Interaction of the Conduction Electrons with Tunneling States in Metallic Glasses

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We consider a model designed to describe the interaction between the conduction electrons and the localized configurational excitations (tunneling states) in metallic glasses. We show that this interaction is dominated by an infinite sequence of Anderson overlap catastrophies. Using perturbation theory and scaling arguments we analyze the low-temperature behavior of the model.

In this Letter we explore some of the consequences of the interaction between tunneling levels and conduction electrons in metallic glasses. These levels, arising from local rearrangements of the amorphous atomic structure, were originally proposed to explain the low-temperature $(T < 1$ K$)$ properties of insulating glasses.[1,2] Moreover, it has been conjectured that they are generic features of the glassy state.[1] Recent ultrasonic saturation experiments[3,4] have dramatically confirmed earlier indications that these local configurational excitations also exist in metallic glasses.[5,6] Then, it becomes an interesting question to ask how do they interact with the electrons? Cochrane et al.[7] and Tsuei[8] have suggested that this coupling leads to precisely the same divergent contribution to the resistivity as occurs in the Kondo problem. However, we find that the metallic-glass problem is quite different. Nevertheless, the infrared-divergent response of the degenerate electron gas to local time-dependent perturbations (due to tunneling between local configurations) plays an important role, and this lends the problem a complexity of its own.

Our analysis is based upon a nonmagnetic model which was proposed by Kondo to describe the interaction between conduction electrons and an atom which can tunnel between two positions.[9] To suit our purpose we reinterpret this model to apply to a group of atoms moving between two configurations. Such two-state systems are most conveniently described by a pseudospin $S_i = \frac{1}{2}\sigma_i$ ($i = x$, y, z), where σ_i are the Pauli spin matrices. Thus, our basic Hamiltonian is

$$H = \sum_k \epsilon_k c_k^\dagger c_k + \Delta S_z + \Delta_0 S_x$$
$$+ K_{\parallel} S_z N^{-1} \sum_{kk'} c_k^\dagger c_{k'}, \qquad (1)$$

where ϵ_k is the single-electron energy, Δ is the energy difference between the two configurational states, Δ_0 is the tunneling frequency in energy

units, N is the total number of atoms in the sample, and $K_{\parallel}$ is the coupling energy. Note that, for the sake of simplicity, we have neglected all S_z-independent potential scattering terms and therefore aim to discuss only the qualitative features of the interaction.

We would like to stress that in our model an electron merely sees a different scattering potential for each state of the configuration but has no effective internal-spin degree of freedom as in Ref. 7. There it is assumed that the single-particle conduction-electron states in the presence of one tunneling configuration are orthogonal to those in the presence of the other configuration. This approach is questionable because the current-carrying electrons are not the electrons which are tightly bound to the atomic cores. Furthermore, if this picture were correct, the conduction electrons would have to be trapped inside the regions defined by the tunneling systems. To avoid such conceptual difficulties, we make no assumptions beforehand about the effect of the tunneling levels upon the electrons.

Let us begin by calculating the scattering rate $\tau_e^{-1}(\omega)$ for an electron of energy ω (measured from ϵ_F) in perturbation theory using $K_{\parallel}$ as a small parameter. To lowest order $(K_{\parallel}^2)$, we find the usual Born-approximation result, which we have shown elsewhere[10] to be unobservably small. In the Kondo problem the third-order contribution to $\tau_e^{-1}(\omega)$ diverges as $J^3 \ln|D/\omega|$, where J is the exchange energy and D is the bandwidth. In contrast we find a contribution of the form $K_{\parallel}^3 \ln|(\omega - E)/(\omega + E)|$, where $E^2 = \Delta^2 + \Delta_0^2$. This term does not contribute to the resistivity because it is an odd function of ω. This difference between the Kondo problem and the problem at hand is due to the difference in the spin algebra. However, the next term diverges as $\omega \to 0$. For $T \ll \omega \ll E$, to leading logarithmic approximation, it is given by

$$[\tau_e^{-1}(\omega)]^{(4)} = -\frac{\pi}{4\hbar}\rho^{-1}(\rho K_{\parallel})^4 \frac{\Delta^2 \Delta_0^2}{E^4}\tanh^2\frac{\beta E}{2}\left(\ln\frac{D}{\omega}\right)^2, \qquad (2)$$

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where ρ is the electronic density of states per atom at ϵ_F and $\beta = (k_B T)^{-1}$. Independently of the signs of $K_{\parallel}$, Δ, and Δ_0 this result indicates a singularity which tends to reduce the resistivity as the temperature is lowered. Thus the situation is similar to, but not identical with, the case of the ferromagnetic Kondo problem for which the effective coupling between the local spin and the conduction electrons decreases as T decreases.

