I. INTRODUCTION

Experimental advances have made it possible to measure the spectral line shape of a single molecule (SM) embedded in a condensed phase. In a disordered condensed phase each molecule is in a unique static and dynamic environment, hence the line shapes of chemically identical SMs vary from molecule to molecule. In this way, the dynamic properties of the host are encoded in the distribution of SM spectral line shapes.

In this paper we investigate the conditions for simple/complex line shape phenomena of SMs interacting with randomly distributed independent two-level systems (TLSs) based on the sudden jump approach of Kubo and Anderson. Examples of simple and complex line shape phenomena can be found in Figs. 5 and 6, respectively. We define simple line shape phenomena as the case where all (or most) SM lines have identical shape, though parameters describing the line can vary from one molecule to the other. For example, cases where all lines are Lorentzian or Gaussian, though the linewidth is a random variable. If all lines are Gaussian or Lorentzian, only one single probability density function (PDF) is needed to characterize the statistical properties of the lines, e.g., the PDF of linewidths. On the other hand, complex line shape phenomena are defined when the functional form of the line shape differs from one molecule to the other. This is expected when splitting phenomena are observed (see the following for details). For this case an infinite number of PDFs are needed to fully characterize the statistical properties of the lines. As we have discussed in Ref. 23, in this complex case each line can be characterized by its cumulants \( \kappa_1, \kappa_2, \ldots \), which vary from one SM to the other, and then the PDFs \( P(\kappa_1), P(\kappa_2), \ldots \) are needed for the full description of the statistical properties of the lines.

In this work we use the approach of Skinner and co-workers, c.f. Refs. 12, 13, and 18. Reilly and Skinner modeled the line shape of SMs interacting with \( N \) identical TLSs on a lattice based on the Kubo–Anderson sudden jump approach. Geva and Skinner considered a SM interacting with a disordered environment. They modeled the line shape of a SM in low temperature glass based on the sudden jump picture and the standard tunneling model of glass. In this model, a random distribution of dynamical defects (i.e., the TLSs) interact with the chromophore via long range interactions. Based on these models, we find (i) for SMs interacting with identical TLSs, which are randomly distributed in space and in the fast modulation limit, that lines are Lorentzian. Under certain conditions we find that the distribution of linewidths of the SMs is a Lévy-stable distribution and we explain that this is a consequence of the generalized central limit theorem. (ii) For SMs in glass and when TLSs are excluded from a sufficiently large spheri-
II. SUDDEN JUMP MODEL

Following Refs. 9, 10, 12, and 26 we assume a chromophore coupled to nonidentical independent TLSs. The SM–TLS interaction is dipolar. The chromophore is on the origin and the position of the \( n \) TLS is \( \mathbf{r}_n \). The TLSs are coupled to phonons or other thermal excitations such that the state of the TLS changes with time. The state of the \( n \)th TLS is described by an occupation parameter, \( \xi_n(t) \), which is equal to 1 or 0 if the TLS is in its ground or excited state, respectively. The transitions between the ground and excited state are described by the up and down transition rates \( K_{n}^{u}, K_{n}^{d} \), which are related to each other by the standard detailed balance condition.

The excitation of the \( n \)th TLS shifts the chromophore’s transition frequency by \( v_n \). Thus, the chromophore’s transition frequency is

\[
\omega(\tau) = \omega_0 + \sum_{n=1}^{N_{\text{act}}} \xi_n(\tau)v_n, \tag{1}
\]

where \( N_{\text{act}} \) is the number of active TLSs in the system (see further details in the following) and \( \omega_0 \) is the bare transition frequency, which differs from one molecule to the other depending on the local static disorder. The frequency perturbation of the \( n \)th TLS is

\[
v_n = 2\pi \alpha \frac{\Psi(\Omega)\Delta_n}{r^3}, \tag{2}
\]

where \( \alpha \) is a coupling constant whose dimensions are Hz m³, \( \Delta_n \) is a dimensionless function of the internal parameters of the TLS, and \( \Psi(\Omega) \) is a dimensionless function of order unity defined by the orientation of the \( n \)th TLS and the SM.

The absorption line shape of the SM is given by the complex Laplace transform of the dipole autocorrelation function (also called the relaxation function)

\[
I_{\text{SM}}(\omega) = \frac{1}{\pi} \text{Re} \left[ \int_0^\infty dt e^{-i\omega t} e^{-t/T_1} \Phi_{\text{SM}}(t) \right], \tag{3}
\]

where \( T_1 \) is the lifetime of the chromophore’s excited state. The relaxation function is

\[
\Phi_{\text{SM}}(t) = \exp \left[ -i \int_0^t d\tau \omega(\tau) \right], \tag{4}
\]

where the bar denotes the average with respect to the stochastic processes \( \xi_n(\tau) \). For simplicity we restrict the analysis to \( \omega_0 = 0 \) in Eq. (1) and \( 1/T_1 = 0 \) in Eq. (3), hence only contributions of the TLSs to the lines are considered. Since the TLSs are independent,

\[
\Phi_{\text{SM}}(t) = \prod_{n=1}^{N_{\text{act}}} \Phi_n(t). \tag{5}
\]

The relaxation function of a single TLS can be evaluated based on methods developed by Anderson and Kubo,

\[
\Phi_n(t) = e^{-\left(\theta_n + i\gamma_n v_n\right)\theta_n} \left[ \cos(\Omega_n t) + \frac{\theta_n}{\Omega_n} \sinh(\Omega_n t) \right] \tag{6}
\]

with
\[ \Omega_n = \sqrt{\frac{K_n^2}{4} - \frac{v_n^2}{4}} - i \left( \frac{p_n - 1}{2} \right) v_n K_n, \]  
\[ \theta_n = \frac{K_n}{2} - i \left( \frac{p_n - 1}{2} \right) v_n, \]

where \( p_n \) is the probability of finding the \( n \)th TLS in its excited state and \( K_n = K_a + K_d \). In the slow modulation limit \( K_n \approx |v_n| \) one finds a much simpler expression,

\[ \Phi_n(t) = 1 - p_n + p_n e^{-i\omega_n t}. \]  

From Eq. (9) we learn that the line shape of a SM coupled to a single TLS, in the slow modulation limit, is described by two delta peaks (splitting phenomena) and it is easy to understand that the line shape of a SM interacting with \( N \) slow TLSs will be described by \( 2^N \) delta peaks.

In the fast modulation limit, \( K_n \gg |v_n| \),

\[ \Phi_n(t) = \exp(-i p_n v_n t) \exp(-\Gamma_n |t|) \]

and \( \Gamma_n = (p_n - p_n^2) v_n^2 K_n \). This means that a line shape of a SM interacting with a single fast TLS is a Lorentzian with half width \( \Gamma_n \). It is clear that the line shape of a SM interacting with a bath of fast TLSs will also yield a Lorentzian shape with a random linewidth

\[ \Gamma = \sum_{n=1}^{N_{act}} p_n (1 - p_n) \frac{v_n^2}{K_n} \]

centered at

\[ \omega_c = \sum_{n=1}^{N_{act}} p_n v_n. \]

For this behavior, the condition \( K_n \gg |v_n| \) must hold for all the TLSs in the system. For TLSs close to the origin the fast modulation condition is not satisfied since

\[ |v_n| = 2 \pi \alpha \frac{\Psi(\Omega_n)}{r^3} \gg K_n \]  

for \( r \to 0 \). Hence for a system to exhibit Lorentzian behavior TLSs should not reside in the close vicinity of the SM.

