Spin-Lattice Relaxation: Non-Bloembergen-Purcell-Pound Behavior by Structural Disorder and Coulomb Interactions

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We study, by Monte Carlo simulation, the spin lattice relaxation rate $1/T_1(\omega,T)$ caused by diffusing ions in disordered structures. We show that both disorder and Coulomb interactions are essential to obtain the typical non-Bloembergen-Purcell-Pound behavior of $1/T_1$. The dependence of $1/T_1$ upon frequency ω and temperature T can be described by the simple scaling form $1/T_1=\omega^{-1}f(\omega\tau)$. We find that the NMR correlation time τ is more highly activated than the conductivity relaxation time τ_σ, which is in agreement with very recent experimental results.

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Nuclear magnetic resonance (NMR) [1] is one of the most common experimental techniques to probe ionic motion in disordered media, such as glass forming melts, electrolyte glasses, and crystalline ionic conductors with local disorder [2-7]. The behavior of the diffusion induced spin lattice relaxation rate $1/T_1(\omega,T)$, as a function of temperature T and Larmor frequency ω, can be summarized as [2-7]

$$\frac{1}{T_1}(\omega,T)\sim\begin{cases} e^{E_1/k_BT}, & T\gg T_{\max}(\omega),\\ \omega^{n-2}e^{-E_2/k_BT}, & T\ll T_{\max}(\omega), \end{cases} \tag{1}$$

with an exponent $n>0$. In an Arrhenius plot, $1/T_1$ shows a maximum at $1/T_{\max}(\omega)$, where $T_{\max}(\omega)$ decreases with decreasing frequency. Since generally $E_1>E_2$, the curve is asymmetric in shape. For fixed temperature T, $1/T_1(\omega,T)$ is constant at low frequencies $\omega\ll 1/\tau$ and decreases as ω^{n-2} for $\omega\gg 1/\tau$. The NMR crossover time τ is considerably larger than the inverse hopping rate ν^{-1} of the mobile ions [8]. In contrast to this overall behavior, the standard Bloembergen-Purcell-Pound (BPP) theory predicts a symmetric maximum of $1/T_1$ in the Arrhenius plot with $n=0$ and a NMR crossover time τ of the order of ν^{-1} [9].

A similar frequency dependence with a fractional exponent $n_\sigma>0$ and a crossover frequency τ_σ^{-1} is observed in the frequency dependent conductivity $\sigma(\omega,T)$ below the GHz regime [10]. For fixed temperature, $\sigma(\omega)$ is constant at low frequencies $\omega\ll 1/\tau_\sigma$ and increases as $\sigma(\omega)\sim(i\omega)^{n_\sigma}$ for $\omega\gg 1/\tau_\sigma$. Again, except at high temperatures, τ_σ is considerably larger than ν^{-1} and the activation energy E_1^σ in the dc regime is larger than the apparent activation energy E_2^σ in the dispersive regime [11]. As the temperature is lowered, $1/\tau_\sigma$ decreases and the exponent n_σ seems to increase [12]. In contrast, standard random walk theory predicts no dispersion to occur; $n_\sigma=0$. Similar anomalies have been observed in quasielastic light or neutron-scattering [13,14] and ultrasonic attenuation [15].

It has been suggested by several authors [10,16-18] that the Coulomb interaction between the mobile ions, which is not taken explicitly into account in the standard theories, is responsible for the anomalous transport behavior. Mean-field [17] and mode-coupling [18] approaches as well as Monte Carlo simulations [19] of tracer diffusion and ionic conductivity in disordered structures have substantiated this idea.

In this Letter we investigate, for the first time, how the spin lattice relaxation rate and the related NMR correlation functions are affected by structural disorder and Coulomb interaction between the mobile ions. We show by Monte Carlo simulations that it is the interplay of both Coulomb interaction and structural disorder that gives rise to the typical non-BPP behavior of $1/T_1(\omega,T)$ with an exponent n being independent of temperature. We find that $1/T_1$ obeys simple scaling behavior. In contrast, the exponent n_σ increases with decreasing temperature and the conductivity $\sigma(\omega,T)$ obeys no simple scaling form. At lower temperatures, n_σ approaches n, and in this case $1/T_1$ and σ may be simply connected, as suggested by mean-field theory [17] and some experiments [3]. The conductivity relaxation time τ_σ is less activated than the NMR correlation time τ, in agreement with very recent experimental results [20,21].