The physical reason for the logarithmically divergent perturbation series above is the infrared-divergent response of the degenerate electron gas to a time-dependent external potential (due to the tunneling term Δ_0 in our Hamiltonian). As is well known, this effect is responsible for the various edge singularities in soft-x-ray spectroscopy where the time-dependent potential is that due to the sudden appearance or disappearance of a core hole.[11] It also accounts for the complexity of the Kondo problem where the time-dependent perturbation is caused by the flipping of the impurity spins.[12] In what follows we shall draw on the expertise developed in these fields to analyze our model beyond low-order perturbation theory.

Anderson, Yuval, and Hamann[12] have obtained a qualitatively correct solution to the Kondo problem by transforming it into a fictitious statistical mechanics problem of one-dimensional charged particles interacting via logarithmic pair potentials and then analyzing the scaling properties of the new problem with changes in the short-range cutoff associated with the pair potentials. (This cutoff is related to the bandwidth in the original problem.) Likewise, it can be shown that our problem, as defined by the Hamiltonian given in Eq. (1) is equivalent[13] to a logarithmic gas whose grand partition function is given by

$$Z = \sum_{n=0}^{\infty} (\tfrac{1}{2}\Delta_0)^{2n} \int_0^{\beta} d\beta_{2n} \cdots \int_0^{\beta_2 - \tau} d\beta_1 \exp\Big\{ \sum_{i>j} (-1)^{i-j}(2-\epsilon)\ln[(\beta_i - \beta_j)/\tau] + \Delta\sum_i (-1)^i \beta_i \Big\}, \tag{3}$$

where $\epsilon = 2 - (2\delta/\pi)^2$, $\tan\delta = \tfrac{1}{2}\pi\rho K_{\parallel}$, and τ is inversely proportional to the bandwidth D. Note that the quantity β is the true inverse temperature and should not be confused with the temperature of the logarithmic gas.

Significantly, Eq. (3) differs from the corresponding Kondo result in that, for weak coupling, we are near $\epsilon = 2$ ($\delta \ll 1$) while in the Kondo case ϵ is near 0. This is illustrated in Fig. 1. Thus, the logarithmic gas for our problem is in the "high-temperature" regime, far removed from the "phase-transition" region, $\epsilon = 0$, of the Kondo problem.

The basic idea of scaling in this context is to transform the problem at low temperatures to an equivalent problem with appropriately altered coupling constants at high T where the logarithmic divergences can be treated in perturbation theory. The fundamental assumption is that the temperature enters only through β/τ so that we may carry out this transformation by increasing τ. Anderson, Yuval, and Hamann[12] derived a set of scaling equations for the coupling constants and argued that it is valid everywhere near the $\tilde{\Delta}_0 = 0$ axis in Fig. 1. Translating their scaling equations into the language of our model we find

$$d\tilde{\Delta}_0/d\ln\tau = (1 - \tfrac{1}{2}\tilde{K}_{\parallel}^2)\tilde{\Delta}_0, \tag{4}$$

$$d\tilde{K}_{\parallel}/d\ln\tau = -(2A)^{-1}\tilde{K}_{\parallel}^3\tilde{\Delta}_0^2,$$

where $\tilde{\Delta}_0 = \Delta_0\tau$, $\tilde{K}_{\parallel} = 2\delta/\pi \approx \rho K_{\parallel}$, and $A = (\tilde{K}_{\parallel}^2)_0$,

the initial value. The scaling trajectories are shown in Fig. 1.