### III. EXAMPLE 1: IDENTICAL TLS MODEL

Let us investigate the fast modulation limit using a simple model. We assume all TLSs are identical though randomly distributed in space, hence we have \( \Delta_n = 1, p_n = p \) and \( K_n = K \). Two additional parameters are needed to define the model—the density of the TLSs \( \rho \) as well as the coupling \( \alpha \). According to the discussion in Sec. II, the SM line shape will be Lorentzian, with a width which varies from one molecule to the other, provided that all TLSs are described by a fast modulation limit. The condition for the fast modulation limit is

\[ K \gg 2 \pi \alpha \frac{\Psi(\Omega_n)}{r^3} \]  

for all TLSs in the system. Since \( \Psi(\Omega) = 1 \), each SM with a TLS in a shell of radius \( r \sim (a/K)^{1/3} \) is not described by the fast modulation limit. For such a TLS to be rare the condition

\[ b_1 \rho \alpha/K \ll 1 \]  

must hold and \( b_1 \) is a constant of order unity determined by statistical properties of \( \Psi(\Omega) \). When Eq. (15) is valid the SMs are described by the fast modulation limit and we anticipate that lines are Lorentzian.

To quantify the transition from the fast modulation limit to the more complex slow modulation limit we define an order parameter. Let

\[ \xi = \frac{1}{2} \int_{-\infty}^{\infty} d\omega |I_{\text{SM}}(\omega) - I_{\text{lin}}(\omega)|, \]

where \( I_{\text{SM}}(\omega) \) is the line shape of the SM and \( I_{\text{lin}}(\omega) \) is the line shape of the molecule in the fast modulation limit [i.e., a Lorentzian with width \( \Gamma \), Eq. (11), centered on \( \omega_c \), Eq. (12)]. Both \( I_{\text{SM}}(\omega) \) and \( I_{\text{lin}}(\omega) \) depend on the realization of disorder the SM is interacting with, hence \( \xi \) is a random variable. We define \( \langle \xi \rangle \) the order parameter and \( \langle \cdots \rangle \) is an average over realizations of disorder. Since according to our definitions \( I_{\text{SM}}(\omega) \) and \( I_{\text{lin}}(\omega) \) are normalized functions the order parameter \( \xi \) is dimensionless and \( 0 \leq \langle \xi \rangle \leq 1 \). The order parameter \( \langle \xi \rangle \to 0 \) in the fast modulation limit (i.e., the ordered case in the sense that all lines are Lorentzian though their width and location are random) while \( \langle \xi \rangle \to 1 \) far from this limit (e.g., when splitting phenomena are expected to be observed).

We generated on our computer many realizations of disordered systems. In simulation we exclude TLSs from a cavity of radius \( l \) around the SM, otherwise the TLSs are uniformly distributed in space. For simplicity we use the two-state model \( \psi(\Omega) = \pm 1 \) with equal probabilities; other more realistic forms of \( \Psi(\Omega) \) will not alter the conclusions we reach. For each realization of disorder we used the fast Fourier transform to calculate the SM line shape and also \( \xi \). In Fig. 1 we show the typical line shapes for different choices of \( K \). In the slow modulation limit we observe the splitting behavior, while in the fast modulation limit we see Lorentzian behavior. The transition between the two behaviors is shown using the order parameter. In Fig. 2 we plot \( \langle \xi \rangle \) versus the dimensionless control parameter \( \alpha \rho/K \). We observe a transition from simple to complex behavior.

When the system is in the fast modulation limit, line shapes are characterized by their line width. The PDF \( P(\Gamma) \) of linewidth fully characterizes the statistical properties of the lines and now we shall calculate this PDF.25 Using Eq. (11) we introduce the dimensionless width

\[ \Gamma' = \frac{\Gamma}{K} = \sum_{n=1}^{N_{act}} p (1 - p) 4 \pi^2 \alpha^2 \frac{\Psi^2(\Omega)}{r^3} \]

As mentioned previously, we have introduced a finite cutoff \( l \) and TLSs are excluded from a sphere of radius \( l \) around the SM. In our case, it is important to note that TLSs close to the origin do not satisfy the condition of fast modulation Eq. (14). Therefore, to be consistent we must consider the TLSs...
in the vicinity of the SM with care. We use the two-state model approach, \( \psi(\Omega) = \pm 1 \), to show that the characteristic function [the Fourier transform of \( P(\Gamma') \) ] is given by

\[
\langle e^{i\Delta \Gamma'} \rangle = \exp \left[ -\rho^* \sqrt{p(1-p)} \sqrt{|k|} \int_{h(k)}^{\infty} dx \left( 1 - e^{i\sqrt{k}x} \right) \right],
\]

with

\[
h(k) = \frac{l^3 k^3 K}{2 \pi \sqrt{|k|} \sqrt{p(1-p)} \alpha}
\]

and

\[
\rho^* = \frac{8 \pi^2 \rho \alpha}{3 K}
\]

is the dimensionless density. We shall always consider the limit \( \rho^* \to 0 \) since only then slow TLSs are rare according to Eq. (15). We do not give the details of the derivations of Eq. (18) since similar derivations are presented in the context of low temperature glass in the following. The Fourier inversion of Eq. (18) can be performed numerically. Only in the limit of \( l \to 0 \) can an analytical approach be used.

We consider the limit \( l \to 0 \) in Eq. (18) yielding \( h(k) = 0 \). For such a limit to be meaningful some care must be taken since there exist two dimensionless length scales in the problem (\( \rho^* \)) and \( (4 \pi p l^3/3)^{1/3} \). It is easy to see that when \( Kl^3/\alpha \to 0 \) the limit \( h(k) \to 0 \) can be taken in Eq. (18). Such a limit will obviously describe well the case \( l = (\alpha/K)^{1/3} \). A slightly more delicate limit is the case \( l = (\alpha/K)^{1/3} \), for which the limit \( h(k) \to 0 \) can be considered provided that \( \rho^* \to 0 \). To see this, use \( l = (\alpha/K)^{1/3} \). Then \( h(k) = [2 \pi p(1-p)k^{3/2}]^{-1} \) and only values of \( k \) which satisfy \( \rho^* \sqrt{p(1-p)} \sqrt{|k|} \sim 1 \) will contribute to the inversion of Eq. (18).

For these values of \( k \), \( h(k) \to 0 \) if \( \rho^* \to 0 \). For \( l = 0 \) we find in the limit of \( \rho^* \to 0 \),

\[
P(\Gamma') = L_{1/2,1}(\Gamma'),
\]

where \( L_{1/2,1}(\Gamma') \) is a one sided Lévy-stable density\(^{29,30}\) given explicitly as

\[
L_{1/2,1}(\Gamma') = \sqrt{2 \pi} \Gamma'^{-3/2} \exp \left[ -\frac{\zeta^{3/2}}{2 \Gamma'} \right]
\]

and

\[
\zeta = \frac{\rho^*}{2} \sqrt{2 \pi p(1-p)}.
\]

For large \( \Gamma' \), \( P(\Gamma') \to \Gamma'^{-3/2} \), implying a broad distribution of \( \Gamma' \). We shall elaborate more on Lévy statistics in the summary and show that Lévy statistics can be used to analyze many other related problems.

