Generalized Peierls-Boltzmann Transport Equations for Phonons and Local Excitation Kinetics

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The Peierls-Boltzmann transport equation for phonons is re-formulated and modified by means of sequences of transport and statistical postulates. The transition probabilities within the collision term are expanded in a comprehensive way. The resulting nonlinear kinetic equations are applied to a simple model system, i. e. a local excitation coupled to a transport system. The steady state solutions reveal the possibility of a hysteresis-type of "transport phase transitions" from the "thermodynamic" branch to a "nonthermodynamic" one via a cumulative excitation. The stability of the solutions is checked and the approximations are discussed.

1. Introduction

Nonequilibrium phenomena have gained increasing interest in the last years. It has turned out that there exist close connections between these dynamical phenomena in engineering, biology, chemistry, physics and related topics[1]. A common feature of these phenomena is the fact that the nonequilibrium systems considered are open systems described by nonlinear evolution equations. Such systems can be driven far away from thermal equilibrium by an external stimulation and in most of the cases they can be stabilized in this nonequilibrium state by a flux through the system.

The manifold of these nonlinear structures seems to be restricted to very few types.

In general in an open system there are two dominant physical entities: an external stimulation (i. e. generalized forces) causing the transport through the system and a quantity being transported in response to the stimulation (i. e. generalized fluxes).

One possible external stimulation is the coupling of the relevant system to other systems of different temperatures (heat baths) thus leading in the case of condensed matter to a flux of phonons. The motivation for our interest in nonlinear phonon transport is twofold. On the one hand it seems important to know what kind of nonlinear structures can be established on the basis of microscopic physical principles, i. e. what types of "transport phase transitions" may arise. On the other hand one is interested in the kind of approximations that are necessary to arrive at solvable nonlinear kinetic equations and in the justification of the crude approximations which are necessary to reach this stage of description.

Nonequilibrium phenomena cannot be handled by the conventional methods like the Peierls-Boltzmann equation (PBE) in a relaxation time approximation. Nevertheless, nonlinear PBE's seem to be a very useful description if modified in an appropriate manner. We thus employ such a generalized and extended PBE for phonons, and take it in its fully nonlinear form.

The emphasis of this paper lies in the derivation of this generalization of the PBEs and in the simplification of these nonlinear equations to a manageable form.

Our starting point is a bilinear phonon density operator. After a series of conventional approximations and assumptions we end up with a set of nonlinear kinetic equations. To find their steady state solutions (nonlinear structures) we choose a model of utmost simplicity: a linear chain coupled to an additional local degree of freedom. We solve the nonlinear PBE and check the stability of the steady state solutions.

The result is a special type of transport phase transition. It is a hysteresis-like solution which indicates a discontinuous transition from the thermodynamic branch to the nonthermodynamic one and vice versa as a function of the phonon flux intensity.

Details of this transport phase transition and of an existing further type are discussed in a forthcoming paper.

2. Derivation of the Modified Peierls-Boltzmann Transport Formalism

Since the fundamental work of Peierls[2] on the heat conduction in crystals there has been great

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progress in phonon transport theory. In particular, very elegant theoretical formulations have been given that are very suitable to perform calculations for the transport properties of crystals which pertain to the neighbourhood of thermal equilibrium ("thermodynamic" branch of solutions)[3]. To avoid this restriction to the linear regime we must extend as well as simplify the equations to a form which enables us to look for nonlinear solutions. This is rather cumbersome, and hence for a first study of effects far from thermal equilibrium, it is absolutely necessary to restrain to a formalism of utmost simplicity.

A very direct approach to formulate a phonon transport theory is via the definition of a phonon density operator

$$\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)=\sum_{\mathbf{k}'\lambda'}[a^{+}(\mathbf{k}\,\lambda,t)\,a(\mathbf{k}'\,\lambda',t)\cdot\exp\{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}\}\cdot X(\mathbf{k}\,\lambda,\mathbf{k}'\,\lambda')+h.\,c.]\,. \quad (1)$$

(Here $\mathbf{k}$ is the wave vector and λ denotes the phonon branches.)

The definition of $\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)$ is not uniquely given. A neccessary condition is that the energy density of the mode $\mathbf{k}\,\lambda$ must be ($\hbar=1$)

$$\hat{\varepsilon}(\mathbf{k}\,\lambda,\mathbf{r},t)=\omega(\mathbf{k},\lambda)\,n(\mathbf{k}\,\lambda,\mathbf{r},t)\,. \quad (2)$$

The function $X(\mathbf{k}\,\lambda,\mathbf{k}'\,\lambda')$ restricts the deviation of $\mathbf{k}'$ from $\mathbf{k}$ in the wave packet and may be chosen as a Wigner function[3b] or as a Gauss function

$$X(\mathbf{k}\,\lambda,\mathbf{k}'\,\lambda')=\frac{1}{2\,V}\,\delta_{\lambda\lambda'}\exp\{-\alpha\,|\mathbf{k}-\mathbf{k}'|^{2}\} \quad (3)$$

as was done by Hardy[4]. (V is the total volume.)

