Theory of Single-Particle Time-Correlation Functions*

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We present a general theory for the calculation of the single-particle time-correlation function $\alpha(t) = \langle [a, a^\dagger(t)] \rangle$ which is the canonical average of the commutator between the particle annihilation a and creation $a^\dagger(t)$ at time t. The theory is based on the projection-operator method. The complex spectral function $\hat{\alpha}(\omega)$ is expressed in terms of the natural frequency of oscillation Ω and the width function $\hat{\gamma}(\omega)$. From the analytical property of $\hat{\alpha}(\omega)$ in the complex ω plane for the weak-coupling limit, the long-time behavior of the correlation function $\alpha(t)$ and the relaxation functions is obtained. For a harmonic oscillator immersed in a heat bath, the perturbation calculations for Ω and $\hat{\gamma}(\omega)$ are given in the power of the coupling constant. By means of this series, the spectral function $\hat{\alpha}(\omega)$ for a single normal mode of an anharmonic system is explicitly calculated as a function of the frequency ω and the temperature T. As a possible application of the results the electrical conductivity due to a localized mode is discussed.

I. INTRODUCTION

Statistical-mechanical theories of transport properties of quantum-mechanical systems are most conveniently described in terms of the single-particle time-correlation function or the Green's function.[1,2] Actual calculation of this function, however, often requires tedious combinatorial and diagrammatic arguments. Another approach to the problem is to use the projection-operator method first developed by Zwanzig[3] and later by others.[4-7] In particular, Mori[4] has shown that this method applied to a dissipative system leads to the generalized Langevin equation of motion of a dynamical quantity. The time correlation of the random force determines the damping function $\gamma(t)$ of the equation.

The purpose of the present work is to calculate the single-particle time-correlation function $\alpha(t)$ by means of the projection-operator method. The essential feature of the theory is based on the fact that the projection-operator method provides the spectral function in terms of the natural frequency Ω and the width function $\hat{\gamma}(\omega)$, which is the imaginary Laplace transformation of the damping function. In a theory of impurity-induced infrared absorption profiles in condensed systems, the authors used a similar approach with the simplifying assumption of the linear coupling of the impurity mode to the bath. As pointed out by Greer and Rice[8] in their recent review article, this approach shifts the emphasis of the calculation from the determination of the frequency dependence of the absorption-profile function or the spectral function to the determination of the width function whose frequency dependence is weaker. This is also precisely what is accomplished through the use of the variational method introduced by Schwinger[9] for calculating the frequency-dependent Green's function.

The present projection operator [Eq. (2.5)] is quite different from those[3-7] previously introduced in the sense that it is directly based on the fundamental commutation relation [Eq. (2.2)] in quantum mechanics. It does not require an additional "normalization" which makes the operator idempotent since the commutation relation itself automatically takes care of it. The operator is so effective that from the simple property of Ω being positive we can deduce the analytical properties of the spectral function $\hat{\alpha}(\omega)$ in the complex ω plane (Sec. II). The pole of $\hat{\alpha}(\omega)$ in the weak-coupling limit determines the long-time behavior of the single-particle correlation $\alpha(t)$ and the various response and relaxation functions between the position and the momentum of the particle (Sec. III). These functions play a fundamental role in many aspects of transport phenomena. In particular, they describe directly the stochastic theory of Brownian motion.[4]

Next, we shall consider a harmonic oscillator immersed in a heat bath. With the assumption of weak coupling we shall develop a perturbation series for the natural frequency Ω and the damping function $\gamma(t)$ up to the order of λ^2, where λ is the coupling constant. In the special case when the coupling is linear with respect to the normal coordinate of the oscillator, the random force reduces to the coupling force. This means that the damping function $\gamma(t)$ becomes the autocorrelation

function of the coupling force, which is a result previously obtained by Lax[10] and Wilson, King, and Kim[6] (Sec. IV). At this stage, the results are still general and applicable to many systems. With the further specification of the Hamiltonian to that of an anharmonic system of small vibrations we obtain the explicit form of the complex spectral function $\hat{\alpha}(\omega)$ as a function of ω and temperature. The actual calculation is carried out up to the quartic order in the normal coordinates in the power-series expansion of the coupling potential. The extension to the higher-order terms does not require much further calculation since the result is given by a general expression of the product of the uncoupled correlations to which all the required terms are reduced by the Wick theorem.[11] As a possible application of the results the electrical conductivity due to a localized mode is discussed.

