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Interactions of two-level systems in glasses

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Abstract. Using methods from polaron theory, we re-derive the elastic interaction between two-level systems (TLS) in glasses in a non-perturbative manner. We then calculate the relaxation rate of the interacting dressed TLS perturbatively. Although this calculation necessitates some approximations, it leads to the statement that for strong TLS-phonon interaction the TLS relaxation rate $1/T_1$ is, at least for asymmetric TLS, considerably different from the prediction of the usual (weak-coupling) expression. The impact of this result on theory and experiment is discussed.

There are two explicit derivations [1, 2] of the interaction, induced by the exchange of virtual phonons, between the now well known two-level systems (TLS) in glasses, which were postulated in 1972 [3, 4]. Both of them are perturbative. In the first [1], an *effective second-order Hamiltonian* of the interaction is constructed. In the second approach [2], the linear coupling of the phonon to the diagonal TLS matrix elements is replaced with the strain field of a classical dipole, but the *remainder of the Hamiltonian is kept unchanged* (e.g. the phonon coupling to the off-diagonal matrix elements). The only problem with these approximations is that the interaction derived turns out to be *strong* [1], which might invalidate its derivation. Therefore it is clearly desirable to obtain the TLS interaction in a non-perturbative way. The present work is a first step in this direction.

Furthermore, there is a series of papers [5, 6] that deal with the influence of strain interactions or local strain fields, which are allowed to be strong, on the density of states of tunnelling units (two- to six-level systems) in glasses. Consequences for the low temperature properties of glasses such as heat capacity and thermal conductivity are investigated. On the other hand, these articles hardly address [5] the question of the microscopic (quantum mechanical) origin of these interactions, which is one of our objectives. The strain fields are introduced phenomenologically and treated semi-classically. Certain many-body effects, such as the renormalisation of the deformation potentials, as well as the TLS relaxation times, which will arise naturally from our calculation, are absent from that approach.

Before exhibiting the details of the calculation, we would like to summarise the main features of the model. Inspection of the Hamiltonian given below reveals its close resemblance to the 'spin-boson' Hamiltonian [7], which has been a topic of considerable interest and innumerable publications during the last few years (see e.g. [7] and references therein). There is one difference, however: our Hamiltonian describes not one

but *many* spins (namely the TLS) coupled to the phonon bath. Clearly, the results of existing elaborate calculations [8] of the dynamics of the single-spin system cannot simply be carried over. This is especially true since the spin–phonon coupling *generates an interaction* between the spins (which is of course impossible in a single-spin system); its derivation is one of the goals of this paper. As it turns out, this interaction is the familiar *elastic coupling* (mediated by virtual *phonon* exchange) between TLS which is known to be stronger [9], in most cases, than the electrostatic interaction (mediated by virtual *photon* exchange). All *static* TLS coupling considered to date are of this indirect type: lack of knowledge on the microscopic nature of the TLS means that it is difficult to conceive of additional, possibly more direct interaction mechanisms.

If the phonon coupling is strong, the TLS are expected to become ‘dressed’ with ‘clouds’ of virtual phonons. Apart from trying to treat the strong coupling correctly, we intend to investigate how the bare system parameters become renormalised through this coupling. The traditional way to attack both of these problems is via polaronic transformations plus perturbation theory. This method, which may be traced back to the early 1950’s [10–12] (and possibly earlier), has become a standard tool in the polaron literature [12–14]. Although more formal methods like functional integral techniques are possible [7, 15], this procedure works well enough to give a semi-quantitative answer. The emphasis of the present work is not so much on the sophistication of the theoretical method as on the physics of the result.

The calculation proceeds as follows. First, we apply the unitary transformation given in equation (8) (later) to the Hamiltonian. This produces an interaction term for the ‘dressed’ TLS which is obtained without any approximation. Second, we calculate the relaxation rate for the dressed TLS using the golden rule, i.e. perturbation theory. The underlying assumption (which is also traditionally made) is that the *dressed* entities *can* be considered as weakly interacting. The final decision as to whether this is true in the present case, rests upon experiment. To obtain a clear picture of the physics, it will be imperative to reduce the number of parameters in the course of the calculation, particularly of those on which little or no experimental information is available. To this end, we keep non-oscillatory terms, which are likely to be large, and neglect certain oscillatory terms. While this approximation may surely be improved upon in later computations, it is clearly the first step to accomplish.

The Hamiltonian of the system we are considering is

$$H = H_1 + H_2 + H_{12} \quad (1)$$

$$H_1 = -\sum_k \frac{1}{2} E^k \sigma_z^k \quad (2)$$

$$H_2 = \sum_q \omega_q b_q^\dagger b_q \quad (\hbar = 1) \quad (3)$$

$$H_{12} = \sum_{q,k} (\Delta_q^k \sigma_z^k + W_q^k \sigma_x^k) (b_q + b_{-q}^\dagger). \quad (4)$$

The TLS operators are given in pseudo-spin representation with Pauli matrices σ_z^k, σ_x^k ($\sigma^2 = 1$). E^k is the energy splitting of the k th (non-interacting) TLS and is given by

$$E^k = [(\Delta^k)^2 + (W^k)^2]^{1/2} \quad (5)$$

where Δ^k and W^k are the asymmetry parameter and the tunnelling matrix element, respectively (W is denoted by Δ_0 in the majority of the literature). q is a quantum number characterising the phonon mode; it may be viewed as shorthand for wavevector plus

polarisation, i.e. $q = (\mathbf{q}, \sigma)$. It should be noted, however, that for glasses the concept of a wavevector q is an approximate one, applicable only to low-energy vibrations.