The choice (3) has the advantage of being rather flexible with respect to the space extension parameter α. It was shown in[4] that the phonon density operator (1) as specified with (3) is a rather good approximation for

$$d<l_{\mathrm{F}}\ll|\alpha^{1/2}\ll L$$

where d is the lattice constant, l_{F} the range of interaction and L the length of the crystal.

The restriction to bilinearity in the definition of $\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)$ is justified also in the case of an anharmonic crystal if there is the possibility of a suitable canonical transformation to quasiharmonicity.

Let us assume now that the total Hamiltonian be given by

$$H=H_{0}+H_{\mathrm{I}} \quad (4)$$

where H_0 is the diagonal harmonic part of the lattice vibrations including some singular additional degrees of freedom and H_{I} the interaction Hamiltonian for all interactions between phonons as well as between phonons and local modes.

The Heisenberg equation of motion for the phonon density operator

$$-i\,\partial_{t}\,\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)=[H_{0}+H_{\mathrm{I}},\,\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)] \quad (5)$$

is the starting point for the derivation of a phonon transport equation. The first commutator

$$[\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t),H_{0}]=-\frac{1}{2\,V}\sum_{\mathbf{k}'}[\omega(\mathbf{k}\,\lambda)-\omega(\mathbf{k}'\,\lambda)]\cdot a^{+}(\mathbf{k}\,\lambda,t)\,a(\mathbf{k}'\,\lambda,t)\cdot\exp\{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}\}\cdot\exp\{-\alpha\,|\mathbf{k}-\mathbf{k}'|^{2}\}-h.\,c. \quad (6)$$

may be approximated by

$$[\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t),H_{0}]=-i\,\mathbf{v}(\mathbf{k}\,\lambda)\,\nabla_{r}\,\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)+O[\alpha^{-1}\,V^{-1}\,\partial_{k}^{2}\,\omega(\mathbf{k}\,\lambda)] \quad (7)$$

where we have made a series expansion

$$\omega(\mathbf{k}'\,\lambda)-\omega(\mathbf{k}\,\lambda)=\nabla_{k}\,\omega(\mathbf{k}\,\lambda)\cdot(\mathbf{k}-\mathbf{k}')+O[\alpha^{-1}\,V^{-1}\,\partial_{k}^{2}\,\omega(\mathbf{k}\,\lambda)]$$

and

$$\nabla_{k}\,\omega(\mathbf{k}\,\lambda)=\mathbf{v}(\mathbf{k}\,\lambda) \quad (8)$$

being the phonon group velocity.

If there would be no interaction H_{I}, the Heisenberg equation of motion could be written in the form

$$[\partial_{t}+\mathbf{v}(\mathbf{k}\,\lambda)\,\nabla_{r}]\,\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)=O[\alpha^{-1}\,V^{-1}\,\partial_{k}^{2}\,\omega(\mathbf{k}\,\lambda)]\,. \quad (9)$$

This pertains to the harmonic, translationally invariant crystal. The right hand side of Eq. (9) may be neglected provided α is chosen large enough or if there is no dispersion [i. e. $\partial_{k}^{2}\,\omega(\mathbf{k}\,\lambda)=0$]. In the general case ($H_{\mathrm{I}}\neq 0$) the Heisenberg equation for $\hat{n}(\mathbf{k}\,\lambda,\mathbf{r},t)$ reads

$$[\partial_{t}+\mathbf{v}(\mathbf{k}\,\lambda)\nabla_{r}]\hat{n}=-i[\hat{n},H_{\mathrm{I}}]+O\,(\alpha^{-1}\,V^{-1}\,\partial_{k}^{2}\,\omega)\,. \quad (10)$$

Equation (10) leads to the general "Boltzmann" equation for phonons. The second term on the left hand side is the conventional linear transport term. Such a type of streaming term is always found if H_0 is a one particle Hamiltonian, even if one starts with the Liouville equation for the density matrix and if one only considers the lowest order of the BBGKY hierarchy of equations[5]. For higher orders a mixing between the transport and collision term [right hand side of Eq. (10)] appears in these derivations, whereas it is not present in our equations. In principal the collision term of Eq. (10) also incorporates higher forms of phonon densities. For these densities further kinetic equations arise and a Bogoljubov hierarchy is established. To avoid this we simplify the collision term in such a way that the first equation of the hierarchy is disentangled from the rest.

3. Simplification of the Streaming Term

If the commutator (7) would be averaged over the whole space, it would vanish as a consequence of the wave packet description. But this commutator plays the role of a phonon source term

$$\partial_t \hat{n}(\boldsymbol{k}\lambda, \boldsymbol{r}, t) = -\operatorname{div}_{\boldsymbol{r}} \hat{j}(\boldsymbol{k}\lambda, \boldsymbol{r}, t) \tag{11}$$

where

$$\hat{j}(\boldsymbol{k}\lambda, \boldsymbol{r}, t) = \boldsymbol{v}(\boldsymbol{k}\lambda)\, \hat{n}(\boldsymbol{k}\lambda, \boldsymbol{r}, t)\,. \tag{12}$$

Until now we have assumed that our system is closed and described by an internal Hamiltonian. To have an open transport system an external stimulus should create and annihilate phonons in certain regions of the system, e. g. at the boundaries (thermal gradient).

