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THEORETICAL STUDIES OF HOMOGENEOUS LINEWIDTHS OF OPTICAL TRANSITIONS IN GLASSES *

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In this paper, we review the recent theories of the homogeneous linewidth of chromophores in glasses, using the Redfield relaxation theory as a starting point. We treat the interaction of phonons with the two-level systems in the glass and discuss the approximations and averaging techniques used by many authors. We also examine the role of fractons and other models for the width.

1. Introduction

In this paper, we review the current theories of the homogeneous linewidth of chromophores embedded in glasses. The recent interest in this phenomenon has led to much experimental and theoretical work [1–15]. In this paper we will concentrate on the latter. We will be unable to treat all the theoretical models; however we hope to give the reader a good overall view of the field.

The standard model is that this width is caused by the interaction of the chromophoric molecule with two-level systems (TLS) assumed to exist in glasses and which provide an explanation of the low-temperature specific heat and thermal conductivity in these systems [16–20]. Interaction with phonons cause these TLS to change state from the lower to upper levels (or vice versa). Since the TLS interact weakly with the chomophore and this interaction is different in the excited and ground states of the chromophore, there is a dephasing produced in the optical transition, All approaches we discuss assume this basic physical model. The differences between them are often only a difference in either the approximations made or the technical aspects of averaging over TLS parameters (energies, tunneling parameters and distances). Instead of giving a detailed description of every model, we will proceed as follows: In section 2, we present the standard model for the chromophore interacting with a single TLS and show how this yields a formula for the width (due to one TLS) which agrees with most of the theoretical papers. In section 3, we discuss the various ways of averaging over the TLS distributions and find the temperature dependence of the width. In section 4, we review three other models for the width, the fracton model of Lyo and Orbach, the model of Osadko and a model assuming more than one effective mechanism. In section 5, we conclude with a discussion of the various ideas presented.

2. Chromophore–TLS interaction

2.1. Energy levels

Consider a single TLS interacting with a chromophore (either an ion or molecule), the latter having two states, ground $|g\rangle$, and excited $|e\rangle$. The assumption usually made is that the energy splitting of the TLS differs slightly in these two states, so that random flipping of the TLS (by

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phonons, for example) will cause the chromophore's energy difference to fluctuate and thereby produce a width in the optical absorption line.

First, consider the TLS. It is usually assumed to be made up of two states $|L\rangle$ and $|R\rangle$ on either side of a barrier with an energy separation Δ and tunneling matrix element $\frac{1}{2}K$. In the localized basis (or L and R states), the Hamiltonian matrix is

$$\frac{1}{2}\begin{pmatrix} -\Delta_i & K \\ K & \Delta_i \end{pmatrix}, \tag{1}$$

where the index i refers to the state of the chromophore (i.e. $|g\rangle$ or $|e\rangle$). This matrix has the eigenvalues and eigenvectors

$$-\tfrac{1}{2}\left(\Delta_i^2 + K^2\right)^{1/2} : \begin{pmatrix} \cos\theta_i \\ \sin\theta_i \end{pmatrix} \tag{2a}$$

and

$$+\tfrac{1}{2}\left(\Delta_i^2 + K^2\right)^{1/2} : \begin{pmatrix} -\sin\theta_i \\ \cos\theta_i \end{pmatrix}, \tag{2b}$$

where

$$\sin 2\theta_i = \frac{K}{\left(\Delta_i^2 + K^2\right)^{1/2}}, \qquad \cos\theta_i = \frac{\Delta_i}{\left(\Delta_i^2 + K^2\right)^{1/2}}. \tag{2c}$$

Thus, when the chromophore is in the ground state $|g\rangle$, the TLS splitting is $(\Delta_g^2 + K^2)^{1/2}$. The normal situation is that $K^2 \ll \Delta^2$, so that the TLS eigenstates are still largely localized.

Now consider the four-state system of a chromophore and one TLS. The states are labelled $|a\rangle$, $|b\rangle$, $|c\rangle$ and $|d\rangle$ and represent the chromophore in $|g\rangle$ and the two TLS eigenstates ($|a\rangle$ and $|b\rangle$) or the chromophore in $|e\rangle$ and the two TLS eigenstates. The phonon induced rates of flipping the TLS are labelled R_{cd} and R_{dc} (in $|e\rangle$), and R_{ab} and R_{ba} (in $|g\rangle$). Note that since $\omega_{dc} \equiv (\Delta_e^2 + K^2)^{1/2}$ is not equal to $\omega_{ba} \equiv (\Delta_g + K^2)^{1/2}$, these rates are *slightly different* in $|g\rangle$ and $|e\rangle$. In fact, if we follow most of the literature and assume that the R_{ij} are caused by *linear* phonon terms in the deformation potential approximation, we find the phonon–TLS interaction to be given by (in both $|g\rangle$ and $|e\rangle$)

$$V = \sum_q g_q\left(b_q + b_{-q}^+\right)\left[\,|L\rangle\langle L| - |R\rangle\langle R|\,\right], \tag{3}$$

where the sum is over phonon modes. The terms which cause TLS flips will then be

$$V_{\text{flip}} = \sum_q g_q\left(b_q + b_{-q}^+\right)\left\{\sin 2\theta_g\left(|a\rangle\langle b| + |b\rangle\langle a|\right) + \sin 2\theta_e\left(|c\rangle\langle d| + |d\rangle\langle c|\right)\right\}. \tag{4}$$