H_2 describes the phonon bath, H_{12} the interaction between the TLS and phonons, which is assumed here to be linear in the deformation field. To make connection with the notation in [1] we note that

$$\Delta_{\mathbf{q},\sigma}^k = -\sum_{\alpha,\beta} \frac{1}{4} (e_\alpha(\mathbf{q}, \sigma)q_\beta + e_\beta(\mathbf{q}, \sigma)q_\alpha) i \left(\frac{\hbar}{2\rho V \omega_{\mathbf{q},\sigma}} \right)^{1/2} \exp(i\mathbf{q}\mathbf{x}^k) G_{\alpha\beta,z}^k \quad (6)$$

where $e_\alpha(\mathbf{q}, \sigma)$, $e_\beta(\mathbf{q}, \sigma)$ are components of the phonon polarisation vector and \mathbf{x}^k is the position vector of the TLS considered. A similar formula holds for W_q^k with $G_{\alpha\beta,z}^k$ replaced by $G_{\alpha\beta,x}^k$.

A derivation of (4), which may be found in [16], shows that if the phonons couple (as is widely believed) more strongly to the *localised* TLS states than to their delocalised superpositions, the quantities Δ_q^k and W_q^k may be written

$$\Delta_q^k = D_q^k \Delta^k / E^k \quad W_q^k = D_q^k W^k / E^k. \quad (7)$$

This form is assumed in [2]. (This is equivalent to neglecting the $\partial\Delta_0/\partial\varepsilon_{\alpha\beta}$ terms in equation (4) of [1]. The magnitude of the D_q^k is largely determined by the phonon deformation potentials.

We now introduce the unitary transformation

$$U = \exp\left(-\sum_{k,q} \frac{\Delta_q^k}{\omega_q} \boldsymbol{\sigma}_z^k (b_q - b_{-q}^\dagger)\right) \quad (8)$$

and rewrite the Hamiltonian (1) in terms of the transformed operators

$$\boldsymbol{\Sigma}_i^k = U^{-1} \boldsymbol{\sigma}_i^k U \quad B_q^\dagger = U^{-1} b_q^\dagger U \quad B_q = U^{-1} b_q U \quad (9)$$

describing two-level systems dressed with virtual phonons and phonons dressed with (virtual) two-level systems, respectively.

This is, of course, done by calculating UHU^{-1} and results in†

$$\begin{aligned} H = & -\sum_k \frac{1}{2} E^k \boldsymbol{\Sigma}_z^k + \sum_q \omega_q B_q^\dagger B_q - \sum_{q,k,l} \frac{1}{\omega_q} \Delta_q^k \Delta_{-q}^l \boldsymbol{\Sigma}_z^k \boldsymbol{\Sigma}_z^l \\ & + \sum_{q,k} \frac{1}{2} W_q^k [\boldsymbol{\Sigma}_+^k \Psi_1^k + \boldsymbol{\Sigma}_-^k \Psi_2^k, B_q + B_{-q}^\dagger]_+ \\ & - \sum_{q,k,l} (1 - \delta_{kl}) \frac{1}{\omega_q} W_q^k \Delta_{-q}^l (\boldsymbol{\Sigma}_+^k \Psi_1^k + \boldsymbol{\Sigma}_-^k \Psi_2^k) \boldsymbol{\Sigma}_z^l \end{aligned} \quad (10a)$$

where $[,]_+$ denotes the anticommutator,

$$\Psi_n^k = \exp\left((-1)^n \sum_q \frac{2}{\omega_q} \Delta_q^k (B_q - B_{-q}^\dagger)\right) \quad (10b)$$

and

$$\boldsymbol{\Sigma}_\pm^k = \boldsymbol{\Sigma}_x^k \pm i\boldsymbol{\Sigma}_y^k. \quad (10c)$$

Obviously, the third term on the right-hand side of (10a) describes a spin–spin interaction

† For the convenience of readers interested in doing the calculation themselves, we give the transformations of operators needed to obtain equation (10):

$$U \boldsymbol{\sigma}_z^k U^{-1} = \boldsymbol{\sigma}_z^k \quad U \boldsymbol{\sigma}_\pm^k U^{-1} = \frac{1}{2} (\psi_1^k \boldsymbol{\sigma}_\pm^k + \psi_2^k \boldsymbol{\sigma}_\pm^k) \quad U b_q^\dagger U^{-1} = b_q^\dagger - \sum_k (\Delta_{\pm q}^k / \omega_q) \boldsymbol{\sigma}_z^k.$$

Here, ψ_n^k is the same as Ψ_n^k with bare instead of dressed phonon operators.

$$\sum_{k,l} J_{zz}^{kl} \Sigma_z^k \Sigma_z^l$$

of the dressed TLS, with

$$J_{zz}^{kl} = -\sum_q (1/\omega_q) \Delta_q^k \Delta_{-q}^l.$$

Using (6), we can verify that this operator corresponds to the $\sigma_z^k \sigma_z^l$ interaction derived in [1], if we employ the same approximations (Debye model, neglect oscillating terms, in space, at the Debye wavevector) as in [1]. Of course, this unitary transformation cannot reproduce the $\sigma_x^k \sigma_x^l$ interaction in [1]. However, since this is supposed to be a very small fraction of the total TLS–TLS interaction (for reasons given in [1, 2]), equation (10) may be a good starting point for further investigations. We discuss a more general unitary transformation below which does lead to a $\sigma_x^k \sigma_x^l$ interaction.

