# Boltzmann Equation Approach to Fröhlich's Vibrational Model of Bose Condensation-Like Excitations of Coherent Modes in Biological Systems

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A modified Peierls-Boltzmann transport equation formalism for phonons is applied to Fröhlich's vibrational model. In this model a set of oscillators it nonlinearly coupled to the rest of the system, which can be taken as a heatbath. An external energy supply leads to an additional excitation of the modes. The Hamiltonian for the model is presented and the kinetic equations are derived. The steady state solutions show that under certain conditions the lowest mode becomes strongly excited, when the phonon flux increases. The resulting excitation far above the thermal value corresponds to a preferred channeling of energy into a single mode (Bose condensation-like excitation). Correspondence with Fröhlich's rate equation approach is established and the quasi phase transition-like behaviour is discussed.

## 1. Introduction

In a series of papers Fröhlich has promoted the ideas that electric vibrations with frequencies of the order of $10^{11}$–$10^{12}$ Hz should be coherently excited in active biological materials [1–8]. These coherent oscillations should play an important role in the order and function of biological systems. Therefore one may expect that excitations of the proposed type possibly could lead to drastic changes in the behaviour of biosystems [3, 6].

Fröhlich's proposal has received increasing interest and support through some rather exciting experimental results. Some evidence for the existence of coherent oscillations in the proposed frequency region has been found in bacteria [9–11] and in yeast [12, 13]. Furthermore Fröhlich has presented some model calculations which present theoretical support for his ideas. In the "High-polarization model" the possibility of the existence of a metastable highly-polarized state has been shown [1, 4]. In the vibrational model on the other hand, a nonlinear mode-mode coupling can lead to the channeling of energy into a single mode ("Bose-condensation") [2].

Fröhlich has extended his basic ideas to give a possible explanation for the extraordinary high sensitivity of certain biological systems to extremely weak external fields [14–17]. This so-called "Brain Wave Model" is based on the assumed existence of coherent oscillations in biological systems. Therefore it is of great importance to find both additional theoretical support and experimental evidence for Fröhlich's proposals.

However, it cannot be overemphasized that the description of complex biological functions by means of single theoretical models is extremely difficult. We want to start in this direction by investigating Fröhlich's "vibrational model" on a microscopic basis. This calculation is intended to supplement the phenomenological rate equation approach [1, 4].

Our model is the same as Fröhlich's one: a set of oscillating units (e.g. dipolar electric oscillators) which form a narrow frequency band and which are suspended in a heatbath. The oscillators are assumed to interact nonlinearly with the heatbath. Furthermore energy is supplied to each mode of the branch from the surroundings. We describe the kinetics of the oscillating system by means of the modified Peierls-Boltzmann transport equations for phonons: The external energy supply is incorporated in a "phonon flux" through the system of oscillators. The heatbath's kinetics is treated in a similar way, but in the respective equations the transport term is omitted.

There have already been some attempts to present a microscopic foundation for Fröhlich's rate equation approach. Bhaumik et al. [18–20] have proposed a model Hamiltonian for Fröhlich's vibrational model and employed transition probabilities of Golden Rule type. The coupling has been restricted to a linear one with respect to the oscillations (phonons) of the dipolar system. Two

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phonon processes then necessitate the application of the second order Golden Rule, which describes transitions via energy non-conserving metastable states, whereas the direct processes are well described by the Fermi Golden Rule itself. Wu and Austin [21, 22] have applied a direct perturbation theoretical method to the equations of motion for a model Hamiltonian, where the nonlinear interaction is quadratic in the phonon variables.

In both approaches the external energy source consists of a set of harmonic oscillators, which couples linearly to the oscillating units. Both results are in a good agreement with Fröhlich's results. Furthermore Bhaumik et al. [18] have presented rough estimates for some parameters (e.g. line width and critical flux) and a comparison with available experimental data.

The purpose of the present work is to apply a well-developed transport formalism to Fröhlich's vibrational model. This formalism has been chosen both to supplement the phenomenological rate equation approach and to extend the above cited microscopic treatments.

We start with a short review of the derivation of modified Peierls-Boltzmann transport equations for phonons. In chapter 3 we present our model system and the Hamiltonian for its description. The transition probabilities are calculated and the resulting transport equations are given. Several assumptions and approximations are applied to these equations to get a solvable system of nonlinear differential equations.

Chapter 4 contains the steady state solutions. In close analogy to Fröhlich's treatment a formal chemical potential is introduced. The conditions under which our result corresponds to that of Fröhlich are discussed. In order to allow for an analytical solution for the steady state excitations, we restrict ourselves to a two-mode approximation. This is done in Chapter 5. In Chapter 6 we investigate approximate steady state solutions of the complete system.

In the last chapter (Chapter 7) the results are discussed. It is shown that a "Bose-condensation-like" excitation is possible, if several conditions with respect to the material parameters are fulfilled. It turns out that the "phase" transition to the excessive excitation of the lowest mode is no sharp one.

## 2. Peierls-Boltzmann Transport Equations for Phonons

The aim of the present study lies in a microscopic approach to the question of Bose condensation like behaviour in certain open and nonlinear phonon-systems. A possible way to describe this problem is via transport equations for phonons.

We start with a short review of the derivation of modified phonon transport equations. Details of these Peierls-Boltzmann equations may be found in [23]. Starting point was a bilinear phonon density operator $\hat{n}(\varkappa\lambda, \boldsymbol{r}, t)$ and a Hamiltonian which consists of two parts: a harmonic one, $H_0$, for the phonons and a second one, $H_1$, which describes interactions between phonons. A series of conventional transport postulates applied to the commutator $[H_0, \hat{n}]$ in the Heisenberg equation of motion led to the wellknown linear transport term. Further simplifications of the transport and the collision terms (i.e. the commutator $[H_1, \hat{n}]$), among which we specifically note a spatial averaging procedure, then have been applied. The result is the general Boltzmann equation (vid. Eq. (I.29))

$$\partial_t \langle \hat{N}_\varkappa \rangle - \Phi(\varkappa, t) = \sum_{m=0}^{n} \left( \sum_{\mu,\nu}^{(1)} - \sum_{\mu,\nu}^{(2)} \right) \varrho_\nu(t)\, \partial_t\, W_{\mu\nu}(t) \qquad (1)$$

with

$$\hat{N}_\varkappa \equiv \hat{N}(\varkappa\lambda, t) = b^+(\varkappa\lambda, t)\, b(\varkappa\lambda, t) \qquad (2)$$

where $b^+$ and $b$ are phonon creation and annihilation operators of mode $(\varkappa\lambda)$. The restrictions for the summations originate from the separation into creation (i.e. gain) and annihilation (i.e. loss) processes, i.e.

$$\sum^{(1)} \to N_\varkappa^{(\mu)} = N_\varkappa^{(\nu)} + m\,,$$
$$\sum^{(2)} \to N_\varkappa^{(\mu)} = N_\varkappa^{(\nu)} - m$$

with $N_\varkappa^{(\mu)} \equiv \langle \mu | a_\varkappa^+ a_\varkappa | \nu \rangle$; $m = 1, 2, \ldots$.