According to the standard theory [1], the spin-lattice relaxation rate $1/T_1$ is determined by the spectral densities $J^{(1)}(\omega)$ and $J^{(2)}(\omega)$,

$$\frac{1}{T_1}=C[J^{(1)}(\omega)+J^{(2)}(2\omega)]\,, \tag{2}$$

which are the Fourier transforms of the correlation functions $G^{(q)}(t)$, $J^{(q)}(\omega)=\int_{-\infty}^{\infty}G^{(q)}(t)e^{i\omega t}dt$, $q=1,2$; ω is the Larmor frequency, and C is a constant depending only on the nuclear properties of the mobile ions. For magnetic dipole-dipole or quadrupolar interactions, $G^{(q)}(t)$ can be written as [1]

$$G^{(q)}(t)=\frac{1}{N}\sum_{i\neq j}^{N}\langle F_{ij}^{(q)*}(t)F_{ij}^{(q)}(0)\rangle\,. \tag{3}$$

The brackets $\langle\rangle$ stand for the thermal average, N denotes the number of particles, and $F_{ij}^{(q)}(t)=q(8\pi/$

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$15)^{1/2}Y_2^q(\Omega_{ij}(t))/r_{ij}^3(t)$ describes the local field between the particles i and j. Y_2^q are the spherical harmonics, and Ω_{ij} and r_{ij} are the spherical coordinates of the vector $\mathbf{r}_{ij}$ pointing from the ith to the jth particle, with respect to the magnetic field. The ansatz $G^{(q)}(t)=G^{(q)}(0)e^{-t/\tau_0}$ leads to the standard BPP behavior.

We consider mobile particles with density ρ in both an ordered and a disordered simple cubic lattice of spacing a with periodic boundary conditions. The magnetic field is aligned along the [100] direction. To model the structural disorder we assume that a certain fraction $1-p$ of sites is inaccessible for the mobile particles, and take the diffusion path that percolates through the lattice as disordered substrate [22]. The particles can hop between accessible neighboring sites, the structural potential barrier between the sites is V. In the absence of Coulomb interactions the hopping rate is simply $\tau_0^{-1}=\tau_\infty^{-1}\times\exp(-V/k_BT)$, where τ_∞^{-1} is an attempt frequency. In the presence of Coulomb interactions, the modified potential barriers are calculated by using Ewald summations, and the hopping rates are chosen according to the standard Metropolis algorithm. For details of the simulation technique, we refer to [19]. The relative strength of the Coulomb interaction with respect to the thermal energy k_BT is characterized by the plasma parameter $\Gamma\equiv e^2/r_sk_BT$, where $\frac{4}{3}\pi r_s^3=\rho^{-1}$, and the relative strength with respect to the structural potential barrier V is $\eta\equiv e^2/r_sV$.

In our numerical simulations we have chosen a lattice of length $L=39a$, and $\rho=10^{-2}/a^3$, $\eta=5$, and $p=0.4$, which is well above the percolation threshold $p_c\cong 0.312$ [22]. Averages were performed over typically 100 configurations.

First we discuss our results for the correlation functions. For sufficiently large Γ ($\Gamma>10$) we found numerically that $G^{(2)}(t)\cong 4G^{(1)}(t)$ for all times t, and thus $G^{(2)}(t)/G^{(2)}(0)\equiv G^{(1)}(t)/G^{(1)}(0)$. Figure 1(a) shows $1-G^{(q)}(t)/G^{(q)}(0)$ versus t/τ_0 for $\Gamma=40$, 60, and 80 (i) in the ordered lattice and (ii) in the disordered system. The typical decay time τ of the correlations is defined by $G^{(q)}(\tau)/G^{(q)}(0)=1/e$. As is shown in the inset of Fig. 1(a), the ratio τ/τ_0 is thermally activated, $\tau/\tau_0=\exp(E_\tau/k_BT)$, with an activation energy $E_\tau\cong 0.04e^2/r_s=0.04\eta V$ in the regular lattice, and $E_\tau\cong 0.09e^2/r_s=0.09\eta V$ in the disordered system. In both systems, $1-G^{(q)}(t)/G^{(q)}(0)$ is proportional to t/τ_0 for small t/τ_0 values. In the disordered system, for $\Gamma>20$, an intermediate time regime can be well identified, where $1-G^{(q)}(t)/G^{(q)}(0)\sim(t/\tau_0)^{1-n}$. The exponent n is independent of temperature, $n\cong 0.73$. Closer inspection [Fig. 1(b)] shows that $G^{(q)}(t)/G^{(q)}(0)$ is only a function of t/τ, and thus $1-G^{(q)}(t)/G^{(q)}(0)\sim(t/\tau)^{1-n}$ for $\tau_0/\tau\ll t/\tau<1$. Hence, the correlation functions show Kohlrausch-Williams-Watts form [23], $G^{(q)}(t)=G^{(q)}(0)\times\exp[-(t/\tau)^{1-n}]$, in the relevant decay regime.