So far we have seen how the known form of the interaction between TLS in glasses can be derived non-perturbatively. However, equation (10) reveals more than that. Whereas in the original form of the Hamiltonian spin-flipping was simply determined by the matrix element W_q^k , we now have two terms (fourth and fifth terms on the right-hand side of (10a)), both inducing spin flips and including complicated phonon operators. If the TLS interaction is strong, we are dealing, in physical systems, with the dressed entities (Σ_z^k, Σ_x^k) rather than with the bare ones (σ_z^k, σ_x^k). In previous approaches [1, 2], calculations were based on the relaxation rates of the latter, even though the spin–spin interaction of the former was taken into account. Yet, in general, the flip rates of the dressed TLS are different from those of the bare ones. They may be computed from the golden rule, which provides the formula

$$\Gamma \equiv \lim_{t \rightarrow \infty} \frac{d}{dt} P_{\{n\} \rightarrow \{m\}}(t) = \int_{-\infty}^{\infty} d\tau \text{Tr}_b \langle \{n\} | H_{\text{flip}} | \{m\} \rangle \langle \{m\} | \tilde{H}_{\text{flip}}(-\tau) \rho_b | \{n\} \rangle. \tag{11a}$$

Here, H_{flip} is the sum of the fourth and fifth terms in (10a) and

$$\tilde{H}_{\text{flip}}(-\tau) = \exp(-iH_0 \tau) H_{\text{flip}} \exp(iH_0 \tau) \tag{11b}$$

H_0 being the sum of the first three terms in (10a). We have rewritten the δ function in the golden rule expression as a time integral, since we are dealing with many-phonon contributions, which can be handled easier this way. The equilibrium density operator ρ_b of the phonon system appears in the formula, because an average over all initial phonon configurations has to be carried out.

$|\{n\} n = |n_1\rangle |n_2\rangle \dots |n_N\rangle$ describes the initial TLS configuration as a product of single TLS states, the eigenstates of the Σ_z^k , $|\{m\}\rangle$ is an analogous product for the final configuration. We consider a transition with a single TLS flipping, i.e. $\{m\}$ is a configuration which is equal to $\{n\}$ in all states except the k th one. For this case, the evaluation of (11) yields

$$\Gamma_{\uparrow/\downarrow}^k = \int_{-\infty}^{\infty} d\tau \exp(\mp i\tilde{E}_{\{n\}}^k \tau) \times \exp\left(-\sum_q 4 \frac{|\Delta_q^k|^2}{\omega_q^2} [n_q (1 - e^{i\omega_q \tau}) + (n_q + 1)(1 - e^{-i\omega_q \tau})]\right)$$

$$\begin{aligned} & \times \left\{ \sum_q |W_q^k|^2 [n_q e^{i\omega_q \tau} + (n_q + 1) e^{-i\omega_q \tau}] \right. \\ & + \left(\sum_q 2 \frac{W_q^k}{\omega_q} \left[\Delta_{-q}^k (n_q e^{i\omega_q \tau} - (n_q + 1) e^{-i\omega_q \tau}) \right. \right. \\ & \left. \left. \mp \sum_l (1 - \delta_{kl}) (-1)^{n_l+1} \Delta_{-q}^l \right] \right)^2 \left. \right\} \end{aligned} \tag{12a}$$

with

$$\tilde{E}_{(n)}^k = E^k + 4 \sum_l (1 - \delta_{kl}) (-1)^{n_l+1} J_{zz}^{kl}. \tag{12b}$$

In this formula, n_q is the thermal occupation number of phonon mode q . Γ_{\uparrow}^k is the flip rate of a TLS from its lower to its upper state (when it absorbs more energy in the many-phonon process than it emits), Γ_{\downarrow}^k the rate of decay into the lower level. The sum of these two quantities is the total relaxation rate Γ^k of the k th TLS for a given configuration of all the other TLS. In order to compare our formula with the familiar [17, 2]†

$$(1/T_1) (= \Gamma_{\text{bare}}) = (\gamma_l^2/c_l^5 + 2\gamma_t^2/c_t^5)(W^2 E/2\pi\hbar^4 \rho) \coth(E/2k_B T) \tag{13}$$

resulting from the same calculation with H_{12} instead of H_{flip} (and a correspondingly different H_0 , of course), we ought to perform an additional thermal average on (12) over all TLS except the k th, which we are looking at (the superscript k has been omitted in (13)). For an accurate evaluation of (12) we need more detailed information than is available for most glasses; therefore, we shall restrict our interest primarily to orders of magnitude. We will then introduce several approximations in the process of evaluation which turn out to render the thermal average unnecessary.