As already mentioned, we numerically generated many line shapes of SMs. For each molecule we extract its line-width, and we consider a set of parameters for which all lines observed are approximately Lorentzian. In Fig. 3 we compare our prediction, Eq. (21), and our numerical simulation, to find good agreement between theory and simulation. In Fig. 4 we show a correlation plot of half width at half maximum from numerical simulations of the lines and \( \Gamma' \) Eq. (11). All the data points fall on a linear curve, indicating Lorentzian behavior of the lines.

In the slow modulation limit, splitting is observed and thus the linewidth gives only partial characterization of the line. Instead of linewidths one can characterize the line by an infinite number of cumulants \( \kappa_1, \kappa_2, \) etc. Then an infinite number of PDFs describe the statistical properties of the lines \( P(\kappa_1), P(\kappa_2), \) etc.\(^{23}\) This situation is far more complicated than the fast modulation limit when a single function \( P(\Gamma) \) describes the statistical properties of the line.

**IV. CONDITIONS FOR GAUSSIAN LINE SHAPES**

For low temperature glass, Brown and Silbey\(^{13}\) showed, based on numerical simulations, that once TLSs are excluded from a sphere of radius \( l \) the line shapes become Gaussian.
They considered a set of parameters relevant to experiment (see details in Table III) and \( l = 7 \) nm. Here we go further by using an analytical approach and show when the Gaussian approximation is valid and how to choose \( l \). We use two criteria for Gaussian behavior—one based on the cumulant expansion and a second that uses an order parameter. In this section we give the general conditions for Gaussian behavior to hold while in Sec. V we discuss the example of a SM in low temperature glass. For discussions of the Gaussian background approximation in the context of inhomogeneous line shapes see Refs. 27 and 31.

We divide the system into two parts. Within the first spherical inner region 1 the system is treated exactly, while the rest of the system, region 2, is treated using a Gaussian approximation. The radius of the inner region is \( l \) and the line shape formula is rewritten as

\[
I_{\text{SM}}(\omega) = \frac{1}{\pi} \text{Re} \left[ \int_0^\infty dt e^{i\omega t} h_1(t) h_2(t) \right]
\]

where \( h_1(t) = \Pi_{n=1}^{\infty} \Phi_{n_1}(t) \) and \( h_2(t) = \Pi_{n=2}^{\infty} \Phi_{n_2}(t) \)

are the autocorrelation functions of regions 1 and 2, respectively. We show that if \( l \) is large enough, and under certain conditions, \( h_2(t) \) can be approximated by a Gaussian. This behavior might be expected based on a standard central limit argument since for large \( l \) the SM is interacting with many TLSs and frequency shifts are small.

This division into two regions is important for three main reasons. (i) If the background region 2 can be approximated by Gaussian behavior and if \( l \) is not too large, we can find an analytical formula for the line shape by treating the TLSs in region 1 exactly. (ii) In some cases, when the density of TLS is low, the choice \( l \to 0 \) can be made and then line shapes are Gaussian. (iii) At least in principle, if the (spherical) molecule is large enough then \( l \) is the radius of the molecule. Hence, region 1 is empty and again lines are Gaussian.

We use the autocorrelation function of region 2, and the cumulant expansion

\[
\ln[h_2(t)] = \sum_{j=1}^{\infty} (-i)^j \frac{\kappa_j}{j!} t^j
\]

to find the cumulants of \( h_2(t) \). The four lowest cumulants \( \kappa_j \) are presented in Table I; higher order cumulants are easily calculated using symbolic programming (e.g., MATHEMATICA). The summation \( \Sigma_{1}^{\infty} \) in Table I is for active TLSs in region 2. When \( l = 0 \) the cumulants in Table I are the line shape cumulants.

From Table I we observe that the first and second cumulants are independent of the rates \( K_n \). Cumulants of order \( j \leq 2 \) are real while generally cumulants of order \( j > 2 \) are complex, implying that the moments of the line shape diverge when \( j > 2 \). The divergence of the moments implies that for large \( \omega \), \( I(\omega) \sim \omega^{-4} \). Thus the tails of \( I(\omega) \) behave
TABLE II. The same as Table I but for the slow modulation limit.

\[ j \quad \kappa_j \]
\[ 1 \quad \Sigma_0 p_n \nu_n \]
\[ 2 \quad \Sigma_0 p_n (1 - p_n) \nu_n^2 \]
\[ 3 \quad \Sigma_0 p_n (1 - 3p_n + 2p_n^3) \nu_n^3 \]
\[ 4 \quad \Sigma_0 p_n (1 - 7p_n + 12p_n^2 - 6p_n^3) \nu_n^4 \]

in a non-Gaussian way. Nevertheless, Gaussian-type behavior can be found in the central part of the \( I(\omega) \) curve.

The slow modulation limit was defined for the case \( \kappa_n \ll \nu_n \), for all the TLSs in the system. For TLSs far from the origin the condition does not hold since \( \nu \sim 1/r^3 \); however, the TLSs situated very far from the molecule do not contribute to the line shape. Let us assume that the TLSs in region 2 are described by the slow modulation limit (this assumption can be checked as we show for the glass model in Sec. VI). The zero-order approximation of the cumulants in the slow modulation limit is found by setting \( \kappa_n = 0 \) in Table I. These cumulants are presented in Table II, and as we see, all cumulants are real, hence moments of the line shape are finite and the power-law tails of the line shape are absent. We note that only active TLSs contribute to the line, hence the condition \( \kappa_n > 1/\tau_{\text{exp}} \) must hold with \( \tau_{\text{exp}} \) the experiment time. This implies that the slow modulation limit described in Table II exists only when the measurement time is infinite, in other cases the cumulants of Table II are approximate.

We now discuss the conditions for the Gaussian approximation. By definition the cumulant expansion of a Gaussian is given by \( \ln[h_2(t)] = -i \kappa_1 t - \kappa_2 t^2/2 \), namely all the cumulants \( \kappa_j \) with \( j > 2 \) are zero. For the Gaussian approximation of \( h_2(t) \) to hold, we use two requirements (these will be relaxed later when we use the order parameter). The first is that TLSs in region 2 must be described by the slow modulation limit because then the moments of the line shape \( I(\omega) \) are finite and the power-law tails of the line shape are absent. Second, in order to truncate the cumulant expansion after the second term, the cumulants in Table II must satisfy

\[ |\kappa_4| \ll 3 \kappa_2^2 \]

and

\[ |\kappa_3| \ll \frac{3}{\sqrt{2}} \kappa_2^{\frac{3}{2}}. \]

From these conditions one can determine the cutoff \( l \). Once these conditions hold, \( h_2(t) \) is approximately a Gaussian

\[ h_2(t) \approx \exp \left( -i \kappa_1 t - \frac{\kappa_2 t^2}{2} \right), \]

with \( \kappa_1 \) and \( \kappa_2 \) defined in Table II. From Eq. (29) it is easy to understand why the line shape of a molecule interacting with the TLS in region 2 is also Gaussian (i.e., when region 1 is empty).