In general we would have to introduce an additional Hamiltonian H_{ext} for the coupling to the external world, yielding additional terms on the right hand side of Equation (10). Since this procedure in most cases is not practicable we henceforth exclude all external source and sink regions from the spatial averaging. Thus

$$[\boldsymbol{v}(\boldsymbol{k}\lambda)\, \nabla_r \hat{n}(\boldsymbol{k}\lambda, \boldsymbol{r}, t)]_{av.\boldsymbol{r}} = -V^{-1}\, \Phi(\boldsymbol{k}\lambda, t) \tag{13}$$

is the driving force for our system producing the phonon flux. To install the space-independent flux $\Phi(\boldsymbol{k}\lambda, t)$ it is necessary to think of an energy "sink-source dipole" at the boundary.

4. Simplification of the Collision Term

There is no difficulty to take the spatial average of the commutator for the collision term. With

$$\int_V \mathrm{d}^3 r\, \hat{n}(\boldsymbol{k}\lambda, \boldsymbol{r}, t) = \hat{N}(\boldsymbol{k}\lambda, t) = a^+(\boldsymbol{k}\lambda, t)\, a(\boldsymbol{k}\lambda, t) \tag{14}$$

and the assumption that the commutator $[\hat{n}, H_{\text{I}}]$ is replaceable by its spatial average we obtain

$$\partial_t \hat{N}(\boldsymbol{k}\lambda, t)\Big|_{\text{Coll}} = -i[\hat{N}(\boldsymbol{k}\lambda, t), H_{\text{I}}]\,. \tag{15}$$

The time derivative of $\hat{N}(\boldsymbol{k}\lambda, t)$ is computed in the usual way, i. e. either

$$\partial_t \langle \hat{N}(\boldsymbol{k}\lambda, t)\rangle_c = \partial_t \langle \Psi(t) | \hat{N}(\boldsymbol{k}\lambda) | \Psi(t)\rangle \tag{16}$$

or

$$\partial_t \langle \hat{N}(\boldsymbol{k}\lambda, t)\rangle_c = \partial_t \operatorname{Tr}[\varrho(t)\, \hat{N}(\boldsymbol{k}\lambda)]\,, \tag{17}$$

where $\langle \hat{N}(\boldsymbol{k}\lambda, t)\rangle$ is the expectation value of $\hat{N}(\boldsymbol{k}\lambda, t)$ and the index c refers to "collision term".

Equation (16) is easily handled by Dirac's perturbation theory, whereas for Eq. (17) the master equation may be employed (see appendix A). For Eq. (16) we get

$$\partial_t \langle \hat{N}(\boldsymbol{k}\lambda, t)\rangle_c = \sum_\mu N_{\boldsymbol{k}}^{(\mu)}\, \partial_t |c_\mu(t)|^2 \tag{18}$$

with

$$\begin{aligned}\partial_t |c_\mu(t)|^2 = i \sum_{\alpha,\beta,\nu} c_\nu(t')\, c_\beta{}^*(t') &\cdot (\exp\{-i(E_\mu - E_\alpha)t\}\, T^+_{\mu\nu}\, T^-_{\beta\alpha}\, H_{\text{I},\alpha\mu} \\ &- \exp\{-i(E_\alpha - E_\nu)t\}\, T^-_{\nu\mu}\, T^+_{\alpha\beta}\, H_{\text{I},\mu\alpha})\end{aligned}$$

and

$$T^+_{\mu\nu} = \langle \mu | T^+ \exp\{-i \int_{t'}^{t} \mathrm{d}\tau\, H_{\text{I}}(\tau)\} | \nu\rangle\,. \tag{19}$$

Equation (17) may be rewritten as

$$\partial_t \langle N(\boldsymbol{k}\lambda, t)\rangle_{\text{c}} = \sum_\mu N_k{}^{(\mu)}\, \partial_t \hat{\varrho}_\mu(t)\,, \tag{20}$$

where $\hat{\varrho}_\mu(t)$ is the diagonal part of the density matrix and which will satisfy the Zwanzig master equation [6] in the gain and loss form:

$$\begin{aligned}\partial_t \hat{\varrho}_\mu(t) = \sum_\mu \int_0^t \mathrm{d}\tau\, [\hat{\varrho}_\nu(t-\tau)\, W_{\nu\mu}(\tau) \\ - \hat{\varrho}_\mu(t-\tau)\, W_{\mu\nu}(\tau)]\end{aligned} \tag{21}$$

with

$$W_{\mu\nu}(\tau) = -[L_{\text{s}} \exp\{-i(L_0 + Q\, L_{\text{s}})\tau\}\, L_{\text{s}}]_{\mu\mu\nu\nu}\,. \tag{22}$$

$L_{\text{s}} = [H_{\text{I}},\ ]$ and $L_0 = [H_0,\ ]$ are the tetradic Liouville operators and $P = 1 - Q$ is the diagonalization projector.

