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Coherent States and Irreversible Processes in Anharmonic Crystals*

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Irreversible phenomena involving phonons in a slightly anharmonic crystal are investigated using coherent states as a basis. This basis retains the advantages of the classical theory, in which phase relations are clearly exhibited, for a quantum-mechanical system. In the coherent-state basis the equation of motion for the density matrix has an obvious correspondence with the classical Liouville equation. In particular, the connection with the action-angle variables of Brout and Prigogine is elucidated. A new, rapid proof of the Brout-Prigogine equation is given using the method of semi-invariants. This technique exhibits higher-order corrections in a usable form. The quantum corrections to the classical equation of motion for the density function are shown to be due to extra terms involving second derivatives in the action-angle variables. The Peierls master equation is then derived from the Brout-Prigogine equation. The important problem of elastic scattering of phonons is treated by our method in an appendix.

I. INTRODUCTION

THE main purpose of the present work is to exhibit the utility of the coherent-state basis[1] for the description of irreversible processes. Although similar techniques may be applied to other systems of interacting bosons, we restrict our attention to the problem of phonons in a slightly anharmonic crystal. Elastic scattering by defects is discussed in the Appendix. In the coherent-state representation, the equation of motion for the density matrix although fully quantum-mechanical, has an obvious correspondence with the classical Liouville equation. The correspondence with the action-angle variables used by Brout and Prigogine[2,3] is elucidated. (For a coherent state $|\alpha\rangle$, the parameter α is related to the action J and the angle ϕ by $\alpha = J^{1/2}\exp(i\phi)$.) The coherent states, which in the classical limit describe classical harmonic-oscillator motion,[1,4] have other advantages when compared to the traditional number states. The phase relations so interesting in a discussion of irreversibility are at all times clearly exhibited. Number eigenstates have completely indeterminate phase.[5] Moreover, the coherent states correspond closely to nearly all intuitive thinking on our subject, based as it is on wave propagation. For the number states $|n\rangle$, the mean oscillator position $\langle n|x(t)|n\rangle$ always vanishes, no matter how large n. In contrast,[4] coherent states give a mean $\langle\alpha|x(t)|\alpha\rangle$ of $\cos(\omega t-\phi)$. Finally, we note that a classical driving force excites the coherent state of an oscillator.[4] A careful treatment of the coupling of crystals to massive heat reservoirs should take this into account.

In Sec. II, the necessary mathematical techniques are developed. These techniques are applied to the evolution of the density matrix in an anharmonic solid in Sec. III. We shall see that the general quantum Liouville equation derived differs from that of Brout and Prigogine by the addition of terms involving second derivatives in the action-angle variables. The latter terms are of order N^{-1} relative to the "classical terms," where N is the mean occupation of an oscillator, and hence establish the classical limit and corrections thereto. In Sec. IV a short derivation of the Brout-Prigogine master equation[2,3] is given. Higher order corrections are exhibited in a useful form. In Sec. V, we use the Brout-Prigogine master equation to derive the Peierls equation[6,7] for the time rate-of-change of the mean number of phonons in a given mode of vibration. Finally, some remarks are made on the derivation of the Peierls equation.

II. MATHEMATICAL PRELIMINARIES

The reader is referred to Refs. 1 and 4 for a full discussion of coherent states. Normalizing the creation and destruction operators for an oscillator, $a^\dagger$ and a, so that $a^\dagger a = N_{\rm op}$, $N_{\rm op}$ having eigenvalues 0, 1, 2, $\cdots$, the coherent state $|\alpha\rangle$ (α is an arbitrary complex number) is given by

$$
\begin{aligned}
a|\alpha\rangle &= \alpha|\alpha\rangle \\
|\alpha\rangle &= \exp(-\tfrac{1}{2}|\alpha|^2)\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle \qquad (2.1) \\
&= \exp(\alpha a^\dagger - \alpha^* a)|0\rangle ,
\end{aligned}
$$

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[1] R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

[2] R. Brout and I. Prigogine, Physica **22**, 621 (1956).

[3] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, New York, 1962).

[4] P. Carruthers and M. M. Nieto, Am. J. Phys. **33**, 537 (1965).

[5] P. Carruthers and M. M. Nieto, Phys. Rev. Letters **14**, 387 (1965).

[6] R. E. Peierls, Ann. Physik **3**, 1055 (1929).

[7] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), Chap. 2.

where $|n\rangle$ denotes the normalized number state. The coherent states are not orthogonal:

$$\langle\alpha|\beta\rangle=\exp(\alpha^*\beta-\tfrac{1}{2}|\alpha|^2-\tfrac{1}{2}|\beta|^2)\,, \tag{2.2}$$

but they are complete, as indicated by the resolution of the identity,

$$\frac{1}{\pi}\int|\alpha\rangle\langle\alpha|d^2\alpha=I. \tag{2.3}$$

The integration in (2.3) is to be taken over the two-dimensional α plane; $d^2\alpha=d(\mathrm{Re}\alpha)d(\mathrm{Im}\alpha)$.

For notational simplicity, let us first consider a single oscillator. In the coherent state representation, the quantum Liouville equation is

$$i\langle\alpha|\frac{\partial\rho}{\partial t}|\alpha\rangle=\frac{1}{\pi}\int d^2\beta \times[\langle\alpha|H|\beta\rangle\langle\beta|\rho|\alpha\rangle-\langle\alpha|\rho|\beta\rangle\langle\beta|H|\alpha\rangle]. \tag{2.4}$$

If the Hamiltonian H is expressed in terms of creation and annihilation operators, we see that Eq. (2.4) involves, in general, terms of the form [H is assumed to be expressible as an ordered polynomial as in Eq. (2.12) below]:

$$\frac{1}{\pi}\int d^2\beta(\alpha^*)^m\beta^n\langle\alpha|\beta\rangle\langle\beta|\rho|\alpha\rangle\,, \tag{2.5}$$

where m, n are integers. This integral can be worked out by using the following formulas:

$$\begin{aligned}
&\text{(a)} && \frac{1}{\pi}\int d^2\beta e^{\alpha^*\beta-|\beta|^2}f(\beta^*)=f(\alpha^*)\,,\\
&\text{(b)} && \frac{1}{\pi}\int d^2\beta e^{\alpha^*\beta-|\beta|^2}\beta^n f(\beta^*)=\left(\frac{\partial}{\partial\alpha^*}\right)^n f(\alpha^*)\,,\\
&\text{(c)} && \frac{1}{\pi}\int d^2\beta e^{\alpha\beta^*-|\beta|^2}f(\beta)=f(\alpha)\,,\\
&\text{(d)} && \frac{1}{\pi}\int d^2\beta e^{\alpha\beta^*-|\beta|^2}(\beta^*)^n f(\beta)=\left(\frac{\partial}{\partial\alpha}\right)^n f(\alpha).
\end{aligned} \tag{2.6}$$