A rough estimate of \( l \) can be made if a slow modulation limit exists, from the condition

\[ \langle |\kappa_4| \rangle \ll \langle \kappa_2^2 \rangle. \]

Let us now quantify the Gaussian behavior of the background, region 2, using a second approach. We define an order parameter in a way similar to that used in Eq. (16),

\[ \xi = \frac{1}{2} \int_{-\infty}^{\infty} d\omega |I_{\text{SM}}(\omega) - I_{\text{Gd}}(\omega)|, \]

where \( I_{\text{Gd}}(\omega) \) is the Gaussian line shape, defined using the first and second cumulants \( \kappa_1 \) and \( \kappa_2 \) in Table II. The average \( \langle \xi \rangle \) is defined to be an order parameter. For small values of \( l \) and for the standard tunneling model parameters in Table III, we expect that \( \langle \xi \rangle \sim 1 \), because the lines show non-Gaussian behavior [i.e., several peaks are observed as shown in Fig. 6]. As \( l \) is increased we might expect \( \langle \xi \rangle \) to decrease, since when the lines are Gaussian \( \langle \xi \rangle \rightarrow 0 \). When \( l \) is very large \( \langle \xi \rangle \) might increase again because then the background TLSs are described by the fast modulation limit (i.e., their contribution is Lorentzian). Thus one cannot expect a monotonic behavior of \( \langle \xi \rangle \) as the parameter \( l \) is increased.

Finally we note that the criteria for Gaussian behavior, based on the cumulant expansion equations (27) and (28) and the order parameter (31) are different. The cumulant approach is sensitive to the behavior of the line in its tails, while the order parameter approach mainly captures the behavior of the line in its center. The main advantage of the cumulant test is that analytical expressions for the cumulants were found in Tables I and II and with these exact expressions it is easy to check the condition for Gaussian behavior of the cumulants. Generally there is no reason to expect that all lines with small values of \( \langle \xi \rangle \) (namely lines which are Gaussian according to order parameter test) also be described by Gaussian cumulants.

V. EXAMPLE 2: STANDARD TUNNELING MODEL

The dependence of the random variables \( p_n, \kappa_n, \nu_n \) on microscopical parameters of the standard tunneling model of
low temperature glass is given in the following. We do not discuss the assumptions of this model and the interested reader is referred to the literature (see, e.g., the citations in Refs. 9 and 13). Later we use this model as an example for our results derived in Sec. IV. There exist a few variants of the standard tunneling model and here we use the model used in the context of SM spectroscopy in low temperature glass.9 In our simulations we follow the procedure in Ref. 9. According to the standard tunneling model:

(a) The frequency shift due to the nth TLS is

\[ v_n = 2 \pi \alpha \frac{A_n}{E_n} \frac{\epsilon_n}{r_n} \],

(32)

where \( \alpha \) is a coupling constant, \( A_n \) is the TLS asymmetry parameter, \( E_n \) is the energy splitting of the nth TLS,

\[ E_n = \sqrt{A_n^2 + J_n^2} \],

(33)

and \( J_n \) is the tunneling parameter describing the nth TLS. \( \epsilon_n \) is the orientation parameter taken to \( \epsilon = +1 \) or \( \epsilon = -1 \) with equal probability.9

(b) The occupation probability of the excited state

\[ p_n = \frac{1}{1 + \exp(\beta E_n)} \],

(34)

with \( \beta = 1/(k_B T) \).

(c) The TLS flipping frequency

\[ K_n = cJ_n^2E_n \coth\left(\frac{\beta E_n}{2}\right) \],

(35)

where \( c \) is the TLS phonon coupling constant.

The random variables of the standard tunneling model of glass \( \epsilon, A, J, r \) are given by four distributions and one constraint.

(i) The PDF of \( \epsilon \) is given by

\[ P(\epsilon) = \frac{1}{2}\left[ \delta(\epsilon - 1) + \delta(\epsilon + 1) \right] \].

(36)

(ii) The PDF of \( A \) and \( J \) is given by

\[ P(A, J) = P(A) P(J) = \frac{1}{N} \frac{A^\mu}{J}, \]

(37)

when \( 0 \leq A \leq A_{\text{max}} \) and \( J_{\text{min}} \leq J \leq J_{\text{max}} \) and the normalization

\[ 1 = \frac{1 + \mu}{N} A_{\text{max}}^{1+\mu} \ln(J_{\text{max}}/J_{\text{min}}). \]

(38)

(iii) For \( r > l \) the TLSs are uniformly distributed in space.

(iv) An important constraint on the random variables is the condition that only TLSs that flip in the time of observation \( \tau_{\text{exp}} \) contribute to the line shape, mathematically the condition reads

\[ K_n > 1/\tau_{\text{exp}} \]

(39)

and only TLSs satisfying this condition are considered. In this way the results we obtain depend on the time of observation. A critical discussion of approximation (39) is given in Ref. 15. The working assumption behind Eq. (39) is that lines are stable. If a TLS will flip only a few times on the time scale of experiment and if this TLS is close enough to the SM, the line shape becomes unstable. It is assumed (but not proven yet) that disregarding these instabilities is a reasonable assumption which follows the procedure of experimental data analysis.

In the simulations we use the parameter set of Table III that describes terrylene in polystyrene.9 One note on the parameter set is in order here. For a single TLS at a distance \( 1 \) nm we find the frequency shift is \( \nu/2\pi = 375 \) GHz (we assumed that \( A/E \approx 1 \) and this assumption is reasonable for many TLSs). Such a shift is huge and might be suspected as unphysical. To see this, consider the ratio of this shift and the temperature \( \hbar \nu/(k_B T) = 18 \) at \( T = 1 \) K. Thus a shift being similar or larger than a TLS energy splitting and simultaneously the approximation of a TLS flipping independently of the shift induced in the chromophore appear questionable. We note that our results for the background with \( l > 7 \) nm (and not too small temperatures) are expected to hold since for large \( r \) values the ratio \( \hbar \nu/(k_B T) \) is small. In what follows we restrict ourselves to the Geva–Skinner model and will report on the study of nearby TLSs in future work.

Finally, deviations between predictions based upon simulations of the SM glass model and measurement of SM linewidth distribution were recently reported in Ref. 16. Good agreement between experiment and simulation was found by introducing an additional distribution of coupling constants \( \alpha \). While the assumption of distribution of coupling constant is not unreasonable, one cannot rule out the possibility of other reasons for deviations between simulation and experiment. It is also still to be seen if distribution of \( \alpha \) is independent of the distribution of other parameters in the model (i.e., \( A \) and \( J \)).