The space-independent phonon flux $\Phi(\varkappa, t)$ is given by

$$\Phi(\varkappa, t) = - V [v(\varkappa\lambda)\, \nabla r\, \hat{n}(\varkappa\lambda, r, t)]_{\text{av. r}}\,. \qquad (3)$$

$V$ is the total volume of the transporting system, $v(\varkappa\lambda)$ the group velocity. The r.h.s. of Eq. (1) represents the collision term. $\varrho_\nu(t)$ is the diagonal part of the density matrix and $W_{\mu\nu}(t)$ is the transition probability from state $|\nu\rangle$ to state $|\mu\rangle$:

$$W_{\mu\nu}(t) = - [L_1 \exp(-i(L_0 + QL_1))\, L_1]_{\mu\mu\nu\nu}\,. \qquad (4)$$

$L_1 = [H_1, \,]$ and $L_0 = [H_0, \,]$ are the tetradic Liouville operators, $P = 1 - Q$ is the diagonalization projector. A kind of Markofficity assumption in the Master equation for $\varrho_\nu(t)$ is incorporated as well as the assumption of vanishing initial correlations [i.e. $Q\varrho(t=0) = 0$], which is equivalent to a random phase approximation (vid. Equation (I.29)). As a next step in the calculations the transition probabilities $W_{\mu\nu}(t)$ have been expanded. With the restriction to "irreducible transitions" and to a specific time scale one is left with transition probabilities of Golden Rule type:

$$\begin{aligned}\partial_t W_{\mu\nu}(t) &= 2\pi\lambda^2 V_{\mu\nu}\,\delta(E_\mu - E_\nu) \\ &\quad + 2\pi\lambda^4 \Big|\sum_\alpha V_{\mu\alpha} V_{\alpha\nu}(E_\alpha - E_\mu)^{-1}\Big|^2 \\ &\quad \cdot \delta(E_\mu - E_\nu) + O(\lambda^6) + \cdots \end{aligned} \tag{5}$$

with

$$\lambda V_{ij} \equiv (H_1)_{ij}\,.$$

$|i\rangle$ and $|j\rangle$ are arbitrary states, $|\mu\rangle$ and $|\nu\rangle$ is the initial and final state, respectively. The detailed structure of the transition probabilities depends on the interaction Hamiltonian $H_1$ of the transport system under consideration.

Independent from the details of the internal phonon interactions the modified phonon-transport equation has the following structure.

$$\begin{aligned}&\partial_t \langle \hat{N}_\varkappa\rangle - \Phi(\varkappa, t) \\ &\quad = -\frac{\langle \hat{N}_\varkappa\rangle - \langle \hat{N}_\varkappa\rangle_0}{\tau_\varkappa} + \partial_t \langle \hat{N}_\varkappa\rangle_c\,. \end{aligned} \tag{6}$$

The excitation of phonon mode $\varkappa$ ($\equiv \boldsymbol{k}\lambda$), i.e. $\langle N_\varkappa\rangle$, is influenced by the phonon flux, relaxation and collision processes and by changes of these quantities. The necessity to add semiphenomenological relaxation path to the kinetic equations was stressed in I: they appear as the first terms on the r.h.s. of Equation (6).

### 3. Model System and Hamiltonian

Following Fröhlich, we suppose that the biological model system consists of the following units:

(a) a set of oscillators, which represents dipolar electric oscillating units. These modes form a narrow frequency band $\{\omega_j\}$ with $\omega_1 \leqq \omega_j \leqq \omega_2$. They are considered not to interact with each other, but to interact with the rest of the system.

(b) the rest of the system, which acts as a heatbath. It is represented by a set of independent oscillators $\{\Omega_\varkappa\}$.

(c) an external energy source, which establishes a phonon flux.

In addition to direct two-, three- and four-phonon processes between the modes $\{\omega_j\}$ and the heatbath, we take into account additional processes, described in a semi-phenomenological way by relaxation paths.

There have been already several attempts to make a microscopic theory for Fröhlich's phenomenological approach [18—22]. We partially follow these approaches, but our particular interest lies on the application of phonon transport equations and on a possible phase-transition behaviour of the system by phonon-flux.

The modes of the electric dipolar oscillations are associated with creation and annihilation operators, $a_i^+$ and $a_i$. The vibrational modes of the heatbath are described by the operators $b_\varkappa^+$ and $b_\varkappa$. The Hamiltonian for this coupled system of oscillators reads

$$H = H_0 + H_1\,. \tag{7}$$

The harmonic part $H_0$ consists of the system (i.e. $\{\omega_i\}$) and bath oscillators (i.e. $\{\Omega_\varkappa\}$), ($\hbar = 1$)

$$H_0 = \sum_i \omega_i a_i^+ a_i + \sum_\varkappa \Omega_\varkappa b_\varkappa^+ b_\varkappa\,. \tag{7a}$$

The interaction between the dipolar modes and the heatbath is assumed to be essentially determined by bilinear, cubic and quartic coupling terms. The interaction Hamiltonian is written as

$$\begin{aligned} H_1 &= \sum_{i,\varkappa} (\lambda_{i\varkappa} a_i^+ b_\varkappa + \lambda_{i\varkappa}^* a_i b_\varkappa^+) \\ &\quad + \sum_{i,j,\varkappa} (\chi_{ij\varkappa} a_i^+ a_j b_\varkappa^+ + \chi_{ij\varkappa}^* a_i a_j^+ b_\varkappa) \\ &\quad + \sum_{i,j,\varkappa} (\beta_{ij\varkappa} a_i^+ a_j^+ b_\varkappa + \beta_{ij\varkappa}^* a_i a_j b_\varkappa^+) \\ &\quad + \sum_{i,\varkappa,l} (\delta_{i\varkappa l} a_i^+ b_\varkappa^+ b_l + \delta_{i\varkappa l}^* a_i b_\varkappa b_l^+) \\ &\quad + \sum_{i,j,\varkappa,l} (\gamma_{ij\varkappa l} a_i^+ a_j b_\varkappa^+ b_l + \gamma_{ij\varkappa l}^* a_i a_j^+ b_\varkappa b_l^+)\,. \end{aligned} \tag{7b}$$

Both systems are assumed to be translationally invariant. Furthermore, the coupling parameters must fulfill this invariance against translation. The coupling coefficients $\lambda$, $\chi$, $\beta$, $\delta$, and $\gamma$ are functions of the wave vectors $(i, j, k \ldots)$ and the energies $(\omega_i, \omega_j, \omega_\varkappa \ldots)$ of the associated phonon operators.

We assume that they are smooth in the energy conserving region. This region is rather restricted, since a narrow frequency band $\{\omega_j\}$ is given in our model. A restriction to frequency and $k$-vector independent coupling parameters will be taken in our calculations.

In Hamiltonian (7b) we have combined all those interaction parts which have been used in the microscopic approaches of either Bhaumik et al. [18—20] or of Wu and Austin [21, 22]. We want to restrict ourselves to those direct and energy conserving two and three phonon processes, which are described by the first two terms of $H_1$. Changes due to the other three terms will be discussed below (vid. Chapter (7) and Appendix B).

Combining Eqs. (1), (5), (6) and (7) we get the kinetic equations ($\beta = \delta = \gamma = 0$)

$$\begin{aligned}\partial_t \langle n_i\rangle = \Phi_i - \frac{\langle n_i\rangle - \langle n_i\rangle_0}{\tau_i} &+ 2\pi \sum_{\varkappa} |\lambda|^2 (\langle N_\varkappa\rangle - \langle n_i\rangle)\, \delta(\omega_i - \Omega_\varkappa) \\ &+ 2\pi \sum_{\substack{j,\varkappa \\ j>i}} |\chi|^2 (\langle n_j N_\varkappa\rangle - \langle n_i N_\varkappa\rangle + \langle n_i n_j\rangle + \langle n_j\rangle\, \delta(\omega_j - \omega_i - \Omega_\varkappa) \\ &+ 2\pi \sum_{\substack{j,\varkappa \\ j<i}} |\chi|^2 (\langle n_j N_\varkappa\rangle - \langle n_i N_\varkappa\rangle - \langle n_i n_j\rangle - \langle n_i\rangle)\, \delta(\omega_i - \omega_j - \Omega_\varkappa) \qquad (8)\end{aligned}$$

with

$$n_j \equiv a_j^+ a_j\,, \quad N_\varkappa = b_\varkappa^+ b_\varkappa\,.$$

It is wellknown that if the phonon collision term is written in a power form, the highest nonlinear terms cancel out, i.e. $\langle n_i N_\varkappa\rangle$ in the two- and $\langle n_i n_j N_\varkappa\rangle$ in the three-phonon process, respectively.