First, we neglect the J_{zz}^{kl} term in the definition of $\tilde{E}_{(n)}^k$, assuming that the sum of the contributions of many TLS with differing signs will add up to something close to zero. This is one of the oscillatory terms to be neglected which was mentioned in the introduction. For the purpose of the calculation it is actually not necessary to replace the sum by zero. It is sufficient to substitute an average value which simply adds to the energy E^k given in (5). Since this does not change the calculation much, it can be done as easily as the one presented here. We chose the value zero, because this choice seems least biased in view of the fact that it is hard to give any quantitative estimate without detailed information on the spatial distribution of the TLS and the resulting actual strengths of the J_{zz}^{kl} . *On average*, the sum will be close to zero for temperatures that are not too low, i.e. temperatures at which the TLS can be thermally excited. At $T = 0$, however, all TLS will be in their ground state (all $n_l = 1$) and zero will no longer be a good approximation to the sum.

Second, consider the term $2\sum_{q,l}(1 - \delta_{kl})(-1)^{n_l+1}(1/\omega_q)W_q^k\Delta_{-q}^l$ in (12a). It has the same structure as the second term in (12b) (see the definition of the J_{zz}^{kl} after equation (10)). The only difference is that Δ_q^k is replaced with W_q^k , meaning a multiplication by W_q^k/Δ_q^k , a small quantity for most TLS. It is therefore consistent to neglect this term as well. With these two approximations, equation (12) no longer depends on the particular TLS configuration. While these may not be good approximations in *all* cases, they seem justified as a first step in order to get an indication of the overall effects of the strong phonon coupling. Anyhow, we do not claim more than qualitative accuracy for our results.

† In the first derivation of this result [17], only one deformation potential was used instead of γ_l and γ_t .

Our third approximation is to use the Debye density-of-states for the phonons as we go to the continuum limit of (12). At low temperatures, this is clearly acceptable for all sums containing a factor n_q (producing a cutoff at high frequencies where the Debye model is not valid), but it is not so obviously a good approximation for the sums containing $(n_q + 1)$, because of the 1. (Of course, the earlier calculations leading to equation (13) also rely on the Debye model.)

With these assumptions in addition to (7), the total relaxation rate becomes

$$\begin{aligned} \Gamma^k = & \frac{1}{4} \frac{G}{\omega_D^2} \left(\frac{W^k}{E^k} \right)^2 \int_{-\infty}^{\infty} d\tau (e^{-iE^k\tau} + e^{iE^k\tau}) \exp(-f(\tau) - ig(\tau)) \\ & \times \left[\int_0^{\omega_D} d\omega \omega^3 \{n(\omega) e^{i\omega\tau} + [n(\omega) + 1] e^{-i\omega\tau}\} \right. \\ & \left. + \frac{G}{\omega_D^2} \left(\frac{\Delta^k}{E^k} \right)^2 \left(\int_0^{\omega_D} d\omega \omega^2 \{n(\omega) e^{i\omega\tau} - [n(\omega) + 1] e^{-i\omega\tau}\} \right)^2 \right] \end{aligned} \quad (14a)$$

where $n(\omega) = 1/(e^{\hbar\omega/k_B T} - 1)$

$$f(\tau) = \frac{G}{\omega_D^2} \left(\frac{\Delta^k}{E^k} \right)^2 \int_0^{\omega_D} d\omega \omega [2n(\omega) + 1] [1 - \cos(\omega\tau)] \quad (14b)$$

$$g(\tau) = \frac{G}{\omega_D^2} \left(\frac{\Delta^k}{E^k} \right)^2 \int_0^{\omega_D} d\omega \omega \sin(\omega\tau) \quad (14c)$$

and

$$G = (\gamma_l^2/c_l^5 + 2\gamma_t^2/c_t^5)(1/\pi^2 \hbar \rho) \omega_D^2 \quad (14d)$$

is a dimensionless constant. Γ_{\uparrow}^k is given by the $e^{-iE^k\tau}$ term, Γ_{\downarrow}^k by the $e^{iE^k\tau}$ term.

The relaxation rate Γ^k of (14) reduces to the simple form of Γ_{bare} , if $f(\tau)$ and $g(\tau)$ as well as the last term on the right-hand side of (14a) are set equal to zero. In fact, for symmetric TLS ($\Delta^k = 0$), these quantities are zero.

Consider now the asymmetric case. Evaluation of G for a standard set of parameters ($\gamma_l = 1.6$ eV, $\gamma_t = 1.0$ eV, $c_l = 3$ km s⁻¹, $c_t = 2$ km s⁻¹, $\rho = 2$ g cm⁻³, $\Theta_D = \hbar\omega_D/k_B = 150$ K) shows that in general G , and hence $f(\tau)$, are *not* small quantities ($G \approx 350$). Therefore, the exponential prefactor $e^{-f(\tau)}$ will substantially reduce the relaxation rate, even for quite small values of the asymmetry parameter ($\Delta^k/E^k \geq 0.1$). This is most easily seen by looking at the limit $t \rightarrow \infty$ of (14b):

$$f(\infty) = G \left(\frac{\Delta^k}{E^k} \right)^2 \left(\frac{1}{2} + \frac{\pi^2}{3\eta^2} + \frac{2}{\eta} \ln(1 - e^{-\eta}) - \frac{2}{\eta^2} \sum_{n=1}^{\infty} \frac{e^{-n\eta}}{n^2} \right) \quad (15)$$

where $\eta = \Theta_D/T$.