II. BASIC THEORY

We define the single-particle correlation function of the form

$$\alpha(t) = \langle [a, a^\dagger(t)] \rangle , \tag{2.1}$$

where $\langle \cdots \rangle$ is the average over the canonical ensemble, a and $a^\dagger$ are the annihilation operator and the creation operator of the "particle," $a^\dagger(t)$ is the Heisenberg operator at time t, and $[A, B]$ is the commutator between A, B. For a boson

$$[a, a^\dagger] = 1 . \tag{2.2}$$

Even though the present theory applies equally well for fermions, in which case the bracket is taken to be the anticommutator, we shall limit ourselves to Bose–Einstein statistics for definiteness.

In the actual calculation of the transport properties we need the Laplace transform $\hat{\alpha}(\omega)$,

$$\hat{\alpha}(\omega) = \int_0^\infty \alpha(t) e^{-i\omega t - \epsilon t} dt , \tag{2.3}$$

where ϵ is an infinitely small positive quantity. As is well known, the real part of $\hat{\alpha}(\omega)$ divided by π is called the spectral function and has many important properties. We may write down some of the properties for later use[1,2]:

$$\frac{\mathrm{Re}\,\hat{\alpha}(\omega)}{\pi} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \alpha(t) e^{-i\omega t - \epsilon |t|} dt ,$$

$$\frac{\mathrm{Re}\,\hat{\alpha}(\omega)}{\pi} \gtreqless 0 \quad \text{for } \omega \gtreqless 0 , \tag{2.4}$$

$$\int_{-\infty}^{+\infty} \frac{\mathrm{Re}\,\alpha(\omega)}{\pi} d\omega = 1 .$$

In order to calculate $\alpha(t)$ by means of the projection-operator method, we introduce a projection operator P defined by

$$Px = a^\dagger \langle [a, x] \rangle , \tag{2.5}$$

where x stands for an arbitrary operator. From the basic commutation relation, $[a, a^\dagger] = 1$, the projection operator thus introduced indeed satisfies the fundamental condition,

$$P^2 = P . \tag{2.6}$$

An analogous projection operator may be introduced whenever there exists a basic commutation relation. For example, from the commutation relation between the coordinate Q and its conjugate momentum $\dot{Q}$, $[Q, \dot{Q}] = i\hbar$, where $\hbar$ is Planck's constant divided by 2π, we have a projection operator defined by

$$P'x = \dot{Q} \langle [Q, x] \rangle / i\hbar . \tag{2.7}$$

The present operator is quite different from that of Mori[4] in the sense that it is not possible to make the bracket between A and B,

$$\{A, B\} \equiv \langle [A^\dagger, B] \rangle , \tag{2.8}$$

have all the necessary properties of the scalar product where $A^\dagger$ is the Hermitian adjoint of A. For instance, $\{A^\dagger, A\}$ is identically zero. In spite of this the present operator is quite effective in the practical calculation of $\alpha(t)$.

Once the projection operator P is introduced, it is a simple matter to obtain the equation of motion of $\alpha(t)$, following Mori[4] and Zwanzig,[3]

$$\dot{\alpha}(t) = i\Omega\alpha(t) - \int_0^t \gamma(s)\, \alpha(t-s) ds , \tag{2.9}$$

where

$$\Omega = \langle [a, La^\dagger] \rangle , \tag{2.10}$$

$$\gamma(s) = \langle [f^\dagger, f(s)] \rangle . \tag{2.11}$$

Here L is the Liouville operator defined by

$$Lx = (1/\hbar)[H, x] , \tag{2.12}$$

$f(s)$ is the random force defined by

$$f(s) = -e^{i(1-P)Ls}(1-P)La^\dagger$$
$$= -(1-P)e^{iL(1-P)s} La^\dagger , \tag{2.13}$$

and $f^\dagger$ is the adjoint of $f(0)$. The random force is obviously "orthogonal" to $a^\dagger$ since

$$Pf(s) = a^\dagger \langle [a, f(s)] \rangle = 0 . \tag{2.14}$$

Mori is the first to identify $f(s)$ as the random force in the generalized Langevin equation.[4] We note, however, that the above definition of the random force is taken differently from Mori's by a factor $-i$ to ensure the physical significance of the concept [see Eq. (4.12)]. If the Hamiltonian is invariant under time reversal, the symmetry of the damping function $\gamma(s)$ follows:

$$\gamma(s) = \gamma(-s)^* . \tag{2.15}$$

The natural frequency Ω is a positive quantity, since it can be expressed as an integral of a positive quantity,

$$\Omega = \hbar \int_0^\beta \langle a(-i\hbar\xi) a^\dagger \rangle d\xi > 0 \ . \tag{2.16}$$