The Eq. (21) is only valied if we assume that the nondiagonal part of the density matrix is negligible for the initial time, i. e.

$$Q\, \hat{\varrho}(t=0) \equiv \hat{\varrho}_{\text{nd}}(t=0) = 0\,. \tag{23}$$

This assumption is a rather crude one and is still very much under discussion, although for mathematical convenience it is used in nearly all practical calculations.

A similar assumption must be incorporated in Equation (19). Here we make use of a kind of random phase approximation

$$c_\nu(t')\, c_\beta^*(t') \to |c_\nu(t')|^2\, \delta_{\nu\beta} . \tag{24}$$

This approximation must only be satisfied for the initial time $t = t'$.

In addition, we introduce a kind of Markofficity assumption in the form

$$\varrho_\mu(t-\tau)\, W_{\mu\nu}(\tau) \approx \varrho_\mu(t)\, W_{\mu\nu}(\tau) . \tag{25}$$

The assumptions (23) and (24) are more or less equivalent. The Markofficity approximation (25) however, requires a detailed analysis with respect to the assumption (23), since they are not independent from each other. Details will be published elsewhere[7].

Furthermore it can be shown that with the assumptions (23) to (25) there is no relevant difference between the two approaches (16) and (17) to the collision term. Applying the Goldberger-Adams-Theorem to the tetradic kernel (22) of Eq. (21), we can derive the same expansion which one gets if one expands equation (19) (see Appendix B). With these assumptions and approximations the general "Boltzmann" equation for phonons [Eq. (10)] reads (henceforth, $\boldsymbol{k}\lambda$ will be abbreviated by k)

$$\partial_t \langle \hat{N}_k \rangle - \Phi(k,t) = \sum_\mu N_k^{(\mu)}\, \partial_t\, \varrho_\mu(t) \tag{26}$$

where

$$\partial_t\, \varrho_\mu(t) = \partial_t \big(\sum_\nu T^+_{\mu\nu}\, T^-_{\nu\mu}\big)\, \varrho_\nu(t) \tag{27}$$

and where we have made use of Eqs. (13), (20) and (B 5). The collision term [r.h.s. of Eq. (26)] can be rearranged in the following way

$$\begin{aligned}\sum_\mu N_k^{(\mu)}\, \partial_t\, \varrho_\mu(t) &= \sum_{\mu,\nu} N_k^{(\mu)}\, \varrho_\nu(t)\, \partial_t W_{\mu\nu}(t)\\ &= \sum_\mu N_k^{(\mu)} \sum_\nu [\varrho_\nu(t) - \varrho_\mu(t)]\, \partial_t W_{\mu\nu}(t)\\ &= \sum_{m=0}^{\infty} m \Big(\overset{(1)}{\sum_{\mu,\nu}} \varrho_\nu(t) - \overset{(2)}{\sum_{\mu,\nu}} \varrho_\nu(t) \Big)\, \partial_t W_{\mu\nu}(t) .\end{aligned} \tag{28}$$

The restrictions for the summations originate from the separation into creation and annihilation processes i. e.

$$\overset{(1)}{\sum} \to N_k^{(\mu)} = N_k^{(\nu)} + m , \tag{1}$$

$$\overset{(2)}{\sum} \to N_k^{(\mu)} = N_k^{(\nu)} - m . \tag{2}$$

We then are left with the general Boltzmann equation

$$\partial_t \langle \hat{N}_k \rangle - \Phi(k,t) = \sum_{m=0}^{\infty} m \Big(\overset{(1)}{\sum_{\mu,\nu}} - \overset{(2)}{\sum_{\mu,\nu}} \Big)\, \varrho_\nu(t)\, \partial_t W_{\mu\nu}(t) \tag{29}$$

with

$$W_{\mu\nu}(t) = T^+_{\mu\nu}\, T^-_{\nu\mu} .$$

5. Expansion of the Transition Probabilities

We choose the most compact form for the transition probability i. e.

$$\partial_t W_{\mu\nu}(t) = \partial_t (T^+_{\mu\nu}\, T^-_{\nu\mu}) . \tag{30}$$

It is convenient to introduce a small parameter λ

$$H_{\mathrm{I}} = \lambda V . \tag{31}$$

Expanding Eq. (30) into a power series with respect to the interaction Hamiltonian λV and restricting ourselves to transitions with energy conservation between initial and final state we are left with

$$\begin{aligned}\partial_t W_{\mu\nu}(t) = \big| &O(\lambda) + O(\lambda^2)\\ &+ O(\lambda^3) + \dots \big|^2\, \frac{2 - 2\cos(E_\mu - E_\nu)\, t}{(E_\mu - E_\nu)^2}\end{aligned} \tag{32}$$

where

$$\begin{aligned}O(\lambda^n) = (-1)^{n+1} &\sum_{\alpha_i} \lambda^n\, V_{\mu\alpha_1} V_{\alpha_1\alpha_2} \dots V_{\alpha_{n-1}\nu}\\ &\cdot (E_{\alpha_1} - E_\nu)^{-1} \dots (E_{\alpha_{n-1}} - E_\nu)^{-1} .\end{aligned} \tag{33}$$

We have discarded all terms of a "mixed" time behaviour, i. e. those terms which contain time-periodicity with respect to intermediate states. In doing so we utilized the philosophy that a given multiple transition respectively is only taken in the lowest order where it first appears and it is assumed, that it is only taken into account, if all the transitions below its order are forbidden.