The matrix elements are calculated with a product state of independent oscillators

$$\begin{aligned}|\nu\rangle &= |\{n_j\}\rangle \cdot |\{N_\varkappa\}\rangle \qquad (9)\\ &= \prod_j \frac{1}{\sqrt{n_j!}} (a_j^+)^{n_j} |0\rangle \cdot \prod_\varkappa \frac{1}{\sqrt{N_\varkappa!}} (b_\varkappa^+)^{N_\varkappa} |0\rangle\,.\end{aligned}$$

At this state we only can proceed if we postulate a factorization procedure, which one always has to employ to separate a subhierarchy from the hierarchy of kinetic equations. We do not want to go into the details of this procedure. In [24, 25] we have been able to show that the structure and stability of steady state solutions of kinetic equations like Eq. (8) are nearly unchanged for different decoupling methods. Therefore we choose the most simple factorization

$$\begin{aligned}\langle n_i n_j\rangle &= \langle n_i\rangle \langle n_j\rangle\,,\\ \langle n_i N_\varkappa\rangle &= \langle n_i\rangle \langle N_\varkappa\rangle\,.\end{aligned}$$

The second factorization seems reasonable, since $\langle N_\varkappa\rangle$ will be replaced by its thermal average with respect to the heatbath. In addition we expand the argument of the $\delta$-functions of Equation (8).

$$\omega_i - \Omega_\varkappa = \partial_{\boldsymbol{k}} \Omega_\varkappa|_{\boldsymbol{k}=\boldsymbol{i}} \cdot (\boldsymbol{j} - \boldsymbol{i} - \boldsymbol{k}) + \cdots$$

and

$$\omega_j - \omega_i - \Omega_\varkappa = \partial_{\boldsymbol{k}} \Omega_\varkappa|_{\boldsymbol{k}=\boldsymbol{j}-\boldsymbol{i}} \cdot (\boldsymbol{j} - \boldsymbol{i} - \boldsymbol{k}) + \cdots$$

leading to

$$\begin{aligned}\delta(\omega_i - \Omega_\varkappa) &\approx |v_i|^{-1}\, \delta(\boldsymbol{i} - \boldsymbol{k})\,,\\ \delta(\omega_j - \omega_i - \Omega_\varkappa) &= |v_{j-i}|^{-1}\, \delta(\boldsymbol{j} - \boldsymbol{i} - \boldsymbol{k})\end{aligned}$$

with

$$\boldsymbol{v}_i \equiv \boldsymbol{v}_{i,\lambda} = \partial_{\boldsymbol{i}}\, \omega_{i,\lambda}\,.$$

With these expansions, one summation in each collision term of Eq. (8) can be performed. The resulting parameters and the factor $2\pi$ are contained in the modified coupling constants, $|\tilde{\chi}|^2$ and $|\tilde{\lambda}|^2$, respectively.

The modified and approximated equations then read

$$\begin{aligned}\partial_t \langle n_i\rangle = \Phi_i - \frac{\langle n_i\rangle - n_i^0}{\tau_i} &+ |\tilde{\lambda}|^2 (\langle N(\omega_i)\rangle - \langle n_i\rangle) \\ &+ \sum_{j>i} |\tilde{\chi}_2|^2 (\langle n_j\rangle (\langle N(\omega_j - \omega_i)\rangle + \langle n_i\rangle + 1) \\ &- \langle n_i\rangle \langle N(\omega_j - \omega_i)\rangle) \qquad (10) \\ &+ \sum_{j<i} |\tilde{\chi}_1|^2 (\langle n_j\rangle \langle N(\omega_i - \omega_j)\rangle \\ &- \langle n_i\rangle (\langle N(\omega_i - \omega_j)\rangle + \langle n_j\rangle + 1))\,.\end{aligned}$$

## 4. Steady State Solutions

We want to solve Eqs. (10) for the time independent case. For $w_i < w_j$ we get

$$\langle n_i\rangle_s = \frac{|\tilde{\lambda}|^2 N^0(\omega_i) + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s + \frac{n_i^0}{\tau_i} + \Phi_i}{\frac{1}{\tau_i} + |\tilde{\lambda}|^2 + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - \langle n_j\rangle_s)} \tag{11}$$

and

$$\langle n_j\rangle_s = \frac{|\tilde{\lambda}|^2 N^0(\omega_j) + \sum_{l<j} |\tilde{\chi}_2|^2 N^0(\omega_j - \omega_l)\langle n_l\rangle_s + \frac{n_j^0}{\tau_j} + \Phi_j}{\frac{1}{\tau_j} + |\tilde{\lambda}|^2 + \sum_{l<j} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_l) + \langle n_l\rangle_s + 1)} \tag{12}$$

where $\langle N_\varkappa\rangle_s$ has been replaced by its thermal value $N_\varkappa^0$. The index s refers to steady state solution. Equation (11) can be rewritten in another way, i.e.

$$\langle n_i\rangle_s = \left(1 + \frac{\Phi_i}{\frac{n_i^0}{\tau_i} + |\tilde{\lambda}|^2 N^0(\omega_i) + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s}\right) (e^{\beta(\omega_i - \mu_i)} - 1)^{-1} \tag{11a}$$

with the formal introduction of a chemical potential

$$e^{-\beta\mu_i} = \frac{\frac{n_i^0}{\tau_i} + |\tilde{\lambda}|^2 N^0(\omega_i) + \sum_{j>i} |\tilde{\chi}_2|^2 e^{-\beta\omega_i} N^0(\omega_j - \omega_i)(1 + \langle n_j\rangle_s)}{\frac{n_i^0}{\tau_i} + |\tilde{\lambda}|^2 N^0(\omega_i) + \sum_{j>i} |\tilde{\chi}_2|^2 e^{\beta(\omega_j - \omega_i)} (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s}\,; \quad (\beta \equiv 1/k_B T). \tag{11b}$$

If one introduces the difference between steady state and thermal solution

$$\delta n_i = \langle n_i\rangle_s - n_i^0$$

one gets

$$\delta n_i = \frac{\sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1 + n_j^0)\,\delta n_j + \Phi_i}{|\tilde{\lambda}|^2 + \frac{1}{\tau_i} + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - n_j^0 - \delta n_j)}\,. \tag{11c}$$

The structure of Eqs. (11a) and (11b) has been chosen in close analogy to that form, in which Fröhlich has presented the steady state solution of his rate equation approach (vid. Appendix A).

The condition $\mu_i > 0$ (i.e. $\exp(-\beta\mu_i) < 1$), which is necessary to permit a Bose-condensation like behaviour, leads to

$$\sum_{j>i} |\tilde{\chi}_2|^2 (\exp(-\beta\omega_i) N^0(\omega_j - \omega_i)(\langle n_j\rangle_s + 1) - (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s) < 0\,. \tag{13a}$$

This inequality can be rewritten as

$$\sum_{j>i} |\tilde{\chi}_2|^2 \frac{N^0(\omega_j)}{N^0(\omega_j - \omega_i)}\,\delta n_j > 0 \tag{13b}$$

which means that one must have (at least for certain $j$)

$$\langle n_j\rangle_s > n_j^0 \tag{14}$$

i.e. an excitation above a thermal one.

It is instructive to consider two limiting cases. If the second-order process is neglected (i.e. $|\tilde{\chi}_2|^2 \to 0$) it follows from Eq. (11b)

$$\exp(-\beta\mu_i) = 1 \rightsquigarrow \mu_i = 0\,. \tag{15}$$

The result is a modified Planck distribution

$$\langle n_i\rangle_s = \left(1 + \frac{\Phi_i}{n_i^0/\tau_i + |\lambda|^2 N^0(\omega_i)}\right) \cdot (\exp(\beta\omega_i) - 1)^{-1}\,. \tag{16}$$

On the other hand a vanishing phonon flux $\Phi_i$ results in the modified distribution [vid. Eq. (11a)]

$$\langle n_i\rangle_s = (\exp(\beta(\omega_i - \mu_i) - 1)^{-1}\,. \tag{17}$$

However, for $\Phi_i = 0$ it follows from Eqs. (11), (12) or from Eq. (11c) that $\langle n_i \rangle_s = n_i^0$ and $\langle n_j \rangle_s = n_j^0$ is one possible solution; it in turn leads to

$$\exp(-\beta \mu_i) = 1 .$$

Furthermore, this thermal equilibrium solution is the only stable solution for zero flux conditions. This can be shown by simple stability theoretical methods, but for brevity these calculations will not be given here. A detailed discussion of Eqs. (11), (12) will be presented in Chapter 7.