Thus, the flipping rates (in the Golden Rule approximation) will be given by

$$R_{dc} = 2\pi\sum_q g_q^2\left(\bar{n}_q + 1\right)\sin^2 2\theta_e\,\delta\left(\omega_q - \omega_{dc}\right) = G\omega_{dc}^3 \cdot \sin^2 2\theta_e \cdot \frac{1}{1 - \exp(-\beta\omega_{dc})}, \tag{5a}$$

$$R_{ba} = G\omega_{ba}^3 \cdot \sin^2 2\theta_g \cdot \frac{1}{1 - \exp(-\beta\omega_{ba})}, \tag{5b}$$

$$R_{cd} = \exp(-\beta\omega_{dc})\,R_{dc}, \tag{5c}$$

$$R_{ab} = \exp(-\beta\omega_{ba})\,R_{ba}, \tag{5d}$$

where G is a collection of constants, the Debye approximation has been made for the long-wavelength phonons and $\beta = (k_B T)^{-1}$. In addition we have assumed the deformation potential result that $g_q^2 \propto \omega_q$. This could be generalized to $g_q^2 \propto \omega_g^\sigma$; we will not concern ourselves with this possibility. Note that the differences between R_{dc} and R_{ba} occur in each term (except G).

One final remark about the model should be made here; the difference δ between ω_{dc} and ω_{ba} is due to the difference in interaction between the TLS and the chromophore, when the chromophore is excited and when it is in its ground state. It is this small quantity which is usually assumed to be a dipole–dipole (or dipole–quadrupole) term: $\delta \sim 1/R^s$ where R is the distance from TLS to chromophore.

2.2. Optical transitions and Redfield theory

The four-level system will have two large optical transition moments, μ_{ac} and μ_{bd}. The moments μ_{ad} and μ_{bc} are much smaller in value and we will neglect them. The optical absorption line shape is governed by the Fourier transform of the

transition dipole correlation function which may be written in the usual way as

$$C(t) = \sigma_{ca}(t) + \sigma_{db}(t), \tag{6}$$

where σ_{ca} and σ_{db} obey the coupled equations (Redfield formalism)

$$\dot{\sigma}_{ca} = [-i\omega_{ca} - T_{ca,ca}]\,\sigma_{ca} - T_{ca,db}\sigma_{db}, \tag{7a}$$

$$\dot{\sigma}_{db} = [-i\omega_{db} - T_{db,db}]\,\sigma_{db} - T_{db,ca}\sigma_{ca}, \tag{7b}$$

subject to the initial conditions

$$\sigma_{ca}(0) = p_a = \frac{e^{-\beta E_a}}{e^{-\beta E_b} + e^{-\beta E_a}}, \tag{8a}$$

$$\sigma_{db}(0) = p_b = \frac{e^{-\beta E_b}}{e^{-\beta E_b} + e^{-\beta E_a}}. \tag{8b}$$

In this we have made, in addition to the weak coupling assumptions, the approximations that the other density matrix elements play no role and can be neglected, and have assumed that the transition moment matrix elements are equal, i.e., $\mu_{ab} = \mu_{cd}$. The diagonal relaxation matrix elements $T_{ij,ij}$ are given by

$$T_{ca,ca} = \tfrac{1}{2}(R_{cd} + R_{ab}) + \gamma_{rad}, \tag{9a}$$

$$T_{db,db} = \tfrac{1}{2}(R_{dc} + R_{ba}) + \gamma_{rad}, \tag{9b}$$

where γ_{rad} is the radiative rate. The phonon assisted terms are simply related to the flipping of the TLS states. The other matrix elements of the relaxation matrix can be found using the model of phonon–TLS interaction discussed above. The use of the standard [21] theory with V_{flip} as the perturbation yields

$$T_{ca,db} = -\frac{1}{2}\left[\frac{\omega_{ba}}{\omega_{cd}}R_{ba} + \frac{\omega_{dc}}{\omega_{ba}}R_{dc}\right], \tag{10a}$$

$$T_{db,ca} = -\frac{1}{2}\left[\frac{\omega_{ba}}{\omega_{dc}}R_{ab} + \frac{\omega_{dc}}{\omega_{ba}}R_{cd}\right]. \tag{10b}$$

Note that if the difference between ω_{ba} and ω_{dc} is neglected *in the relaxation terms*, we find

$$T_{ca,ca} - \gamma_{rad} = -T_{db,ba} \equiv R_{\uparrow} \tag{11a}$$

$$T_{db,db} - \gamma_{rad} = -T_{ca,db} \equiv R_{\downarrow}, \tag{11b}$$

where $R_{\uparrow}$ and $R_{\downarrow}$ are the upward and downward rate of flipping. Then the relaxation matrix becomes identical to the usual exchange theories.