To confirm this qualitative discussion, we have evaluated (14) numerically. For small values of E^k (which we are mainly interested in) the computation turns out to be a tricky matter, because the (outer) integrand is a slowly decaying oscillating function at low temperatures. Details of the integration procedure will be given elsewhere.

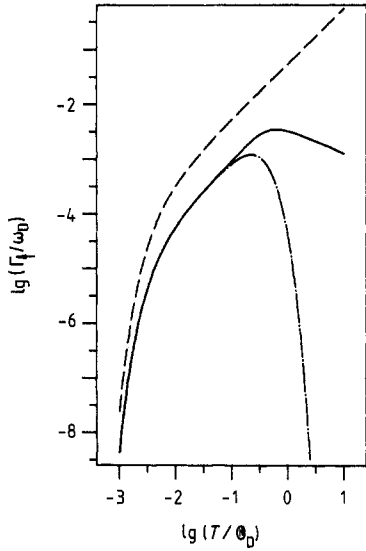


Figure 1. Rate Γ_{\uparrow} of flips from the lower level of a TLS into the upper level, as a function of temperature, in the range $10^{-3} \Theta_D$ to $10 \Theta_D$. Double logarithmic plot. Parameters used are given in the text. Full curve, rate for dressed TLS according to equation (14); broken curve, rate for bare TLS (equation (13)). The chain curve represents $e^{-f(\infty)}\Gamma_{\uparrow \text{bare}}$.

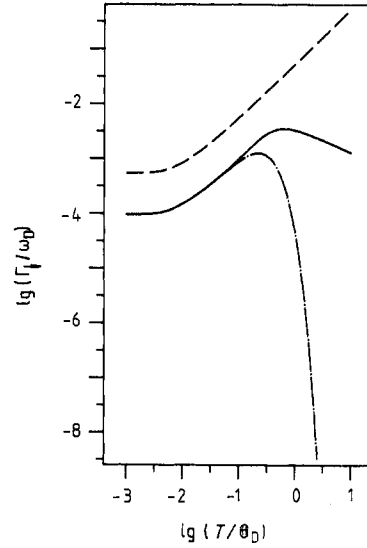


Figure 2. Rate Γ_{\downarrow} of flips from the upper TLS level into the lower one, as a function of temperature. Double logarithmic plot. Parameters used are given in the text. Full curve, dressed TLS (equation (14)); broken curve, bare TLS (equation (13)). Chain curve $e^{-f(\infty)}\Gamma_{\downarrow \text{bare}}$.

Using the parameter set given above and a ratio $\Delta^k/E^k = 0.1$ with $E^k = 0.01\omega_D$, we obtain Γ_{\uparrow}^k and Γ_{\downarrow}^k as displayed in figures 1 and 2. In addition, we give the absorption ($\propto n(E/\hbar)$) and emission parts ($\propto [n(E/\hbar) + 1]$) of formula (13) and the product of these quantities with $e^{-f(\infty)}$. It is obvious that the relaxation rates are indeed reduced by about an order of magnitude at low T in comparison with the naive result (13). Moreover, we find that at sufficiently low temperatures the relation $\Gamma_{\text{dressed}} = e^{-f(\infty)}\Gamma_{\text{bare}}$ is a good approximation to the exact result. The deviations of this formula are less than 1% (of Γ_{dressed}) below $0.03 \Theta_D$ and less than 10% below $0.09 \Theta_D$. In our example, the reduction factor is $e^{-f(\infty)} = 0.176$ below $\approx 0.1 \Theta_D$. It decreases very quickly with increasing Δ^k : for $\Delta^k/E^k = 0.3$ we have $e^{-f(\infty)} = 1.6 \times 10^{-7}$ for $\Delta^k/E^k = 0.5$, $e^{-f(\infty)} = 1.3 \times 10^{-19}$.

At high temperatures ($T > \Theta_D$), our result has little physical significance, since we have not considered non-linear couplings in the Hamiltonian, which will then become important. Also the Debye model fails in that region. We have extended the calculations to these temperatures only in order to show (qualitatively) that the phenomenon of *dynamic localisation* may occur, i.e. the relaxation rate goes through a maximum and decreases again.

Our main result is the *strong reduction of flip rates for strongly coupled TLS*. The consequences of this result are as manifold as the application of (13).

We will give examples below. However, it may be useful to recall a few general facts first. At present, there seems to exist a set of by-and-large consistent experimental values for quantities like deformation potentials, TLS densities-of-states, and TLS relaxation times, in several glasses. These quantities are, of course, not measured directly. Direct experimental observation concerns different things, e.g. the decrease in signal amplitude

due to ultrasound attenuation, the variation of sound velocity as a function of frequency, the amplitudes of phonon or photon echoes.