Now, the Laplace transform of the equation of motion yields

$$\hat{\alpha}(\omega) = -i/[\omega - \Omega - i\hat{\gamma}(\omega)] \ , \tag{2.17}$$

where $\hat{\gamma}(\omega)$ is defined analogously to $\hat{\alpha}(\omega)$, defined in Eq. (2.3). We may call $\hat{\gamma}(\omega)$ the width function since its real part describes the width of the spectral function. Separation of $\hat{\gamma}(\omega)$ into the real and imaginary parts gives

$$\hat{\gamma}(\omega) = \gamma_1(\omega) - i\gamma_2(\omega) \ . \tag{2.18}$$

These two parts are related by the well-known Kramers–Kronig relation. Substitution of this into $\hat{\alpha}(\omega)$ gives

$$\mathrm{Re}\alpha(\omega) = \frac{\gamma_1(\omega)}{[\omega - \Omega - \gamma_2(\omega)]^2 + \gamma_1^2(\omega)} \ , \tag{2.19}$$

$$\mathrm{Im}\alpha(\omega) = \frac{-\omega + \Omega + \gamma_2(\omega)}{[\omega - \Omega - \gamma_2(\omega)]^2 + \gamma_1^2(\omega)} \ . \tag{2.20}$$

From the first of these and the sign of the spectral function given in Eq. (2.4) we have

$$\gamma_1(\omega) \gtrless 0 \quad \text{for} \quad \omega \gtrless 0 \ . \tag{2.21}$$

The direct proof of this important property from the definition of $\hat{\gamma}(\omega)$ is not very simple since the random force $f(t)$ does not obey the usual dynamical law of motion.

Now we are ready to discuss the analytical properties of $\alpha(\omega)$. So far, all the results obtained above are exact and independent of the specific form of the Hamiltonian. If we assume, however, that the interaction energy between "particles" is small compared to the characteristic energy of oscillation, $\Omega \gg |\hat{\gamma}(\omega)|$, we may conclude that the pole of $\hat{\alpha}(\omega)$ from Eq. (2.17) must be located in the vicinity of Ω. Thus in the first approximation we have for the location of the pole ω_p

$$\omega_p = \Omega + i\hat{\gamma}(\omega_p) \cong \Omega + \gamma_2(\Omega) + i\gamma_1(\Omega) \ , \tag{2.22}$$

which is in the upper half of the complex ω plane, since Ω is positive [from Eq. (2.16)] and, accordingly, $\gamma_1(\Omega)$ is also positive [from Eq. (2.21)]. This means that in the weak-coupling limit the amplitude function $\mathrm{Re}\alpha(\omega)/\pi$ is Lorentzian. From the inverse Fourier transform of Eq. (2.4) we obtain the long-time behavior[12] of the correlation function $\alpha(t)$,

$$\alpha(t) \sim e^{i\nu t - \Gamma|t|} \ , \tag{2.23}$$

where $|t|$ denotes the absolute value of t and

$$\nu = \Omega + \gamma_2(\Omega) \ , \tag{2.24}$$

$$\Gamma = \gamma_1(\Omega) > 0 \ . \tag{2.25}$$

It is well known that one could make an analogous argument in terms of the analytical properties of the one-particle Green's function. The beauty of the present approach is that it gives the width explicitly in terms of the random force. Later, in Sec. IV, we shall calculate the frequency dependence of the width function of a single normal mode of vibration for a system of small oscillation. In Sec. III, however, we shall calculate the so-called response function and the relaxation function between the coordinate and the momentum from the long-time expression of $\alpha(t)$ given by Eq. (2.23).

III. RESPONSE AND RELAXATION FUNCTION FOR ONE PARTICLE

The position Q and the momentum $\dot{Q}$ of a particle are related to a and $a^\dagger$ as follows:

$$Q = \left(\frac{\hbar}{2\omega_0}\right)^{1/2} (a + a^\dagger) \ , \qquad \dot{Q} = -i\left(\frac{\hbar\omega_0}{2}\right)^{1/2} (a - a^\dagger) \ , \tag{3.1}$$

where ω_0 is the intrinsic frequency of the particle which may or may not equal the natural frequency Ω. The results which follow do not depend on ω_0 explicitly.

