associated with living systems.

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