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A TWO-STATE MODEL FOR NON-EXPONENTIAL RELAXATION IN CONDENSED MATTER*

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A two-state model is presented for polarization relaxation in condensed matter. The dynamics of relaxation is treated with quantum transition theory. The physical meaning of the so-called time-dependent transition rate is clarified. The new model not only gives the fractional exponential and power-law relaxation functions naturally, but also indicates that the universality of the relaxation law results from the scaling behavior of low-frequency effective spectrum.

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I. INTRODUCTION

It has been shown experimentally that in a large variety of relaxation phenomena in condensed matter the relaxation function follows the fractional exponential form or power-law form, or a combination of the two forms[1-6], namely,

$$q(t) = \exp(-at^b) \quad a > 0,\ 0 < b < 1\ , \tag{1}$$

$$q(t) \sim t^{-\alpha} \quad t \to \infty,\ \alpha > 0\ . \tag{2}$$

These two "universal" relaxation forms depart strongly from the traditional Debye exponential form ($b = 1$). The models that are concerned with the two forms can be divided into two major classes. One is the distribution of relaxation time theory, in which $q(t)$ is expressed as a superposition of exponential decay terms, $q(t) = \int f(\tau)\exp(-t/\tau)\mathrm{d}\tau$. The main task of the theory is to find the weight distribution $f(\tau)$ of the relaxation time. This approach is microscopically arbitrary and does not explain the universality of the relaxation laws. The other uses the following phenomenological rate equation:

$$\mathrm{d}q(t)/\mathrm{d}t = -W(t)q(t) \tag{3}$$

and tries to determine the so-called time-dependent rate function $W(t)$ from microscopical models. In Ngai's correlated state model[1] and Dissado and Hill's double-well potential model[7], the essential importance of low frequency excitations of certain correlated-states in dynamics of relaxation was stressed. But the dynamical origin of the correlated-state and

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the physical meaning of time-dependent rate are not clear at present.[8] So there is still no satisfactory theory to account for these two relaxation forms (1) and (2).

In this paper, we shall confine our attention to the polarization relaxation (dielectric and paramagnetic relaxation) and present a two-state model treated with quantum transition theory. In contrast to previous models the present model not only treats the dissipation more rigorously but also gives the two relaxation forms naturally.

II. THE DYNAMICAL MODEL

Consider a set of dipoles (or Ising spins) localized on the lattice. Suppose each dipole moves in the same mean-field provided by the lattice and other dipoles in the absence of external electrical field. Denote the Hamiltonian of the static part ($T = 0$) of this field as H_d. It has two degenerate eigenstates $|\pm\rangle$ representing the two equivalent sites of each dipole, in which its dipole moment assumes values $\pm\mu$. The dynamical part of the lattice is taken as a heat bath modeled as a set of harmonic oscillators (henceforth $\hbar = k_B = 1$),

$$H_l = \sum_n \omega_n (p_n^2 + q_n^2)/2 \,, \tag{4}$$

where P_n is the dimensionless momentum of mode n and q_n is the dimensionless coordinate. The eigenstates of $H_0 = H_d + H_l$ are

$$|\pm n_i\rangle = |\pm\rangle|n_1, n_2, \cdots\rangle \,, \tag{5}$$

in which there are n_i phonons on the i-th mode. Suppose the dipole is linearly coupled to the phonons,

$$H' = \sum_n \lambda_n q_n V \,, \tag{6}$$

where λ_n is the dimensionless coupling constant and V is only related to the dipole. We shall show later that the relaxation of dipoles from a polarized state to a nonpolarized state after removal of an external electrical field corresponds to the quantum transition process from initial state $|+\rangle$ to final state $|-\rangle$ under the perturbation H'. Following the conventional treatment of first-order time-dependent perturbation, we get the transition probability $P(t)$ that the dipole is in state $|-\rangle$ at time t and was in state $|+\rangle$ initially,

$$P(t) = \sum{}' 2|\langle +n_i|H'|-n_i'\rangle|^2 (1 - \cos\Delta E t)/(\Delta E)^2 \,, \tag{7}$$

where $\sum'$ represents the summation over all possible final states and the thermal average of the initial phonon states.