The response function between Q and $\dot{Q}$ is given by

$$\phi_1(t) = (1/i\hbar)\langle [Q, \dot{Q}(t)] \rangle = \mathrm{Re}\alpha(t) \ . \tag{3.2}$$

From the long-time behavior of $\alpha(t)$ we have immediately

$$\phi_1(t) = e^{-\Gamma t}\cos\nu t, \qquad \Gamma t \gg 1 \ . \tag{3.3}$$

By differentiation with respect to t we obtain the autocorrelation function of momentum,

$$\phi_2(t) = \frac{1}{i\hbar}\langle [\dot{Q}, \dot{Q}(t)] \rangle = e^{-\Gamma t}(\Gamma\cos\nu t + \nu\sin\nu t), \tag{3.4}$$

and by integration we have the autocorrelation function of position,

$$\phi_0(t) = \frac{1}{i\hbar}\langle [Q, Q(t)] \rangle = -\mathrm{Re}\int_t^\infty \alpha(t')dt' = \frac{e^{-\Gamma t}}{\nu^2 + \Gamma^2}(\nu\sin\nu t - \Gamma\cos\nu t) \ . \tag{3.5}$$

The relaxation function of A and B is defined by Kubo[13] as follows:

$$\langle \tilde{A}, B(t) \rangle = \beta^{-1}\int_0^\beta \langle A(-i\hbar\xi)B(t) \rangle d\xi = (i\hbar\beta)^{-1}\int_t^\infty \langle [A, B(t')] \rangle dt' \ , \tag{3.6}$$

assuming that the zero-frequency component of

$A(t)$ or $B(t)$ is zero. From the last formula we obtain the following relaxation functions:

$$\Phi_0(t) = \langle \tilde{Q},\ Q(t)\rangle = \beta^{-1}\int_t^\infty \phi_0(t')\,dt'$$
$$= \frac{kT}{(\nu^2+\Gamma^2)^2}\, e^{-\Gamma t}\left[(\nu^2-\Gamma^2)\cos\nu t + 2\nu\Gamma\sin\nu t\right], \tag{3.7}$$

$$\Phi_1(t) = \langle \tilde{Q},\ \dot{Q}(t)\rangle = -kT\phi_0(t)\ , \tag{3.8}$$

$$\Phi_2(t) = \langle \dot{\tilde{Q}},\ \dot{Q}(t)\rangle = kT\phi_1(t)\ . \tag{3.9}$$

These quantities enter into the various aspects of the transport properties. For example, these describe the stochastic theory of the Brownian motion of a simple-harmonic oscillator. Similar results are obtained by Mori[4] and others.[14–17] Their results appear different from the above by an order of Γ/ν. The reason for this is that Ω and $\hat{\gamma}(\Omega)$ are expressed in terms of the commutator in the present work, whereas in Mori's work Ω and $\hat{\gamma}(\Omega)$ are expressed in terms of the Kubo scalar product given by Eq. (3.6).

The results given above are only their first approximations. We can improve the results starting from the more accurate calculation of the pole of $\hat{\alpha}(\omega)$. In many applications, however, we need only the Fourier transforms of these functions, which can be expressed in terms of $\hat{\alpha}(\omega)$. For example, for the Laplace transform of $\phi_1(t)$ defined by Eq. (3.2) we have

$$\phi_1(\omega) = \int_0^\infty \phi_1(t)e^{-i\omega t-\epsilon t}dt = \tfrac{1}{2}\left[\alpha(\omega)+\alpha^*(-\omega)\right]. \tag{3.10}$$

If necessary, we can calculate $\phi_1(t)$ from the inverse transform of this. We shall use this formula in Sec. V.

IV. PERTURBATION SERIES FOR Ω AND $\gamma(t)$

As an application of the basic theory developed in Sec. II we shall calculate the one-particle correlation function for a harmonic oscillator immersed in a heat bath. The system Hamiltonian may be described by

$$H = H^0 + \lambda V\ ,$$
$$H^0 = H_0 + H_B\ , \tag{4.1}$$

where H_0, H_B, and λV represent the harmonic oscillator, the heat bath, and their coupling. H_0 is given by

$$H_0 = (a^\dagger a + \tfrac{1}{2})\hbar\omega_0\ , \tag{4.2}$$

where ω_0 is the intrinsic frequency of the harmonic oscillator. To proceed, it is safe to assume that the coupling potential V can be expanded as a power series in q_0,

$$V(q_0, q_B) = \sum_{n=0}^{\infty} b_n(q_B)q_0^n, \qquad q_0 = a + a^\dagger \tag{4.3}$$