The formal solution to eq. (7) is

$$\begin{pmatrix}\sigma_{ca}\\ \sigma_{db}\end{pmatrix} = \{\exp[-i\boldsymbol{\omega} - \boldsymbol{T}]t\}\begin{pmatrix}p_a\\ p_b\end{pmatrix}, \tag{12}$$

so that

$$C(t) = (1, 1)\{\exp(-i\boldsymbol{\omega} - \boldsymbol{T})t\}\begin{pmatrix}p_a\\ p_b\end{pmatrix}. \tag{13}$$

This agrees, in form, with the spectral diffusion of Huber [12] (and in detail if the relaxation terms are approximated by eq. (11)) as well as the theories of Molenkamp and Wiersma [56].

As is evident from eq. (13), the width of the optical absorption line is determined by the real part of the eigenvalues of the matrix $i\boldsymbol{\omega} + \boldsymbol{T}$. Note that $\omega_{ca} = \omega_{eg} - \frac{1}{2}(\omega_{dc} - \omega_{ba})$ and $\omega_{db} = \omega_{eg} + \frac{1}{2}(\omega_{dc} - \omega_{ba})$, so that the ω_{eg} is just a constant term as is γ_{rad} in both transitions; both will be left out of the remaining formulas. That is, frequency will be measured with respect to ω_{eg} and widths given without the additive contribution of the radiative rate. There are two simple limits for which the linewidth can be easily found: $\delta = (\omega_{dc} - \omega_{ba})$ large compared to the rates R_{ij} and δ small compared to these. Since $\delta \sim 1/r^s$, the nearby ions will give large δ and the ions far away from the chromophore will give small δ; there are, however, many more of the latter.

Case (1): $\delta > R_{ij}$

In this case the four-level system will have two optical transitions, one at frequency $-\delta/2$ with width $\frac{1}{2}(R_{cd} + R_{ab})$ and one at frequency $\delta/2$ with width $\frac{1}{2}(R_{dc} + R_{ba})$. Using the one-phonon TLS interaction, we find that the widths are

$$\tfrac{1}{2}G\left[\omega_{dc}^3\{\bar{n}(\omega_{dc}) + 1\}\right]\frac{K^2}{\omega_{dc}^2} + \tfrac{1}{2}G\left[\omega_{ba}^3\{\bar{n}(\omega_{ba}) + 1\}\right]\frac{K^2}{\omega_{ba}^2}, \tag{14a}$$

and

$$\tfrac{1}{2}G\left[\omega_{dc}^3\bar{n}(\omega_{dc})\right]\frac{K^2}{\omega_{dc}^2} + \tfrac{1}{2}G\left[\omega_{ba}^3\bar{n}(\omega_{ba})\right]\frac{K^2}{\omega_{ba}^2}. \tag{14b}$$

Thus, as $T \to 0$, one of the lines becomes very narrow (i.e., width equal to γ_{rad}) while the other

has a width governed by the *downward* flip rate of the TLS (i.e., phonon emission term), which is nonzero at $T=0$. This formula for the widths agrees with the results of Small et al. [6], Lyo [8b, d], Molenkamp and Wiersma [5b], and Reineker et al. [9d, e], before averaging over TLS parameters. This limit has been called the UPS (uncorrelated phonon scattering) limit or the slow modulation limit.

The standard approximation employed to find the width from these expressions has been to average these widths over the initial populations of $|a\rangle$ and $|b\rangle$ to get the width Γ, and to assume $\omega_{ba}=\omega_{dc}=\epsilon$ in all the subsequent expressions

$$\Gamma = G\frac{K^2}{\epsilon^2}\cdot\epsilon^3\left\{[\bar{n}(\epsilon)+1]\times\frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}+\bar{n}(\epsilon)\frac{1}{1+e^{-\beta\epsilon}}\right\}, \tag{15a}$$

$$=\frac{G}{2}\frac{K^2}{\epsilon^2}\left[\epsilon^3\coth\left(\frac{\beta\epsilon}{2}\right)\right]\cdot\operatorname{sech}^2\left(\frac{\beta\epsilon}{2}\right)$$

$$\equiv\tau^{-1}(\epsilon)\operatorname{sech}^2\left(\frac{\beta\epsilon}{2}\right). \tag{15b}$$

where we have written the last form in terms of the "spin–lattice" relaxation rate of the TLS, $\tau^{-1}=\frac{1}{2}(R_\uparrow+R_\downarrow)=\frac{1}{2}GK^2\epsilon\coth(\beta\epsilon/2)$.