The formulas (a)–(d) can be derived by expanding f in the integrand in a Taylor series and using the following formula[1]:

$$\frac{1}{\pi}\int d^2\beta e^{-|\beta|^2}\beta^l(\beta^*)^m d^2\beta=\delta_{lm}(l!m!)^{1/2}. \tag{2.7}$$

To illustrate the application of these formulas, we shall evaluate the integral

$$\frac{1}{\pi}\int d^2\beta\beta\langle\alpha|\beta\rangle\langle\beta|\rho|\alpha\rangle. \tag{2.8}$$

The expression $\langle\beta|\rho|\alpha\rangle$ in the integrand involves a factor $\langle\beta|\alpha|\rangle$, so we shall factor it out and write

$$\langle\beta|\rho|\alpha\rangle\equiv\langle\beta|\alpha\rangle\rho(\beta^*,\alpha). \tag{2.9}$$

The functional dependence of $\rho(\beta^*,\alpha)$ on β^* and α is a result of the left- and right-handed properties of the states $\langle\beta|$ and $|\alpha\rangle$. Notice that

$$\langle\alpha|\rho|\alpha\rangle=\rho(\alpha^*,\alpha). \tag{2.10}$$

Using these definitions and Eq. (2.6b) to do the integration, we get:

$$\begin{aligned}
\frac{1}{\pi}\int d^2\beta\beta\langle\alpha|\beta\rangle\langle\beta|\rho|\alpha\rangle
&=e^{-|\alpha|^2}\frac{1}{\pi}\int d^2\beta e^{\alpha^*\beta-|\beta|^2}\beta[e^{\beta^*\alpha}\rho(\beta^*,\alpha)]\\
&=e^{-|\alpha|^2}\frac{\partial}{\partial\alpha^*}[e^{\alpha^*\alpha}\rho(\alpha^*,\alpha)]\\
&=\left(\alpha+\frac{\partial}{\partial\alpha^*}\right)\rho(\alpha^*,\alpha).
\end{aligned} \tag{2.11}$$

In such calculations, it is essential that α^* be considered independent of α. Note that $\exp(\beta^*\alpha)\rho(\beta^*,\alpha)$ is identical to the function $R(\beta^*,\alpha)$ defined by Glauber.[1]

The latter result can be generalized, and the form (2.9) clarified, as follows. Consider an operator A expandable in terms of the ordered series:

$$A=\sum_{mn}A_{mn}(a^\dagger)^m(a)^n\equiv A(a^\dagger,a). \tag{2.12}$$

Then we find

$$\frac{\langle\alpha|A(a^\dagger,a)|\beta\rangle}{\langle\alpha|\beta\rangle}=\sum_{mn}A_{mn}(\alpha^*)^m\beta^n\equiv A(\alpha^*,\beta). \tag{2.13}$$

We shall call the quantity $A(\alpha^*,\beta)$ the *reduced matrix element* of the operator A. Given sufficiently well-behaved expansion coefficients A_{mn}, the function $A(\alpha^*,\beta)$ is an analytic function of two complex variables.[8] It is therefore sufficient to calculate $A(\alpha^*,\alpha)$, which is a boundary value $(\beta=\alpha)$ of $A(\alpha^*,\beta)$.[9] In fact, Eq. (2.11) can be generalized to the matrix element $\langle\alpha|A(a^\dagger,a)\rho|\alpha\rangle$.

$$\begin{aligned}
\langle\alpha|A(a^\dagger,a)\rho|\alpha\rangle
&=\frac{1}{\pi}\int d^2\beta|\langle\alpha|\beta\rangle|^2A(\alpha^*,\beta)\rho(\beta^*,\alpha)\\
&=e^{-|\alpha|^2}\sum_{mn}A_{mn}(\alpha^*)^m\int\frac{d^2\beta}{\pi}e^{\alpha^*\beta-|\beta|^2}\beta^n[e^{\beta^*\alpha}\rho(\beta^*,\alpha)]\\
&=e^{-|\alpha|^2}\sum_{mn}A_{mn}(\alpha^*)^m\left(\frac{\partial}{\partial\alpha^*}\right)^n[e^{\beta^*\alpha}\rho(\beta^*,\alpha)]_{\beta^*=\alpha^*}\,,
\end{aligned}$$

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[8] S. Bochner and W. T. Martin, *Several Complex Variables* (Princeton University Press, Princeton, New Jersey, 1948).

[9] An important consequence is therefore the reduction of the number of descriptive real variables from four (α,β) to two (α).

so

$$\langle\alpha|A(a^\dagger,a)\rho|\alpha\rangle=e^{-|\alpha|^2}A\left(\alpha^*,\frac{\partial}{\partial\alpha^*}\right)\left[e^{\alpha^*\alpha}\rho(\alpha^*,\alpha)\right]. \quad (2.14)$$

From Eq. (2.14), we can also obtain the expectation value of the operator A immediately

$$\begin{aligned}\langle A\rangle&=\mathrm{Tr}(A\rho)\\&=\frac{1}{\pi}\int d^2\alpha e^{-|\alpha|^2}A\left(\alpha^*,\frac{\partial}{\partial\alpha^*}\right)\left[e^{\alpha^*\alpha}\rho(\alpha^*,\alpha)\right].\end{aligned} \quad (2.15)$$

The method of integration used in deriving Eq. (2.11) and Eq. (2.14) will be used repeatedly when we consider specific models. It is important to note in Eq. (2.15) that all averages can be expressed in terms of the diagonal elements of the density matrix. This is an attractive feature of this representation. According to Eq. (2.15) the average of the number operator is

$$\langle N\rangle=\frac{1}{\pi}\int d^2\alpha\alpha^*\left(\alpha+\frac{\partial}{\partial\alpha^*}\right)\rho(\alpha^*,\alpha). \quad (2.16)$$