where q_0 and q_B are the coordinates of the harmonic oscillator and the bath molecules. In what follows we use the Liouville operators L, L^0, and L', corresponding to H, H^0, and V, respectively. From the assumed Hamiltonian we immediately obtain

$$La^\dagger = \omega_0 a^\dagger + \lambda V'\ ,$$
$$La\ \ = -\omega_0 a - \lambda V'\ , \tag{4.4}$$

where $-V'$ is the coupling force defined by

$$V' = \frac{1}{\hbar}\frac{\partial V}{\partial q_0}\ , \tag{4.5}$$

which has the dimension of frequency. Now we are ready to calculate the natural frequency Ω and the damping function $\gamma(t)$.

A. Natural Frequency

From Eqs. (2.10) and (4.4) we obtain

$$\Omega = \langle [a,\ La^\dagger]\rangle = \omega_0 + \lambda\langle V''\rangle\ , \tag{4.6}$$

where

$$V'' = \frac{1}{\hbar}\frac{\partial^2 V}{\partial q_0^2}\ . \tag{4.7}$$

That is, the shift is given by the average gradient of the coupling force $-V'$. Accordingly, in the special case of linear coupling, the natural frequency Ω reduces to ω_0. The above result is still exact. If we use the perturbation theory to reduce the canonical average $\langle\cdots\rangle$ into the canonical average $\langle\cdots\rangle_0$ of the uncoupled system described by H^0, we obtain

$$\Omega - \omega_0 = \lambda\langle V''\rangle_0 - \lambda^2\int_0^\beta \langle V(-i\hbar\xi)\,\delta V''\rangle_0 d\xi + O(\lambda^3)\ , \tag{4.8}$$

where

$$\delta V'' = V'' - \langle V''\rangle_0\ .$$

B. Damping Function $\gamma(t)$

According to Eq. (2.11), the damping function $\gamma(t)$ is given by the correlation of the random force $f(t)$, which is related to the true coupling force $-V'$ as follows:

$$f(t) = -\lambda e^{i(1-P)Lt}(1-P)V'\ , \tag{4.9}$$

where use has been made of Eq. (4.4).

Following the perturbation scheme developed in a previous paper,[7] we separate the projector P into two parts:

$$P = P^0 + \lambda P'\ , \tag{4.10}$$

where P^0 is defined by

$$P^0X = a^\dagger\langle [a,\ X]\rangle_0\ , \tag{4.11}$$

which obviously commutes with L^0. Substitution of Eq. (4.10) into Eq. (4.9) yields

$$f(t) = -\lambda e^{iL^0t}(1-P^0)V' + O(\lambda^2)$$

$$= -\lambda(e^{iL^0 t}V' - e^{i\omega_0 t}a^\dagger\langle V''\rangle_0) + O(\lambda^2)\,. \quad (4.12)$$

In the special case of linear coupling, the random force coincides with the coupling force up to the order of λ. Substitution of the above result into the definition of $\gamma(t)$ given by Eq. (2.11) yields

$$\gamma(t) = \lambda^2\{\langle[V',\ V'(t)]\rangle_0 - e^{i\omega_0 t}\langle V''\rangle_0^2\} + O(\gamma^3)\,, \quad (4.13)$$

where $-V'(t)$ describes the uncoupled motion of the force

$$V'(t) = e^{iL^0 t}V'\,. \quad (4.14)$$

To see the significance of the second term we take the Fourier transform to obtain the width,

$$\frac{\gamma_1(\omega)}{\lambda^2} = \frac{1}{2}\int_{-\infty}^{+\infty}\langle[V',\ V'(t)]\rangle_0 e^{-i\omega t}dt - \pi\delta(\omega-\omega_0)\langle V''\rangle_0^2 + O(\lambda)\,. \quad (4.15)$$

One notices immediately that the second term diverges at $\omega=\omega_0$. However, according to Eq. (2.21) $\gamma_1(\omega)$ is positive when $\omega>0$. This means that the first term must contain a divergent component at $\omega=\omega_0$ which cancels the second term. This is actually the case. When $\langle V''\rangle_0\neq 0$, $V'(t)$ must depend on $q_0(t)$, which contributes a Fourier component with the frequency ω_0.