Case (2): $\delta \ll R_{ij}$

In this case, the TLS flipping is rapid compared to h/δ, so that fast modulation occurs. As we pointed out above, a natural assumption is to neglect δ in all of the relaxation rates, $T_{ij,kl}$ and only include δ in the frequency shift. Then the eigenvalues of $i\omega+T$ can easily be written down as

$$\tfrac{1}{2}(R_\uparrow+R_\downarrow)\pm\tfrac{1}{2}\left[(R_\uparrow+R_\downarrow)^2-2i\delta(R_\uparrow+R_\downarrow)-\delta^2\right]^{1/2}. \tag{16}$$

The relevant eigenvalue is the one with the smaller width, the other one leading to very little intensity. This eigenvalue is, to order δ^2,

$$+\frac{i\delta}{2}\frac{(R_\uparrow-R_\downarrow)}{R_\uparrow+R_\downarrow}+\frac{\delta^2R_\uparrow R_\downarrow}{(R_\uparrow+R_\downarrow)^3}, \tag{17}$$

yielding a width $\delta^2R_\uparrow R_\downarrow(R_\uparrow+R_\downarrow)^{-3}=\frac{1}{4}\delta^2\tau\operatorname{sech}^2(\beta\epsilon/2)$, in agreement with Lyo [8b, d], Molenkamp and Wiersma [5b] and others in this limit. Note that these authors finally average this width over the distribution of TLS parameters to obtain the average width.

If one does *not* make the assumption that δ can be neglected in the $T_{ij,kl}$, then additional terms (to order δ^2) appear in the width. The relevant eigenvalue of the matrix is then given by

$$+\frac{i\delta}{2}\frac{(R_\uparrow-R_\downarrow)}{R_\uparrow+R_\downarrow}+\delta^2\frac{R_\uparrow R_\downarrow}{(R_\uparrow+R_\downarrow)^3}+\frac{\delta^2}{\epsilon^2}\frac{R_\uparrow R_\downarrow}{R_\uparrow+R_\downarrow}\left[\frac{\beta\epsilon}{2}\coth\left(\frac{\beta\epsilon}{2}\right)-2\right], \tag{18}$$

which differs from the last formula in the last term. The width of the optical transition then has two contributions. At low T, the first goes as cosech $\beta\epsilon$ while the second goes as $\beta\epsilon$ cosech $\beta\epsilon$, so that which is dominant depends on the coupling constants, etc. At $T>\epsilon/k_B$, the first term goes like $1/T$ (narrowing) while the second goes like T and can even be negative; thus, at high enough T, this formula will predict a nonsensical result. The breakdown of this approximation is due to the increasing importance of the other matrix elements σ_{da} and σ_{cb} in determining the dynamics. We are able to neglect them only if the mixing of the various transitions is small. When $T>\epsilon/k_B$ the mixing can be large and we should examine the Redfield equations for the four coupled matrix elements, σ_{db}, σ_{ca}, σ_{da}, σ_{cb}. It turns out that these equations can be solved exactly, and Kassner and Reineker [9c–e] did so. The resulting expressions are prohibitively complicated but, in the limit we are discussing, turn out to yield (for the eigenvalue we are considering) the same imaginary part and a real part equal to

$$\delta^2\frac{R_\uparrow R_\downarrow}{(R_\uparrow+R_\downarrow)^3}+\frac{\delta^2}{\epsilon^2}\frac{R_\uparrow R_\downarrow}{R_\uparrow+R_\downarrow}\times\left(\frac{\beta\epsilon}{2}\coth\left(\frac{\beta\epsilon}{2}\right)-1\right). \tag{19}$$

This agrees with the earlier result at low T, and does not have the unphysical behavior discussed above at high T. In fact, both terms now yield a

$1/T$ behavior at high T, thus the high-T narrowing is preserved. In addition, for the generally accepted parameter values of K, Δ, G, etc., the second term is much smaller than the first at all but the lowest temperatures.

This dicussion shows clearly that not only the averaging procedure but also the approximations made are a delicate matter. Small differences in approximate forms can yield very different behavior. Thus, for example, both Lyo and Orbach [8a] and Reineker and Morawitz [9a, b] got a linear T dependence at high T because of their approximation (in a mathematical sense) of setting $R_{ab}/\sin^2 2\theta_g$ equal to $R_{cd}/\sin^2 2\theta_e$ and $R_{ba}/\sin^2 2\theta_g$ equal to $R_{dc}/\sin^2 2\theta_e$.

