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Dynamics of two-level systems in glasses

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We investigate the relaxation of a two-level system (TLS) in the golden-rule approximation by taking into account phonon-mediated interactions between TLS's.

INTRODUCTION

Amorphous solids, particularly inorganic glasses, exhibit strikingly anomalous behavior in low-temperature heat-capacity, thermal-conductivity, and optical properties of doped ions or molecules.[1] The unique properties of glass are believed to arise out of low-energy excitations or two-level systems (TLS's).[2] In recent work two-level or tunneling systems have been found from numerical simulations of Lennard-Jones-type glass.[3,4] A glass is described by an ensemble of TLS's, each being coupled to phonons of the heat bath. Exchange of virtual phonons produces an effective interaction between the TLS's.

Sometime back, Kassner and Silbey[5] (KS) derived an effective TLS-TLS interaction mediated by the exchange of virtual phonons by using a polaron-type unitary transformation. The work of KS is an extension of earlier work[6] with single TLS systems. A multi-TLS system must be considered to take into account TLS-TLS interactions in the dynamics of a TLS.

A TLS Hamiltonian can be written as

$$H_{\text{TLS}}=E_l|l\rangle\langle l|+E_u|u\rangle\langle u|+\frac{W}{2}(|l\rangle\langle u|+|u\rangle\langle l|)\ , \tag{1}$$

where the localized basis of the TLS is denoted by $\{|l\rangle,|u\rangle\}$, representing, respectively, the lower and upper states of the asymmetric double well; the asymmetry parameter is $\Delta=E_u-E_l$, while $W/2$ is the tunneling matrix element.

The work of KS, as well other theoretical work[7] on the TLS, proceeds by carrying out a diagonalization of H_{TLS}. In this basis the eigenstates are given by a linear combination of the localized states $|l\rangle$ and $|u\rangle$. In this paper we show that a polaronic transformation produces a simpler interaction between the "dressed" TLS and "dressed" phonons if one works in the localized basis rather than the basis of the diagonalized H_{TLS}. It may be noted that the localized basis was also used in Ref. 4 to estimate the deformation potential that arises from TLS-strain interactions. Using the localized basis, we calculate the relaxation rate of a TLS using golden-rule perturbation theory and compare our result with that of KS.

TWO-LEVEL SYSTEM

It is convenient to use the pseudo-spin-$\frac{1}{2}$ notation to describe the TLS system. The two spin configurations correspond to the upper or lower occupied states of a TLS. H_{TLS} for an N-TLS system is given by

$$H_{\text{TLS}}=\sum_{k=1}^{N}\left[\frac{(E_l^k+E_u^k)}{2}-\frac{\Delta^k}{2}\sigma_z^k+\frac{W^k}{2}\sigma_x^k\right]\ , \tag{2}$$

the σ's being Pauli matrices.

The phonon and TLS-phonon Hamiltonians[7] are

$$H_{\text{phonon}}=\sum_q \omega_q b_q^\dagger b_q\ , \tag{3}$$

$$H_{\text{TLS-phonon}}=\sum_k\sum_q (S_q^k+D_q^k\sigma_z^k)(b_q+b_{-q}^\dagger)\ , \tag{4}$$

where q denotes both wave vector and polarization indices. The coupling constants S_q and D_q are given in terms of $h_{q,l}$ and $h_{q,u}$, the latter being proportional to the deformation potential. We have

$$S_q^k=(h_{q,l}^k+h_{q,u}^k)/2 \quad\text{and}\quad D_q^k=(h_{q,l}^k-h_{q,u}^k)/2\ .$$

We note once again that the structure of the TLS-phonon Hamiltonian is different from that obtained by using the diagonal basis of H_{TLS}. The total Hamiltonian is now given by

$$\begin{aligned}H&=H_{\text{TLS}}+H_{\text{phonon}}+H_{\text{TLS-phonon}}\\&=\sum_k\left[\frac{(E_l^k+E_u^k)}{2}-\left[\frac{\Delta^k}{2}\right]\sigma_z^k\right]+\sum_q\omega_q b_q^\dagger b_q\\&\quad+\sum_{q,k}\left[(S_q^k+D_q^k\sigma_z^k)(b_q+b_{-q}^\dagger)+\left[\frac{W^k}{2}\right]\sigma_x^k\right]\ .\end{aligned} \tag{5}$$