For further calculation of the *complex width function* $\hat{\gamma}(\omega)$, it is necessary to give the explicit form of H_B and V. Previously we have calculated the impurity-induced infrared absorption for an imperfect crystal system and obtained a similar but less general width function with the assumption of linear coupling. In that calculation, however, we neglected the terms $\langle a^\dagger a^\dagger(t)\rangle$ and $\langle aa(t)\rangle$, so that the final result is valid only in the vicinity of $\omega=\omega_0$.

In order to show the effectiveness of the present method, which is based on the perturbation series of Ω and $\gamma(t)$ given by Eqs. (4.8) and (4.13), we shall calculate the width function $\hat{\gamma}(\omega)$ and the frequency Ω of a single normal mode of vibration for a system of small vibration with higher-order coupling.

V. SPECTRAL FUNCTION $\alpha(\omega)$ OF A SINGLE NORMAL MODE

Consider a system of small vibration. Then the Hamiltonian introduced in Eq. (4.1) takes the form

$$H^0 = \sum_{i=0}^{N}(a_i^\dagger a_i + \tfrac{1}{2})\hbar\omega_i\,, \quad (5.1)$$

$$V = \frac{\hbar}{3!}\sum_{rsp=0}^{N}V_{rsp}q_r q_s q_p + \frac{\hbar}{4!}\sum_{rspu=0}^{N}V_{rspu}q_r q_s q_p q_u + \cdots\,, \quad (5.2)$$

where

$$q_i = a_i^\dagger + a_i\,,\quad i=0,\ 1,\ \ldots,N \quad (5.3)$$

and a_i and $a_i^\dagger$ are the annihilation and creation operators of the ith normal mode of vibration and N is the total number of the normal modes. In the calculation which follows we shall take only the cubic and quartic coupling in q, neglecting the higher-order terms in the coupling potential V. As before, we write simply $a^\dagger$ and a for $a_0^\dagger$ and a_0. According to Eq. (4.13), the damping function $\gamma(t)$ for the zeroth phonon takes the form

$$\gamma(t) = \langle[V',\ V'(t)]\rangle_0 - e^{-i\omega_0 t}\langle V''\rangle_0^2\,, \quad (5.4)$$

where we have neglected the $O(\lambda^3)$ term and set $\lambda=1$. If we use Wick's theorem[11] it is a simple matter to calculate this. From the explicit form of the potential V given by Eq. (5.2) we can write $\gamma(t)$ in the following compact form:

$$\gamma(t) = \sum_{s=0}^{N}\left[\sum_{r=0}^{N}V_{0srr}\left(n_r+\frac{1}{2}\right)\right]^2 C_s(t) + \frac{1}{2}\sum_{r,s=0}^{N}(V_{0rs})^2 C_{rs}(t) + \frac{1}{6}\sum_{rsp=0}^{N}(V_{0rsp})^2 C_{rsp}(t) - e^{i\omega_0 t}\sum_{r=0}^{N}V_{00rr}\left(n_r+\frac{1}{2}\right)\,, \quad (5.5)$$

where n_r is the average phonon number of the rth normal mode of vibration,

$$n_r = (e^{\beta\hbar\omega_r}-1)^{-1}\,, \quad (5.6)$$

and the functions $C_s(t)$, $C_{rs}(t)$, and $C_{rsp}(t)$ are the first three members of the following general function:

$$C_{12\cdots\mu}(t) = 2i\,\mathrm{Im}G_{12\cdots\mu}(t)\,,$$
$$G_{12\cdots\mu}(t) = \prod_{j=1}^{\mu}\langle q_j q_j(t)\rangle_0\,, \quad (5.7)$$

where the subscripts $12\cdots\mu$ are obvious shorthand notations for v, s, p, $\cdots$ μth phonons. Hereafter, whenever it is convenient we write these simply as $C^{(\mu)}(t)$ and $G^{(\mu)}(t)$, respectively. In order to obtain a general and symmetric expression of $G^{(\mu)}(t)$ we write the one-particle correlation in the form

$$\langle q_j q_j(t)\rangle_0 = 2Z_j\cos(\omega_j t - \tfrac{1}{2}i\beta\hbar\omega_j)\,, \quad (5.8)$$

where Z_j is the harmonic-oscillator partition function

$$Z_j = \tfrac{1}{2}\mathrm{cosech}(\tfrac{1}{2}\beta\hbar\omega_j)\,. \quad (5.9)$$