3. The effect of many-TLS

As mentioned above, the approximation of taking the total linewidth as the sum over all TLS of the individual width due to each TLS (after averaging over the TLS parameters) has been widely used. This approximation has recently been questioned by Huber et al. [12c, d], but for didactic reasons we will use it in the following.

The averaging over the distribution of Δ (TLS energy differences in the absence of tunneling), K (the tunneling matrix element) and the distribution of δ (or distances of the TLS from the chromophore) is not straightforward. To arrive at a result for the temperature dependence within the approximations we have made, we only need consider the distribution of ϵ (the final) TLS splittings) and δ.

The simplest procedure is to assume that δ is large, use eq. (15) and write

$$\langle\Gamma\rangle = \int_0^{\epsilon_{max}} d\epsilon\, \rho(\epsilon)\, \tau^{-1}(\epsilon)\, \mathrm{sech}^2(\beta\epsilon/2), \qquad (20)$$

where $\rho(\epsilon)$ is the density of TLS as a function of the splitting ϵ, which we assume varies at low ϵ as ϵ^μ. At low T, we can change variables to $\beta\epsilon$ and replace $\beta\epsilon_{max}$ by ∞ to find

$$\langle\Gamma\rangle \sim T^{2+\mu}, \qquad \epsilon_{max}/T \gg 1, \qquad (21)$$

since $\tau^{-1} \propto \epsilon$ when we take the explicit ϵ dependence of eq. (15b). If we follow many authors and assume $|f^+|^2 \equiv K^2/\epsilon^2$ has little or no ϵ dependence, then $\tau^{-1} \sim \epsilon^3$ and $\Gamma \sim T^{4+\mu}$. At high T, τ^{-1} varies as T, so

$$\langle\Gamma\rangle \sim T, \qquad \epsilon_{max}/T \ll 1. \qquad (22)$$

Lyo [8b] pointed out that one should sum only over those TLS such that δ is larger than the TLS flipping rates, so the width arises from those TLS within a radius R_c given by (remember $\delta = b/R^s$)

$$R_c \cong \left(\frac{b}{\hbar\tau^{-1}}\right)^{1/s}. \qquad (23)$$

He then sums Γ over this volume and then over the distribution in ϵ:

$$\langle\langle\Gamma\rangle\rangle \propto \int_0^{\epsilon_{max}} d\epsilon\, \rho(\epsilon) \int_0^{R_c} dR\, R^2 \cdot \Gamma \cdot n, \qquad (24)$$

where n is the spatial density of TLS. Since in this limit (δ large) Γ is independent of δ, we have

$$\langle\langle\Gamma\rangle\rangle \propto \int_0^{\epsilon_{max}} d\epsilon\, \rho(\epsilon)\, \tau^{-1+3/s}\, \mathrm{sech}^2(\beta\epsilon/2). \qquad (25)$$

Lyo assumes $\tau^{-1} \propto \epsilon^3$ for phonon-assisted processes to find

$$\langle\langle\Gamma\rangle\rangle \propto T^{1+\mu+3(1-3/s)}, \qquad \epsilon_{max}/T \gg 1. \qquad (26)$$

(That is, Lyo writes K^2/ϵ^2 as $|f^+|^2$ so that $\tau^{-1} \propto |f^+|^2\epsilon^3$ and assumes that the ϵ dependence of $|f^+|^2$ can be neglected, whereas we have included it explicitly.) If we assume that $\tau^{-1} \propto \epsilon$, as above, then $\langle\langle\Gamma\rangle\rangle \propto T^{1+\mu+(1-3/s)}$ as pointed out by Jankowiak and Small [6]. In either case, for dipole–dipole coupling ($s = 3$), we find the width varying as $T^{1+\mu}$.

Now, consider the fast modulation realm. Summing over the distant TLS, which have $\delta \ll \tau^{-1}$, we obtain

$$\langle\langle\Gamma\rangle\rangle \propto \int_0^{\epsilon_{max}} d\epsilon\, \rho(\epsilon) \int_{R_c}^{\infty} dR\, R^2\delta^2\tau\, \mathrm{sech}^2(\beta\epsilon/2). \qquad (27)$$

But $\delta \sim 1/R^s$ and performing the integral over R and examining the result at low T, we again find

$$\langle\langle\Gamma\rangle\rangle \propto T^{1+\mu+3(1-3/s)}, \qquad (28)$$

using Lyo's assumption $\tau^{-1} \propto \epsilon^3$. These results were confirmed by Molenkamp and Wiersma [5b].