Consider phonon echoes. They are known to provide a measurement of the deformation potential γ which is independent of the TLS density-of-states [18]. However, quite elaborate theoretical considerations are necessary before one arrives at the seemingly direct result for the dephasing rate and then the deformation potential.

Hence the aforementioned consistent set of experimentally determined parameters relies on a—presumably equally consistent—set of underlying theoretical assumptions, i.e. not only the specific model, within which the data are interpreted, but also the general theoretical framework.

Our result seems to imply that at least one of the equations widely used within this framework does not fit together with another statement made within the same theoretical building, namely that the interaction between TLS and phonon is ‘extremely strong’ [19]. We have merely calculated the TLS relaxation rate. We expect our argument to apply to other quantities such as the phonon relaxation rate as well (which would directly affect the interpretation of ultrasound attenuation measurements). In the following discussion, however, we can only examine the most immediate consequences of our result.

For instance, deformation potentials γ obtained by way of measurements of TLS relaxation rates [18] may have to be corrected (if one is interested in the bare quantities) towards larger values to compensate for the decrease by a factor $e^{-f(x)}$, unless the experimental results were dominated by relaxation of symmetric or near symmetric TLS. This may have been the case, but then it is difficult to explain the observation of additional faster relaxation processes in terms of spectral diffusion [18]. Inspection of (10a) and (7) shows that, in the present approximation, the spin–spin interaction of symmetric TLS is zero, hence these are not affected by spectral diffusion. (We will slightly modify this statement below.)

Of course, experimentalists have known for a long period of time that the deformation potentials obtained from measurements were *effective*, i.e. averaged values, and most certainly it was also suspected that these quantities were *renormalised* through the interaction—even though we are not aware of any explicit statement about this in the TLS literature. On the other hand, merely switching to a description in terms of effective quantities whilst sticking to the old formulae may not be sufficient, because the renormalisation changes functional dependencies as well, as we have seen. In our case, this change may hardly be visible in the temperature direction of parameter space, because it is well described by a simple prefactor over the experimentally relevant range of temperatures, but it is quite pronounced in the Δ -direction.

To check on the possible effects of this strong Δ -dependence, we consider, in some detail, the distribution of TLS relaxation rates. We will assume that the distribution of Δ and λ is constant in accord with the original ideas in [3] and [4]: $P(\Delta, \lambda) = \bar{P}$. We then transform this distribution to new variables $r = T_1^{-1}/T_{1\min}^{-1}$ and E , given by equation (5). In the usual framework, $r = (W/E)^2$ and $P(E, r) = \bar{P}/2r(1-r)^{1/2}$, which we call the weak-coupling result. Within the present theory, however, we have for temperatures below $0.03\Theta_D$

$$r = (W/E)^2 e^{-G'(\Delta/E)^2} \quad (16)$$

with (see (15))

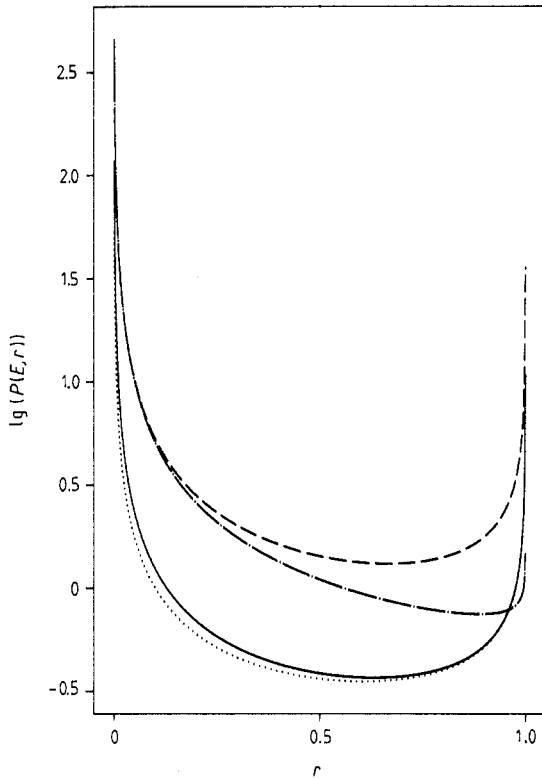


Figure 3. Logarithmic plot of the TLS distribution $P(E, r)$. Full curve, strong coupling result (equation (18)), $G' = 10$; broken curve, usual weak-coupling result (corresponding to $\mu = 0$ in [20]); chain curve, the formula of [20] with their suggested value $\mu = \frac{2}{3}$; dotted curve, approximation (20). \bar{P} is set equal to 1 for convenience.