From this and Eq. (5.7) we obtain

$$G^{(\mu)}(t) = Z^{(\mu)}\sum_{k=1}^{2^\mu}\cos(\alpha_k t - \tfrac{1}{2}i\beta\hbar\alpha_k)\,, \quad (5.10)$$

where α_k is one of the 2^μ combination of the fre-

quencies of the normal modes,

$$\{\alpha_k\} = \pm\omega_1 \pm \omega_2 \pm \cdots \pm \omega_\mu \,. \tag{5.11}$$

From the imaginary part of $G^{(\mu)}(t)$ we obtain the required result,

$$C^{(\mu)}(t) = 2iZ^{(\mu)} \sum_{k=1}^{2^\mu} \sinh(\tfrac{1}{2}\beta\hbar\alpha_k) \sin\alpha_k t \,. \tag{5.12}$$

This completes the expression for $\gamma(t)$ given by Eq. (5.5). What we need for the transport properties is the complex with function. This in turn requires the Laplace transform $\hat{C}^{(\mu)}(\omega)$ of $C^{(\mu)}(t)$,

$$\hat{C}^{(\mu)}(\omega) = \int_0^\infty C^{(\mu)}(t)\, e^{-i\omega t - \epsilon t} dt \,. \tag{5.13}$$

The real and imaginary parts are

$$\mathrm{Re}\hat{C}^{(\mu)}(\omega) = 2\pi Z^{(\mu)} \sinh(\tfrac{1}{2}\beta\hbar\omega) \,|\omega| \sum_k \delta(\omega^2 - \alpha_k^2) \,, \tag{5.14}$$

$$\mathrm{Im}\hat{C}^{(\mu)}(\omega) = 2Z^{(\mu)} \sum_k \sinh(\tfrac{1}{2}\beta\hbar\omega)\, P\frac{\alpha_k}{\alpha_k^2 - \omega^2} \,, \tag{5.15}$$

where $|\omega|$ is the absolute value of ω and P denotes the principal value. One notices that $\mathrm{Re}\hat{C}^{(\mu)}(\omega)$ is an odd function of ω and is positive when $\omega > 0$, whereas $\mathrm{Im}\hat{C}^{(\mu)}(\omega)$ is an even function of ω.

Similar symmetry does not hold for the complex width function $\hat{\gamma}(\omega)$ unless the second term in Eq. (4.13) or in Eq. (4.15) is negligible. As one can see more clearly from the basic equation for the damping function given by Eq. (2.11), the function $\gamma(\omega)$ does not have to satisfy such a symmetry, since the random force $f(t)$ is not Hermitian. However, very often the contribution from the second term of Eq. (4.13) is negligibly small compared to the first term, so that we can approximately assume such a symmetry for $\gamma(\omega)$ in the weak-coupling limit. In the following we give the limiting expression of these functions with respect to temperature.

A. High-Temperature Limit

$$\mathrm{Re}\hat{C}^{(\mu)}(\omega) \sim \pi\left(\frac{kT}{\hbar}\right)^{\mu-1} \omega\,|\omega| \left(\prod_{j=1}^{\mu}\omega_j\right)^{-1} \sum_k \delta(\omega^2 - \alpha_k^2) \,, \tag{5.16}$$

$$\mathrm{Im}\hat{C}^{(\mu)}(\omega) \sim \left(\frac{kT}{\hbar}\right)^{\mu-1} \left(\prod_{j=1}^{\mu}\omega_j\right)^{-1} \sum_k \frac{\alpha_k^2}{\alpha_k^2 - \omega^2} \,. \tag{5.17}$$

B. Low-Temperature Limit

$$\mathrm{Re}\hat{C}^{(\mu)}(\omega) \sim 2\pi\omega\delta(\omega^2 - \alpha_x^2) + O(e^{-\beta\hbar\omega_n}) \,, \tag{5.18}$$

$$\mathrm{Im}\hat{C}^{(\mu)}(\omega) \sim P\frac{2\alpha_x^2}{\alpha_x^2 - \omega^2} + O(e^{-\beta\hbar\omega_n}) \,, \tag{5.19}$$

where α_x is the maximum frequency of α_k given by

$$\alpha_x = \omega_1 + \omega_2 + \cdots + \omega_\mu \tag{5.20}$$

and ω_n is the minimum frequency of $1, 2, \ldots, \omega_\mu$.

The drastic simplification in the low-temperature limit is easily understood by means of a physical picture that describes one-photon ($\hbar\omega > 0$) interactions with μ phonons. In the low-temperature limit all the phonons are in the lowest-energy levels. As a result, the minimum work which a photon can do is to promote the μ phonons involved in the interaction to the next-higher-energy levels. This obviously requires the energy $\hbar\omega_x$.