These two results show the strong dependence

of the temperature dependence on the assumptions made in the averaging process, even though these results both make the major assumption that the total width is the sum of the width from each TLS. Reineker and Morawitz [9a] and recently Huber [12c, d] pointed out that in fact one should average the line shape or the equivalent, average the correlation function. Since the spatial distribution of the TLS is random, he suggests that the configuration average of $C(t)$ (eq. (13)) should be treated as in other disordered system theories, i.e.,

$$\langle\langle e^{i\Omega t}\rangle\rangle_{\text{conf}} = \exp\left\{-n\left[\int dR\, R^2\langle(1-e^{-i\Omega t})\rangle\right]\right\}, \tag{29}$$

where the inner average is over the TLS parameters. Since Huber's paper in this volume treats this, we will not discuss it further, except to say that Huber's form for the single TLS–chromophore interaction is the same as ours, within the approximations noted above (eq. (11)) and that within the dipole–dipole coupling model, he also finds a width proportional to $T^{1+\mu}$.

At this point, we see that this model predicts that in order to obtain a $T^{1.3}$ dependence at low temperature (as found in many experiments) entirely from the TLS interactions, one must postulate that the density of TLS modes varies as ϵ^{μ} as $\epsilon \to 0$, $\mu = 0.3$, and that the interaction is dipole–dipole. If there is a *universal* form for the low-frequency density of TLS states $\epsilon^{0.3}$, then the important open problem is to understand why this is true. This becomes even more important when one realizes that there is little evidence for this density of states in other kinds of experiments. Acoustic measurements in silicate glasses have been explained [15a] with the original model [16] which yields a constant TLS distribution and logarithmically varying TLS density of states. For most purposes, the latter can be taken to be constant. In addition, measurements in polymers [15c] have been interpreted to yield *higher* density of states at *lower* energies, directly contradicting the $\epsilon^{0.3}$ behavior. The often quoted specific heat measurements [17], which were explained by an $\epsilon^{0.3}$ density of states, have been reconciled with the original model by invoking the time dependence of the specific heat [18,19]; a more recent conjecture [20] also removes the need for the $\epsilon^{0.3}$ density of states to explain the specific heat.

There are three other calculations of the homogeneous linewidth due to TLS interactions [15b, 9d, 9e, 6] that use the original density of states and yield a temperature dependence close to $T^{1.3}$ over the relevant range. Hunklinger [15b] uses a stochastic model of spectral diffusion, which we will not discuss, Kassner and Reineker [9d, e] use the model we have set forth here, however they derive a formula for the line shape of the full many-body problem of one chromophore interacting with N TLS. Arguments are given that the low-temperature line intensity is dominated by a few narrow lines whose widths are calculated *numerically* as the sum over the exact linewidths of the chromophore one TLS problem. Care has to be taken to include all nonnegligible contributions, so that a large interaction volume around the chromophore is considered. At low T, the contributions of quite weakly coupled TLS are important (since the TLS flip rates are so low) and only extremely weakly coupled TLS can be neglected. The numerical results [9d, e] give a temperature dependence roughly consistent with $T^{1.3}$ over the relevant T range, in both the dipole–dipole and the dipole–quadrupole case, and using the original TLS distribution and the Debye phonon density of states. It is clear fom this numerical evaluation of the linewidth that the average over the tunneling matrix elements (K or overlaps, $\exp(-\lambda)$) is subtle and can lead to a change in the temperature dependence, *especially* at very low T. It is this averaging which leads to a deviation from the Lyo prediction ($T^{1+\mu}$), at low T, to a linewidth varying more quickly with T. Thus even with $\mu = 0$, the temperature dependence is consistent with (but not exactly equal to) $T^{1.3}$. A drawback of this theory is that as yet no analytical formulas for the linewidth have been given, although approximate analytical expressions for the average over Δ and K are available. The complete average over δ, Δ and K has not been found, except numerically. It is even less likely that an analytic form can be given if the Huber formulation for the linewidth is used. Recently Jankowiak and Small [6] have introduced a new averaging procedure which also yields a $T^{1+\mu_{\text{eff}}}$ result.

4. Other theoretical models

4.1. Fractons

Lyo and Orbach [8c] suggested a modification of Lyo's form based on the postulated existence of fracton modes in disordered systems by Alexander and Orbach [22]. The argument starts with the postulate that in a disordered system there exists a range of length scales (neither too long nor too short) for which the geometric structure is self-similar, i.e., the mass density scales with distance from any point like $n^{\bar{d}-d}$, where $\bar{d}$ is the fractal dimension and d the Euclidean dimension. Alexander and Orbach [22] then examined the consequences of this for the vibrational modes of the system and found that in a certain frequency range (connected to the distance range over which the system is self-similar) the density of states of the localized modes (fractons) produced will scale as $\omega^{1/3}$ instead of the Debye form ω^{d-1}. Note that the existence of fractons does *not* mean that the long-wavelength phonons are absent.