Further simplifications occur when ρ depends only on the number operator $a^\dagger a$. In this case $\rho(\alpha^*,\alpha)$ is a function of the product $\alpha^*\alpha$. Suppose $B(a^\dagger,a)$ depends on $a^\dagger a$; as a special case of Eq. (2.12) we write

$$B=\sum_n b_n(a^\dagger a)^n. \quad (2.17)$$

Since B is diagonal in the number basis we use Eq. (2.1) to obtain

$$\begin{aligned}\langle\alpha|B|\beta\rangle&=\sum_n b_n\sum_k\frac{k^n(\alpha^*\beta)^k}{k!}\exp\left[-\tfrac{1}{2}|\alpha|^2-\tfrac{1}{2}|\beta|^2\right]\\&=B_1(\alpha^*\beta)\langle\alpha|\beta\rangle,\end{aligned} \quad (2.18)$$

where

$$\begin{aligned}B_1(\alpha^*\beta)&=\sum_n b_nF_n(\alpha^*\beta),\\F_n(z)&=e^{-z}\sum_k\frac{k^nz^k}{k!}.\end{aligned} \quad (2.19)$$

Thus, if an operator B is a function of $a^\dagger a$, its reduced matrix element $\langle\alpha|B|\beta\rangle/\langle\alpha|\beta\rangle$ is a function of the product $\alpha^*\beta$. Trivial examples show that this is not the case for all operators, e.g. $(a^\dagger a^2)^2$ has reduced matrix element $(\alpha^*\beta^2)^2+2\alpha^*\beta^3$ which is not a function of $\alpha^*\beta$ alone.

Next we describe the transition to action-angle variables. The action J is defined to be the mean excitation number of the state $|\alpha\rangle$, and ϕ the corresponding phase:

$$\alpha=J^{1/2}e^{i\phi};\quad J=\alpha^*\alpha,\quad \phi=\frac{1}{2i}\ln\left(\frac{\alpha}{\alpha^*}\right). \quad (2.20)$$

Noting that α^* should be considered independent of α (see derivation of Eq. (2.11) and Eq. (2.14), for example), we find

$$\begin{aligned}\frac{\partial}{\partial\alpha}&=J^{1/2}e^{-i\phi}\left(\frac{\partial}{\partial J}-\frac{i}{2J}\frac{\partial}{\partial\phi}\right),\\\frac{\partial}{\partial\alpha^*}&=J^{1/2}e^{i\phi}\left(\frac{\partial}{\partial J}+\frac{i}{2J}\frac{\partial}{\partial\phi}\right).\end{aligned} \quad (2.21)$$

Integrations over the α plane become, in terms of the action-angle variables

$$\int d^2\alpha=\frac{1}{2}\int_0^\infty dJ\int_0^{2\pi}d\phi. \quad (2.22)$$

To illustrate this transformation, consider the Liouville equation for a free harmonic oscillator:

$$i\frac{\partial\rho}{\partial t}=[H_0,\rho]\equiv L_0\rho, \quad (2.23)$$

where $H=\omega a^\dagger a$. A short calculation shows that $\rho(\beta^*,\alpha)$ evolves as

$$\begin{aligned}i\frac{\partial\rho(\beta^*,\alpha)}{\partial t}&=L_0(\beta^*,\alpha)\rho(\beta^*,\alpha),\\L_0(\beta^*,\alpha)&=\omega\left(\beta^*\frac{\partial}{\partial\beta^*}-\alpha\frac{\partial}{\partial\alpha}\right).\end{aligned} \quad (2.24)$$

Note that if at $t=0$, $\rho(\beta^*,\alpha)$ is a function of $\beta^*\alpha$, then ρ is independent of time. This corresponds to the trivial remark that $[\rho(N),N]$ vanishes.

For $\alpha=\beta$, Eq. (2.24) reduces to

$$L_0(\alpha^*,\alpha)=i\omega\frac{\partial}{\partial\phi} \quad (2.25)$$

independent of the action. The analogy to the classical oscillator[2,3] should now be obvious. Generalizing to an arbitrary number of independent oscillators of frequency ω_k, we have

$$L_0=\sum_k i\omega_k\frac{\partial}{\partial\phi_k}. \quad (2.26)$$

The eigenfunctions of L_0 play an important role in the perturbation expansion for the density matrix. These eigenfunctions are the same as in the classical analysis:

$$\begin{aligned}f\{\nu\}&=(2\pi)^{-(N/2)}\exp\left[-i\sum_k\nu_k\phi_k\right],\\L_0f\{\nu\}&=\left(\sum_k\nu_k\omega_k\right)f\{\nu\},\end{aligned} \quad (2.27)$$

where the ν_k vary over all the positive and negative integers and the sum over k covers all N normal modes.

The set $\{\nu\}$ should never be mistaken for the occupation numbers; rather it specifies the phase of the oscillator.

The normalization in Eq. (2.27) has been chosen according to the inner product

$$(g|h)=\int g^*\{\phi\}h\{\phi\}\prod_k d\phi_k\,, \tag{2.28}$$

so that the eigenfunctions $f\{n\}$ are normalized as follows:

$$(f\{\nu\}|f\{\nu'\})=\delta_{\{\nu\}\{\nu\}}\,. \tag{2.29}$$

The Kronecker delta in Eq. (2.29) means that $\nu_k=\nu_k'$ for all $k=1,\ \cdots N$. We have used round brackets to denote inner products in the space of the eigenfunctions (2.27) to avoid confusion with the usual quantum mechanical inner product, which will be written with sharp brackets.

To conclude this section, we calculate some averages of functions of the number operator, for density matrices which depends only on N (or $\alpha^*\alpha$). In this case $\rho(\alpha^*,\alpha)$ depends on J alone and Eqs. (2.16), (2.21), (2.22) show that

$$\langle N\rangle=\int dJJ\rho(J)+\int dJJ\frac{\partial}{\partial J}\rho(J)\,. \tag{2.30}$$

Integrating the second term by parts and applying the normalization condition for $\rho(J)$, we get

$$\langle N\rangle=\int dJJ\rho(J)-1$$

or

$$\langle\langle J\rangle\rangle\equiv\int dJJ\rho(J)=\langle N\rangle+1\,. \tag{2.31}$$

