Paley-Wiener criterion for relaxation functions

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It is shown how the Paley-Wiener theorem in Fourier-transform theory can provide the bound for physically acceptable relaxation functions for long times. In principle the linear exponential decay function, and hence also a superposition of linear exponential decay functions, does not provide an acceptable description of relaxation phenomenon although the Paley-Wiener bound can be made to approach arbitrarily close to linear exponential. A class of relaxation functions proposed recently obeys the Paley-Wiener bound. The general necessity for time-dependent relaxation rates is emphasized and discussed.

It is traditional[1,2] to discuss the residual part of relaxing quantities in terms of linear exponential decay, viz.,

$$\exp(-t/\tau) \ , \tag{1}$$

where τ is the "relaxation time", or a superposition[3-14] of exponential decay terms with a distribution of τ. In fact, deviations from this exponential behavior are usually observed in experimental measurements.[3-21] Other functional forms, namely,

$$\exp[-a(t/\tau_s)^b], \quad a > 0, \ 0 < b < 1 \tag{2a}$$

and

$$(t/\tau_s)^{-\alpha}, \quad \alpha > 0 \ , \tag{2b}$$

have proved to be widely applicable in the description of a large variety of relaxation phenomena in condensed matter physics.[10,15-21] Here τ_s is a characteristic time in the system. There have been many attempts[15-20] to understand the latter dependences in terms of a distribution of relaxation times. Alternatively, the functional forms [(2a) and (2b)] have been viewed as fundamental in themselves and based on mechanistic origins.[21] The purpose of the present paper is to employ the Paley-Wiener theorem[22] on Fourier transforms together with physical requirements that have to be satisfied by any relaxation process to discriminate between the two viewpoints.

In Eq. (1) τ is traditionally the result of calculating the linear time-proportional transitional probability given by the golden rule. The physical picture of relaxation here is that the system which is relaxing is in contact with a heat bath. The heat bath in turn is described by a Hamiltonian which is not affected by interaction with the relaxing system. It is the interaction between the system and the heat bath which leads to the relaxation process.[23-25] An alternative scheme to this is the master equation approach.[26] Here again, the linear time-proportional transitional probabilities play a crucial role in setting up the master equation. The physical model for relaxation is, however, still the same—relaxing system, heat bath, and mutual interaction.[27] After eliminating the heat-bath variables, the relaxing system is treated by means of a model Hamiltonian such as Glauber's kinetic Is-

ing model where the linear time-proportional transitional probability is an essential input.[28,29]

In view of the experimental observation that the relaxation is described by a fractional exponential in condensed matter systems, it appears that the linear time-proportional transition probability may have to be changed suitably. This points to the fact that there is a failure of the application of the golden rule to the relaxing system plus heat bath. Since the heat bath is assumed to be very large compared to the relaxing system, the energy spectrum of the heat bath may be considered to be a continuum. The relaxing system has a spectrum which is embedded in this and the breakdown of the golden rule seems possible here, as in bremsstrahlung in quantum electrodynamics and the x-ray–edge problem in solid-state physics. The new time dependence of the transition rate indicates that the heat bath plays an active role in relaxation phenomena unlike in the traditional picture where it serves only to define the temperature of the system.[24]

In a separate context, the idea of decay of unstable states in quantum mechanics has been discussed in a manner quite analogous to our discussion of the relaxation of a system in contact with the heat bath.[30-32] Here the decay of a state is caused by a perturbation. In the discussion to follow, we focus on the time dependence of the relaxing system using the formalism developed by Chiu, Sudarshan, and Misra.[32] We find a bound for the effective transition rate for relaxation which replaces the constant transition rate used hitherto in the master equation or any other theory of relaxation. We believe that the scheme outlined here is an "effective" description of relaxation processes in condensed matter systems.