Lyo and Orbach [8c] consider the TLS flipping rates to be caused by TLS–fracton interactions instead of TLS–phonon interactions, and suggest that these rates ($\tau^{-1}(\epsilon)$) will vary as $\epsilon^{4/3}$ (i.e., $\epsilon^{1/3}$ from the density of fracton states and ϵ from the fracton–TLS interaction). When this form is averaged in the same manner as before, these authors find $\langle\langle\Gamma\rangle\rangle \propto T^{1+\mu+4(1-3/s)/3}$, thus for dipole–dipole interactions ($s=3$) $\langle\langle\Gamma\rangle\rangle \propto T^{1+\mu}$. These authors suggest that a possible explanation of the 1.3 exponent is that the relevant interaction is dipole–quadrupole ($s=4$) and $\mu \simeq 0$.

For this explanation to be valid, one must accept a number of conjectures; for example, (a) the TLS–fracton interaction term $|g_q|^2$ varies as ω_q, (b) the term K^2/ω^2 (i.e. the $\sin^2 2\theta$) is averaged separately from the term $\tau^{-1}(\epsilon)$, (c) the phonon–TLS interaction is too weak to cause TLS flips. Since the fractons are local modes, (a) can be challenged and the procedure in (b) is open to question, especially given the delicacy of the various averaging procedures as mentioned in the last section. In addition, the fracton density of states should be less important than the phonon density of states at very low ω, or equivalently, very low T. Thus, as T is lowered the fractons should play less of a role. In spite of these objections, this remains an interesting suggestion which should be probed by further experiment and theory.

Recently Dixon et al. [23] have suggested that fractons play a role in the homogeneous linewidths even at high T (10 K $< T <$ 200 K). They assume that the fractons (or localized vibrational modes of the glass) dephase the optical transition via a two-fracton interaction (just as a two-phonon interaction causes dephasing). Using the McCumber–Sturge [24] formulation they find that $\Gamma_{\text{fracton}} \sim T^2$ at essentially all the temperatures of their experiment, in agreement with their data. Since the phonon contribution to the linewidth is also proportional to T^2 for $T > \theta_D/2$, and Huber has pointed out [12a] that the phonon density of states in glasses becomes non-Debye-like at rather small ω so that $\Gamma \sim T^2$ even at $T < \theta_D/2$, it is difficult to see the need for invoking fractons for this range of T. Since fractons can be thought of as vibrational modes of the glass, i.e. local modes, whether the introduction of them in this context is useful or not depends a little on one's beliefs.

4.2. Osadko's theory

Osadko [13] has suggested that the TLS should be treated as a thermal bath in just the same manner that phonons are treated in the standard theories of line broadening. His theory is nonperturbative, but the essential flavor and results can be found using perturbation theory and the standard McCumber–Sturge [24] line-shape formula.

Consider the chromophore to be a two-state system ($|g\rangle$ and $|e\rangle$ as before and assume that the relevant interaction between the TLS and the chromophore is an operator which flips *two* TLS (note the resemblance to the low-T linewidth due to quadratic phonon terms), i.e.

$$V_{\text{TLS-chromophore}} = [\,|e\rangle\langle e| - |g\rangle\langle g|\,] \sum_{i \neq j} v_{i,j} \sigma_i^+ \sigma_j^- , \tag{30}$$

where σ_i^+ is an operator which flips the ith TLS from the lower to the upper levels, σ_i^- is the reverse, and v_{ij} is the interaction matrix element. The physical picture is then that TLS dephase the

optical transition by their constant flipping. The standard formula for the linewidth at low T then yields

$$\Gamma = \tfrac{1}{2}\int_{-\infty}^{+\infty} \mathrm{d}\tau \langle [V_{ee}(\tau) - V_{gg}(\tau)] \times [V_{ee}(0) - V_{gg}(0)] \rangle, \tag{31}$$

where the $V_{ee} - V_{gg}$ is the instantaneous change in the optical transition frequency due to the TLS (i.e. the matrix elements of $V_{\text{TLS-chromophore}}$) and the average is over the thermal distribution of TLS. Then

$$\Gamma = \tfrac{1}{2}\int_{-\infty}^{+\infty} \mathrm{d}\tau \sum_{\substack{i,j \\ i \neq j}} |v_{ij}|^2 \times \langle \sigma_i^+(\tau)\sigma_i^-(0)\rangle \langle \sigma_j^-(\tau)\sigma_j^+(0)\rangle, \tag{32a}$$

and

$$\Gamma \propto \int_0^{\epsilon_{\max}} \mathrm{d}\epsilon [\rho(\epsilon)]^2 |v(\epsilon)|^2 n_{\text{TLS}}^{\ell}(\epsilon)\, n_{\text{TLS}}^{\text{u}}(\epsilon), \tag{32b}$$