A useful generalization is easily proved

$$\begin{aligned}\langle(a^\dagger)^n a^n\rangle=(-1)^n\int_0^\infty \rho(J)L_n(J)dJ\\ \equiv(-1)^n\langle\langle L_n(J)\rangle\rangle\,,\end{aligned} \tag{2.32}$$

where L_n is the Laguerre polynomial.[10] Many interesting relations of this sort hold. For a collection of oscillators with a density matrix depending only on $\{N_k\}$

$$[\rho(\{\alpha_k^*\},\{\alpha_k\})=\rho(\{J_k\})]$$

where N_k is the occupation number of the kth mode, one finds

$$\begin{aligned}\langle N_{k_1}\rangle&=(-1)\langle\langle L_1(J_{k_1})\rangle\rangle=\langle\langle J_{k_1}\rangle\rangle-1\\ \langle N_{k_1}N_{k_2}\rangle&=(-1)^2\langle\langle L_1(J_{k_1})L_1(J_{k_2})\rangle\rangle=\langle\langle J_{k_1}J_{k_2}\rangle\rangle\\ &\quad-\langle\langle J_{k_1}\rangle\rangle-\langle\langle J_{k_2}\rangle\rangle+1\\ &\cdots\\ \langle N_{k_1}N_{k_2}\cdots N_{k_n}\rangle&=(-1)^n\langle\langle L_1(J_{k_1})\cdots L_1(J_{k_n})\rangle\rangle\\ &=(-1)^n\langle\langle\prod_{i=1}^n(1-J_{k_i})\rangle\rangle\,.\end{aligned} \tag{2.33}$$

To give an example, consider an oscillator in thermal equilibrium, for which

$$\rho=\frac{e^{-\beta\omega a^\dagger a}}{\mathrm{Tr}e^{-\beta\omega a^\dagger a}}\,, \tag{2.34}$$

where $\beta=(kT)^{-1}$;

$$\rho(J)=\frac{\langle\alpha|e^{-\beta\omega a^\dagger a}|\alpha\rangle}{\mathrm{Tr}e^{-\beta\omega a^\dagger a}}\,. \tag{2.35}$$

Using Eqs. (2.18), (2.19), we find

$$\rho(J)=\frac{\exp[-J(1-e^{-\beta\omega})]}{(1-e^{-\beta\omega})^{-1}}\,. \tag{2.36}$$

Then we obtain the expected results

$$\begin{aligned}\langle\langle J\rangle\rangle&=\int dJJ\rho(J)=\frac{1}{1-e^{-\beta\omega}}\,,\\ \langle N\rangle&=\langle\langle J\rangle\rangle-1=\frac{1}{e^{\beta\omega}-1}\,.\end{aligned} \tag{2.37}$$

III. EVOLUTION OF THE DENSITY MATRIX IN ANHARMONIC SOLIDS; ACTION-ANGLE VARIABLES

If we denote the displacement of the atoms from the mth equilibrium lattice site by $\mathbf{u}_m$, the Hamiltonian is[11]

$$\begin{aligned}H&=H_0+V_3\\ H_0&=\tfrac{1}{2}\sum_m M\dot{\mathbf{u}}_m{}^2+\tfrac{1}{2}\sum_{mn}A_{mn}{}^{ij}u_m{}^iu_n{}^j\\ V_3&=\frac{1}{3!}\sum_{\substack{lmn\\ ijk}}B_{lmn}{}^{ijk}u_l{}^iu_m{}^ju_n{}^k\,,\end{aligned} \tag{3.1}$$

where M is the mass of the atom and i, j, k denotes the x, y, z components. In normal mode coordinates[12]

$$\dot{\mathbf{u}}_m=\sum_k\left(\frac{1}{2MN\omega_k}\right)^{1/2}(a_ke^{i\mathbf{k}\cdot\mathbf{m}}+a_k{}^\dagger e^{-i\mathbf{k}\cdot\mathbf{m}})\mathbf{e}_k\,, \tag{3.2}$$

where k denotes the wave vector $\mathbf{k}$ and the polarization index; $\mathbf{e}_k$ is the polarization vector, and we adopt the convention $\mathbf{e}_{-k}=-\mathbf{e}_k$. Hence,

$$\begin{aligned}H_0&=\sum_k\omega_k(a_k{}^\dagger a_k+\tfrac{1}{2})\\ V_3&=-\sum_{kk'k''}(\omega_k\omega_{k'}\omega_{k''})^{-1/2}\\ &\qquad\times(V_{kk'-k''}a_{k''}{}^\dagger a_{k'}a_k+\mathrm{H.c.})\,,\end{aligned} \tag{3.3}$$

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[10] *Higher Transcendental Functions*, edited by A. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1953), Vol. II, p. 188.

[11] Notation is the same as given by P. Carruthers, Rev. Mod. Phys. 33, 92 (1961).

[12] The restriction to crystals having real polarization vectors is of no concern to the purpose of this paper. Similarly, the optical modes are never considered explicitly.

where

$$V_{kk'k''}=3\times\frac{1}{3!}\left(\frac{1}{2MN}\right)^{3/2}b_{kk'k''}$$

$$b_{kk'k''}=\sum_{ijk}e_k{}^i e_{k'}{}^j e_{k''}{}^k\sum_{lmn}B_{lmn}{}^{ijk}e^{i(\mathbf{k}\cdot\mathbf{l}+\mathbf{k}'\cdot\mathbf{m}+\mathbf{k}''\cdot\mathbf{n})}\,. \tag{3.4}$$

The factor of three in $V_{kk'k''}$ comes from cyclic permutation of k, k', k''. We have omitted the terms which create and destroy three phonons, since they do not conserve energy. They can and must be considered when higher order terms are considered.

If we consider the quantum Liouville equation between states $|\{\alpha_k\}\rangle$, where $\{\alpha_k\}$ denotes a set of amplitudes α_k for all the modes, we get

$$\begin{aligned}i\langle\{\alpha_k\}|\frac{\partial\rho}{\partial t}|\{\alpha_k\}\rangle&=\frac{1}{\pi^N}\int\prod_k d^2\beta_k[\langle\{\alpha_k\}|H|\{\beta_k\}\rangle\langle\{\beta_k\}|\rho|\{\alpha_k\}\rangle\\&\quad-\langle\{\alpha_k\}|\rho|\{\beta_k\}\rangle\langle\{\beta_k\}|H|\{\alpha_k\}\rangle]\,.\end{aligned} \tag{3.5}$$

As remarked in Sec. II, it is sufficient to consider the diagonal elements of ρ in this basis. Off-diagonal elements are found by analytic continuation of α^* to β^*. The right hand side of Eq. (3.5) contains the following terms:

(i) From H_0:

$$\begin{aligned}\sum_q\omega_q\frac{1}{\pi^N}\int\prod_k d^2\beta_k[\alpha_q{}^*\beta_q\langle\{\alpha_k\}|\{\beta_k\}\rangle\langle\{\beta_k\}|\rho|\{\alpha_k\}\rangle\\-\beta_q{}^*\alpha_q\langle\{\alpha_k\}|\rho|\{\beta_k\}\rangle\langle\{\beta_k\}|\{\alpha_k\}\rangle]\end{aligned} \tag{3.6}$$

which upon integration by the methods outlined in Sec. II becomes

$$\sum_k\omega_k\left(\alpha_k{}^*\frac{\partial}{\partial\alpha_k{}^*}-\alpha_k\frac{\partial}{\partial\alpha_k}\right)\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle; \tag{3.7}$$

(ii) From V_3:

$$\begin{aligned}&-\sum_{qq'q''}(\omega_q\omega_{q'}\omega_{q''})^{-1/2}\Big\{V_{qq'-q''}\frac{1}{\pi^N}\int\prod_k d^2\beta_k[\alpha_{q''}{}^*\beta_{q'}\beta_q\langle\{\alpha_k\}|\{\beta_k\}\rangle\langle\{\beta_k\}|\rho|\{\alpha_k\}\rangle\\&\qquad\qquad-\beta_{q''}{}^*\alpha_{q'}\alpha_q\langle\{\alpha_k\}|\rho|\{\beta_k\}\rangle\langle\{\beta_k\}|\{\alpha_k\}\rangle]+\text{H.c.}\Big\}\\&=-\sum_{kk'k''}(\omega_k\omega_{k'}\omega_{k''})^{-1/2}\left\{V_{kk'-k''}\left[\alpha_{k''}{}^*\left(\alpha_{k'}+\frac{\partial}{\partial\alpha_{k'}{}^*}\right)\left(\alpha_k+\frac{\partial}{\partial\alpha_k{}^*}\right)-\left(\alpha_{k''}{}^*+\frac{\partial}{\partial\alpha_{k''}}\right)\alpha_{k'}\alpha_k\right]+\text{H.c.}\right\}\\&\qquad\qquad\times\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle\,.\end{aligned} \tag{3.8}$$

Therefore, the Liouville equation in the coherent-state representation becomes

$$\begin{aligned}i\frac{\partial}{\partial t}\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle&=\sum_k\omega_k\left(\alpha_k{}^*\frac{\partial}{\partial\alpha_k{}^*}-\alpha_k\frac{\partial}{\partial\alpha_k}\right)\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle\\&-\sum_{kk'k''}(\omega_k\omega_{k'}\omega_{k''})^{-1/2}\left\{V_{kk'-k''}\left[\alpha_{k''}{}^*\left(\alpha_{k'}+\frac{\partial}{\partial\alpha_{k'}{}^*}\right)\left(\alpha_k+\frac{\partial}{\partial\alpha_k{}^*}\right)-\left(\alpha_{k''}{}^*+\frac{\partial}{\partial\alpha_{k''}}\right)\alpha_{k'}\alpha_k\right]+\text{c.c.}\right\}\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle\,.\end{aligned} \tag{3.9}$$

Using Eqs. (2.20)–(2.21) to transform to the action-angle variables, we obtain:

$$\begin{aligned}i\frac{\partial}{\partial t}\rho(\{J_k,\phi_k\},t)&=i\sum_k\omega_k\frac{\partial}{\partial\phi_k}\rho(\{J_k,\phi_k\},t)\\&+i\sum_{kk'k''}\left\{\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}V_{kk'-k''}e^{i(\phi_k+\phi_{k'}-\phi_{k''})}\left[i\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}\right)-\frac{1}{2}\left(\frac{1}{J_k}\frac{\partial}{\partial\phi_k}+\frac{1}{J_{k'}}\frac{\partial}{\partial\phi_{k'}}+\frac{1}{J_{k''}}\frac{\partial}{\partial\phi_{k''}}\right)\right.\right.\\&\left.\left.+\left(i\frac{\partial^2}{\partial J_k\partial J_{k'}}-\frac{1}{2J_{k'}}\frac{\partial^2}{\partial J_k\partial\phi_{k'}}-\frac{1}{2J_k}\frac{\partial^2}{\partial J_{k'}\partial\phi_k}-i\frac{1}{4J_{k'}J_k}\frac{\partial^2}{\partial\phi_{k'}\partial\phi_k}\right)\right]+\text{c.c.}\right\}\rho(\{J_k,\phi_k\},t)\,.\end{aligned} \tag{3.10}$$

Apart from a difference in sign convention, and the addition of terms involving second derivatives in J and ϕ, Eq. (3.10) is identical to that given by Brout and Prigogine. The "quantum corrections" are clearly of order $1/J$ relative to the "classical" terms and hence vanish in the classical limit. We thus obtain the advantages of physical interpretation of the classical approach while keeping the quantum-mechanical accuracy.

In writing Eq. (3.9) and Eq. (3.10) we have omitted those contributions which do not conserve energy in the dominant approximation (see next section). A similar calculation shows that these contribute the following terms to Eq. (3.9)

$$\sum_{kk'k''}(\omega_k\omega_{k'}\omega_{k''})^{-1/2}\left\{V_{kk'k''}\left[\left(\alpha_k+\frac{\partial}{\partial\alpha_k{}^*}\right)\left(\alpha_{k'}+\frac{\partial}{\partial\alpha_{k'}{}^*}\right)\left(\alpha_{k''}+\frac{\partial}{\partial\alpha_{k''}{}^*}\right)-\alpha_k\alpha_{k'}\alpha_{k''}\right]+\text{c.c.}\right\}\langle\{\alpha_k\}|\rho|\{\alpha_k\}\rangle. \quad (3.11)$$

In action-angle variables, this contributes the following terms to (Eq. 3.10):

$$\sum_{kk'k''}\left\{\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}V_{kk'k''}e^{i(\phi_k+\phi_{k'}+\phi_{k''})}\left[\left(1+\frac{\partial}{\partial J_k}+\frac{i}{2J_k}\frac{\partial}{\partial\phi_k}\right)\right.\right.$$

$$\left.\left.\times\left(1+\frac{\partial}{\partial J_{k'}}+\frac{i}{2J_{k'}}\frac{\partial}{\partial\phi_{k'}}\right)\left(1+\frac{\partial}{\partial J_{k''}}+\frac{i}{2J_{k''}}\frac{\partial}{\partial\phi_{k''}}\right)-1\right]+\text{c.c.}\right\}\rho(\{J_k,\phi_k\},t). \quad (3.12)$$