Let H be the Hilbert space formed by the totality of the relaxing states and those which are stable. The time evolution of this total system is then described by the evolution operator $U(t) = \exp(-iHt)$, where H is the self-adjoint Hamiltonian operator of the system. (Units with $\hbar = 1$ are used in this paper.) For the sake of simplicity, it is assumed that there is only one relaxing state represented by the vector $|R\rangle$ of H. The state $|R\rangle$ is associated with the continuous spectrum of H and is orthogonal to all bound stationary states of the Hamiltonian. It is assumed that the Hamiltoni-

an H has no singular continuous spectrum. If F_ϵ denotes the spectral projections of H,

$$H = \int \epsilon \, dF_\epsilon = \int \epsilon |\epsilon\rangle \langle \epsilon| d\epsilon \ , \tag{3}$$

then the function $\langle R | F_\epsilon | R \rangle$ is absolutely continuous, and its derivative

$$\rho(\epsilon) = \frac{d}{d\epsilon} \langle R | F_\epsilon | R \rangle = \langle R | \epsilon \rangle \langle \epsilon | R \rangle \tag{4}$$

can be interpreted as the energy distribution of the state $|R\rangle$. In other words, the integral $\int_E^{E+\Delta E} \rho(\epsilon) d\epsilon$ is the probability that the energy of the state $|R\rangle$ lies in the interval $(E, E + \Delta E)$. The function $\rho(\epsilon)$ has the following properties:

(i) $\rho(\epsilon) \geq 0$;

(ii) $\int \rho(\epsilon) d\epsilon = 1$

corresponding to the normalization condition, $\langle R | R \rangle = 1$; and

(iii) $\rho(\epsilon) = 0$

for ϵ outside the spectrum of H. In order that the system have a stable ground state, the spectrum of H must have a finite lower bound. Therefore $\rho(\epsilon)$ is semibounded.

The residual part of a relaxing quantity, $Q(t)$, at an instant t for the relaxing state $|R\rangle$ is[33]

$$Q(t) \propto |\langle R | \exp(-itH) | R \rangle|^2 \ . \tag{5}$$

The residual relaxing amplitude

$$c(t) = \langle R | \exp(-itH) | R \rangle \tag{6}$$

may be seen to be the Fourier transform of the energy distribution function $\rho(\epsilon)$,

$$c(t) = \int \exp(-i\epsilon t) \rho(\epsilon) d\epsilon \ . \tag{7}$$

The Paley-Wiener theorem[22] turns out to be the touchstone for the determination of the bounds on the long-time behavior of relaxation processes. This theorem stated in the present context is as follows: The necessary and sufficient condition that there exists a function $\rho(\epsilon)$, which is the Fourier transform of a square integrable function $c(t)$ and which vanishes below some value of ϵ, say zero [i.e., $\rho(\epsilon)$ is semibounded in the ϵ variable], is

$$\int_{-\infty}^{\infty} \frac{|\ln|c(t)||}{1+t^2} dt < \infty \ . \tag{8}$$

This condition is guaranteed if, for $(t/\tau_s) \to +\infty$,[30]

$$|c(t)|^2 \geq \exp[-a(t/\tau_s)^b], \quad a > 0, \ 0 < b < 1 \ . \tag{9}$$

Here τ_s is a characteristic time so that a is dimensionless. It should be noted that both the forms (2a) and (2b) satisfy this inequality whereas the linear exponential form (1) does not. Thus the two cases, Eqs. (1) and (2), are mutually exclusive. Although b may approach arbitrarily close to 1, the case $b = 1$ corresponds to a physically unrealistic, unbounded $\rho(\epsilon) \propto a\tau_s^{-1}[(a/\tau_s)^2 + \epsilon^2]^{-1}$, and therefore violates the conditions of the Paley-Wiener theorem. Since a single linear exponential form is unphysical, a superposition of them is also unphysical. Hence the idea of superposition of exponentially decaying functions must also be ruled out as a

viable description of relaxation phenomena.

Also, in general, the case $b = 0$ in Eq. (2a) is excluded. This follows from the fact that the corresponding $c(t)$ would violate the condition of square integrability, which is also physically untenable since then $Q(t)$ cannot then be proportional to $|c(t)|^2$. However, when $b \to 0$ in such a way that $ab \to \alpha$ where α is nonzero, it may be shown that

$$|c(t)|^2 \geq (t/\tau_s)^{-\alpha} \ , \tag{10}$$

with $\alpha > 1$ for $t/\tau_s \to \infty$. Therefore, the requirements of the Paley-Wiener theorem are again met. It is remarkable that both the Paley-Wiener limiting form, Eq. (2a), and the simple inverse power decay, Eq. (2b), have been repeatedly found to govern many different relaxation processes in condensed matter physics. Both of these have also been predicted from microscopic models.[21]