where we have assumed (a) that $|v_{ij}|^2$ is a function of $\epsilon_i = \epsilon_j$ only, (b) $\rho(\epsilon)$ is the density of TLS energies and (c) $n_{\text{TLS}}^{\ell}(\epsilon)$ is the thermal population of the lower TLS level and $n_{\text{TLS}}^{\text{u}}(\epsilon)$ is the thermal population of the upper level. At equilibrium, $n_{\text{TLS}}^{\ell} = (1 + \mathrm{e}^{-\beta\epsilon})^{-1}$ and $n_{\text{TLS}}^{\text{u}} = \mathrm{e}^{-\beta\epsilon}(1 + \mathrm{e}^{-\beta\epsilon})^{-1}$ so that

$$\Gamma \propto \int_0^{\epsilon_{\max}} \mathrm{d}\epsilon\, \rho^2(\epsilon)\, |v(\epsilon)|^2\, \mathrm{sech}(\beta\epsilon/2). \tag{33}$$

The temperature dependence now depends on the *assumed* form for $\rho^2(\epsilon)|v(\epsilon)|^2$. If this is assumed constant, the $\Gamma \propto T \tanh(\epsilon_{\max}/2k_{\text{B}}T) < T$; if it is assumed to vary as ϵ^x, then $\Gamma \propto T^{1+x}$ at low temperature. Oskadko can fit the experimental data with a particular (and perhaps reasonable) form for $|v(\epsilon)|^2\rho^2(\epsilon)$.

4.3. Two mechanisms operating

The simplest, and perhaps least innovative, procedure to obtain a $T^{1+\mu}$ dependence of the linewidth is to assume that there are two mechanisms operating simultaneously. For example, Jackson and Silbey [25] assumed that the TLS contribution to the linewidth is linear in T (i.e. the dipole–dipole interaction, $\mu = 0$ form) at low T while the local librational modes, known to dephase the optical transition in *crystals*, gave a typical optical phonon contribution. Thus at low temperatures, where acoustic phonon direct contributions can be neglected,

$$\Gamma = AT + \sum_{\substack{\text{local} \\ \text{modes}}} \lambda_i [\mathrm{e}^{-\beta\omega_i}/(1 - \mathrm{e}^{-\beta\omega_i})]. \tag{34}$$

Here λ_i is the coupling constant to the ith local mode. This predicts that at low enough temperatures ($T < \omega_i/k_{\text{B}}$) the linewidth is linear in T, but as the temperature is raised Γ varies as $T^{1+\delta}$, where δ is small. Local mode frequencies of a few cm^{-1} and coupling constants taken from crystalline studies can fit most of the data in glasses.

The original Jackson–Silbey model assumed the local modes were *librations* of the chromophore; however, local modes of the glass give a contribution of exactly the same form. Thus one may suggest that direct local mode contributions (of all sorts) when added to a linear T dependence can fit the data, at least for $T > 1$ K. This model, however, clearly suggests that for $T < \omega_i/k_{\text{B}}$ (i.e. temperatures well below the lowest local mode frequencies) the linewidth will be linear T (assuming $\mu = 0$, as these authors do).

5. Conclusions

We wish that a review of the various theoretical models of the homogeneous width of the optical transitions in glasses could end by pointing out the correct one. Unfortunately, we cannot do this because in all the theoretical calculations (each based on the same physical model), approximations are made which, because of the delicacy of the various averaging techniques, can lead to small changes in the temperature dependence, especially at very low temperatures. For several, if not most, of these approximations there is no real knowledge about their validity. In spite of this and the different averaging procedures for dipole–dipole coupling of the TLS to the chromophore (either electric or elastic), most authors find a $T^{1+\mu}$ dependence at low T, where μ is an additional parameter (due to the intrinsic density of states of

the TLS varying as ϵ^{μ}). Other authors find a similar temperature dependence without μ by more carefully averaging over the tunneling parameters. As we have seen, the universal variation of the TLS density of states does not seem to show up in other measurements. If we try to explain the $T^{1.3}$ dependence by a dipole–quadrupole form ($s = 4$) and fracton TLS coupling [8c] or by $s = 4$ and $\tau^{-1}(\epsilon) \propto \epsilon$ (see the discussion under eq. (26) where this will predict $T^{1.25}$), then the form of the line shape will not be Lorentzian (i.e. the decay will not be exponential [12d]). This is not verified experimentally.

The TLS Raman process of Osad'ko and the two-mechanism model (section 4) can also fit the data with appropriate untested assumptions.

In short, the $T^{1.3}$ dependence can be explained by the TLS model, but it requires assumptions about which there is little or no independent support. It would be desirable for the theorists to make explicit predictions of other properties or experimental results, while ensuring that the models give consistent results for thermodynamic properties so that the various theories can be distinguished. For example, what do the theories predict for hole-burning efficiencies and time dependence?

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