VI. TRANSITION FROM NON-GAUSSIAN TO GAUSSIAN BEHAVIOR OF THE BACKGROUND

Let us consider the line shapes for a SM interacting with TLSs described by the standard tunneling model. We consider only the TLS in region 2 and use \( l = 7 \) nm. We generate the line shapes of six randomly chosen SMs based on the parameter set presented in Table III. The line shapes obtained by numerical integration are presented in Fig. 5. The lines presented in Fig. 5 depend on a huge set of parameters describing the TLSs interacting with the SMs. We also show Gaussian approximation obtained with no fitting parameters. Each Gaussian line is defined by its mean and variance, i.e., \( \kappa_1 \) and \( \kappa_2 \) both defined in Table I, the mean and variance being random variables. In Fig. 5 we show good agreement between the line shape and the Gaussian approximation for six molecules. For comparison we show in Fig. 6 also the case \( l = 1 \) nm, for which, as observed already by Geva and Skinner, most SM lines are different in shape from each other.

To quantify the transition from simple (i.e., Fig. 5) to complex (i.e., Fig. 6) line shape phenomena we have used numerical simulations to evaluate to order parameter \( \langle \xi \rangle \), Eq. (31), as a function of the cutoff \( l \). A transition from a non-Gaussian behavior for small values of \( l \) to a Gaussian behavior with \( \langle \xi \rangle < 1 \) for larger values of \( l \) is shown in Fig. 7. The error bars in Fig. 7 are computed from the standard
deviation of the random variable $\xi$. We note that $\langle \xi \rangle$ is small when the limit of Gaussian behavior is approached ($l>7$ nm). In principle, one can characterize the Gaussian behavior on the basis of the $\xi$ distribution and not on the average as we did here. We leave this issue for future work. We note that the transition to Gaussian behavior shown in Fig. 7 is smooth and slow (i.e., nonexponential) due to the long-range $1/r^3$ interaction considered here.

We now consider the cumulants of line shapes. In Eqs. (27) and (28) we have specified the conditions for the Gaussian approximation. We have calculated the cumulants $\kappa_3$ and $\kappa_4$ defined in Table I for 3000 molecules using the parameter set in Table III and $l=1$ nm. For this value of $l$ we anticipate a non-Gaussian behavior since according to Fig. 6 splitting is observed. In the upper part of Fig. 8 $|\Re[\kappa_4]|$ vs $3\kappa_2^2$ is displayed for 3000 molecules. The line $\Re[\kappa_4]=3\kappa_2^2$ is also given as a guide to the eye. This line separates those molecules which satisfy the condition $|\Re[\kappa_4]|>3\kappa_2^2$ (and hence according to our cumulant test are non-Gaussian) from those that follow $|\Re[\kappa_4]|<3\kappa_2^2$ (and hence exhibit a Gaussian behavior). From Fig. 8 we learn that cumulants of most of the molecules exhibit a non-Gaussian behavior, as expected. In the lower part of Fig. 8 we show simulation results for the case when the rates are set to zero. We see that the results are not altered by the transition rates $K$. Thus for $l=1$ nm, the system is described by the slow modulation limit. This result is compatible with previous numerical results obtained by

![Fig. 5. Simple line shape phenomena for SMs in glass based on the sudden jump standard tunneling model. Line shapes of six SMs interacting with a set of TLSs described by the data of Table III are given by full lines for $T=1.7$ K and $l=7$ nm. The Gaussian approximation obtained by using the first two (random) cumulants of the line shape are given by dash-dotted curves. No fitting was used. The frequency is given in units of (rad GHz) and the intensity in units of (rad GHz)$^{-1}$. In all panels we set $\omega_0=0$.](image.png)

![Fig. 6. Complex line shape phenomena for SMs in glass based on sudden jump standard tunneling model. The parameters are the same as in Fig. 5 but with $l=1$ nm. Note the very different scales. The Gaussian approximation clearly fails in general.](image.png)
Pfluegl, Brown, and Silbey,\textsuperscript{12} who showed that distribution of linewidths of the full standard tunneling model is very similar to the distribution of linewidths obtained using a model where all rates are set to zero.

In Fig. 9 we present the cumulants for $l = 7$ nm and with the other parameters identical to those in Fig. 8. The upper part of Fig. 9 demonstrates that the cumulants are again different than Gaussian. This is surprising since the order parameter for this case is $\langle \xi \rangle = 0.05$. In the lower part of Fig. 9 we show the results of simulations where all rates are set to zero. The large deviation between the full simulation and the simulation with $K = 0$ indicates that for $l = 7$ nm the slow modulation limit does not work well. Generally we expect that the slow modulation limit will not work well for some choice of large $l$ since the shifts $\nu \sim 1/r^3$ are typically smaller as $l$ is increased. In Fig. 10 we show the same as in Figs. 8 and 9 with the temperature $T = 1$ K and $l = 7$ nm. Now most of the cumulants exhibit a Gaussian behavior, though exceptions are still found and, in addition, the slow modulation limit is valid.

To conclude, we have observed a rich type of behavior.

(a) When $l = 1$ and $T = 1.7$ K a non-Gaussian behavior is manifested in the test of cumulants as well as by the fact that $\langle \xi \rangle = 0.5$. This is compatible with the direct observation of the line shapes which exhibit a non-Gaussian behavior. We have also shown that this case is compatible with the slow modulation limit.

(b) When $l = 7$ nm and $T = 1.7$ K, according to the order parameter $\langle \xi \rangle = 0.05$ and most SM lines are characterized as Gaussian. However, a closer look at the cumulants of the line shapes reveals non-Gaussian behavior. There is no contradiction between these two observations since the cumulants of the line shapes are sensitive to the behavior of the tails of the line shape and these tails decay like power laws exhibiting a non-Gaussian behavior. On the other hand, the order parameter captures the features of the line shape, at its center, and is therefore more relevant to the experimental situation for which the tails of the line are not resolved.

(c) For $l = 7$ nm and $T = 1$ K a Gaussian behavior of the cumulants is observed, supported by the order parameter $\langle \xi \rangle = 0.08$. In addition, we showed that to a good approximation the slow modulation limit is valid. The slow modulation works better for this case [as compared with case (b)] since as the temperature is decreased the rate $K$ becomes smaller while the shifts $\nu$ are not changed.

\section*{VII. DISTRIBUTION OF VARIANCE}

In Sec. VI we showed (under certain conditions) that for SM in low temperature glass, a Gaussian approximation of background TLSs is valid for large enough $l$. The approximate Gaussian correlation function $h_2(t)$, Eq. (29), is de-
scribed by only two random parameters, $k_1$ and $k_2$, and the distribution of these variables gives the full statistical properties of the background. $k_1$ contributes only a shift to the lines and is unimportant from a practical point of view since other shifts always exist in SM-glass systems (i.e., static disorder contribution to $\omega_0$). In this section we calculate the PDF of variance $P_l(k_2)$.