In Appendix A we compare our microscopic approach (kinetic equations of Peierls-Boltzmann type) with the phenomenological approach of Fröhlich (rate equation method). It is shown that our results are identical with those of Fröhlich under the conditions that in our approach

a) a factorization procedure is applied,
b) thermal values for the $N_\varkappa$ variables are chosen,
c) relaxation processes are neglected,
d) the coupling constants are modified and simplified. This in turn means that the frequency dependence of the chemical potential is neglected,
e) the phonon fluxes $\{\Phi_j\}$ are taken as a system independent external energy supply.

## 5. Two-Mode-Approximation

It would be difficult to solve the system of quadratic equations [Eqs. (11) and (12)] exactly. To get a better understanding of the general behaviour of $\langle n_i \rangle_s$, we start by restricting ourselves to a system of two oscillators. The same method also applies if there are more than 2 modes. The complete set of equations will be discussed in the following chapter. With $\omega_i = \omega_1$, $\omega_j = \omega_2$ and $\Omega_\varkappa = \omega_2 - \omega_1$ we have two kinetic equations [vid. Eq. (10)]:

$$\begin{aligned}\partial_t \langle n_1 \rangle = \Phi_1 - \frac{\langle n_1 \rangle - n_1^0}{\tau_1} + |\tilde{\lambda}|^2(\langle N_\varkappa \rangle - \langle n_1 \rangle) \\ + |\tilde{\chi}|^2((\langle n_2 \rangle - \langle n_1 \rangle)\langle \tilde{N}_\varkappa \rangle \\ + \langle n_1 \rangle \langle n_2 \rangle + \langle n_2 \rangle) ,\end{aligned} \tag{18}$$

$$\begin{aligned}\partial_t \langle n_2 \rangle = \Phi_2 - \frac{\langle n_2 \rangle - \langle n_2 \rangle^0}{\tau_2} + |\tilde{\lambda}|^2(\langle \tilde{N}_\varkappa \rangle - \langle n_2 \rangle) \\ + |\tilde{\chi}|^2((\langle n_1 \rangle - \langle n_2 \rangle)\langle \tilde{N}_\varkappa \rangle \\ - \langle n_1 \rangle \langle n_2 \rangle - \langle n_2 \rangle)\end{aligned} \tag{19}$$

with

$$\begin{aligned}\langle N_\varkappa \rangle &= \langle N(\omega_1) \rangle , \\ \langle \tilde{N}_\varkappa \rangle &= \langle N(\omega_2) \rangle , \\ \langle \tilde{N}_\varkappa \rangle &= \langle N(\omega_2 - \omega_1) \rangle .\end{aligned}$$

We wish to solve these equations for the stationary case, i.e. when

$$\partial_t \langle n_1 \rangle = 0 = \partial_t \langle n_2 \rangle .$$

From Eqs. (17) and (18) we find

$$\langle n_1 \rangle_s = \frac{|\tilde{\lambda}|^2 N_\varkappa^0 + |\tilde{\chi}|^2(\tilde{N}_\varkappa^0 + 1)\langle n_2 \rangle_s + \Phi_1 + n_1^0/\tau_1}{1/\tau_1 + |\tilde{\lambda}|^2 + |\tilde{\chi}|^2(\tilde{N}_\varkappa^0 - \langle n_2 \rangle_s)} , \tag{20}$$

$$\langle n_2 \rangle_s = \frac{|\tilde{\lambda}|^2 \tilde{N}_\varkappa^0 + |\tilde{\chi}|^2 \tilde{N}_\varkappa^0 \langle n_1 \rangle_s + \Phi_2 + n_2^0/\tau_2}{1/\tau_2 + |\tilde{\lambda}|^2 + |\tilde{\chi}|^2(\tilde{N}_\varkappa^0 + \langle n_1 \rangle_s + 1)} . \tag{21}$$

Furthermore, summing up Eqs. (18) and (19) we can derive the relation

$$\begin{aligned}\langle n_2 \rangle_s \left(\frac{1}{\tau_2} + |\tilde{\lambda}|^2\right) + \langle n_1 \rangle_s \left(\frac{1}{\tau_1} + |\tilde{\lambda}|^2\right) \\ = \Phi_1 + \Phi_2 + \frac{n_1^0}{\tau_1} + \frac{n_2^0}{\tau_2} + |\tilde{\lambda}|^2(N_\varkappa^0 + \tilde{N}_\varkappa^0)\end{aligned}$$

between the two variables $\langle n_2 \rangle_s$ and $\langle n_1 \rangle_s$. One possible realization is of course given by $\langle n_2 \rangle_s = n_2^0$ and $\langle n_1 \rangle_s = n_1^0$ for vanishing phonon fluxes $\Phi_1$ and $\Phi_2$, respectively.

If one eliminates $\langle n_2 \rangle_s$ in Eq. (20) and $\langle n_1 \rangle_s$ in Eq. (21) one arrives at two quadratic equations for the steady state values. They are found to have the following structure

$$\begin{aligned}a\langle n_1 \rangle_s^2 + (b_1 - \alpha_1(\Phi_1 + \Phi_2))\langle n_1 \rangle_s \\ - (c_1 + \beta_1 \Phi) = 0 ,\end{aligned} \tag{22}$$

$$\begin{aligned}a\langle n_2 \rangle_s^2 - (b_2 + \alpha_2(\Phi_1 + \Phi_2))\langle n_2 \rangle_s \\ + (c_2 + \beta_2 \Phi) = 0\end{aligned} \tag{23a}$$

where all parameters are positive,

$$a, b_2, c_1, c_2, \beta_1, \beta_2, \alpha_1, \alpha_2 > 0 \tag{23b}$$

with the exception of $b_1$, i.e. $b_1 \gtrless 0$.

From the quadratic Eqs. (22) two pairs of steady state solutions can be calculated

$$\text{SS 1:} \quad \begin{aligned}\langle n_1 \rangle_{s,1} &\geqq n_1^0 , \\ \langle n_2 \rangle_{s,1} &\geqq n_2^0\end{aligned} \tag{24}$$

(SS 1 stands for "steady state solution 1").

$$\text{SS 2:} \quad \begin{aligned}\langle n_1 \rangle_{s,2} &< 0 , \\ \langle n_2 \rangle_{s,2} &\gg n_2^0 > 0 ,\end{aligned} \tag{25}$$

(SS 2 stands for "steady state solution 2"), where the sign of equality holds for $\Phi_1 = 0 = \Phi_2$. A detailed investigation shows that the SS 2-solution is unstable. Both from a mathematical (i.e. unstable) and a physical (i.e. both unstable and negative) point of view the latter solution must be neglected. We are left with the SS 1, a qualitative picture of which is shown in Figure 1.

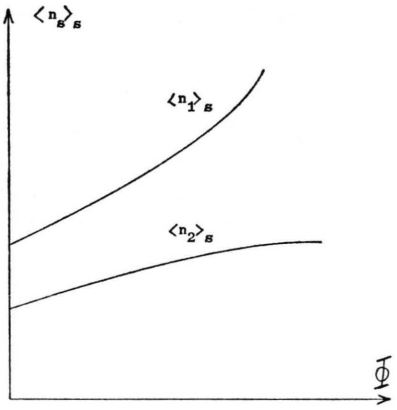


Fig. 1. Steady state excitation $\langle n_s \rangle_s$ ($s = 1,2$) as a function of the external phonon flux $\Phi$ [vid. Eq. (20)] in the 2-mode approximation. Only the stable solutions are drawn (arbitrary units are used).

An extension of these calculations to a set of $n$ oscillators is straightforward but very cumbersome. One must solve a set of $n$ coupled quadratic equations, leading to $n$ separated quadratic equations which in principle can be solved. The result would be two sets of solutions

$$\{\langle n_1 \rangle_{s,1}, \langle n_2 \rangle_{s,1} \dots \langle n_n \rangle_{s,1}\},$$
$$\{\langle n_1 \rangle_{s,2}, \langle n_2 \rangle_{s,2} \dots \langle n_n \rangle_{s,2}\}$$

the stability of which must be checked.