In this way we only consider "irreducible transitions". These are those transitions, which neither contain the initial nor the final states as an intermediate state. We end up with the Golden Rules:

$$\begin{aligned}\partial_t W_{\mu\nu}(t) = {} & 2\pi \lambda^2\, V_{\mu\nu} V_{\nu\mu}\, \delta(E_\mu - E_\nu)\\ &+ 2\pi\lambda^4 \Big| \sum_\alpha V_{\mu\alpha} V_{\alpha\nu} (E_\alpha - E_\nu)^{-1} \Big|^2\, \delta(E_\mu - E_\nu)\\ &+ 2\pi\lambda^6 \Big| \sum_{\alpha,\beta} V_{\mu\alpha} V_{\alpha\beta} V_{\beta\nu} (E_\alpha - E_\nu)^{-1}\\ &\qquad \cdot (E_\beta - E_\nu)^{-1} \Big|^2\, \delta(E_\mu - E_\nu) + \dots\end{aligned} \tag{34}$$

where we have introduced the least problematic of our assumptions i. e.

$$\partial_t\, \frac{1 - \cos(E_\mu - E_\nu)\, t}{(E_\mu - E_\nu)^2} \to \pi\, \delta(E_\mu - E_\nu) . \tag{35}$$

This postulate requires a high density of states or a great number of degrees of freedom such that the poincaré periodicity t_p is large compared with the "physical" time t, and it leads to irreversibility.

The first term on the right hand side of Eq. (34) is the well known Fermi Golden Rule, the expressions for $n = 2, 3$ are the first, second ... Higher Golden Rules. For the latter energy conservation is required only between initial and final state but not for transitions to intermediate states. Thus, the Fermi Golden Rule describes direct processes whereas the Higher Golden Rules describe indirect transitions via energy non conserving intermediate states.

6. Further Simplifications and Application to a Model System[8]

The application of our general Boltzmann equation (29) to arbitrary phonon transporting systems requires further approximations. It is advantageous to illustrate this procedure at a specific example. To keep the frame of this study within a reasonable limits we choose a model of utmost simplicity. Our model consists of a linear chain, representing the phonon transporting system S_1, and a non-transporting system S_2, e.g. a single additional degree of freedom with excitation energy ω_s. The total Hamiltonian of the coupled system is given by

$$H = H_p + H_s + H_{I,1} + H_{I,2} \equiv H_0 + H_I \quad (36)$$

where

$$H_p = \sum_{\boldsymbol{k}} \omega_k \, a_k^+ \, a_k \quad (37)$$

and

$$H_s = \omega_s \, b_s^+ \, b_s \quad (38)$$

are the diagonal parts H_0 describing the harmonic part of the chain vibrations and of the additional degree of freedom respectively. Anharmonic contributions of the linear chain are contained in $H_{I,1}$. $H_{I,2}$ represents the interaction between the transporting and nontransporting system and needs further specification.

For the transporting system S_1 we get from Eqs. (29) and (36) the kinetic equation

$$\partial_t \langle \hat{N}_k \rangle - \Phi(k,t) = -\frac{\langle \hat{N}_k \rangle - \langle \hat{N}_k \rangle_0}{\tau_k} + \sum_{m=0}^{\infty} m \left(\sum_{\mu,\nu}^{(1)} - \sum_{\mu,\nu}^{(2)} \right) \varrho_\nu(t) \, \partial_t W_{\mu\nu}(t) \quad (39)$$

and for the local excitation

$$\partial_t \langle \hat{N}_s \rangle = -\frac{\langle \hat{N}_s \rangle - \langle \hat{N}_s \rangle_0}{\tau_s} + \sum_{m=0}^{\infty} m \left(\sum_{\mu,\nu}^{(1)} - \sum_{\mu,\nu}^{(2)} \right) \varrho_\nu(t) \, \partial_t W_{\mu\nu}(t) \, . \quad (40)$$

The first term on the right hand side of Eq. (39) and of Eq. (40) is a relaxation term. It describes additional relaxations which originate either from the anharmonic Hamiltonian $H_{I,1}$ or from defects in the chain or from those coupling terms which are not considered explicitely. Such additional relaxation paths are always present in realistic systems. We handle these contributions in a BKG approximation, i. e. as a linear relaxation term. The relaxation times τ_k and τ_s play a very important role in the stability conditions of the steady state solutions of Eqs. (39) and (40).

In equilibrium, i. e. $\langle \hat{N}_k \rangle = \langle \hat{N}_k \rangle_0$ and $\langle \hat{N}_s \rangle = \langle \hat{N}_s \rangle_0$ the relaxation terms are zero. Away from equilibrium, they express the irreversibility. They guarantee that the systems tend to assume thermal equilibrium even without a coupling between S_1 and S_2, if there is no flux.