The distribution of variances was calculated previously for a simple mean field model which neglects the distribution of $\{A,J\}$. Within this approach $k_2 = p(1-p)\Sigma 1/j_{0}^{2}$ (and $p(1-p) = (p_n(1-p_n))$). Due to the wide distribution of TLS parameter it is worthwhile checking if such an approach works well. The calculation of the variance distribution was motivated by the conjecture that the variance distribution is directly related to the measured distribution of full width at half maximum (FWHM) $\Delta \nu$. It was suggested that $\Delta \nu = c_1 \sqrt{k_2}$, where $c_1$ is a fitting parameter being identical for all SMs. Using this approach the PDF of linewidth is

$$P(\Delta \nu) = \frac{d\nu}{d\Delta \nu} P_l(k_2)$$

and within this approach the cutoff $l$ is a fit parameter. Due to the lack of experimental data it is difficult to determine if this approach works well. The main motivation for this approach was (briefly) as follows. (i) TLSs within region 1 are responsible for the splitting, they do not contribute to the distribution of linewidth and hence are neglected. (ii) Background TLSs contribution to the lines is approximately Gaussian and then the linear relation $\Delta \nu = c_1 \sqrt{k_2}$ holds. This

FIG. 9. The same as Fig. 8, however here $l=7$ nm. When we set $K=0$ (the bottom panel) in simulation a Gaussian behavior is observed for all molecules. It is indicated that the background is not well approximated by the slow modulation limit since the results for $K = 0$ and $K \neq 0$ are very different.

FIG. 10. $|\text{Re}[k_2]|$ vs $3k_2^2$ for 3000 molecules, $T = 1$ K and $l=7$ nm. Now 2903 molecules exhibit Gaussian behavior (the top panel). Comparing between the cases $K \neq 0$ (the top panel) and $K = 0$ (the bottom panel) we see that most molecules environments are described by the slow modulation limit.
implies that the distribution of linewidth is a poor measure of the complexity of the lines. The TLSs located in the vicinity of the molecule and thus being responsible for the details of the line shapes are in effect neglected. Here we first calculate the distribution of variance and no claim is made that it is directly related to the distribution of \( \Delta \nu \). We then discuss further the \( \Delta \nu = c_1 \sqrt{\kappa_2} \) approach.

The variance of the line shape of a single chromophore \( \kappa_2 \) is rewritten using Eq. (34),

\[
\kappa_2 = \sum_{n=1}^{N_{\text{act}}} \frac{1}{4} \text{sech}^2 (\beta E_n/2) \nu_n^2,
\]

(41)

where the sum is over all active TLSs in the system and TLSs in region 1 are excluded from the summation (though we shall also consider the case \( l = 0 \)). We remind the reader that Eq. (41) is exact (i.e., independent of the shape of the line). Not all TLSs in the system are active on the time scale of experiment and \( N_{\text{act}} \) in Eq. (41) is the number of TLSs which satisfy the constraint Eq. (39), \( K > 1/\tau_{\text{expt}} \). The probability that a TLS is active is

\[
f = \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \, P(A,J) \times \Theta [cJ^2 E \coth(\beta E/2) - 1/\tau_{\text{expt}}],
\]

(42)

where \( \Theta [\cdot] \) denotes the heaviside step function. Therefore the effective density of the TLSs is \( \rho_{\text{eff}} = N_{\text{act}} / V \), \( V \) being the volume of the system and

\[
\rho_{\text{eff}} = \rho f,
\]

(43)

which in turn depends on temperature and time of experiment. The average variance is

\[
\langle \kappa^2_2 \rangle = \pi \alpha^2 \frac{4 \pi \rho_{\text{eff}}}{3 \beta^3} \left( \text{sech}^2 (\beta E/2) \frac{A}{E} \right)^2_{AJ}
\]

(44)

and

\[
\langle \cdots \rangle_{AJ} = \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \{ P(A,J) \cdots \}
\times \Theta [cJ^2 E \coth(\beta E/2) - 1/\tau_{\text{expt}}] / f,
\]

(45)

where the denominator \( f \) guarantees normalization. To derive Eq. (44) we have averaged over the orientation and the random locations of the TLS in space (using uniform distribution for \( r > 1 \)). From Eqs. (44) and (45),

\[
\langle \kappa^2_2 \rangle = \pi \alpha^2 \frac{4 \pi \rho}{3 \beta^3} \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \, P(A,J) \text{sech}^2 (\beta E/2)
\times \frac{A}{E} \Theta [cJ^2 E \coth(\beta E/2) - 1/\tau_{\text{expt}}].
\]

(46)

Notice that \( \langle \kappa^2_2 \rangle \) depends explicitly on the density \( \rho \) and not on the effective density \( \rho_{\text{eff}} \). Also, when \( l \rightarrow 0 \) we find \( \langle \kappa^2_2 \rangle = \infty \). The calculation of the integral in Eq. (46) can be performed using MATHEMATICA. An analytical approach for the solution of this integral is given in the Appendix. In a similar way one can derive expressions for \( \langle \kappa^2_3 \rangle, \langle \text{Re} |\kappa_4| \rangle \), etc.

The characteristic function of the variance [i.e., the Fourier transform of \( P_\nu(\kappa_2) \)] is

\[
\langle \exp (ik \kappa_2) \rangle_{\text{eff}} = \lim_{N_{\text{act}} \rightarrow \infty} \left\{ \frac{1}{N_{\text{act}}} \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \left[ P (A,J) \right] \right\}
\times \exp \left[ ik B(A,J) \frac{A}{E} \right]_{AJ}^{N_{\text{act}}},
\]

(47)

with

\[
B(A,J) = \pi^2 \alpha^2 \text{sech}^2 (\beta E/2) \left( \frac{A}{E} \right)^2
\]

(48)

and \( \langle \cdots \rangle_{AJ} \) is an average over the random variables \( A, J, r, \) and \( \epsilon \). Using a standard trick,

\[
\langle \exp (ik \kappa_2) \rangle_{\text{eff}} = \lim_{N_{\text{act}} \rightarrow \infty} \left\{ \frac{1}{N_{\text{act}}} \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \left[ P (A,J) \right] \right\}
\times \left[ \frac{1}{3} \rho_{\text{eff}} \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \left[ P (A,J) \right] \right]^{N_{\text{act}}}_{AJ},
\]

(49)

we find

\[
\langle \exp (ik \kappa_2) \rangle_{\text{eff}} = \exp \left[ - \frac{4 \pi \rho_{\text{eff}}}{3} \int_{J_{\min}}^{J_{\max}} \int_{A_{\min}}^{A_{\max}} dJ \, dA \left[ P (A,J) \right] \right]
\times \left[ \frac{A}{E} \right]_{AJ}^{2} \left( 1 - \exp \left[ ik \frac{2 \pi \alpha^2}{3} \text{sech}^2 (\beta E/2) \right] \right)_{AJ}^{N_{\text{act}}},
\]

(50)

and \( \langle \cdots \rangle_{AJ} \) is an average over the TLS parameters \( A \) and \( J \). When \( l = 0 \) we find

\[
\langle \exp (ik \kappa_2) \rangle_{\text{eff}} = \exp \left[ - \frac{Z_{1/2}}{k} (1 - i \frac{k}{|k|}) \right]
\]

(51)

and

\[
Z_{1/2} = \frac{1}{6} (2 \pi)^{5/2} \alpha \rho_{\text{eff}} (\text{sech} (\beta E/2) (A/E))_{AJ}.
\]

(52)

More explicitly,

\[
Z_{1/2} = \frac{1}{6} (2 \pi)^{5/2} \alpha \rho \int_{A_{\min}}^{A_{\max}} dA \int_{J_{\min}}^{J_{\max}} dJ \, P (A,J) \text{sech} (\beta E/2)
\times \text{sech} (\beta E/2) \left( \frac{A}{E} \right) \Theta [cJ^2 E \coth(\beta E/2) - 1/\tau_{\text{expt}}].
\]

(53)

The characteristic function Eq. (51) is a one sided Lévy-stable characteristic function \( L_{1/2,1}(k) \) and therefore the PDF of variance, \( P_0(\kappa_2) \), is a one-sided Lévy-stable density,

\[
P_0(\kappa_2) = L_{1/2,1}(\kappa_2).
\]

(54)
and $L_{1/2,1}(\kappa_2)$ is defined in Eq. (22) with the scaling constant Eq. (53). Equations (51) and (54) are valid only when $l=0$. For the parameters in Table III we find $Z_{1/2}=2.15$ GHz when $\mu=1/3$ and $Z_{1/2}=17.25$ GHz when $\mu=0$.