In practice this method can only be applied for a low number of oscillators at most. Approximate methods must be taken into account if one wants to know the behaviour of the $\langle n_\varkappa \rangle_s$ with varying flux.

## 6. Approximate Steady State Solutions

The steady state solution $\langle n_i \rangle_s$ is a function of all other steady state solutions $\{\langle n_j \rangle_s\}$ with $\omega_j > \omega_i$ and the phonon flux $\Phi_i$. The $\{\langle n_j \rangle_s\}$ in turn are functions of the set of phonon fluxes $\{\Phi_j\}$ and of the $\{\langle n_1 \rangle_s\}$ with $\omega_1 < \omega_j$. We want to discuss the $\langle n_i \rangle_s$-solution as a function of the energy supply by phonon transport and of the coupling parameters alone with the $\langle n_j \rangle_s$ eliminated. Instead of a rather difficults elimination procedure for the $\langle n_j \rangle_s$ variables of Eq. (11), we try an approximate method. We assume that the $\langle n_j \rangle_s$ are essentially determined by the one-phonon processes and by phonon fluxes. In a first approximation we neglect the two-phonon processes in Equation (12). The result is

$$\langle n_j \rangle_s^{(1)} = \frac{|\tilde{\lambda}|^2 N^0(\omega_j) + \frac{n_j^0}{\tau_j} + \Phi_j}{1/\tau_j + |\tilde{\lambda}|^2}. \tag{26}$$

For $\Phi_j = 0$, the solution must be

$$\langle n_j \rangle_s^{(1)}|_{\Phi_j = 0} = n_j^0 \tag{27}$$

leading to $N^0(\omega_j) = n_j^0$. Equation (26) can be simplified to

$$\langle n_j \rangle_s^{(1)} = n_j^0 + \frac{\Phi_j \tau_j}{1 + \tau_j |\tilde{\lambda}|^2} \equiv n_j^0 + \delta n_j^{(1)} \tag{28}$$

which means that the excitation of the modes is approximately given by its thermal value plus an increase proportional to the phonon flux. We replace $\langle n_j \rangle_s$ of Eq. (11) by $\langle n_j \rangle_s^{(1)}$. Then the result is

$$\langle n_i \rangle_s^{(1)} = \frac{|\tilde{\lambda}|^2 N^0(\omega_i) + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1)\left(n_j^0 + \frac{\Phi_j \tau_j}{1 + \tau_j |\tilde{\lambda}|^2}\right) + \frac{n_i^0}{\tau_i} + \Phi_i}{\frac{1}{\tau_i} + |\tilde{\lambda}|^2 + \sum_{j>i} |\tilde{\chi}_2|^2 \left(N^0(\omega_j - \omega_i) - n_j^0 - \frac{\Phi_j \tau_j}{1 + \tau_j |\tilde{\lambda}|^2}\right)}. \tag{29}$$

The above approximation [Eqs. (26), (29)] is a reasonable one, if the phonon fluxes $\{\Phi_j\}$ are small. But this latter restriction is to a certain extend already recommended in the derivation of the transport term [vid. Eq. (3)], where one has restricted to a linear transport term. We emphasize that the fluxes $\{\Phi_j\}$ have to be made consistent with the definition (3) after the approximate or exact steady state solutions have been found.

Equation (29) is restricted to processes with $\omega_i < \omega_j$. The complete steady state solution for an

arbitrary frequency $\omega_i$ is given by a combination of Eqs. (11) and (12) or directly from Eq. (10). It reads

$$\langle n_i\rangle_s^{(1)} = \frac{|\tilde{\lambda}|^2 N^0(\omega_i) + \Phi_i + \frac{1}{\tau_i} n_i^0 + A_1}{|\tilde{\lambda}|^2 + \frac{1}{\tau_i} + A_2} \tag{30}$$

with

$$A_1 = \sum_{j<i} |\tilde{\chi}_1|^2 (N^0(\omega_i - \omega_j)\langle n_j\rangle_s^{(1)} + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s^{(1)},$$

and

$$A_2 = \sum_{j<i} |\tilde{\chi}_1|^2 (N^0(\omega_i - \omega_j) + \langle n_j\rangle_s^{(1)} + 1) + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - \langle n_j\rangle_s^{(1)}).$$

$\langle n_j\rangle_s$ has been replaced by $\langle n_j\rangle_s^{(1)}$ (vid. Equation (28)).

A qualitative behaviour of the steady state excitation $\langle n_i\rangle_s^{(1)}$ as a function of the external phonon fluxes $\{\Phi_j\}$ is given in Figure 2. For simplicity we have drawn the steady states for equal fluxes, i.e. $\Phi_i = \Phi_j = \Phi_\varkappa = \cdots$. Details of the behaviour depend on the model parameters. These include the average spacing of the energy levels within the frequency band and their width, the number of oscillators (i.e. frequencies within the band) and the coupling strengths for the different processes. However, changes of some or all of these parameters do not alter the global behaviour which is shown in Figure 2.

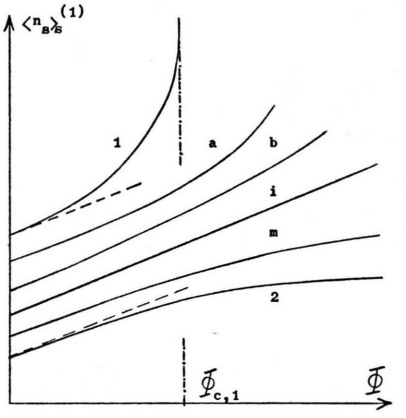


Fig. 2. Qualitative behaviour of the steady state excitation $\langle n_s\rangle_s^{(1)}$ as a function of the external phonon flux $\Phi$ [vid. Eq. (30)]. Only the excitations for the lowest, the highest and some intermediate frequencies are drawn, i.e. $\omega_1 = \omega_{\min} < \omega_a < \omega_b < \omega_i < \omega_m < \omega_2 = \omega_{\max}$. The dashed lines represent the steady state excitations for vanishing nonlinear coupling, i.e. $|\chi_1|^2, |\chi_2|^2 \to 0$. The low frequencies are determined by the $|\chi_2|^2$-processes, the high-frequency excitations by the $|\chi_1|^2$-processes. For $\Phi \to \Phi_{c,1}$, the lowest mode becomes strongly excited (arbitrary units are used, $\Phi = 0$ are the thermal values).

## 7. Results and Discussion

To give an interpretation of the preceding results it is useful to start with Eqs. (11) to (13). The steady state solutions can be divided into two groups with respect to the three phonon processes:

I. $a_i^+ a_j b_\varkappa^+ + cc$ including the energy conservation condition $\omega_i = \omega_j - \Omega_\varkappa$ and the steady state occupation $\langle n_i\rangle_s$ [vid. Equation (11)].

II. $a_i^+ a_j b_\varkappa + cc$ including the energy conservation condition $\omega_i = \omega_j + \Omega_\varkappa$ and the steady state occupation $\langle n_i\rangle_s$ [vid. Eq. (12)].

Only in processes of the type I a minus sign appears in the denominator of the steady state solution. This means that a strong excitation is only achievable for the lower frequency part of the set of oscillators. The condition for a strong excitation ("Bose-condensation" like behaviour) reads [vid. Eq. (11)]

$$\frac{1}{\tau_i} + |\tilde{\lambda}|^2 + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - \langle n_j\rangle_s) \to 0^+. \tag{31}$$

The same condition follows from Eq. (11b) with $\omega_i - \mu_i \to 0^+$. The $|\tilde{\chi}_1|^2$-processes [vid. Eq. (30)] can be neglected for frequencies $\omega_i$ of the lower part. For at least some of the $j$'s ($j > i$) one must have: (condition (31) can be split into several parts):

a) $\langle n_j\rangle_s > n_j^0$ or equivalently $\delta n_j > 0$. This condition must be valid since one always has $N^0(\omega_j - \omega_i) > n_j^0$. This means that at least some of the oscillators with higher frequencies must be excited above their thermal values.

b) $N^0(\omega_j - \omega_i) - n_j^0 - \delta n_j < 0$ for at least some of the $j$'s, since the first two terms of (30) are positive. The value $\delta n_j$ for which this condition can be fulfilled is given by $\omega_i = \omega_{\min}$, i.e. for the smallest frequency $\omega_i$. Thus it is the lowest mode which first can undergo a transition to a "Bose-condensation" like behaviour.

c) $\sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - n_j^0 - \delta n_j) < 0$, i.e. the combination of the complete set of three phonon processes with $\omega_j > \omega_i$ must lead to a negative contribution in the denominator of Equation (11).