The use of the kinetic Eqs. (39) and (40) has the advantage that there is no need to specify the coupling Hamiltonian to the external world which would have been necessary if we had not taken the transport $\Phi(k,t)$ as an external stimulus. We emphasize, however, that Φ has to be made consistent with the definition (13) after the solutions have been found.

7. Steady State Solutions

Let us assume now that a predominant part of the nondiagonal interaction Hamiltonian $H_{I,2}$ be given by

$$H_{I,2} \equiv \lambda V = \lambda \sum_k \gamma(k,s) \, (a_k + a_{-k}^+) \, (b_s + b_s^+) \, , \quad (41)$$

where b_s^+ represents the single local excitation and the a's are the phonon operators.

Further let us assume that a 3-phonon process is necessary for the excitation of the local degree of freedom,

$$\omega_s = \omega(k) + \omega(k') + \omega(k'') \equiv \{\omega(k)\} \, . \quad (42)$$

Then the second Higher Golden Rule [$n = 3$ in Eq. (34)] is necessary to allow for a process with energy conservation between initial and final states. This then would be a cumulative excitation via energy non conserving intermediate states. For the collision term of the transporting system we would have then

$$\partial_t \langle N_k \rangle_c = 2\pi \sum_{\mu,k,k'} \varrho_\mu(t) A(k,k',k'')\ \delta[\omega_s - \{\omega(k)\}]$$
$$\cdot [(N_s^{(\mu)})^3 (N_k^{(\mu)}+1)(N_{k'}^{(\mu)}+1)(N_{k''}^{(\mu)}+1) - (N_s^{(\mu)}+1)^3 N_k^{(\mu)} N_{k'}^{(\mu)} N_{k''}^{(\mu)}] \equiv F(N_s, N_k) \qquad (43)$$

where $$A(k,k',k'') = \gamma(k,s)^2 \gamma(k',s)^2 \gamma(k'',s)^2 \left(\frac{1}{E_s+E_k}\left(\frac{1}{E_s-E_{k''}} + \frac{1}{E_s-E_{k'}}\right) + \text{cycl.}\right)^2 .$$

For the local degree of freedom this equation reads

$$\partial_t \langle \hat{N}_s \rangle_c = -\sum_k F(N_s, N_k) . \qquad (44)$$

Thus we have to solve the two kinetic Eqs. [vid. (39) and (40)]

$$\partial_t \langle \hat{N}_k \rangle - \Phi(k,t) = -\frac{\langle \hat{N}_k \rangle - \langle \hat{N}_k \rangle_0}{\tau_k} + F(N_s, N_k) , \qquad (45)$$

$$\partial_t \langle \hat{N}_s \rangle = -\frac{\langle \hat{N}_s \rangle - \langle \hat{N}_s \rangle_0}{\tau_s} - \sum_k F(N_s, N_k) . \qquad (46)$$

It is immediately evident that the thermal equilibrium

$$\langle \hat{N}_s \rangle_0 = (e^{\beta\omega_s} - 1)^{-1} \qquad (47)$$
$$\beta = (k_B T)^{-1}$$
$$\langle \hat{N}_k \rangle_0 = (e^{\beta\omega(k)} - 1)^{-1} \qquad (48)$$

is a stationary solution, since for this solution $F(N_s, N_k)$ is zero. If we perform the summation over μ in Eq. (43) the function $F(N_s, N_k)$ will not be of a product form which may be seen from the expression

$$\sum_\mu \varrho_\mu(t)(N_s^{(\mu)})^3 (N_k^{(\mu)}+1)(N_{k'}^{(\mu)}+1)(N_{k''}^{(\mu)}+1)$$
$$= \overline{N_s^3 (N_k+1)(N_{k'}+1)(N_{k''}+1)} . \qquad (49)$$

At this stage 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 factorization procedure. In a forthcoming paper[9] we will show that the structure and stability of the steady state solutions of Eqs. (45) and (46) is nearly unchanged for different decoupling methods. A necessary condition is that the procedure has to be such that the thermal equilibrium remains a solution for vanishing phonon input, i. e. $\Phi(k,t) = 0$.

To be specific, we choose

$$\overline{N}_s = (e^{\beta_s \omega_s} - 1)^{-1}, \quad \beta_s = (k_B T_s)^{-1} \qquad (50)$$

where T_s is the "eigentemperature" for the local excitation.

Since there is a great number of phonon-modes which contribute to the flux, we may assume that each single mode in the transporting system is only slightly excited beyond thermal equilibrium. Then there are analytic correlations between N_k, $N_{k'}$ and $N_{k''}$. Then our multivariable system of kinetic equations [Eqs. (45) and (46)] is reduced to a two variable system.

This restriction is profitable for mathematical convenience. Yet, it turns out that a sufficient condition for the phonon excitations will be that they might be treated as parameters which are slightly changing with the phonon flux. One has to keep in mind, therefore that the chosen values for these "parameters" must be consistent with the external stimulus.