When $l\neq 0$ we find

$$\langle \exp(i\kappa_2) \rangle_{A/J} = \exp\left(-\frac{4\pi}{3} \rho_{\text{eff}} \right) \frac{\pi}{|y|} S(\sqrt{|y|})$$

$$-\left(1 - e^{i\pi/2}\right)_{A/J},$$

where $y$ is a dimensionless variable,

$$y = \frac{2\sqrt{\pi} \kappa_2^2}{l^6} \sech^2\left(\frac{\beta E}{2}\right) \left(\frac{A}{E}\right)^2,$$

and $S(x)$ and $C(x)$ are tabulated Fresnel sine and cosine integrals.

For $l\neq 0$ the distribution of variance can be found numerically in two steps. First we use Eq. (45) to find $\langle \cdots \rangle_{A/J}$ in Eq. (55) and then use the inverse Fourier transform. The result is shown in Fig. 11. For small $l$ we find a Lévy-type behavior, as predicted in Eq. (54), while for larger values of $l$ we find that distribution of $\kappa_2$ behaves more like a Gaussian. For large values of $l$, the interaction of background TLSs with the SM is described by $\kappa_2$ and therefore the distribution of $\kappa_2$ completely characterizes the background. Thus for example 2 we found that for $l>7$ nm the background is Gaussian [i.e., $h_2(t)\approx\exp(-\kappa_2^2 t/2)$] and in this section we showed that $\kappa_2$ is (approximately) a Gaussian random variable]. Finally we note that our results for $l\neq 0$ are different from the results obtained within the mean field approach. A cusp found in Refs. 3 and 12 is not seen here due to additional averaging over the $A/J$. For $l=0$ the functional form of $P_0(\kappa_2)$ is identical to what was found previously in Ref. 12. As we discuss in Sec. VIII, the Lévy result is not sensitive to the modeling and that is why the mean field result is identical to the result found here based on the full standard tunneling model in this $l=0$ limit.

Can we use the distribution of variance to predict the distribution of linewidths? In Fig. 12 we show a histogram of linewidths obtained from numerical simulation and a fit based on Eq. (40). The fit was obtained using a distribution of variance and fit parameters $l$ and $c_1$ indicated in Fig. 12. Both $c_1\sim 1$ and $l<7$ nm are in agreement with what might have been expected. However according to Fig. 11 the distribution of variance is very sensitive to the cutoff $l$ and hence also the distribution of FWHM $P(\Delta \nu)$. Therefore there is the possibility of fitting the PDF of FWHM, $P(\Delta \nu)$, to a large number of shapes. Since $l$ is considered as a fit parameter the theory is not predictive. To further investigate the simple approach, we plot in Fig. 13 correlations $c_1 \sqrt{\kappa_2}$ vs $\Delta \nu$ for $l=5$. We use $c_1=2(2\ln 2)^{1/2}$, which is based on the assumption of Gaussian line shapes. From Fig. 13 it is clear that a theory whose starting point is the linear relation $\Delta \nu = c_1 \sqrt{\kappa_2}$, is not totally consistent with numerical data and is expected to yield only qualitative results. Choosing other values of $l$ did not alter this conclusion. The analysis of the FWHM distribution based on an analytical approach is left to future investigations.

Finally we have checked that the simulation of FWHM (with no cutoff) is consistent with the slow modulation limit. In Fig. 14 we show the correlation plot of the FWHM. The FWHM, calculated for the case where all rates are set to zero, are plotted versus the FWHM obtained from the full simulation. We used the parameters of Table III and no cutoff was considered. The nearly linear curve in Fig. 14 indicates that the slow modulation limit is valid for most of the molecules. This is compatible with the finding that the cumulants of the full SM-glass model are well described by the slow modulation limit (i.e., see Fig. 8 and Ref. 23) and with Ref. 12.
VIII. SUMMARY AND DISCUSSION

Zumofen and Klafter\textsuperscript{4} have shown that the spectral diffusion kernel of SM interacting with identical TLS on lattice (ordered case) is a Lévy kernel. For dimension $d=3$ and dipolar interaction the result in Ref. 4 is identical to the well-known Lorentzian kernel found by Klauder and Anderson\textsuperscript{33} (the Lorentzian is a symmetrical Lévy distribution with index 1). This type of Lévy spectral diffusion was observed in experiments (see Ref. 34, and references therein). Here we have considered disordered systems and showed that for both of our working examples, Lévy statistics plays an important role in describing the statistical properties of the lines. For example 1 we showed that in the fast modulation limit the distribution of linewidth is a one sided Lévy-stable density, while for the glass model, described by the slow modulation limit (and $l=0$), the distribution of variance is also a one-sided Lévy-stable density. This is a consequence of the generalized central limit theorem, thus even though our two working examples describe very different physical behaviors, a unifying mathematical theory can be used to understand some of our results.

Lévy-stable distributions serve as a natural generalization of the normal Gaussian distribution.\textsuperscript{29,30} The importance of the Gaussian in statistical physics stems from the central limit theorem. Lévy-stable laws are used when analyzing sums of the type $\sum x_i$, with $\{x_i\}$ being independent identically distributed random variables characterized by a diverging variance. Then the ordinary Gaussian central limit theorem must be replaced with the generalized central limit theorem. With this generalization, Lévy-stable probability densities, $L_{\gamma,\alpha}(x)$, replace the Gaussian of the standard central limit theorem. Here (and in many other works in the field) we are considering similar sums, e.g., the variance $\kappa_2 = \sum x_i$ and $x_i = p_i(1-p_i)\nu_i^2$, for which it is easy to verify that the divergence of $x_i$ is due to the random distribution of TLSs in space (hence when a large cutoff $l$ is introduced, we do not get Lévy behavior). The Lévy behavior of our model is determined by the dimensionality of the problem, $d=3$, and the power law interaction $v \sim \nu^\delta$ with $\delta=3$ for dipolar interaction. One can generalize our results for $\delta$ and $d$ not equal 3, by replacing $L_{1/2,1}$ in Eqs. (21) and (54) with $L_{d/4,2d/2}$ for $d/\delta < 2$ (the index one in $L_{d/4,2d/2}$ describes one-sided Lévy-stable densities, this is the case since $x_i > 0$). We have found that other features of our model describing the TLSs (e.g., distribution of $A$ and $J$) do not influence the Lévy type of behavior and these parameters determine only the scaling constants $z_{1/2}$. Thus the Lévy-stable behavior is not sensitive to the details of the modeling.