This means that the term

$$\sum_{j>i} |\tilde{\chi}_2|^2 \langle n_i \rangle (\langle n_j \rangle - \langle N(\omega_j - \omega_i) \rangle)$$

of Eq. (10) must be positive. Thus an autocatalytic or positive feedback type of process must become effective in the original kinetic equations. A more detailed discussion of this behaviour is in Appendix C.

The conditions a), b) and c) are necessary but not sufficient for Eq. (31) to be valid. In addition one must have the following situation:

d) The three-phonon processes (represented by $|\tilde{\chi}_2|^2$) must be strong, i.e. they must be comparable to the two-phonon ($|\lambda|^2$) and the relaxation processes ($1/\tau_i$). Thus the direct processes system-heatbath and the additional relaxation paths are not the only dominating processes, contrary to the situation which one would usually expect for simple oscillator systems. This demonstrates the essential importance of nonlinear interactions in systems which model biological order and function. Furthermore the necessity for an athermal excitation of at least some modes (i.e. $\langle n_j \rangle_s > n_j^0$) requires non-vanishing phonon fluxes. This can be seen from Eq. (17) and the comment following it and also in a more direct way from Equation (29). By means of the latter one Eq. (30) can be rewritten in an approximated version

$$\frac{1}{\tau_i} + |\tilde{\lambda}|^2 + \sum_{j>i} |\tilde{\chi}_2|^2 \cdot \left( N^0(\omega_j - \omega_i) - n_j^0 - \frac{\Phi_j \tau_j}{1 + \tau_j |\tilde{\lambda}|^2} \right) \to 0^+ . \tag{32}$$

As a result of Eq. (32), the phonon flux $\Phi_j$ for at least some of the $j$'s must exceed a certain value $\Phi_{j,c}$,

$$\Phi_{j,c} = (1 + \tau_j |\tilde{\lambda}|^2)(N^0(\omega_j - \omega_i) - n_j^0) \tag{33}$$

in order to permit a highly excited low frequency mode $\omega_i$. Since the critical flux $\Phi_{j,c}$ is smallest for the lowest frequency (i.e. $\omega_i = \omega_{\min}$), a strong excitation will preferably take place for the lowest mode.

The above considerations show a preferential excitation of the lower modes. Under rather restricted conditions this may lead to a very strong excitation of the lowest mode ("Bose-condensation" into the lowest mode). However, this can only be achieved if the system is externally pumped with a pump strength above a critical value and if the coupling between the oscillator system and the bath is strong and nonlinear. Then a redistribution of the externally supplied energy between the various degrees of freedom becomes possible. The resulting excitation and stabilization of a single mode far above thermal equilibrium (i.e. coherent excitation of an electric vibration) may in turn lead to a new order and function of the system.

However, there is no sharp transition from a normal to a "Bose-condensed" state. The modes which are next to the lowest one participate on the excitation of the lowest mode, although their excitations are appreciably smaller. Details of the excitations of the different modes depend on the system's parameter, i.e. the coupling strength for the different processes, the number of oscillators, the average spacing of the energy levels within the band and their width etc. A suitable choice of these parameters can be done in such a way that the excitation of higher frequencies is almost completely suppressed against that of the lowest one. Furthermore, the coupling parameters are frequency and temperature dependent, a fact one should take into account if one wants to study the detailed quantitative behaviour of the steady state excitation. Such an extended investigation only makes sense if the model is replaced by a more realistic one, i.e. by one in which the set of oscillators can be attributed to a specific and somewhat well-defined active part of a biological system.

It should be emphasized that our results rest on particular material conditions, above all on the large magnitude of the nonlinear interaction $|\tilde{\chi}_2|^2$. The latter condition has been chosen in close analogy to Fröhlich's original proposal. If this condition is not valid, higher nonlinear processes involving three or more quanta of the system must be considered.

This would lead to additional conditions for a possible "Bose-type" of excitation, although the number of suitable nonlinear processes is extremely restricted. In Appendix C it is shown that processes of "autocatalytic" nature are necessary. Other terms, e.g. nonlinear direct interactions within the set of oscillators could also be important and may well give rise to a further competition between exciting and de-exciting processes.

If one takes into account double creation and double annihilation processes (i.e. $\beta a_i^+ a_j^+ b_\varkappa + cc$, $\Omega_\varkappa = \omega_j + \omega_i$) one has to modify Equation (11).

A combination of this latter equation and Eq. (B.6) (vid. Appendix B) leads to $(|\tilde{\chi}_2|^2 - |\tilde{\beta}|^2)\langle n_j\rangle_s$ instead of $|\tilde{\chi}_2|^2\langle n_j\rangle_s$ alone in the denominator of Equation (11). For $|\tilde{\chi}_2|^2 = |\tilde{\beta}|^2$, the only term with a negative sign would cancel, a "Bose-type" of excitation would become impossible. However, it can be shown by a more detailed investigation of the coupling constants that usually one has $|\tilde{\chi}_2|^2 > |\tilde{\beta}|^2$. This has also been shown in (22). In a more realistic model system one should also take into account a coupling to nonoscillating systems, (e.g. free ions — mobile ionic groups — low lying electronic levels) in addition to the simple heatbath (26). Under certain conditions then two phonon absorption or emission processes might become impossible, since only $\Omega_\varkappa = \omega_j - \omega_i$ but not $\Omega_\varkappa = \omega_j + \omega_i$ is allowed for energy conserving processes.

## 8. Summary and Outlook

We have applied a modified Peierls-Boltzmann transport equation formalism to study the problem of a possible "Bose-condensation" like excitation of simple model system. This formalism has been chosen in order to supplement Fröhlich's rate equation approach by a microscopic treatment. It has been shown that our result corresponds to that of Fröhlich if some approximations and simplifying assumptions are applied to our microscopic kinetic equations (vid. Chapter 4 and Appendix A). One of these approximations was the replacement of the steady state values of the bath variables $\langle N_\varkappa\rangle_s$ by their thermal values $N_\varkappa{}^0$. This replacement corresponds to the assumption of detailed balance in the rate equation approach. However, the possible existence of a "Bose-condensation"-like behaviour does not depend on this approximation. The only condition with respect to our model is that a set of externally pumped oscillators $S_1$ (transporting system) is nonlinearly coupled to a system of non-pumped oscillators (nontransporting system $S_2$).

An alternative kind of a model would be the nonlinear coupling of a phonon transporting system (similar to $S_1$) to a singular local degree of freedom, which would replace the system of oscillators (e.g. heatbath) $S_2$ [27—29]. It has been shown that the local degree of freedom gets strongly excited if the phonon flux in system $S_1$ exceeds a threshold value $\Phi_c$ [23, 24]. Depending on the details of the internal nonlinear kinetics, a hysteresis type of transport phase transition is possible. In this model a singular mode is coherently excited instead of the lowest one of a set of oscillators. In both cases, however, the externally supplied energy is preferably channeled into a single mode where it gets stored.