$$G' = G \left(\frac{1}{2} + \frac{\pi^2}{3\eta^2} + \frac{2}{\eta} \ln(1 - e^{-\eta}) - \frac{2}{\eta^2} \sum_{n=1}^{\infty} \frac{e^{-n\eta}}{n^2} \right) \quad (17)$$

which is only weakly temperature-dependent in the temperature range considered. This leads to

$$P(E, r) = \bar{P}/2ru(r)\{1 + G'[1 - u(r)^2]\} \quad (18)$$

where $u(r) = \Delta/E$ is the inverse function of

$$r(u) = (1 - u^2) e^{-G'u^2}. \quad (19)$$

This distribution is plotted in figure 3, together with the weak-coupling result and a modified distribution used in [20], namely $P(E, r) = \bar{P}/2r(1 - r)^{1/2-\mu}$, with $\mu = \frac{2}{3}$. The dotted line gives an analytical approximation to (18), valid for small values of u

$$P(E, r) = \bar{P}/2r(1 + G')^{1/2}(\ln(1/r))^{1/2}. \quad (20)$$

We have chosen the rather small value of G' ($= 10$) in order to keep this approximation (which improves with increasing G') distinguishable from the solid curve representing the exact formula (18). The general shapes of the strong-coupling and the weak-coupling curves are, for the r values considered, very similar to each other, much more so than to the modified distribution. However, for the *same* value of \bar{P} , the strong-coupling distribution is reduced by approximately a factor $(1 + G')^{1/2}$ (close to $r = 1$) with respect to the weak-coupling one. From the figure, it cannot be seen that the *total* number of

TLS is the same in both cases, because the curves are drawn for a common r range. However, for given cutoffs in λ and Δ of the distribution $P(\Delta, \lambda)$, the strong-coupling result extends down to much lower rates r .

Of course, equation (18) may be used to calculate the time dependence of the specific heat. If we set $r_{\min} = T_{1\min}/t$, where t is the experimental time of observation, and integrate (18) from r_{\min} to 1, we obtain the (exact) time dependent density-of-states:

$$n(E, t) = (\bar{P}/2) \ln\{[1 + u(T_{1\min}/t)]/[1 - u(T_{1\min}/t)]\}. \quad (21)$$

This yields the following short-time and long-time results for the specific heat:

$$C(T, t) = (\pi^2/6\rho)k_B^2 T\bar{P}\{[1/(1 + G')]\ln(t/T_{1\min})\}^{1/2} \quad (t \geq T_{1\min}) \quad (22)$$

$$C(T, t) = (\pi^2/12\rho)k_B^2 T\bar{P}[\ln(4t/T_{1\min}) - G'] \quad (t \gg e^{G'} T_{1\min}). \quad (23)$$

Given the constancy of the TLS distribution in the variables Δ and λ , the first equation constitutes a new prediction for the short-time behaviour of the specific heat. The second result is, apart from the summand $-G'$, identical to the familiar logarithmic time dependence from weak-coupling theory. Note, however, that in the present theory this result holds only in the *extreme* long-time limit.

On the other hand, for experiments taking place on *short* time scales the *effective* distribution of the TLS asymmetry parameter Δ may be much narrower than theoretically anticipated [3, 4] due to the slowing down of asymmetric TLS. This could yield an explanation, along the lines suggested in [18] for the discrepancy between TLS densities-of-states inferred from ultrasound experiments and specific heat measurements. Since the time scale of the former is much shorter, they may just not probe many slow asymmetric TLS.

Noting that our result differs from the frequently used formula (13) by just a factor (which is, however, Δ -dependent) over a wide temperature range, we conclude that previous results depending only on the *functional* form of Γ^k may merely be affected within prefactors. This explains to some extent the success of these theories despite their failure to account properly for the strong TLS-phonon interaction. Whether the parameters needed in modified prefactors are still physically reasonable has to be reviewed in each case. Even if it turns out that current theories need not be altered much if all bare parameters are replaced with dressed ones, the present work opens up the possibility actually to *calculate* the bare quantities. This may have important consequences regarding our microscopic picture of the TLS. Furthermore, we may speculate that certain puzzling scaling relations like the constancy of the product $\bar{P}\gamma^2/\rho c^2$ for a wide variety of glasses [21] will find an explanation in terms of the proper relations between bare and dressed quantities.

Let us discuss two final theoretical examples. In [2], an expression was derived for the decay time of phonon echoes in the presence of spectral diffusion, which was later employed in the explanation of homogeneous optical linewidths in glasses [22, 23]. This formula contains the TLS relaxation rate $1/T_1$, which, however, has no influence on the temperature dependence of the *infinite-time* result for the linewidth. Yet, a general reduction of relaxation rates for asymmetric TLS should, in principle, make the *intermediate-time* result in [23] applicable to a wider range of experimental situations. Again, there may be a quantitative problem, because the *fastest* relaxing TLS (the symmetric ones) which were supposed to contribute most, contribute *least* to spectral diffusion.

Theories of homogeneous optical linewidths not invoking spectral diffusion ([24] and references therein) should be affected, too. In these theories, the *relative* contribution of

symmetric TLS to the linewidth will become *more* important. Because the symmetric TLS generally have much smaller energy splittings than the asymmetric ones, most of them can be described in the high-temperature approximation even at fairly low temperatures. Therefore, we expect the theoretical temperature dependence to be modified somewhat towards linearity (T^1). It remains to be examined if this effect is strong enough to change the temperature exponents presently obtained to values which no longer agree with experiment, thus indicating the necessity of major modifications of the theory. On the other hand, since at low temperatures the TLS with large energy splittings contribute little to the linewidth anyway, it is also possible that the alterations are not remarkable.