The polaronic transformation is now performed by a unitary transformation U given by[5]

$$U=\exp\left[-\sum_{k,q}\frac{1}{\omega_q}(D_q^k\sigma_z^k+S_q^k)(b_q-b_{-q}^\dagger)\right]\ . \tag{6}$$

Denoting the transformed (dressed) operators by

$$\Sigma_z^k = U^{-1}\sigma_z^k U,\quad B_q^\dagger = U^{-1} b_q^\dagger U\ ,$$
$$B_q = U^{-1} b_q U,\quad \Sigma_\pm^k = U^{-1}\sigma_\pm U\ , \tag{7}$$

we have,

$$B_q^\dagger = b_q^\dagger + \sum_k \frac{1}{w_q}(S_q^k + D_q^k \sigma_z^k)\ , \tag{8}$$

$$B_q = b_q + \sum_k \frac{1}{w_q}(S_{-q}^k + D_{-q}^k \sigma_z^k)\ . \tag{9}$$

The Hamiltonian in terms of dressed variables is

$$H = \sum_k \left[\frac{(E_l^k + E_u^k)}{2} - \sum_{l,q} \frac{1}{\omega_q} S_{-q}^k S_q^l - \left[\frac{\Delta^k}{2} + \sum_{l,q} \frac{1}{\omega_q} 2 S_q^l D_{-q}^k \right] \Sigma_z^k - \sum_{l,q} \frac{D_{-q}^k D_q^l}{\omega_q} \Sigma_z^k \Sigma_z^l \right] + \sum_q \omega_q B_q^\dagger B_q + \sum_k \frac{W^k}{4}(\psi_1 \Sigma_+^k + \psi_2 \Sigma_-^k)\ , \tag{10}$$

where

$$\psi_n(n=1,2) = \exp\left[(-1)^n \sum_q \frac{2D_q^k}{\omega_q}(B_q - B_{-q}^\dagger) \right]\ . \tag{11}$$

The last term of the Hamiltonian representing phonon-mediated TLS flipping is considerably simpler in form than that obtained by KS. This simplicity is a result of the choice of the localized states of H_{TLS}. We now calculate the flip rate of a TLS by using golden-rule perturbation theory using as perturbation the expression

$$H^{\text{flip}} = \sum_k \frac{W^k}{4}(\psi_1 \Sigma_+^k + \psi_2 \Sigma_-^k)\ . \tag{12}$$

RELAXATION RATE

The details of the calculation follows KS and will not be repeated here. We obtain

$$\Gamma_{\uparrow/\downarrow}^k = \tfrac{1}{4}(W^k)^2 \int_{-\infty}^{+\infty} dt\, \exp(\mp i E_{\{n\}}^k t) \times \exp\left[-\sum_q \frac{4}{\omega_q^2} |D_q^k|^2 [n_q(1 - e^{i\omega_q t}) + (n_q+1)(1 - e^{-i\omega_q t})] \right]\ , \tag{13}$$

where

$$E_{\{n\}}^k = 4 \sum_{l,q} \frac{1}{\omega_q} S_{-q}^l D_q^k + \Delta^k + 4 \sum_{l,q} \frac{1}{\omega_q} D_q^k D_{-q}^l (1 - \delta_{kl})(-1)^{n_l + 1}\ . \tag{14a}$$

In the above expression, $n_l = 0$ if the lth TLS is in the upper state and $n_l = 1$ if it is in the lower state; n_q is the average number of phonons in the mode q. It should be noted that $E_{\{n\}}^k$ given above is not quite the same as $\tilde{E}_{\{n\}}^k$ of KS even if one sets S_q^k equal to zero; Δ^k occurring in Eq. (14a) is the difference in energies of the u and l states in the absence of tunneling. The total relaxation rate Γ^k is the sum of $\Gamma_\uparrow^k$ and $\Gamma_\downarrow^k$.

The flip rate obtained by us has the same mathematical form as that obtained by Leggett *et al.*[6] However, in that work many-TLS effects were not considered. KS have discussed the approximation of neglecting the last term of Eq. (14a), which makes the need to thermal average over all TLS's except the kth unnecessary. We also make the same approximation. Nevertheless, spin-spin effects are still contained in Eq. (14a).