Before discussing the relation between $q(t)$ and $P(t)$, we would like to show that the above two-state model can be derived from the practical dipole-dipole (or spin-spin) interaction,

and the coupling constant λ and V can be determined microscopically. Now we study the interaction between dipole and its surroundings, which causes dipole-flip. We introduce a dipole-dipole coupling with the general form

$$H_{\mathrm{I}} = \sum_{ij} J(\boldsymbol{r}_{ij}) \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \ , \tag{8}$$

where $\boldsymbol{\mu}_i$ is a one-component dipole vector localized at site i. To consider the effect of lattice vibration we expand $J(\boldsymbol{r}_{ij})$ at the equilibrium position of the lattice to the first order

$$J(\boldsymbol{r}_{ij}) = J_0(\boldsymbol{r}_{ij}) + \nabla J_0(\boldsymbol{r}_{ij}) \cdot \Delta \boldsymbol{r}_{ij} \ . \tag{9}$$

Inserting Eq. (9) into Eq. (8), we get

$$H_{\mathrm{I}} = \sum_{ij} (J_0(\boldsymbol{r}_{ij}) + \nabla J_0 \cdot \Delta \boldsymbol{r}_{ij}) \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \ . \tag{10}$$

Noting the fact that the temperature of practical interest is much higher than that of phase transition, we can take mean-field approximation to rewrite Eq. (10) as

$$H_{\mathrm{I}} = \sum_i (\boldsymbol{B}_i + \boldsymbol{C}_i) \cdot \boldsymbol{\mu}_i \ , \tag{11}$$

$$\boldsymbol{B}_i \equiv \sum_j J_0(\boldsymbol{r}_{ij}) \boldsymbol{\mu}_j \ , \tag{12}$$

$$\boldsymbol{C}_i \equiv \sum_j (\nabla J_0 \cdot \Delta \boldsymbol{r}_{ij}) \boldsymbol{\mu}_j \ . \tag{13}$$

Therefore, a set of coupled dipoles become a set of independent dipoles which move in the mean fields $\boldsymbol{B}$ and $\boldsymbol{C}$.

It can be proved that $\boldsymbol{B}$ contributes to $P(t)$ just a constant of time so it has nothing to do with the relaxation. We need only consider the dipole-lattice coupling term $\boldsymbol{C}$. Now with phonon coordinates the Hamiltonian of a dipole-lattice system can be written as $H = H_{\mathrm{d}} + H_{\mathrm{l}} + H'$, where H_{l} and H' are given by Eqs. (4) and (6), respectively. λ_n and V are determined by the expansion of Eq. (13) with phonon coordinates.

For a set of Ising spins with spin-spin coupling, similar results can be obtained under the same condition. So one can see that in contrast to previous models this two-state model, though simple, can be determined microscopically.

III. RELATIONSHIP BETWEEN $q(t)$ AND $P(t)$

The normalized relaxation function $q(t)$ describes the decay of polarization following the removal of a constant field at $t = 0$,

$$q(t) = (N_+(t) - N_-(t))/N \ , \tag{14}$$

where $N_{\pm}(t)$ is the number of dipoles which occupy state $|\pm\rangle$, and N is the total number of dipoles. If the motion of dipoles can be described by the mean field approximation, which is realized in most cases of practical interest, the expression of $q(t)$ can be explained as an average over the ensemble which consists of statistically independent dipoles. From a microscopic point of view, after the removal of external field, the motion of statistically independent dipoles can be regarded as quantum transitions between states $|\pm\rangle$ caused by the mean field which is determined by interactions between dipole and its surroundings. Within the ensemble average explanation of $q(t)$, it can be considered as a measure of the probability that a dipole has not lost its memory of initial state until time t. According to quantum transition theory, once the transition from initial state $|+\rangle$ to final state $|-\rangle$ occurs, the information of early state is totally lost. Then $q(t)$ is equal to the probability that a dipole remains in its initial state $|+\rangle$ until time t. We shall call this probability the lifetime probability of initial state and refer to it as $Q(t)$, then