IV. THE BROUT-PRIGOGINE EQUATION

The development of the preceding section has shown that the time evolution of the ensemble is given by the solution of the differential equation for the reduced matrix element $\rho(\{J_k,\phi_k\},t)$.

$$i\frac{\partial}{\partial t}\rho(\{J_k,\phi_k\},t)=(L_0+L_1)\rho(\{J_k,\phi_k\},t), \quad (4.1)$$

where the unperturbed Liouville operator L_0 is given by Eq. (2.26) and L_1 by Eq. (3.10)

$$L_1=i\sum_{kk'k''}\left\{\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}V_{kk'-k''}e^{i(\phi_k+\phi_{k'}-\phi_{k''})}\left[i\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}\right)-\frac{1}{2}\left(\frac{1}{J_k}\frac{\partial}{\partial\phi_k}+\frac{1}{J_{k'}}\frac{\partial}{\partial\phi_{k'}}+\frac{1}{J_{k''}}\frac{\partial}{\partial\phi_{k''}}\right)\right.\right.$$

$$\left.\left.+\left(i\frac{\partial^2}{\partial J_k\partial J_{k'}}-\frac{1}{2J_{k'}}\frac{\partial^2}{\partial J_k\partial\phi_{k'}}-\frac{1}{2J_k}\frac{\partial^2}{\partial J_{k'}\partial\phi_k}-i\frac{1}{4J_{k'}J_k}\frac{\partial^2}{\partial\phi_{k'}\partial\phi_k}\right)\right]+\text{c.c.}\right\}. \quad (4.2)$$

In the present paper, we shall solve (4.1) by well known perturbation techniques. First define the interaction-picture density matrix

$$\rho_I(\{J_k,\phi_k\},t)\equiv\exp(-iL_0t)\rho(\{J_k,\phi_k\},t). \quad (4.3)$$

ρ_I satisfies the equation

$$i\frac{\partial\rho_I}{\partial t}=L_I(t)\rho_I, \quad (4.4)$$

where

$$L_I(t)=e^{-iL_0t}L_1e^{iL_0t}. \quad (4.5)$$

The formal solution of Eq. (4.4) is

$$\rho_I(t)=T\exp\left(-i\int_{t_0}^{t}L_1(t')dt'\right)\rho_I(t_0), \quad (4.6)$$

where T is the usual time-ordering operator. We shall generally take t_0 to be zero.

$\rho_I(t)$ may be expanded in terms of the eigenfunctions of L_0, the $f\{\nu\}$ from Eq. (2.27):

$$\rho_I(t)=\sum_{\{\nu\}}\rho_I(\{J_k\}\{\nu\},t)f\{\nu\}, \quad (4.7)$$

where the expansion coefficients are

$$\rho_I(\{J_k\}\{\nu\},t)=[f\{\nu\}|\rho_I(\{J_k,\phi_k\},t)]$$

$$=\int f^*\{\nu\}\rho_I(\{J_k,\phi_k\},t)\prod_k d\phi_k. \quad (4.8)$$

The coefficients $\rho_I(\{J_k\}\{\nu\},t)$ resolve the density matrix into the phase functions $f\{\nu\}$. Inserting Eq. (4.6) into Eq. (4.8) yields (using the completeness of $f\{\nu\}$)

$$\rho_I(\{J_k\}\{\nu\},t)=\sum_{\{\nu'\}}\left(f\{\nu\}|T\exp\left(-i\int_0^t L_I(t')dt'\right)f\{\nu'\}\right)$$

$$\times(f\{\nu'\}|\rho_I(\{J_k,\phi_k\},0)). \quad (4.9)$$

This relation is independent of $\{\phi\}$ but still contains derivatives $\partial/\partial J_k$.

We next examine the consequences of the random-phase initial condition:

$$\rho_I(\{J_k\}\{\nu\},0)=0, \quad \{\nu\}\neq\{0\}. \quad (4.10)$$

As explained in Sec. II, the independence of ρ from the phase angles only occurs if ρ is a function of the number

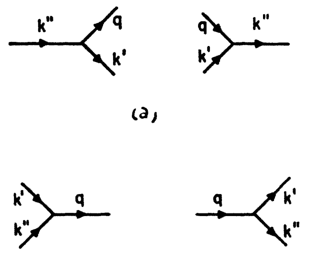

FIG. 1. The three-phonon collision terms entering in the Peierls equation are illustrated graphically. Figure 1(a) corresponds to Eq. (5.9), in which phonon **q** is emitted or absorbed. Figure 1(b), which corresponds to Eq. (5.10) shows processes in which phonon **q** is produced by the coalescence of the phonons or destroyed by splitting into two phonons.

operators $\{N_k\}$. Hence the coefficient

$$\rho_I(\{J_k\}\{0\},t)\equiv\rho_E(\{J_k\},t)$$

describes the number of phonons, or the energy distribution among the normal modes.

The energy-distribution function at time t is then given by

$$\rho_E(\{J_k\},t)=\left(f\{0\}\,|\,T\exp\left(-i\int_0^t L_I(t')dt'\right)f\{0\}\right)\times\rho_E(\{J_k\},0). \quad (4.11)$$

Quantities of the type

$$\left\langle T\exp\left(-i\int_0^t L_I(t')dt'\right)\right\rangle_0=\left(f\{0\}\,|\,T\exp\left(-i\int_0^t L_I(t')dt'\right)f\{0\}\right) \quad (4.12)$$

often arise in statistical and quantum mechanics. A systematic way exists for the evaluation of such expressions.[13,14] In Eq. (4.9) we have to calculate the average of an exponential over the phase angles. As is well-known, such an average can be expressed as the exponential of a modified series.