From Eq. (2) we obtain $1/T_1(\omega,T)$ by Fourier transformation. Figure 2 shows $1/T_1(\omega,T)$ as a function of V/k_BT for (a) the ordered lattice, and (b) the disordered system. In both cases, $1/T_1$ is independent of ω at the high temperature side of the maximum. In case (b), when both disorder and Coulomb interactions are present, we obtain the typical non-BPP behavior: The curves are asymmetric in shape, the maximum occurs at $\omega\tau$

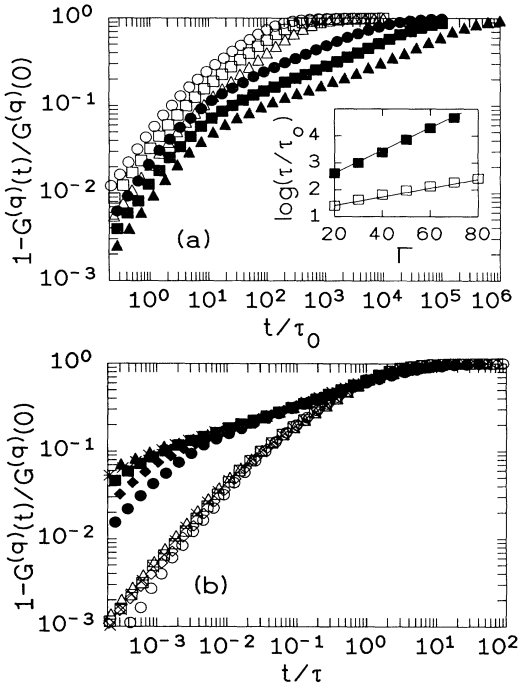

FIG. 1. Plot of $1-G^{(2)}(t)/G^{(2)}(0)$ in the ordered lattice (open symbols) and in the disordered system (filled symbols) (a) as a function of t/τ_0 for $\Gamma=40$ (○,●), 60 (□,■), and 80 (△,▲), and (b) as a function of the scaling variable t/τ for $\Gamma=40$ (○,●), 50 (◇,◆), 60 (□,■), 70 (×,∗), 80 (△,▲). The inset in (a) shows the ratio τ/τ_0 as a function of the plasma parameter Γ.

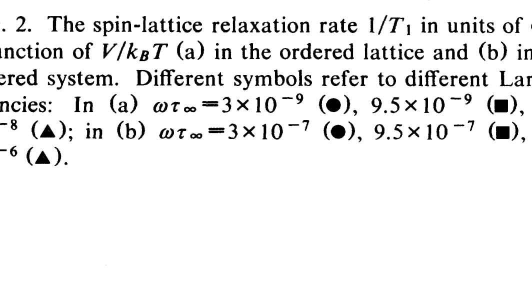

FIG. 2. The spin-lattice relaxation rate $1/T_1$ in units of $C\tau_\infty$ as a function of V/k_BT (a) in the ordered lattice and (b) in the disordered system. Different symbols refer to different Larmor frequencies: In (a) $\omega\tau_\infty=3\times10^{-9}$ (●), 9.5×10^{-9} (■), and 3×10^{-8} (▲); in (b) $\omega\tau_\infty=3\times10^{-7}$ (●), 9.5×10^{-7} (■), and 3×10^{-6} (▲).

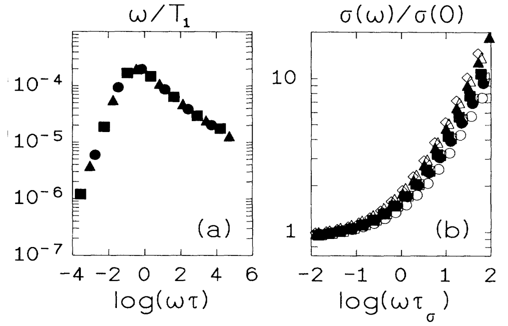

FIG. 3. Scaling plots of (a) ω/T_1 versus $\log(\omega\tau)$ and (b) $\sigma(\omega)/\sigma(0)$ versus $\log(\omega\tau_\sigma)$ for the disordered system. In (a) the symbols refer to the same frequencies as in Fig. 2(b), in (b) the symbols refer to different temperatures $V/k_BT=10$ (○), 20 (●), 30 (□), 40 (■), 50 (△), 60 (▲), and 70 (◇).