The integral (13) does not converge according to the usual definition of convergence. However, by taking the mean value of the oscillations, the integral converges in the same sense as Cesàro's method of summation for infinite series.[8] The integral in Eq. (13) can be written as

$$\Gamma_{\uparrow/\downarrow}^k = \frac{1}{2}(W^k)^2 \int_0^\infty dt\, \cos\left[E_{\{n\}}^k t \pm \sum_q \frac{4}{\omega_q^2} |D_q^k|^2 \sin\omega_q t \right] \exp\left[-\sum_q \frac{4}{\omega_q^2} |D_q^k|^2 (2n_q + 1)(1 - \cos\omega_q t) \right]\ . \tag{14b}$$

The improper integral (14b) is not defined in the usual sense, viz.,

$$\lim_{R\to\infty} \int_0^R I(t)dt\ ,$$

since, for large R, (14b) is of the form

$$\int_0^R I(t)dt \sim \alpha + \beta \sin(E_{\{n\}}^k R)\ ,$$

where α and β are constants. Accordingly, α represents the value of the integral when averaging over the oscillations. The parameter W^k appears as an overall factor in (13), and Δ^k appears only in (13) through the variable $E_{\{n\}}^k$ defined by (14a). This is in direct contrast to KS where these parameters appear in the combinations

$$[(\Delta^k)^2 + (W^k)^2]^{1/2},$$

$$\Delta^k / [(\Delta^k)^2 + (W^k)^2]^{1/2}\ ,$$

and

$$W^k / [(\Delta^k)^2 + (W^k)^2]^{1/2}\ .$$

The interesting region of small $[(\Delta^k)^2 + (W^k)^2]^{1/2}$ is delicate to integrate in the work of KS. Their integral representations for the relaxation rates are governed by integrands which are slowly decaying oscillating functions at low temperatures.[5] Our result (13) is easy to analyze for small Δ^k and W^k. The first term in (14a) makes the integral (13) convergent in the symmetric TLS ($\Delta^k=0$) case and when the third term in (14a) is set equal to zero. Therefore, in our case, the first term in Eq. (14a) is all important for symmetric TLS's.

We now discuss some useful limiting cases. Consider first the limit $|D_q^k|^2 \to 0$. To first order in $|D_q^k|^2$, we have

$$\Gamma_\downarrow^k \simeq \left[\frac{W^k}{2}\right]^2 \int_{-\infty}^{+\infty} d\tau \exp(i\tau E^k)\left[1-\sum_q \frac{4}{\omega_q^2}|D_q^k|^2[(1-e^{+i\omega_q\tau})n_q+(1-e^{-i\omega_q\tau})(n_q+1)\right] . \tag{15}$$

where

$$E^k=\Delta^k+4\sum_{q,l}\frac{1}{\omega_q}S^l_{-q}D_q^k .$$

The first term gives a δ function which does not contribute since E^k cannot vanish. We note that only the term containing $e^{-i\omega_q\tau}$ will make a contribution. Hence

$$\Gamma_\downarrow^k \simeq \left[\frac{W^k}{2}\right]^2 \sum_q \frac{4}{\omega_q^2}|D_q^k|^2(n_q+1)2\pi\delta(\Delta^k-\omega_q) . \tag{16}$$

Similarly,

$$\Gamma_\uparrow^k \simeq \left[\frac{W^k}{2}\right]^2 \sum_q \frac{4}{\omega_q^2}|D_q^k|^2 n_q 2\pi\delta(\Delta^k-\omega_q) . \tag{17}$$

The total relaxation rate of the kth TLS Γ^k $(=\Gamma_\uparrow^k+\Gamma_\downarrow^k)$ is given by

$$\Gamma^k=\frac{(W^k)^2}{4}\sum_q \frac{4}{\omega_q^2}|D_q^k|^2 2\pi(2n_q+1)\delta(\Delta^k-\omega_q) . \tag{18}$$

Using the Debye approximation, the above expression can be further evaluated to give (suppressing the index k)

$$\Gamma=\sum_\sigma \frac{f_\sigma^2}{4c_\sigma^5}\frac{W^2\Delta}{2\pi\rho\hbar^4}\coth\left[\frac{\beta\Delta}{2}\right] , \tag{19a}$$

where $f_\sigma^2=|f_\sigma^l-f_\sigma^u|^2$ and the various quantities occurring in Eq. (19a) are defined in Ref. 1. This result has been obtained earlier[9] with the difference that Γ depends on E $(=\sqrt{\Delta^2+W^2})$ instead of Δ as in our result. In the limit of weak tunneling, i.e., small W, the two results become the same. KS obtain Eq. (19a), albeit with Δ replaced by $[\Delta^2+W^2]^{1/2}$, for symmetric TLS's. However, to second order in D_q^k, the result of KS also reduces to the analog of (19a) just as in our case. This weak TLS-phonon interaction limit was not discussed by KS.