Evidently the $\tilde{K}_{\parallel}$ equation implies that the coupling gets *weaker* as τ increases. As was explained above, increasing τ amounts to decreasing T. From the $\tilde{\Delta}_0$ equation it follows that the tunneling frequency $\tilde{\Delta}_0\tau^{-1}$ also decreases as T is
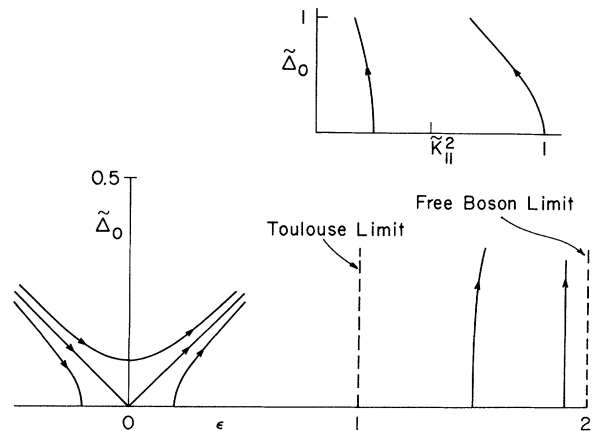

FIG. 1. Scaling curves for the logarithmic gas with charges $\pm (2 - \epsilon)^{1/2}$ and fugacity $\tilde{\Delta}_0$. The Kondo-problem curves begin near $\epsilon = 0$, $\tilde{\Delta}_0 = 0$. The metallic-glass curves begin near $\epsilon = 2$, $\tilde{\Delta}_0 = 0$. The two exactly solvable limits are shown by vertical lines. The inset shows the scaling curves near $\epsilon = 2$ reexpressed in terms of $K_{\parallel}$ to emphasize the decreasing behavior.

lowered. In fact, if we ignore the weak decrease in $\tilde{K}_{\parallel}$ we can integrate Eq. (4) from $\tau_0 = D^{-1}$ to $\tau = \beta$ to obtain

$$\Delta_0(T) = \Delta_0(T/D)^{\tilde{K}_{\parallel}^2/2}. \tag{5}$$

Equations (4) and (5) are our main results. They imply that the net effect of the logarithmic divergences encountered in perturbation theory is to reduce the tunneling frequency $\Delta_0(T)$ as the temperature decreases. A similar result was conjectured by Kondo on the basis of low-order perturbation theory.[9]

It may clarify matters if we note that the above behavior derives from the long-time limit of the correlation function $F(t) = \langle S_+(t)S_-(0) \rangle$. The direct analog of this quantity also appears in x-ray spectroscopy where it is related to the x-ray photoemission cross section. In that context it is well known[12] to behave as $F(t) \sim (t/\tau)^{-(2\delta/\pi)^2}$ because of the Anderson overlap catastrophe.[14] Thus, the other types of infrared divergences which lead to enhancement of the emission and absorption edge and the resistivity increase in the Kondo effect are not part of the metallic-glass problem. Here, we have only the overlap catastrophe which always reduces the appropriate transition amplitudes.

To proceed further with our analysis we now use Eq. (4) to define a characteristic temperature T_0 which separates the high- and low-temperature regimes. Evidently scaling breaks down when $\tilde{\Delta}_0 = 1$. Thus we may define T_0 as the value of τ^{-1} at which $\tilde{\Delta}_0 = 1$. This yields

$$T_0 = \Delta_0(\Delta_0/D)^{\tilde{K}_{\parallel}^2/2} \tag{6}$$

as was conjectured by Kondo[9] from the $T=0$ limit of the tunneling rate. Taking $D = 10$ eV, $\tilde{\Delta}_0 = 10^{-6}$ eV, and $\tilde{K}_{\parallel} = 0.1$, we estimate $T_0/\Delta_0 = 0.9$, which is not a very significant reduction. We note, however, that T_0 [and also the result in Eq. (5)] is a very sensitive function of $K_{\parallel}$.

Unfortunately the scaling equations do not tell us how to calculate such interesting quantities as the resistivity and the "spin"-lattice relaxation rate T_1^{-1} relevant to ultrasonic measurements. However, they may be used as bases for a number of conjectures. The scaling of $K_{\parallel}$ towards zero strongly suggests that the coupling between the electrons and the tunneling levels becomes weaker as T is lowered towards T_0. Therefore, it is reasonable to expect that the electron scattering rate (and hence the resistivity) due to the tunneling levles decreases with T. This supports our earlier conclusion based on perturbation

theory. For $T < T_0$ we would expect no temperature-dependent contribution to the resistivity from the mechanisms described in this paper.