Lévy statistics can be used to analyze other related problems; for example, the PDF of the mean of the line, $\kappa_1$, is $P(\kappa_1) = L_{d/2,0}(\kappa_1)$ and for $d = \delta = 3$ we have a Lorentzian behavior while for $d/\delta = 2$ one has a Gaussian behavior. According to the statistical method of Stoneham\textsuperscript{35} the distribution of $\kappa_1$ gives the TLS contribution to the inhomogeneous line since $\kappa_1$ describes the shifts of the lines (i.e., when $\omega_0 = 0$). It is interesting to note that Stoneham’s theory of inhomogeneous line shapes is compatible with Lévy statistics, as shown in Table IV for different types of interaction. For additional discussion on the relation between the theory of inhomogeneous line shapes, Lévy statistics (and financial markets) see the work of Kador.\textsuperscript{34} In our recent publication,\textsuperscript{23} we showed that SM line shape cumulants in low temperature glass are Lévy distributed. Geva and Skinner\textsuperscript{30} have shown that moments of a dynamical autocorrelation function describing dynamics of SM in glass are described by a certain universal distribution. This distribution is a Lévy distribution.

All these results (and others) indicate that very much
like ordinary Brownian motion, which is described by Gaussian central limit theorem, some parts of line shape phenomena, in systems with long-range interaction, are deeply related to Lévy’s generalized central limit theorem.

We have investigated a transition from simple to complex line shape phenomena. When identical TLSs are distributed randomly in space (example 1), we showed that in the fast modulation limit lines exhibit simple Lorentzian behavior and the linewidth is a random variable. In the slow modulation limit, lines exhibit complex splitting behavior (i.e., several peaks are observed). We have quantified the transition from simple to complex line shape phenomena using an order parameter. Such a transition can be controlled by the rate $K$, which is usually temperature dependent. Thus at least in principle one could observe such a transition by changing the temperature of a system.

Several experimental studies have investigated the distribution of linewidth of SM in glass. The distribution of linewidth does not give direct statistical information on the splitting phenomena and complexity of the lines. We find these features of the lines most interesting. In fact there is not a single definition of linewidth for a structured line with several peaks. The distribution of line shapes is sensitive mainly to the behavior of the background TLSs. To see this, imagine a glass composed of background TLSs, giving Gaussian contribution to the line, plus a single slow TLS in the vicinity of the SM. The single TLS will split the line shape into two (usually the height of the two peaks will be non identical) and the linewidth in such a case is a measure of the background Gaussian width. It is therefore important to consider besides the distribution of linewidths, other statistical measures (e.g., order parameter) which are sensitive to the complex structure of the lines.

ACKNOWLEDGMENTS

Helpful discussions with Professor U. P. Wild, E. Donley, and Dr. T. Plakhotnik are gratefully acknowledged. This work was supported by the NSF.

APPENDIX

It might be convenient to carry out some of the integrations using $K,E$ instead of $A,J$. A standard transformation shows

$$
\int_0^{A_{\max}} dA \int_{J_{\min}}^{J_{\max}} dJ \frac{A^\mu}{N^\frac{1}{2}} \cdots = \frac{1}{2N} \int_{E_{\min}}^{E_{\max}} dE \int_{K_{\min}(E)}^{K_{\max}(E)} dK \frac{E^\mu}{K} \\
\times \left( 1 - \frac{K}{K_{\max}(E)} \right)^{\frac{\mu - 1}{2}} 
$$

(A1)

where

$$
E_{\min} = J_{\min},
$$

(A2)

$$
E_{\max} = \sqrt{A_{\max}^2 + J_{\max}^2},
$$

(A3)

$$
K_{\min}(E) = c E^3 \coth \left( \frac{\beta E}{2} \right),
$$

(A4)

$$
K_{\min}(E) = c \max \left( 2 J_{\min}^2 E^2 - A_{\max}^2 \right) E \coth \left( \frac{\beta E}{2} \right),
$$

(A5)

$$
K_{\max}(E) = c \min \left( 2 J_{\max}^2 E^2 \right) E \coth \left( \frac{\beta E}{2} \right),
$$

(A6)

and

$$
1 = \frac{1 + \mu}{N \cdot \ln(K_{\max}/J_{\min})}.
$$

(A7)

Many times a simplification can be made in the limits of the $K$ integration. When averaging over functions which are vanishing when $\beta E \gg 1$ and when using physical parameters of the standard tunneling model one can use

$$
K_{\min}(E) = J_{\min}^2 E \coth \left( \frac{\beta E}{2} \right)
$$

(A8)

and

$$
K_{\max}(E) = K_{\max}(E).
$$

(A9)

See Ref. 9 for comparison.

To calculate the averaged variance $\langle \kappa_2 \rangle$ it is convenient to use the random variables $E,K$ rather then $A,J$. Using Eqs. (44), (A1), and the identity

$$
A^2 = E^2 \left[ 1 - \frac{K}{K_{\max}(E)} \right]
$$

(A10)

we have

$$
\langle \kappa_2 \rangle = \pi^2 \alpha^2 \frac{4 \pi \rho}{l^3} \int_{E_{\min}}^{E_{\max}} dE \int_{K_{\min}(E)}^{K_{\max}(E)} dK \\
\times \frac{\sigma^2}{\Theta(\kappa_2)}.
$$

(A11)

Since $E_{\max} \beta \gg 1$ we may take the upper limit of the first integral to $\infty$ and since $\beta E_{\min} \ll 1$ we may take the lower limit of the first integral to $0$. Also since $K_{\min}(E) < 1/\tau_{\text{expt}}$ for $\beta E \sim 1$ we set the lower limit of the $K$ integral to 0, and we find after changing variables of integration
\[ \langle \kappa_2 \rangle = \frac{\pi a^2}{\lambda^3} \frac{4 \pi p}{2N} \left( k_B T \right)^{1+\mu} \]

\[ \times \int_0^{\infty} \frac{dx}{x} \left[ \Gamma_{\text{exp}}^3 \coth(\nu/2) \right] \Theta(x-1) \]  

(A12)

and \( \Gamma_{\text{exp}} = e^{(k_B T)^I \tau_{\text{exp}}} \).

Note that the prefactor \( 1/N \) depends on the cutoffs \( A_{\text{max}} \) and logarithmically on the cutoffs \( J_{\text{min}}, J_{\text{max}} \). This seems not to be consistent with the requirement that cutoffs do not affect the final results. However, \( \rho/N \) is a constant which is determined from the measurements (see details of Appendix B of Ref. 9). Hence the prefactors are constants independent of the choice of the cutoffs. This is not obvious from Eq. (A12).

25We shift all the lines to a common origin and do not treat the distribution of line centers which is discussed in summary.
32The TLSs located very far from the SM are unimportant because they do not contribute to the line shape of the SM (i.e., when region 1 is not empty). Depending on the parameters of the model, it might be worthwhile considering an approximate scheme similar to ours however with a Lorentzian background (i.e., if the TLSs in region 2 are in the fast modulation limit then a Lorentzian rather than Gaussian behavior of the background is expected to hold).