Since $|c(t)|^2$ is monotonic for large t/τ_s, it follows from Eqs. (5) and (9) that

$$-\frac{dQ}{dt} \propto -\frac{d|c(t)|^2}{dt} \leq a(b/\tau_s)(t/\tau_s)^{b-1}|c(t)|^2 \ ,$$

$$t/\tau_s \to \infty \quad (0 < b < 1) \tag{11}$$

The effective transition rate $W(t)$ has a bound

$$W(t) \leq a(b/\tau_s)(t/\tau_s)^{b-1} \quad (0 < b < 1) \ . \tag{12}$$

Thus $W(t)$ has an essential dependence on t. The impact of time-dependent transition rates in relaxation processes has recently been discussed elsewhere.[34] Again the limit of $b = 1$ would lead to a constant transition rate, as is the familiar result for a linear exponential decay. As noted above, this case was ruled out so that the transition rate must be a function of time and must have the bound given by Eq. (12).

As mentioned above, Eq. (12) may be extended to include the case $b \to 0$ such that $ab \to \alpha$, where α is nonzero. Then

$$W(t) \leq \alpha t^{-1} \ . \tag{13}$$

This corresponds to the case described by Eq. (10). It is interesting to note that Eqs. (9), (12), and (13) provide a hierarchy of bounds for a relaxing quantity and their corresponding transition rates.

The fact that the effective transition rate has an essential dependence on time shows that it is not compatible with the traditional derivation of constant transition rates by means of the Fermi golden rule.[35] In fact the breakdown of the Fermi golden rule has been noted very often in the literature.[36-40] The familiar expression for the transition rate[35] is a good approximation for long times $t \gg (\Delta E)^{-1}$, where ΔE is the energy difference between the two states between which the transition is taking place. The explicit examples of the breakdown of this are in bremsstrahlung in quantum electrodynamics and the x-ray–edge problem in solid-state physics. In the relaxation regime, such characteristic energy differences may also approach zero. This indicates the breakdown of the approximation in the derivation of the constant transition rate. In this situation, one must carry out a more careful calculation which leads to a time-dependent transition rate as discussed above.

The occurrence of apparent constant transition rates for the "elementary excitations"[41] commonly observed spectroscopically in condensed matter, viz., neutron, Raman, microwave, far infrared, infrared, visible, ultraviolet, x ray,

etc., may be understood to be consistent with the Paley-Wiener theorem if b is taken to approach unity but never quite attain it. Such cases probe either the discrete states or continuum states of the many-particle Hamiltonian H with typical energies in the range $\geq 10^{10}$ Hz such as electrons, phonons, magnons, etc., and the approximation $t\,\Delta E \gg 1$ is good. For relaxation phenomena, b rarely approaches unity. What are involved in the low-frequency relaxation processes are low-frequency excitations of the system below, say 10^{10} Hz. It is clear that an experimental effort should be made to observe these excitations directly. In fact, they may already have been observed in recent experiments.[42]

In general, the effect of these excitations should occur in any of a number of long-tail transient spectroscopic observations made possible by modern electronic advances.

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[33]It is useful here to make a comment elucidating the meaning of relaxing states to characterize relaxation. Equation (5) may be generalized to the assertion that the approach to equilibrium of the system density matrix is controlled by the vanishing of relaxing states. After an appropriate ensemble average, we may assume that the density matrix is diagonal so that a typical element may be written as

$$\sigma_T(\epsilon,t) = \sum_R \langle \epsilon | R(t) \rangle \sigma_R(0) \langle R(t) | \epsilon \rangle + \sigma(\epsilon,t) \ .$$

Here

$$\int \sigma_T(\epsilon,t)\,d\epsilon = \lim_{t\to\infty} \int \sigma(\epsilon,t)\,d\epsilon = 1 \ ,$$

so that $\int \sigma(\epsilon,t)\,d\epsilon < 1$ for general t. The first term on the right-hand side is the contribution from relaxing states that vanishes in accordance with the Paley-Wiener bound that occurs as described below Eq. (7). On the other hand, although the $\sigma(\epsilon,t)$ must adjust to become the equilibrium stationary value such that

$$\lim_{t\to\infty} \int \sigma(\epsilon,t)\,d\epsilon = 1 \ ,$$

their rearrangement is dominated by the vanishing of the relaxing states for large times which therefore control the approach to equilibrium

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