The method of semi-invariants (or cumulants), explained in Ref. 13, offers a rapid and powerful way of exhibiting this exponentiation. Complicated summations are thereby avoided. We state a few relations for clarity. Consider the moment generating function $\langle\exp(ixt)\rangle$, where the average is taken over some probability distribution $P(x)$. The logarithm of this quantity expands as

$$\ln\langle\exp(ixt)\rangle=\sum_{n=1}^{\infty}\frac{(it)^n}{n!}M_n, \quad (4.13)$$

where the first few semi-invariants M_n are given by

$$\begin{aligned}M_1&=\langle x\rangle,\\ M_2&=\langle x^2\rangle-\langle x\rangle^2,\\ M_3&=\langle x^3\rangle-2\langle x^2\rangle\langle x\rangle+2\langle x\rangle^3,\\ M_4&=\langle x^4\rangle-4\langle x^3\rangle\langle x\rangle-3\langle x^2\rangle^2+12\langle x^2\rangle\langle x\rangle-6\langle x\rangle^4.\end{aligned} \quad (4.14)$$

The case of a time-ordered exponential of an operator is not much more complicated.[13]

For the problem at hand (cubic anharmonicities) all odd M_n vanish.

$$\ln\left\langle T\exp\left(-i\int_0^t L_I(t')dt'\right)\right\rangle_0=\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}M_n(t), \quad (4.15)$$

$$\begin{aligned}M_1&=\int_0^t\langle L_I(t')\rangle_0 dt'=0,\\ M_2&=\int_0^t dt_1\int_0^t dt_2[\langle TL_I(t_1)L_I(t_2)\rangle_0-\langle L_I(t_1)\rangle_0\langle L_I(t_2)\rangle_0]\\ &=\int_0^t dt_1\int_0^t dt_2\langle TL_I(t_1)L_I(t_2)\rangle_0,\\ M_4&=\int_0^t dt_1\cdots\int_0^t dt_4[\langle TL_I(t_1)\cdots L_I(t_4)\rangle_0\\ &\quad-3\langle TL_I(t_1)L_I(t_2)\rangle_0\langle TL_I(t_3)L_I(t_4)\rangle_0].\end{aligned} \quad (4.16)$$

For long times, the M_n are proportional to t. Measuring the perturbation by a parameter λ, we see that the contributions are of order $M_n\sim\lambda^n t$ in this limit. Our procedure provides a simple method of estimating higher order corrections to transport quantities.[15,16]

Thus we find $\rho_E(\{J_k\},t)$ to be given by

$$\rho_E(\{J_k\},t)=\exp\left[\sum_n\frac{(-i)^n}{n!}M_n(t)\right]\rho_E(\{J_k\},0), \quad (4.17)$$

$$\rho_E(\{J_k\},t)\approx\exp[-\tfrac{1}{2}M_2(t)]\rho_E(\{J_k\},0). \quad (4.18)$$

In the last expression we have kept only the term of order $\lambda^2 t$. For times substantially longer than that in which the system adjusts to the perturbation (of order $1/\omega_D$ where ω_D is the Debye frequency) $-\frac{1}{2}M_2(t)$ goes over into the Brout-Prigogine operator $\lambda^2 t\Theta_0$ where Θ_0 is given by

$$\begin{aligned}\Theta_0&=-\sum_{\{\nu\}}(f\{0\}\,|\,L_If\{\nu'\})\\ &\quad\times\delta_+(\textstyle\sum\nu_k'\omega_k)(f\{\nu'\}\,|\,L_If\{0\})\\ \pi\delta_+(x)&=\pi\delta(x)+i\frac{P}{x},\end{aligned} \quad (4.19)$$

P being the principal value.

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[13] R. Brout and P. Carruthers, *Lectures on the Many-Electron Problem* (Interscience Publishing Company, New York, 1962).

[14] R. Brout, Phys. Rev. **115**, 824 (1959).

[15] The extension to more general interactions should be obvious.

[16] P. Carruthers, Phys. Rev. **126**, 1448 (1962). In this work the possible importance of higher order corrections is stressed. Less convincing techniques were used in that work.

In differential form, Eq. (4.16) becomes

$$\frac{\partial}{\partial t}\rho_E(\{J_k\},t)=\mathfrak{S}_0\rho_E(\{J_k\},t) \tag{4.20}$$

which is the Brout-Prigogine master equation.

The invalidity of this equation for $0\leqslant t\leqslant 1/\omega_D$ is of no physical consequence, as the assumed initial condition is unphysical, involving as it does the introduction of bare phonons.

V. DERIVATION OF THE PEIERLS MASTER EQUATION

Our expression for $\partial\rho_E/\partial t$ differs from the classical one only by the addition of second derivative terms. These give rise to the spontaneous decay of the phonons, a process not present in the classical theory. To see this, we shall derive the Peierls equation from the Brout-Prigogine equation.

Explicitly, the matrix elements $(f\{\nu\}|L_If\{\nu'\})$ are

$$(f\{\nu\}|L_If\{\nu'\})=\frac{1}{(2\pi)^N}\int_0^{2\pi}\cdots\int_0^{2\pi}\prod_k d\phi_k \times\exp(-i\sum_k \nu_k\phi_k)L_I\exp(i\sum_k \nu_k'\phi_k). \tag{5.1}$$

Using Eq. (4.2), we see that the nonvanishing elements of $(f\{0\}|L_If\{\nu'\})$ and $(f\{\nu'\}|L_If\{0\})$ are

$$\text{(i)}\quad (f\{0\}|L_I|f\{-1_k-1_{k'}1_{k''};0\})=-V_{kk'-k''}\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}\right.$$
$$\left.+\frac{1}{2J_k}+\frac{1}{2J_{k'}}-\frac{1}{2J_{k''}}+\frac{\partial^2}{\partial J_k\partial J_{k'}}+\frac{1}{2J_k}\frac{\partial}{\partial J_{k'}}+\frac{1}{2J_{k'}}\frac{\partial}{\partial J_k}+\frac{1}{4J_kJ_{k'}}\right)e^{-i(\omega k+\omega k'-\omega k'')t} \tag{5.2}$$

which can be written as

$$(f\{0\}|L_If\{-1_k-1_{k'}1_{k''};0\})=-V_{kk'k''}\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}+\frac{\partial^2}{\partial J_k\partial J_{k'}}\right)\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}e^{-i(\omega k+\omega k'-\omega k'')t} \tag{5.3}$$

$$\text{(ii)}\quad (f\{-1_k-1_{k'}1_{k''};0\}|L_If\{0\})=V_{kk'-k''}{}^*\left(\frac{J_kJ_{k'}J_{k''}}{\omega_k\omega_{k'}\omega_{k''}}\right)^{1/2}\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}+\frac{\partial^2}{\partial J_k\partial J_{k'}}\right)e^{i(\omega k+\omega k'-\omega k'')t} \tag{5.4}$$

so the Brout-Prigogine equation becomes

$$\frac{\partial}{\partial t}\rho_E(t)=2\pi\sum_{kk'k''}\delta(\omega_k+\omega_{k'}-\omega_{k''})\frac{|V_{kk'-k''}|^2}{\omega_k\omega_{k'}\omega_{k''}}$$
$$\times\left[\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}+\frac{\partial^2}{\partial J_k\partial J_{k'}}\right)J_kJ_{k'}J_{k''}\left(\frac{\partial}{\partial J_k}+\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_{k''}}+\frac{\partial^2}{\partial J_k\partial J_{k'}}\right)\right]\rho_E(t). \tag{5.5}$$

The factor of 2 on the right hand side comes from adding the complex conjugate term and the principal part of δ_+ does not contribute because it is an odd function of $\{\nu_k'\}$.