Restricting ourselves to steady state solutions, we have computed the excitation $\langle \hat{N}_s \rangle_{SS}$ as a function of external phonon flux $\Phi(k,t)$. In Fig. 1 the result for the local excitation $\langle \hat{N}_s \rangle_{SS}$ above thermal equilibrium is shown for different values of the effective additional relaxation time τ_s. We realize that for increasing flux Φ there is a critical value Φ_{cu} where the steady state solution "jumps" from the "thermodynamic" branch to a "non-thermodynamic" one above. On the other hand, if the flux continuously decreases from a value above Φ_{cu} there again is a critical value Φ_{cl}, where the "non-thermodynamic" solution falls down to the "thermodynamic" one. Features of particular interest are the "phase-transition" behaviour and the "hysteresis" in the transition region. After its existence has been established, it must be proven that the "nonthermodynamic" branch can be stable. In Fig. 2 the result for the stability discussion of the solutions is given. For the stability calculations Ljapunov's first method has been used [10]. By direct computation it has been found that there are extended regions on both sides of the stationary solutions where the trajectories will run towards the stable steady states. Thus global stability can be proved.

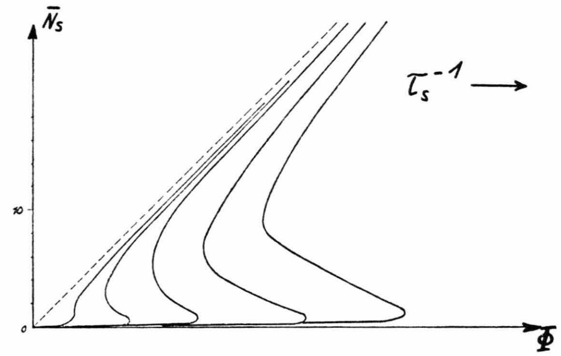

Fig. 1. Excitation of a local mode coupled to a one-dimensional phonon system. $\bar{N}_S$ is the occupation deviation from thermal equilibrium. Φ is the average phonon flux and τ_S the relaxation time for additional scattering processes. For each curve τ_S is a fixed parameter.

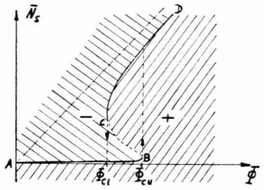

Fig. 2. Transport-phase-transition for a local mode coupled to a one-dimensional phonon system. The + and − sign regions indicate that there a non-stationary solution would tend to higher or lower values respectively. For increasing flux the critical value is Φ_{cu}, for decreasing it is Φ_{cl}. The transition exhibits a hysteresis. Excitations A—B and C—D are stable (stable node behaviour), B—C is absolutely unstable (saddle point).

8. Summary and Outlook

To give an interpretation of the preciding results it is useful to conceive the local excitation as an incoherent cumulative phenomenon. In our particular case 3 phonons combine in succession to create the high-energetic local excitation. An important feature is the stabilization of the local energy storage by means of the phonon flux. It is interesting to note that the stabilization requires additional relaxation terms, which represent "local heat baths" (anharmonicity, defects, etc.). But in physically realistic systems such additional paths are always present. So our result seems to make physical sense. Also, the order of magnitude for the phonon flux near the critical region does not seem to be exorbitantly high for realistic values of the relevant chain parameters.

We must note, however, that the employed approximations and assumptions cannot be justified yet in a satisfactory manner. First of all we have tried to derive – from a microscopic basis – transport equations for phonons. The assumptions (1), (13) and (15) are the transport postulates that are conventional in the theory of phonon transport, whereas the assumptions (23) to (25) are well-adopted in statistical physics though they are still very much under discussion.

We have investigated about 30 different forms of the interactions and their related processes. It turns out that only the above hysteresis-like behaviour and a threshold-like behaviour are found as a solution. Thus, the relevant behaviour of the solutions of our generalized Boltzmann equation does not depend critically on the structural form of the nondiagonal Hamiltonian λV nor on the order of the perturbation theoretical expansion. The only prerequisite for this result is the coupling of a local, nontransporting degree of freedom to a transporting system (i. e. many degrees of freedom) and the restriction to processes with energy conservation between initial and final states. The details of this study will be given elsewhere [9].

To circumvent the problem of approximations as well as to establish experience for their examination it would be highly desirable to study exactly solvable models and to supplement the formalism by experimental results. There is hope that in the near future both investigations will be possible.

Appendix A: Derivation of Equation (19)

The wave function $|\Psi(t)\rangle$ of the system is projected to the known complete set of eigenfunctions of the unperturbed Hamiltonian H_0

$$|\Psi(t)\rangle = \sum_\nu c_\nu(t) \exp\{-i E_\nu t\} |\nu\rangle \qquad \text{(A 1)}$$

with $$H_0 |\nu\rangle = E_\nu |\nu\rangle \,.$$

From Eq. (16) we get with the expansion (A 1)

$$\partial_t \langle \hat{N}(k\lambda, t)\rangle_c = \sum_\mu N_k{}^{(\mu)} \, \partial_t |c_\mu(t)|^2 \qquad \text{(A 2)}$$

with

$$N_k^{(\mu)} = \langle \mu | \hat{N}(k\lambda) | \mu \rangle \,. \tag{A 3}$$

The wave function $| \Psi(t) \rangle$ satisfies the Schrödinger equation

$$i\,\partial_t | \Psi(t) \rangle = H | \Psi(t) \rangle \tag{A 4}$$

where H is given by Equation (4). A formal solution of Eq. (A 4) is

$$| \Psi(t) \rangle = U_s(t,t') | \Psi(t') \rangle \tag{A 5}$$

where

$$U_s(t,t') = \exp\{-i H (t-t')\} \tag{A 6}$$

is the U-matrix for H not depending on time.