$$q(t) = Q(t) \,. \tag{15}$$

According to the linear response theory[2,3], it is easy to find that $q(t)$ is equal to the normalized dipole correlation function $S(t) = \langle\mu(t)\mu(0)\rangle$ under the condition of $\omega_n \ll T$, which is realized in practice, then

$$q(t) = S(t)/S(0) \,. \tag{16}$$

Now we discuss how to determine $Q(t)$ and $q(t)$ from microscopic dynamics.

It should be pointed out that there are two essentially different kinds of descriptions for the dipole-flip process. The description in terms of lifetime is a macroscopic one, in which lifetime of initial state is considered as a measurable quantity. For example, the lifetime of excited state of a two-level atom is corresponding to the time interval between the preparation time for exciting the atom and the time of receiving radiation emitted during the transition from excited state to ground state. But in the conventional treatment of quantum transition with the picture "interaction causing transition", when the perturbation is applied to the state of the system, no longer stationary, is a coherent superposition of eigenstates of H_0. The lifetime of any eigenstate of H_0 cannot be defined. How can we describe an irreversible and discontinuous quantum transition process by a continuous and coherent description? The key point of the conventional treatment is to derive a transition rate (golden rule) under the following three conditions: the spectrum of H_0 is very dense (the number of freedom of the system tends to infinity), the time $t \to \infty$, and $|\langle +n_i|H'|-n_i'\rangle|^2$ is a slow variation function of energy. Under these conditions, the transition probability $P(t) \propto t$ and $\mathrm{d}P/\mathrm{d}t$ gives the transition rate. But what is the probability meaning of transition rate? To the best of our knowledge, there has been little discussion so far. In

most practical cases, it is postulated that the transition rate is proportional to the number of transitions per unit time. This implies that it should be th probability intensity that the transition occurs at time t. But owing to the coherence of eigenstates of H_0, $P(t)$ is generally an oscillating function of time and the positiveness of $\mathrm{d}P/\mathrm{d}t$ is not guaranteed. Only in the macroscopic lifetime description, can a well-defined transition probability intensity, which is proportional to the number of transitions per unit time, be introduced. We shall refer to it as the time-dependent transition rate $R(t)$, which is defined as

$$R(t) \equiv -(\mathrm{d}Q(t)/\mathrm{d}t)/Q(t) \,. \tag{17}$$

It can be proved that $R(t)\mathrm{d}t$ is the conditional probability that the transition occurs in the time interval $(t, t+\mathrm{d}t)$, given that the lifetime of initial state is longer than t.[9] From Eq. (17) it turns out that the time-dependent transition rate $R(t)$ uniquely determines the lifetime probability of initial state $Q(t)$.

$$Q(t) = \exp(-\int_0^t R(s)\mathrm{d}s) \,. \tag{18}$$

It has been clear that the golden rule is the right result and what has been unclear is its solid dynamical foundation.[10] However, here we do not deal with this problem but only discuss the physical meaning of the conventional treatment. We point out that $\mathrm{d}P/\mathrm{d}t$ can be identified as time-dependent transition rate only when the microscopic description has been transformed to macroscopic one under certain transition conditions which guarantee the monotony of $P(t)$. These conditions are in essence the the same as those used in deriving the master equation from quantum Liouville's equation by using a coarse-graining method which cancels coherence between quantum states and allows a classical lifetime description of the master equation. It was pointed out that the limit of infinite numbers of freedom, i.e., the thermodynamic limit, is essential in introducing relaxation.[11] In fact, only this condition is used in the present model, which leads to the situation that the transition rate $R(t)$ is generally time-dependent. Therefore, under the conditions mentioned above, $\mathrm{d}P/\mathrm{d}t$ can be identified as time-dependent transition rate $R(t)$, i.e.,

$$\mathrm{d}P(t)/\mathrm{d}t = R(t) \,. \tag{19}$$

From Eq. (18), noting $P(0) = 0$, we get

$$Q(t) = \exp(-P(t)) \,. \tag{20}$$

This is the formula that determines relaxation function $q(t)$ and lifetime probability $Q(t)$ from microscopic dynamics.