This is not to say that the interaction between the tunneling states and the conduction electrons will have no observable effects. As has been established by Golding et al.[4] the Korringa relaxation rate (T_1^{-1}) of the tunneling levels, which is proportional to $K_{\parallel}^2\Delta_0^2$, has observable consequences in ultrasonic attenuation. Moreover, there are a number of other observable quantities which are proportional to Δ_0^2 such as the resonant ultrasonic absorption coefficient and the phonon contribution to the tunneling-level relaxation rate. On the basis of the above discussion we suggest that these quantities may show power-law anomalies if the exponent $0 < \frac{1}{2}\tilde{K}_{\parallel}^2 < \frac{1}{2}$ turns out to be large enough in some systems. Furthermore, in the superconducting state, where it is expected that the tunneling-level–conduction-electron interaction is completely frozen out on account of the gap, we would predict that in addition to the Korringa rate going to zero all the tunneling frequencies will be shifted upwards. It is hoped that ultrasonic experiments to test these ideas can be devised.

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X-Ray Study and Microscopic Study of the Reentrant Nematic Phase

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We report results from x-ray experiments on mixtures of N-(p-hexyloxybenzylidene)-
p-aminobenzonitrile (HBAB) in N-p-cyanobenzylidene-p-n-octloxyaniline (CBOOA); very
recent microscopic observations on mixtures of cyanohexyloxybiphenyl in cyanooctyloxy-
biphenyl are in agreement with these results. The evidence suggests that the reentrant
nematic phase is similar to the classical nematic phase but may coexist with crystalline
fluctuations.

It has been shown recently[1] that mixtures
formed with two liquid crystals could exhibit with
decreasing temperature the following sequence
of phases: nematic, smectic A, and then again
nematic. The nematic phase which occurs at low
temperature is called the reentrant nematic
phase (Fig. 1). The same phenomenom has also
been observed with pure compounds under pres-
sure.[2] By increasing the pressure from the
nematic phase, we observe the smectic phase
and then again a nematic phase at high pressure.
The nematic phase which occurs at high pressure
is also called the reentrant nematic phase. All
these results have been obtained using the light
microscope.

A model has been proposed[3] for the organiza-
tion of the molecules in this reentrant nematic
phase. In this model, the molecules are assumed
to be associated in antiparallel pairs in the
smectic-A phase, which then can be destabilized
as shown in Fig. 2.

Here we present for the first time the results
of an x-ray investigation of this unusual phase,
and also very recent results of a microscopic
study with a new mixture of thermotropic liquid
crystals (Fig. 1). The observations obtained with
the two techniques are in agreement and suggest
that the reentrant nematic phase with its very
close packing gives rise to the unusually slow
nucleation of a crystallinelike phase some 20°C
below the normal melting temperature. Further,

this crystalline phase *melts* at exactly the reen-
trant transition temperature to the smectic-A
phase.

We have used an improved x-ray diffraction
system equipped with a rotating anode and a bent-
quartz-crystal monochromator. The patterns are
registered with a stable position-sensitive x-ray
detector. This apparatus has been previously de-
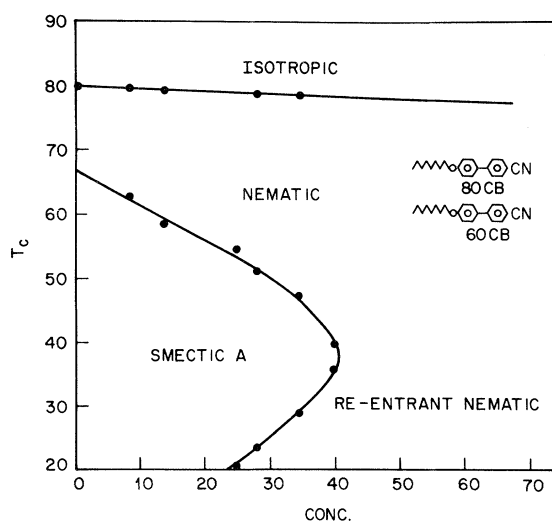scribed.[4] The exposure time for each pattern

FIG. 1. Transition temperatures versus concentra-
tion for equal-weight 6OCB (cyanohexyloxybiphenyl) in
8OCB (cyanoctyloxybiphenyl).