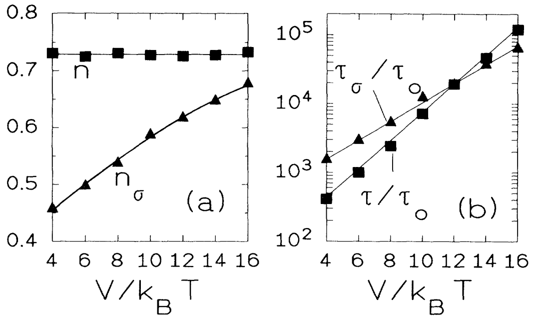

FIG. 4. Plot of (a) the exponents n and n_σ and (b) the relaxation times τ/τ_0 and τ_σ/τ_0 as a function of V/k_BT in the disordered system.

$\approx 1 \gg \omega\tau_0$ with τ from Fig. 1(b), and $1/T_1$ decreases as $1/T_1 \sim \tau(\omega\tau)^{-2+n}$ at low temperatures ($\omega\tau \gg 1$), with the same exponent n as in Fig. 1(b). The activation energies are $E_1 \cong 1.5$ V and $E_2 \cong 0.4$ V. It is important to note that in the absence of disorder, Fig. 2(a), the deviations from the standard behavior are much less pronounced, and an anomalous frequency dependence is hardly seen. The same is true in the disordered system, when the Coulomb interaction is absent [24]. This shows that the presence of *both* structural disorder and Coulomb interactions is needed to obtain the experimentally observed non-BPP behavior. In the following we concentrate on this relevant case only.

As a consequence of the scaling behavior of $G^{(q)}(t)$, $1/T_1(\omega,T)$ is described by the simple scaling ansatz [see Fig. 3(a)]

$$\frac{1}{T_1}(\omega,T)=\frac{1}{\omega}f(\omega\tau)\,, \tag{4}$$

where $f(x) \propto x$ for $x \ll 1$ and $f(x) \propto x^{n-1}$ for $x \gg 1$. Equation (4) implies $E_1 = E_\tau + V$ and the relation $E_2 = (1-n)E_1$ first proposed by Ngai [16].

The scaling ansatz (4) as well as the corresponding scaling ansatz for $\sigma(\omega)$, $\sigma(\omega,T)=\tau_\sigma^{-1}g(\omega\tau_\sigma)$ has been suggested by several authors [16,25]. To see if this scaling relation also holds for $\sigma(\omega,T)$, we have calculated, for exactly the same systems as above, the conductivity $\sigma(\omega,T)$ (for details of the simulation see [19]). We determined τ_σ from the crossover between the dc plateau and the dispersive region, and n_σ from the slope of $\log\sigma$ versus $\log\omega$ in the dispersive region. The result for $\sigma(\omega,T)/\sigma(0,T)$ is shown in Fig. 3(b), as a function of $\omega\tau_\sigma$. The absence of a data collapse shows that, in contrast to $1/T_1(\omega,T)$, there is no simple scaling behavior of $\sigma(\omega,T)$. The reason for this is that the exponent n_σ increases with decreasing temperature [see Fig. 4(a)], and therefore the temperature dependence of σ cannot be described alone by changing the frequency scale (which is indeed possible for $1/T_1$ since n is temperature independent). At lower temperatures, however, n_σ seems to approach n, and we expect mean-field approaches [3,17] yielding $n=n_\sigma$ to be applicable. Figure 4(b) shows the normalized time scales τ/τ_0 and τ_σ/τ_0 as a function of V/k_BT. It is important to note that the conductivity relaxation time τ_σ is less activated than the NMR relaxation time τ, and therefore $\tau/\tau_\sigma \gg 1$ at lower temperatures. This is in accordance with very recent experimental results for $(\mathrm{LiCl})_{0.6}(\mathrm{Li_2O})_{0.7}(\mathrm{B_2O_3})_{1.0}$ [20] and glassy $\mathrm{Li_2AlSi_2O_6}$ [21].

The different temperature dependence of the exponents n and n_σ and of the relaxation times τ and τ_σ show explicitly that in general a universal description of spin-lattice relaxation and conductivity cannot be made. The reason for this is that although the phenomena observed in both experiments originate from the same ion transport mechanism, they are governed by different correlation functions. In spin lattice relaxation, the correlation functions are determined by diffusion of ion pairs, while in conductivity the current-current correlation function is mainly determined by the diffusion of single ions. The deviations from the standard behavior arise from forward-backward correlations of the mobile ions, which occur at length scales between 1 and 3 jump distances [17,19]. Since short distances are weighted considerably more heavily in NMR than in conductivity, the effect of these forward-backward correlations becomes much stronger in NMR than in conductivity. Hence we expect larger deviations from the standard behavior in NMR measurements, with a larger exponent n and a larger activation energy E_τ, in agreement with our findings.

When submitting this paper we learned from K. L. Ngai that a generalized version of the coupling scheme [26] is in agreement with our results.

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