From the definition of $R(t)$ and the equivalence between $Q(t)$ and $q(t)$ in the present model, we can identify the coefficient $W(t)$ in the phenomenological rate equation (3) as

$R(t)$ and find out that the rate equation is the exact one for depolarization relaxation of the model, which clarifies the physical meaning of the so-called time-dependent rate function.

IV. CALCULATION OF $P(t)$

Noting that $q_n = \sqrt{2}(a_n^+ + a_n)/2$ and taking continuous spectrum limit, we have

$$P(t) = A\int(2n(\omega)+1)(1-\cos\omega t)F(\omega)\mathrm{d}\omega/\omega^2 \ , \tag{21}$$

$$F(\omega) \equiv \lambda^2(\omega)\rho(\omega) \ , \tag{22}$$

where $A = |\langle +|V|-\rangle|^2$, $n(\omega) = 1/(\exp(\omega/T)-1)$, $\rho(\omega)$ is the density of states of phonon, and $F(\omega)$ is called the effective spectrum. It can be shown that if $F(\omega)$ is an integrable function, then the higher frequency part of integration (21) ($\int_c^\infty \mathrm{d}\omega, c > 0$) tends to a constant of time when $t \to \infty$, and contributes a pre-exponential factor to $q(t)$. So the long time relaxation is only determined by the low-frequency behavior of $F(\omega)$, which confirms the arguments of other authors on the importance of low-frequency modes. It is conventional to suppose that $F(\omega)$ follows a power law:

$$F(\omega) = a\omega^\beta \quad \omega \le \omega_0 \ , \tag{23}$$

where ω_0 is the top cutoff frequency for the scaling behavior. The physical significance of the scaling law will be discussed in the next section. Now we consider the case of temperature $T \gg \omega_0$. In this case $n(\omega) \approx T/\omega \gg 1$, Eq. (21) becomes

$$P(t) = 2aAT\int_0^{\omega_0}(1-\cos\omega t)\omega^{\beta-3}\mathrm{d}\omega \ ; \tag{24}$$

when $0 < \beta < 2$, $P(t) = 2aAT t^{2-\beta} f(\omega_0 t)$,

$$f(x) \equiv \int_0^x (1-\cos y)y^{\beta-3}\mathrm{d}y \ . \tag{25}$$

Since $f(x)$ is a monotonously increasing and bounded function, it turns out that $P(t)$ is a monotonously increasing function and $f(x)$ can be well approximately replaced by its limit value $f(\infty)$ when $\omega_0 t \gg 1$,

$$f(\infty) = B(\beta) = \pi/[2\Gamma(2-\beta)\sin(\pi(2-\beta)/2)] \ . \tag{26}$$

When $\beta = 2$, $\omega_0 t \gg 1$,

$$P(t) = 2aAT(\gamma + \ln\omega_0 t + O(1/t)) \ , \tag{27}$$

where $\gamma \approx 0.577$ is Euler's constant. When $\beta < 0$, the integral (24) is divergent. In the case of $\beta > 2$, $P(t) \to$constant when $t \to \infty$ and the coupling of the dipole to the environment is too weak to cause an irreversible relaxation. From Eqs. (15) and (20), when $T \gg \omega_0$, we get

$$0 < \beta < 2, \quad q(t) = Q(t) = \exp(-2aAB(\beta)Tt^{2-\beta}) \ ; \tag{28}$$

$$\beta = 2, \quad q(t) = Q(t) = Q_0(\omega_0 t)^{-\alpha} \quad \omega_0 t \gg 1 , \tag{29}$$