We can now calculate the time rate of change of the average number of phonons in a certain mode q.

$$\frac{d}{dt}\langle N_q\rangle=\int(\prod_k dJ_k)J_q\frac{\partial\rho_E}{\partial t}. \tag{5.6}$$

When we substitute $\partial\rho_E/\partial t$ from Eq. (5.5) into Eq. (5.6), the sum over k, k', k'' will contain four types of terms:

$$\begin{array}{lll} \text{(a)} & k,\,k',\,k''\neq q, & \\ \text{(b)} & k=q; & k',\,k''\neq q, \\ \text{(c)} & k'=q; & k,\,k''\neq q, \\ \text{(d)} & k''=q; & k,\,k'\neq q. \end{array} \tag{5.7}$$

Doing the integration of each of these terms by parts, we see that the first type does not contribute. The second and third types give

$$\langle\langle J_{k'}J_{k''}\rangle\rangle+\langle\langle J_qJ_{k''}\rangle\rangle-\langle\langle J_qJ_{k'}\rangle\rangle-\langle\langle J_{k''}\rangle\rangle. \tag{5.8}$$

Note that the last term of Eq. (5.8), which comes from the second-derivative term, does not appear in a classical theory and is what gives rise to the spontaneous decay process. Transforming by Eq. (2.33) to the number representation, Eq. (5.8) becomes

$$\langle N_{k'}N_{k''}\rangle+\langle N_qN_{k''}\rangle-\langle N_qN_{k'}\rangle+\langle N_{k''}\rangle$$
$$=\langle(N_q+1)(N_{k'}+1)N_{k''}\rangle-\langle N_qN_{k'}(N_{k''}+1)\rangle \tag{5.9}$$

which corresponds to the processes of Fig. 1(a). The fourth type gives

$$\langle\langle J_{k'}J_{k''}\rangle\rangle-\langle\langle J_qJ_{k'}\rangle\rangle-\langle\langle J_qJ_{k''}\rangle\rangle+\langle\langle J_q\rangle\rangle$$
$$=\langle N_{k'}N_{k''}\rangle-\langle N_qN_{k'}\rangle-\langle N_qN_{k''}\rangle-\langle N_q\rangle$$
$$=\langle N_{k'}N_{k''}(N_q+1)\rangle-\langle N_q(N_{k'}+1)(N_{k''}+1)\rangle, \tag{5.10}$$

which corresponds to the processes of Fig. 1(b).

Therefore, changing the index q into k, we have derived the Peierls equation[6,7]:

$$\frac{d}{dt}\langle N_k\rangle = 2\pi \sum_{k'k''} \frac{|V_{kk'-k''}|^2}{\omega_k\omega_{k'}\omega_{k''}}$$
$$\times\{2\delta(\omega_k+\omega_{k'}-\omega_{k''})[\langle(N_k+1)(N_{k'}+1)N_{k''}\rangle$$
$$-\langle N_kN_{k'}(N_{k''}+1)\rangle]+\delta(\omega_k-\omega_{k'}-\omega_{k''})$$
$$\times[\langle N_{k'}N_{k''}(N_k+1)\rangle-\langle N_k(N_{k'}+1)(N_{k''}+1)\rangle]\}. \tag{5.11}$$

This result is not sufficient for the rigorous derivation of a transport equation since the density matrix corresponds to a homogeneous (but nonequilibrium) spatial distribution. When we use the Wigner distribution function formalism for transport processes, other components of the density matrix besides $\rho_E(t)$ have to be considered. This problem will be dealt with in a subsequent paper.

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APPENDIX

Consider the following interaction Hamiltonian for scattering by defects:

$$V_3=\frac{1}{4MN}\sum_{qq'}\frac{1}{(\omega_q\omega_{q'})^{1/2}}C_{qq'}a_q{}^\dagger a_{q'}+\text{H.c.}$$
$$\equiv\sum_{qq'}U_{qq'}a_q{}^\dagger a_{q'}+\text{H.c.} \tag{A1}$$

For example, expressions of this form describe strain field or isotope scattering.[11] The perturbation L_1 is

$$L_1=\sum_{kk'}U_{kk'}(J_kJ_{k'})^{1/2}e^{i(\phi_{k'}-\phi_k)}$$
$$\times\left(\frac{\partial}{\partial J_{k'}}+i\frac{1}{2J_{k'}}\frac{\partial}{\partial\phi_{k'}}-\frac{\partial}{\partial J_k}+i\frac{1}{2J_k}\frac{\partial}{\partial\phi_k}+\text{c.c.}\right). \tag{A2}$$

The nonvanishing elements of $(f\{0\}|L_If\{\nu'\})$ and $(f\{\nu'\}|L_I|f\{0\})$ are:

$$(f\{0\}|L_I|f\{1_k-1_{k'};0\})$$
$$=U_{kk'}\left(\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_k}\right)(J_kJ_{k'})^{1/2}e^{-i(\omega_k-\omega_{k'})t}$$
$$(f\{1_k-1_{k'};0\}|L_I|f\{0\})$$
$$=U_{kk'}{}^*(J_kJ_{k'})^{1/2}\left(\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_k}\right)e^{i(\omega_k-\omega_{k'})t} \tag{A3}$$

so

$$\Theta_0=2\pi\sum_{kk'}\delta(\omega_k-\omega_{k'})|U_{kk'}|^2$$
$$\times\left(\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_k}\right)J_kJ_{k'}\left(\frac{\partial}{\partial J_{k'}}-\frac{\partial}{\partial J_k}\right). \tag{A4}$$

From this result, we get

$$\frac{d\langle N_k\rangle}{dt}=2\pi\sum_{k'}|U_{kk'}|^2(\langle N_{k'}\rangle-\langle N_k\rangle). \tag{A5}$$

This is simply the "Golden rule" result; see for example Eq. (4.14) of Ref. 11.