In the description of the spectral function $\alpha(\omega)$ given by Eq. (2.17) we need the natural frequency Ω in addition to $\gamma(\omega)$. We may rewrite Eq. (4.8) for Ω in the following form:

$$\Omega - \omega_0 = \langle V'' \rangle_0 - \left(\frac{1}{i\hbar}\right) \int_0^\infty \langle [V,\, V''(t)] \rangle_0 dt \,, \tag{5.21}$$

where we have neglected the $O(\lambda^3)$ term and set $\lambda = 1$. Following the same procedure as in the case of the damping function we obtain

$$\Omega - \omega_0 = \sum_{r=0}^{N} V_{00rr}\left(n_r + \frac{1}{2}\right) - \sum_{r,s=0}^{N} V_{rrs}V_{00s}\left(n_r + \frac{1}{2}\right) \mathrm{Im}\hat{C}_s(0) - \frac{1}{2}\sum_{rsp=0}^{N} V_{rrsp}V_{00sp}\left(n_r + \frac{1}{2}\right)\mathrm{Im}\hat{C}_{sp}(0) \,, \tag{5.22}$$

where $\mathrm{Im}\hat{C}^{(\mu)}(0)$ is given by

$$\lim_{\omega\to 0} \mathrm{Im}\hat{C}^{(\mu)}(\omega) = 2Z^{(\mu)} \sum_{k=1}^{2^\mu} \alpha_k^{-1} \sinh(\tfrac{1}{2}\beta\hbar\alpha_k) \tag{5.23}$$

from Eq. (5.15). Here care must be taken when one of the α_k equals zero. In such a case it is understood that

$$X^{-1}\sinh X\,\big|_{X=0} = 1. \tag{5.24}$$

The calculation of $\hat{\gamma}(\omega)$ and Ω for the assumed potential V completes the calculation of the spectral function $\hat{\alpha}(\omega)$ unless further information for the potential coefficients is assumed. As a possible application of the present result we may consider the U-center infrared absorption. This problem has been studied extensively by Maradudin[18–20] and others.[7]

According to the Green–Kubo formalism[21] the absorption due to the localized mode is described by the complex conductivity $\sigma(\omega)$, which is shown to be given by the complex spectral function $\alpha(\omega)$ as follows [see Eq. (3.11)]:

$$\sigma(\omega) = \frac{e^2}{i\hbar} \int_0^\infty \langle [Q_0,\, \dot{Q}_0(t)] \rangle\, e^{-i\omega t - \epsilon t} dt$$

$$= \tfrac{1}{2}e^2[\alpha(\omega) + \alpha^*(-\omega)], \qquad (5.25)$$

where eQ_0 is the effective electric-dipole moment of the localized mode. The results by the previous workers for $\sigma(\omega)$ are equivalent to the present one, even though the present result is much more general in the sense that the higher-order coupling does not require much further calculation because of the general expression of the function given in Eqs. (5.14) and (5.15).

VI. CONCLUDING REMARKS

We have used the projection-operator method to calculate the single-particle time-correlation function which provides in a simple manner all the necessary spectral and response functions for the calculation of the various transport properties. The perturbation theory applied to the correlation of the single normal mode amply demonstrates the effectiveness of this approach. Because of the generality of our results, they should be applicable to a host of transport problems in the condensed state. We have in mind application to the vibrational relaxation in liquid systems where Greer and Rice[8] have recently made progress with an interesting suggestion for the coupling terms. Further, the problem of laser-excited vibrational fluorescence[22] of molecular impurities in solids at low temperature, such as CO in solid argon, is worth looking into with the present method.

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Measurements of the Electronic Recombination Coefficient in a Helium Plasma Jet

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The three-body recombination coefficient has been measured in a partially ionized plasma jet mainly by using a spectroscopic technique. Experimental data were treated by the consideration that the net number of particles that were deexcited across a minimum in the total rate of deexcitation of atoms was substantially equal to the number of electronic recombinations. Experimental results are in good agreement with other investigated values and show $T_e^{-4.4}$ dependence of the recombination coefficient.

I. INTRODUCTION

The electron-electron-ion three-body recombination in an optically thin plasma of moderate density has been the subject of numerous studies for a long time, and a large amount of attention has focused on this phenomenon. Considerable progress has been made in the theory of electronic recombination by the appearance of a collisional-radiative recombination theory of Bates, Kingston, and McWhirter, [1] and a quantitative agreement between observed and calculated values has been ob-