$$\alpha = 2aAT, \quad Q_0 = \exp(-2aAT\gamma) .$$

In the case of $0 < T < \omega_0$, we can divide the integral (24) into two parts: $(0, \omega_1)$ and (ω_1, ω_0), choosing $\omega_1 \ll T$. The integral on (ω_1, ω_0) is a constant when $t \to \infty$ and high temperature approximation is applicable on $(0, \omega_1)$. Then similar results can be obtained by replacing ω_0 in Eq. (29) by ω_1 and adding a pre-exponential factor determined by the integral (24) on (ω_1, ω_0). For $T = 0$, Eq. (21) becomes

$$P(t) = aA \int_a^{\omega_0} (1 - \cos \omega t)\omega^{\beta-2} \mathrm{d}\omega . \tag{30}$$

Similar calculation gives

$$-1 < \beta < 1 , \qquad \begin{array}{l} q(t) = Q(t) = \exp(-aAB'(\beta)t^{1-\beta}) , \\ B'(\beta) = \pi/[2\Gamma(2-\beta)\sin(\pi(1-\beta)/2)] ; \end{array} \tag{31}$$

$$\beta = 1 , \qquad \begin{array}{l} q(t) = Q(t) = Q_0(\omega_0 t)^{-\alpha} \quad \omega_0 t \gg 1 , \\ \alpha = aA , \quad Q_0 = \exp(-aA\gamma) . \end{array} \tag{32}$$

From the equivalence between $q(t)$ and $S(t)/S(0)$, the form of correlation function $S(t)$ is the same as $q(t)$. In fact, when $T \gg \omega_0$, $S(t)$ can be calculated exactly and a result consisting with Eqs. (20) and (24) was obtained[8], which is a natural corollary of the general relation between $q(t)$ and $S(t)$ and shows the efficiency of the first order perturbation used here.

V. DISCUSSIONS

The above results show the relaxation form depends critically on the low-frequency scaling behavior of the effective spectrum $F(\omega)$, which is determined by the product of the dynamical coupling and phonon state density. Both factors can have a profound effect on the behavior of $F(\omega)$. It should be stressed that not all of the modes of phonon enter the effective spectrum $F(\omega)$, but only a small part of modes, which is coupled to the localized dipole (or spin), make contribution to $F(\omega)$. On the other hand, the properties of phonon states coupled to a local dipole or spin can also affect the form of $F(\omega)$. Because the localized phonon states are not coupled to local dipoles in the same way as extended phonon states, so the form of $F(\omega)$ can be quite different from the phonon state density $\rho(\omega)$. If we express $F(\omega)$ in Debye's form ω^{d-1}, the fractional exponential law(1) requires $2 < d < 3$ $(1 < \beta < 2)$. It seems a natural result from the viewpoint of fraction. But the fraction model cannot be used here for th reasons given above. And it is a common belief that most amorphous materials cannot be characterized by fractals. It has been shown[12] that for amorphous metals, owing to the breakdown of momentum conservation, the low-frequency part of the effective phonon spectrum will be much softened, namely, the scaling index decreases compared with

the index of perfect lattice. Although the effective spectrum of amorphous insulators has not yet been definitely explained, we suggest that the softened property of effective spectrum might be a general feature of amorphous materials and this feature leads to the universality of the fractional exponential relaxation law. However, a great deal of work should be done, both theoretically and experimentally, in order to know the exact relation between disorder and localization and their effect on the effective spectrum.

In conclusion, a two-state model has been presented for the polarization relaxation in condensed matter. The dynamics of relaxation is treated with quantum transition theory. Through the analysis of relationship between the microscopic and macroscopic descriptions of quantum transition, the formula connecting the quantum transition probability and relaxation function is established. The physical meaning of the so-called time-dependent transition rate and the conventional rate equation for relaxation are clarified. The present model can not only give the fractional exponential and power-law relaxation functions naturally, but also indicate that the softened property of effective phonon spectrum leads to the universality of relaxation law. Finally, we would like to point out that in comparison with phenomenological treatment of coupling in previous models, we introduce coupling through dipole-dipole (or spin-spin) interaction, which allows further first-principle calculation for the effective phonon spectrum.

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