## Appendix A

*Fröhlich's Rate Equation Approach*

In a series of papers Fröhlich [2, 4, 7] has presented his vibrational model. In this phenomenological approach the following steady state solution has been given by [vid. Eqs. (3.11) and (3.15) of Ref. [4]]

$$n_i = \left(1 + \frac{\varphi}{\chi}\frac{S_i}{S}\right) \cdot (1 - \exp(-\beta\mu))(\exp(\beta(\omega_i - \mu) - 1))^{-1} \tag{A.1}$$

with the chemical potential $\mu$ given by

$$\exp(-\beta\mu) = \frac{\varphi + \chi\sum_j (1 + n_j)}{\varphi + \chi\sum_j n_j \exp(\beta\omega_j)} \tag{A.2}$$

and

$$S = \sum s_i = \varphi \sum_i (n_i \exp(\beta\omega_i - (n_i + 1))) . \tag{A.3}$$

Together with Eqs. (A.2) and (A.3) Eq. (A.1) can be rewritten

$$n_i = \left(1 + \frac{S_i}{\varphi + \chi\sum_j n_j \exp(\beta\omega_j)}\right) \cdot (\exp(\beta(\omega_i - \mu) - 1))^{-1} . \tag{A.4}$$

The total rate of change of mode $k$ has been given by the rate equation for first- and second-order processes (i.e. two- and three-phonon processes):

$$\begin{aligned}\dot{n}_i = S_i &- \varphi(n_i \exp(\beta\omega_i) - (n_i + 1)) \\ &- \chi\sum_j (n_i(1 + n_j)\exp(\beta\omega_i) \\ &- (1 + n_i) n_j \exp(\beta\omega_j)) .\end{aligned} \tag{A.5}$$

If one replaces the chemical potential $\exp(-\beta\mu)$ (Eq. (A.2)), one can derive the steady state solution in the form

$$n_i = \frac{S_i + \varphi + \chi\sum_j n_j \exp(\beta\omega_j)}{(\exp(\beta\omega_i) - 1)\varphi + \chi\sum_j (\exp(\beta\omega_i)(1 + n_j) - \exp(\beta\omega_j) n_j)} . \tag{A.6}$$

In order to compare this phenomenological result with our steady state solution of the Peierls-Boltzmann transport equation [vid. Eqs. (11) and (12)], we have to introduce the relations

$$\chi \to \tilde{\chi}_2 \exp(-\beta\,\omega_i)\, N^0(\Omega_\varkappa = \omega_j - \omega_i), \quad \text{(A.7)}$$

$$\varphi \to \tilde{\varphi}\, N^0(\Omega_\varkappa = \omega_i), \quad \text{(A.8)}$$

$$S_i \to \Phi_i . \quad \text{(A.9)}$$

In a similar way one can derive the relations

$$\chi \to \tilde{\chi}_1 \exp(-\beta\,\omega_i)(N(\Omega_\varkappa = \omega_i - \omega_j) + 1)$$
$$\equiv \tilde{\chi}_1 \exp(-\beta\,\omega_j)\, N(\Omega_\varkappa = \omega_i - \omega_j), \quad \text{(A.10)}$$

$$\beta \to \beta\, N(\Omega_\varkappa = \omega_j + \omega_i), \quad \text{(A.11)}$$

if one takes into account second-order processes with $\omega_i > \omega_j$ and processes with double phonon creation and annihilation, respectively.

Equation (A.6) can then be rewritten

$$n_i = \frac{\Phi_i + \tilde{\varphi}\, N^0(\omega_i) + \sum_j \tilde{\chi}(N^0(\omega_j - \omega_i) + 1)\, n_j}{\tilde{\varphi} + \sum_j \tilde{\chi}(N^0(\omega_j - \omega_i) - n_j)} \quad \text{(A.12)}$$

where the relations

$$N^0(\omega_j) = (\exp(\beta\,\omega_j) - 1)^{-1}$$

and

$$(N^0(\omega_j) + 1) = e^{\beta\omega_j} N^0(\omega_j)$$

i.e. thermal distributions, have been used.

A comparison between Eqs. (11) and (A.12) shows that the steady state solutions are identical, if one neglects the relaxation process in Eq. (11) and if one identifies the coupling constants $\tilde{\varphi}$ and $\tilde{\chi}$ with $|\tilde{\lambda}|^2$ and $|\tilde{\chi}_2|^2$, respectively. It should be noted that the assumption of thermal values for the $\{N_\varkappa\}$ is not necessary in Eqs. (11), but is indispensable if one proceeds from Eq. (A.6) to Equation (A.12). Furthermore, from Eq. (A.12) we can see that the rate equation approach (Eq. (A.5)) describes the second order process with $\omega_j > \omega_i$. The case with $\omega_i > \omega_j$ is considered if one makes the replacement (A.10) instead of (A.6) in Equation (A.6). In this way Eq. (13) would result.

It is rather obvious that under the same conditions an identity between Eqs. (A.2) and (11 b) and between Eqs. (A.4) and (11 a) can be established.

A useful version of Eq. (A.6) is given by

$$\delta n_i = \frac{S_i + \chi \sum_j n_i^0 \exp(\beta\,\omega_i)(\exp(\beta\,\omega_j) - 1)\,\delta n_j}{(\exp(\beta\,\omega_i) - 1)\left(\varphi + \sum_j \chi\, n_j^0 \exp(\beta\,\omega_j)\right) + \chi \sum_j (\exp(\beta\,\omega_i) - \exp(\omega_j))\,\delta n_j} \quad \text{(A.13)}$$

with $\delta n_i = n_i - n_i^0$.

## Appendix B

The complete interaction Hamiltonian [Eq. (7)] leads to the kinetic equation

$$\partial_t \langle n_i \rangle = \Phi_i - \frac{\langle n_i \rangle - n_i^0}{\tau_i} + C_\lambda + C_\delta + C_\chi^{(1)} + C_\chi^{(2)} + C_\beta + C_\gamma \quad \text{(B.1)}$$

with

$$C_\lambda = 2\pi \sum_\varkappa |\lambda|^2 (\langle N_\varkappa \rangle - \langle n_i \rangle)\, \delta(\omega_i - \Omega_\varkappa), \quad \text{(B.2)}$$

$$C_\delta = 2\pi \sum_{\varkappa, l} |\delta|^2 (\langle n_i N_l \rangle - \langle n_i N_\varkappa \rangle + \langle N_\varkappa N_l \rangle + \langle N_l \rangle)\, \delta(\omega_i + \Omega_\varkappa - \Omega_l), \quad \text{(B.3)}$$

$$C_\chi^{(2)} = 2\pi \sum_{\substack{j,\varkappa \\ j>i}} |\chi|^2 (\langle n_j N_\varkappa \rangle - \langle n_i N_\varkappa \rangle + \langle n_i n_j \rangle + \langle n_j \rangle)\, \delta(\omega_j - \omega_i - \Omega_\varkappa), \quad \text{(B.4)}$$

$$C_\chi^{(1)} = 2\pi \sum_{\substack{j,\varkappa \\ j<i}} |\chi|^2 (\langle n_j N_\varkappa \rangle - \langle n_i N_\varkappa \rangle - \langle n_i n_j \rangle - \langle n_j \rangle)\, \delta(\omega_i - \omega_j - \Omega_\varkappa), \quad \text{(B.5)}$$

$$C_\beta = 2\pi \sum_{j,\varkappa} |\beta|^2 (\langle n_i N_\varkappa \rangle + \langle n_j N_\varkappa \rangle + \langle N_\varkappa \rangle - \langle n_i n_j \rangle)\, \delta(\omega_j + \omega_i - \Omega_\varkappa), \quad \text{(B.6)}$$

$$C_\gamma = 2\pi \sum_{j,\varkappa,l} |\gamma|^2 (\langle n_i n_j N_l \rangle + \langle n_j N_\varkappa N_l \rangle - \langle n_i N_\varkappa N_l \rangle - \langle n_i n_j N_\varkappa \rangle - \langle n_i n_j N_l \rangle$$
$$- \langle n_i N_\varkappa \rangle)\, \delta(\omega_i - \omega_j + \Omega_\varkappa - \Omega_l). \quad \text{(B.7)}$$