We next consider the limit

$$\frac{(\hbar\omega_D)^2}{2\sum_q |D_q^k|^2(2n_q+1)} \ll 1 . \tag{19b}$$

We have

$$\sum_q \frac{4}{\omega_q^2}|D_q^k|^2(2n_q+1) \geq \frac{1}{\omega_D^2}\sum_q 4|D_q^k|^2(2n_q+1) .$$

Note that

$$\sum_q |D_q^k|^2=\tfrac{1}{16}(\hbar\omega_D)^2 G ,$$

where

$$G=\frac{\omega_D^2}{\pi^2\hbar\rho}\sum_\sigma \frac{f_\sigma^2}{4c_\sigma^5} .$$

Therefore the limit (19b) is valid for all values of the temperature provided $G \gg 8$. Typically,[5] G is ≈ 350. For small values of G, (19b) would still be valid at high temperatures, $kT \gg \hbar\omega_D$, provided also $kT \gg 3\hbar\omega_D/G$. In the limit (19b), the region close to $t=0$ determines the value of the integral (see the Appendix). Therefore we calculate the integral in $\Gamma_\downarrow^k$ by keeping terms up to τ^2 and we have

$$\Gamma_\downarrow^k \simeq \left[\frac{W^k}{2}\right]^2 \int_{-\infty}^{+\infty} d\tau \exp\left[i\left[E^k-\sum_q \frac{4}{\omega_q}|D_q^k|^2\right]\tau\right] \times\exp\left[-\sum_q 2|D_q^k|^2(2n_q+1)\tau^2\right] . \tag{20}$$

This can be integrated to give

$$\Gamma_\downarrow^k=\left[\frac{W^k}{2}\right]^2\frac{\sqrt{\pi}}{A}\exp\left[-\frac{B^2}{4A^2}\right] , \tag{21}$$

where

$$A^2=2\sum_q |D_q^k|^2(2n_q+1) \quad\text{and}\quad B=E^k-\sum_q \frac{4}{\omega_q}|D_q^k|^2 . \tag{22}$$

Similarly, we find

$$\Gamma_\uparrow^k=\left[\frac{W^k}{2}\right]^2\frac{\sqrt{\pi}}{A}\exp\left[-\frac{C^2}{4A^2}\right] , \tag{23}$$

where

$$C=E^k+\sum_q \frac{4}{\omega_q}|D_q^k|^2 . \tag{24}$$

A calculation of the relaxation rate using a Hamiltonian with undressed TLS's but dressed phonon variables, given by Eq. (10) with $\Psi_1=\Psi_2\equiv 1$ and $\Sigma_\pm=\sigma_\pm$, produces identical results to those in Eqs. (21) and (23). We get, as expected, $\Gamma_\downarrow^k > \Gamma_\uparrow^k$. The ratio of the downward to upward flip ratios becomes

$$\Gamma_{\downarrow}^{k}/\Gamma_{\uparrow}^{k}=\exp\left[\left[4E^{k}\sum_{q}\frac{1}{\omega_q}|D_q^k|^2\right]\Big/A^2\right] . \qquad (25)$$

Note that Eq. (25) reduces to the result $e^{\beta E^k}$ and $\ln\Gamma_{\uparrow/\downarrow}^{k}=-\frac{1}{2}\ln(kT/\hbar\omega_D)$ for $kT \gg \hbar\omega_D$. It is interesting that the latter behavior is in agreement with the graphical results of KS, given in Figs. 1 and 2 of Ref. 5.

CONCLUSION

In conclusion, we would like to point out some important differences between the results obtained by us and those obtained earlier by KS and others. The use of localized states of a TLS has produced a relaxation rate which is significantly different from that obtained by KS using the basis which diagonalizes $H_{\rm TLS}$, viz., linearly superposed states of localized states. All calculations use first-order perturbation theory to calculate a constant rate of transition, i.e., the golden rule.