Finally, we would like to point out that this is only the beginning of the story. Had we taken the strong phonon coupling even more seriously, we would have introduced, instead of (8), a unitary transformation with the exponent

$$-\sum_{q,k} (1/\omega_q)(\Delta_q^k \sigma_z^k + W_q^k \sigma_x^k)(b_q - b_{-q}^\dagger)$$

which is diagonal in the *localised* TLS states, to get rid of the entire linear coupling H_{12} . This changes the spin-spin interaction term into

$$-\sum_{q,k,l} \frac{1}{\omega_q} D_q^k D_{-q}^l \left(\frac{\Delta^k}{E^k} \Sigma_z^k + \frac{W^k}{E^k} \Sigma_x^k \right) \left(\frac{\Delta^l}{E^l} \Sigma_z^l + \frac{W^l}{E^l} \Sigma_x^l \right).$$

Hence the symmetric TLS are no longer special in not having reduced relaxation rates and zero interaction, but for them the interaction does not contain any pure $\Sigma_z^k \Sigma_z^l$ terms (however, $\Sigma_z^k \Sigma_x^l$ and $\Sigma_x^k \Sigma_x^l$ terms are present). The main features obtained with this transformation are similar to the results presented above. However, the energy splitting of the TLS changes somewhat, because H_1 is non-diagonal in the localised basis. It is not clear *a priori* which of the two transformations produces a better zeroth-order Hamiltonian.

We need not stop at linear TLS-phonon interactions and the corresponding unitary transformations. If the ideas in [23] about the importance of the Raman process are correct, it is almost mandatory to include *quadratic* phonon coupling (even though we have already taken *some* many-phonon processes into account). This can also be treated in the framework of unitary transformations, as shown in [25]. The calculations are much more complicated but may lead to drastic new effects including a change of the phonon dispersion law.

As to the present state of the art, there are many publications claiming success in explaining thermal, acoustic, and optical properties of glasses on the basis of the TLS model. However, they do not take strong coupling effects into account, even though the strong TLS-phonon interaction is sometimes emphasised [19]. It would therefore seem from the above considerations that *the dynamics of TLS in glasses are still not well understood*. At the very least, it has to be explained (i) why weak-coupling theories have been so successful, (ii) which parameters must be changed in which direction in order to account for strong coupling, and (iii) why this is uncritical. In the worst case, the erroneous or unrealistic assumptions in these theories must be found, and it is interesting whether this will lead to new physical insights.

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References

- [1] Joffrin J and Levelut A 1975 *J. Physique* **36** 811
- [2] Black J L and Halperin B I 1977 *Phys. Rev. B* **16** 2879
- [3] Anderson P W, Halperin B I and Varma C M 1972 *Phil. Mag.* **25** 1
- [4] Phillips W A 1972 *J. Low Temp. Phys.* **7** 351
- [5] Klein M W, Fischer B, Anderson A C and Anthony P J 1978 *Phys. Rev. B* **18** 5887
- [6] Klein M W 1984 *Phys. Rev. B* **29** 5825
Klein M W 1985 *Phys. Rev. B* **31** 1114
- [7] Leggett A J, Chakravarty S, Dorsey A T, Fisher M P A, Garg A and Zwerger W 1987 *Rev. Mod. Phys.* **59** 1
- [8] Rivier N and Coe T J 1977 *J. Phys. C: Solid State Phys.* **10** 4471
- [9] Huber D L, Broer M M and Golding B 1984 *Phys. Rev. Lett.* **52** 2281
- [10] Huang K and Rhys A 1950 *Proc. R. Soc. A* **204** 406
- [11] Lax M 1952 *J. Chem. Phys.* **20** 1752
- [12] Lee T D, Low F and Pines D 1953 *Phys. Rev.* **90** 297
- [13] Holstein T 1959 *Ann. Phys., NY* **8** 325; 343
- [14] Kuper C G and Whitfield G (eds) 1963 *Polarons and Excitons* (New York: Plenum)
- [15] Caldeira A O and Leggett A J 1981 *Phys. Rev. Lett.* **46** 211
Bray A J and Moore M A 1982 *Phys. Rev. Lett.* **49** 1546
Chakravarty S and Kivelson S 1983 *Phys. Rev. Lett.* **50** 1811
- [16] Reineker P and Kassner K 1986 *Optical Spectroscopy of Glasses* ed. I Zschokke (Dordrecht: Reidel) p 65
- [17] Jäckle J 1972 *Z. Phys.* **257** 212
- [18] Graebner J E and Golding B 1979 *Phys. Rev. B* **19** 964
- [19] Golding B and Graebner J E 1981 *Amorphous Solids* ed. W A Phillips (Berlin: Springer) p 107
- [20] Doussineau P, Levelut A, Matecki M, Schön W and Wallace W D 1985 *J. Physique* **46** 979
- [21] Freeman J J and Anderson A C 1986 *Phys. Rev. B* **34** 5684
- [22] Reinecke T L 1979 *Solid State Commun.* **32** 1103
- [23] Hunklinger S and Schmidt M 1984 *Z. Phys.* **B 54** 93
- [24] Kassner K and Reineker P 1987 *Phys. Rev. B* **35** 828
- [25] Munn R W and Silbey R 1978 *J. Chem. Phys.* **68** 2439