We perform the factorization procedure and apply the same approximations as in Chapter 3. For the time independent problem we find the steady state solution

$$\langle n_i\rangle_s = \left(\frac{n_i^0}{\tau_i} + \Phi_i + A\right)\Big/\left(\frac{1}{\tau_i} + B\right) \qquad \text{(B.8)}$$

where $A$, $B$ are given by

$$\begin{aligned}
A = {} & |\tilde{\lambda}|^2 N(\omega_i) \\
& + \sum_{\varkappa} |\tilde{\delta}|^2 N^0(\omega_i + \Omega_\varkappa)(N^0(\omega_i + \Phi_\varkappa) + 1) \\
& + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) + 1)\langle n_j\rangle_s \\
& + \sum_{j<i} |\tilde{\chi}_1|^2 (N^0(\omega_i - \omega_j)\langle n_j\rangle_s \\
& + \sum_{j} |\tilde{\beta}|^2 (N^0(\omega_i + \omega_j))(\langle n_j\rangle_s + 1) \\
& + \sum_{i,\varkappa} |\tilde{\gamma}|^2 \langle n_j\rangle_s (N^0(\omega_i - \omega_j + \Omega_\varkappa) + 1) \\
& \cdot N^0(\omega_j + \Omega_\varkappa - \omega_i); \\
B = {} & |\tilde{\lambda}|^2 + \sum_{\varkappa} |\tilde{\delta}|^2 (N^0(\omega_i - \Omega_\varkappa) - N^0(\omega_i + \Omega_\varkappa)) \\
& + \sum_{j>i} |\tilde{\chi}_2|^2 (N^0(\omega_j - \omega_i) - \langle n_j\rangle_s) \\
& + \sum_{j<i} |\tilde{\chi}_1|^2 (N^0(\omega_i - \omega_j) + 1 + \langle n_j\rangle_s) \\
& + \sum_{j} |\tilde{\beta}|^2 (\langle n_j\rangle_s - N^0(\omega_i + \omega_j)) \\
& + \sum_{j,\varkappa} |\tilde{\gamma}|^2 (N^0(\omega_j + \Omega_\varkappa - \omega_i) \\
& \cdot (N^0(\omega_i + \Omega_\varkappa - \omega_j) + 1 + \langle n_j\rangle_s) \\
& - N^0(\omega_i + \Omega_\varkappa - \omega_j)\langle n_j\rangle_s) .
\end{aligned}$$

For all possible values of the parameters and variables one finds $A > 0$, the numerator of Eq. (B.8) is always positive. In the denominator of Eq. (B.8) there are two terms which can lead to negative contributions

$$|\chi_2|^2 (N^0(\omega_j - \omega_i) - \langle n_j\rangle_s)$$

and

$$\begin{aligned}
& |\gamma|^2 (N^0(\omega_j + \Omega_\varkappa - \omega_i) \\
& \quad - N^0(\omega_i + \Omega_\varkappa - \omega_j))\langle n_j\rangle_s .
\end{aligned}$$

Both terms can only become negative for $\omega_i < \omega_j$.

## Appendix C

The applied kinetic equations have the structure

$$\partial_t \langle n_i\rangle = \Phi_i - \frac{\langle n_i\rangle - \langle n_i\rangle_0}{\tau_i} + F(\{n_j\}) . \qquad \text{(C.1)}$$

The nonlinear function $F(\{n_j\})$ is determined by both the interaction Hamiltonian $H_1$ and the transition probability $W_{\mu\nu}$. Quite generally, the highest nonlinear term cancels out. With

$$\begin{aligned}
F(\{n_j\}) = {} & a_i n_i + \sum_j a_j n_j + \sum_\varkappa a_\varkappa n_\varkappa + \cdots \\
& + \sum_j b_{ij} n_i n_j + \sum_\varkappa b_i n_i n_\varkappa + \sum_{j,\varkappa} b_{j\varkappa} n_j n_\varkappa + \cdots \\
& + \sum_{j,\varkappa} C_{ij} n_i n_j n_\varkappa + \cdots \qquad \text{(C.2)}
\end{aligned}$$

the steady state solution reads

$$\langle n_i\rangle_s = \qquad \text{(C.3)}$$

$$\frac{\Phi_i + \dfrac{\langle n_i\rangle}{\tau_i} + \sum\limits_{j,\varkappa} (a_j n_j + a_\varkappa n_\varkappa + b_{j\varkappa} n_j n_\varkappa + \cdots)}{\dfrac{1}{\tau_i} - a_i - \sum\limits_j b_{ij} n_j - \sum\limits_\varkappa b_{i\varkappa} n_\varkappa - \sum\limits_{j,\varkappa} C_{ij\varkappa} n_j n_\varkappa} .$$

A strong excitation of the mode $i$ requires a small or nearly vanishing denominator in Equation (C.3). At least one of the coefficients $b_{ij}$, $b_{i\varkappa}$ or $c_{i\varkappa}$ must be positive. From Eqs. (C.1) and (C.2) it then follows that

$$\partial_t \langle n_i\rangle = \cdots + n_i f + \cdots \qquad \text{(C.4)}$$

is required, with $f = f(n_j, n_\varkappa \ldots) > 0$. Equation (C.4) indicates that phonon processes with an "autocatalytic" reaction type of structure are necessary for Bose-condensation like behaviour.

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[1] H. Fröhlich, in: Theoretical Physics and Biology, ed. by M. Marois, North-Holland, Amsterdam 1969, p. 13.
[2] H. Fröhlich, Phys. Letters **26A**, 402 (1968).
[3] H. Fröhlich, Intern. J. Quantum Chem. **2**, 641 (1968).
[4] H. Fröhlich, Riv. Nuovo Cim. **7**, 399 (1977).
[5] H. Fröhlich, in: Synergetics, ed. by H. Haken, Teubner, Stuttgart 1973.
[6] H. Fröhlich, Phys. Letters **39A**, 21 (1975).
[7] H. Fröhlich, Proc. Nat. Acad. Sci. **72**, 4211 (1975).
[8] H. Fröhlich, IEEE: Microwave Theory **26**, 613 (1978).
[9] S. J. Webb and M. E. Stoneham, Phys. Letters **60A**, 267 (1977).
[10] S. J. Webb, M. E. Stoneham, and H. Fröhlich, Phys. Letters **63A**, 407 (1977).
[11] J. Berteaud, M. Dardalhon, N. Rebeyrotte, and D. Averbeck, C. R. Acad. Sci. **281**, 843 (1975).
[12] N. D. Devyatkov, Sov. Phys. USPEKHI **16**, 568 (1974).

[13] W. Grundler and F. Keilmann, Z. Naturforsch. **33c**, 15 (1978).
[14] W. R. Adey and S. M. Bawin (contribution Fröhlich), Neurosci. Res. Prog. Bull. **15**, 67 (1977).
[15] Fr. Kaiser, Phys. Letters **62A**, 63 (1977).
[16] Fr. Kaiser, Biol. Cybernetics **27**, 155 (1977).
[17] Fr. Kaiser, Z. Naturforsch. **33a**, 294 (1978), and **33a**, 418 (1978).
[18] D. Bhaumik, K. Bhaumik, and B. Dutta-Roy, Phys. Letters **56A**, 145 (1976).
[19] D. Bhaumik, K. Bhaumik, and B. Dutta-Roy, Phys. Letters **59A**, 77 (1976).
[20] D. Bhaumik, K. Bhaumik, B. Dutta-Roy, and M. H. Engineer, Phys. Letters **62A**, 197 (1977).
[21] T. M. Wu and S. Austin, Phys. Letters **64A**, 151 (1977).
[22] T. M. Wu and S. Austin, Phys. Letters **65A**, 74 (1978).
[23] Fr. Kaiser and M. Wagner, Z. Naturforsch. **32a**, 375 (1977) (henceforth referred to as I).
[24] Fr. Kaiser, Z. Naturforsch. **32a**, 697 (1977).
[25] Fr. Kaiser, Z. Naturforsch. **32a**, 805 (1977).
[26] H. Fröhlich, (private communication).
[27] M. Wagner in: Cooperative Phenomena, ed. by H. Haken and M. Wagner, Springer-Verlag, Berlin 1973, p. 381.
[28] M. Wagner in: Synergetics, ed. by H. Haken, Teubner, Stuttgart 1973, p. 246.
[29] M. Wagner in: Cooperative Effects, Progress in Synergetics, ed. by H. Haken, North-Holland, Amsterdam 1974, p. 215.