First, we have shown that in both our work and that of KS the familiar $\coth(E/2k_BT)$ behavior of the total relaxation rate Γ is obtained in the limit of weak TLS-phonon interactions, i.e., to second order in $|D_q^k|^2$. This behavior of Γ is termed $\Gamma_{\rm bare}$ by KS, the relaxation rate of an unrenormalized TLS. Of course, in our case E is replaced by Δ as expected. However, KS obtained $\Gamma_{\rm bare}$ also for a symmetric TLS ($\Delta^k=0$) for all values of $|D_q^k|^2$. Our result [Eq. (13)] for Γ does not reduce to $\Gamma_{\rm bare}$, with E replaced by Δ, for a symmetric TLS. Note that in the work of Leggett *et al.*[6] their integral representation for Γ diverges for the symmetric TLS owing to the absence of the S_q^k coupling to the phonon field. Such terms are included in our work and thus lead to convergent integrals for symmetric TLS's. The absence of the S_q^k coupling may be the cause also for the tricky nature of the numerical computation in the work of KS for small values of E.

Second, we obtain simple analytical expressions for the relaxation rates [Eq. (13)] in the limit (19b). These expressions are given by Eqs. (21) and (23), which assume simple forms for large T. In fact,

$$\Gamma_{\uparrow}^{k}=\frac{C_1}{\sqrt{T}}e^{-C_2/k_BT} ,$$

where C_1 and C_2 are positive constants and $\Gamma_{\downarrow}^{k}=\Gamma_{\uparrow}^{k}e^{E^k/k_BT}$ with $C_2>E^k$. The $T^{-1/2}$ high-temperature behavior agrees with the numerical results of KS.

Finally, as discussed by Leggett *et al.*,[6] the eigenstates of the $H_{\rm TLS}$ are approximately eigenstates of σ_Z when W/Δ is small. In this case it is more appropriate to use localized states to describe the system. Otherwise, the eigenstates are delocalized and appropriate linear combinations should be considered.

APPENDIX

In this appendix we show how Eq. (21) is obtained from Eq. (13) in the limit of (19b).

Equation (13) can be written as

$$\begin{aligned}\Gamma_{\downarrow}^{k}=&\frac{(W^k)^2}{4}\int_{-\infty}^{+\infty}dt\,\exp(iE^kt)\\&\times\exp\left\{-i\sum_q\frac{4}{\omega_q^2}|D_q^k|^2\sin\omega_qt\right\}\\&\times\exp\left\{-\sum_q\frac{4}{\omega_q^2}|D_q^k|^2(2n_q+1)(1-\cos\omega_qt)\right\} .\end{aligned}\qquad (A1)$$

The first and second exponentials are oscillatory, while the third is less than or equal to zero and vanishes in the limit considered except in a region of small values of t, that is, $\omega_q|t|\le\omega_D|t|\le\varepsilon\ll1$, owing to the $(1-\cos\omega_qt)$ factor.

Therefore

$$\Gamma_{\downarrow}^{k}\simeq\frac{(W^k)^2}{4}\int_{-\varepsilon/\omega_D}^{\varepsilon/\omega_D}dt\,e^{iBt}e^{-A^2t^2} , \qquad (A2)$$

where A and B have been defined in Eq. (22).

Now introduce a change of variable $x=At$. We obtain

$$\Gamma_{\downarrow}^{k}\simeq\frac{(W^k)^2}{4}\int_{-\varepsilon A/\omega_D}^{\varepsilon A/\omega_D}\frac{dx}{A}e^{iBx/A}e^{-x^2} . \qquad (A3)$$

If $\varepsilon A/\omega_D\gg1$, that is, $\omega_D/A\ll\varepsilon$, then the region of integration may be extended to $\pm\infty$ without altering the value of the integral, and so

$$\begin{aligned}\Gamma_{\downarrow}^{k}&\simeq\frac{(W^k)^2}{4}\int_{-\infty}^{+\infty}\frac{dx}{A}e^{iBx/A-x^2}\\&=\frac{(W^k)^2}{4}\frac{\sqrt{\pi}}{A}e^{-B^2/4A^2} .\end{aligned}\qquad (A4)$$

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