$|\Psi(t)\rangle$ and $|\Psi(t')\rangle$ in Eq. (A 5) are replaced by the expansion (A 1) and $U_s(t,t')$ is expanded with the aid of the Goldberger Adams Theorem [11]:

$$U_s(t,t') = \exp\{-i H_0 t\} \cdot T^+ \exp\{-i \int_{t'}^{t} \mathrm{d}\tau\, H_{\mathrm{I}}(\tau)\} \exp\{i H_0 t'\} \tag{A 7}$$

where

$$H_{\mathrm{I}}(\tau) = \exp\{i H_0 \tau\} H_{\mathrm{I}} \exp\{-i H_0 \tau\} \tag{A 8}$$

and T^+ is the time ordering operator of Dyson.

From Eq. (A 5) we get

$$c_\mu(t) = \sum_\nu T^+_{\mu\nu}\, c_\nu(t')$$

$$T^+_{\mu\nu} = \langle \mu | T^+ \exp\{-i \int_{t'}^{t} \mathrm{d}\tau\, H_{\mathrm{I}}(\tau)\} | \nu \rangle \,. \tag{A 9}$$

In a similar way one can derive

$$c_\mu^*(t) = \sum_\nu T^-_{\nu\mu}\, c_\nu^*(t') \tag{A 10}$$

with

$$T^-_{\nu\mu} = (T^+_{\mu\nu})^* \,.$$

The same procedure but with Eq. (A 4) instead of (A 5) leads to

$$i\,\partial_t c_\mu(t) = \sum_{\nu,\alpha} \exp\{i(E_\mu - E_\alpha)t\} (H_{\mathrm{I}})_{\mu\alpha} T^+_{\alpha\nu}\, c_\nu(t') \,. \tag{A 11}$$

(A 9) and (A 11) together with

$$\partial_t | c_\mu(t) |^2 = \partial_t c_\mu(t) \cdot c_\mu^*(t) + c.\,c.$$

lead to Equation (19).

Appendix B

From Eq. (19) and the random phase approximation (24) we get ($H_{\mathrm{I}} \equiv \lambda V$)

$$\partial_t | c_\mu(t) |^2 = i \sum_{\alpha,\beta,\nu} [\exp\{-i(E_\mu - E_\alpha)t\} \cdot T^+_{\mu\nu} T^-_{\nu\alpha} \lambda V_{\alpha\mu} - c.\,c.] \, | c_\nu(t') |^2 \,. \tag{B 1}$$

This equation can be written as

$$\partial_t | c_\mu(t) |^2 = \partial_t \sum_\nu (T^+_{\mu\nu} T^-_{\nu\mu}) | c_\nu(t') |^2 \tag{B 2}$$

which can be verified by direct inspection. [$T^+_{\mu\nu}$ is given by Eq. (A 9).] On the other side the transition probability $W_{\mu\nu}(\tau)$ [Eq. (22)] can be transcribed by means of $(L_s)_{ijkl} = (H_{\mathrm{I}})_{ik}\, \delta_{jl} - (H_{\mathrm{I}})_{lj}\, \delta_{ik}$. This yields

$$W_{\mu\nu}(\tau) = -\sum_{i,j} \lambda^2 [V_{\nu i} (T^+_{i\nu j\mu} V_{j\mu} - T^+_{i\nu\mu j} V_{\mu j}) + V_{i\nu} (T^+_{\nu i\mu j} V_{\mu j} - T_{\nu ij\mu} V_{j\mu})]$$

where

$$T^+_{\nu i\mu j} = \exp\{-i\tau(L_0 + Q L_s)\}\big|_{\nu i\mu j} \tag{B 3}$$

which can be rewritten as

$$T^+_{ijkl} V_{kl} = \exp\{-i(E_i - E_j)t\}\, T^+_{ik} V_{kl} T^-_{lj} \tag{B 4}$$

with T^+_{ij} given by Equation (A 9).

Equations (21) and (25) put together with (B 3) and (B 4) result in a very simple looking equation

$$\partial_t \varrho_\mu(t) = \partial_t [\sum_\nu (T^+_{\mu\nu} T^-_{\nu\mu})]\, \varrho_\nu(t) \tag{B 5}$$

which has the same structure as Equation (B 2). But there exists a remarkable difference. On the right hand side of Eq. (B 2) we have $| c_\mu(t') |^2$ i. e. the initial time t' whereas in Eq. (B 5) there appears the same time t on both sides of the equation.

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