Lévy Distribution of Single Molecule Line Shape Cumulants in Glasses

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(Received 21 December 1999)

We investigate the distribution of single molecule line shape cumulants, $\kappa_1, \kappa_2, \ldots$, in low temperature glasses based on the sudden jump, standard tunneling model. We find that the cumulants are described by Lévy stable laws, thus the generalized central limit theorem is applicable for this problem.

Recent experimental advances [1] have made it possible to measure the spectral line shape of a single molecule (SM) embedded in a condensed phase. Because each molecule is in a unique static and dynamic environment, the line shapes of chemically identical SMs vary from molecule to molecule [2]. In this way, the dynamic properties of the host are encoded in the distribution of single molecule spectral line shapes [1–8]. We examine the statistical properties of the line shapes and show how these are related to the underlying microscopic dynamical events occurring in the condensed phase.

We use the Geva-Skinner [5] model for the SM line shape in a low temperature glass based on the sudden jump picture of Anderson and Kubo [9,10]. In this model, a random distribution of low-density (and noninteracting) dynamical defects [e.g., spins or two level systems (TLS)] interacts with the molecule via *long-range interaction* (e.g., dipolar). We show that Lévy statistics fully characterize the properties of the SM spectral line in both the *fast* and *slow modulation limits,* while far from these limits Lévy statistics describe the mean and variance of the line shape. We then compare our analytical results, derived in the slow modulation limit, with results obtained from numerical simulation. The good agreement indicates that the slow modulation limit is correct for the parameter set relevant to experiment.

Lévy stable distributions serve as a natural generalization of the normal Gaussian distribution. 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. In this case the ordinary Gaussian central limit theorem must be replaced with the generalized central limit theorem. With this generalization, Lévy stable probability densities, $L_{\gamma,\eta}(x)$, replace the Gaussian of the standard central limit theorem. Lévy stable characteristic functions, $\hat{L}_{\gamma,\eta}(k)$, are of the form [11]

$$\ln[\hat{L}_{\gamma,\eta}(k)] = i\mu k - z_\gamma |k|^\gamma \left[1 - i\eta \frac{k}{|k|} \tan\left(\frac{\pi\gamma}{2}\right) \right]$$

(1)

for $0 < \gamma \leq 2$ (for the case $\eta \neq 0$, $\gamma = 1$, see [11]). Four parameters are needed for a full description of a stable

law. The constant γ is called the characteristic exponent, the parameter μ is a location parameter which is unimportant in the present case, $z_\gamma > 0$ is a scale parameter, and $-1 \leq \eta \leq 1$ is the index of symmetry. When $\eta = 0$ ($\eta = \pm 1$) the stable density $L_{\gamma,\eta}(x)$ is symmetrical (one sided). Lévy statistics is known to describe several long-range interaction systems in diverse fields such as astronomy [11], turbulence, and spin glass [12]. Stoneham's theory [13] of inhomogeneous line broadening in defected crystal is based on long-range forces and parts of it can be interpreted in terms of Lévy stable laws.

An important issue is the slow and fast modulation limits [6,10]. Briefly, the fast (slow) modulation limit is valid if important contributions to the line shape are from TLSs which satisfy $\nu \ll K$ ($\nu \gg K$), where ν is the frequency shift of the SM due to SM-TLS interaction and K is the transition rate of the flipping TLS (see details below). In the fast modulation limit, all (or most) lines are Lorentzian with a width that varies from one molecule to the other. For this case, the (Lévy) distribution of *linewidths* fully characterizes the statistical properties of the lines. The second, more complicated, case corresponds to the slow modulation limit. Then the SM line is typically composed of several peaks (splitting) and is not described well by a Lorentzian. If a SM shows splitting, one can investigate the validity of the standard tunneling model of glass [14] in a direct way, since the splitting of a line is directly associated with SM-TLS interaction [7]. As mentioned, we demonstrate the existence of a slow modulation limit in SM-glass system.

Following [5] we assume a SM coupled to nonidentical independent TLSs at distances **r** in dimension d. Each TLS is characterized by its asymmetry variable A and tunneling element J. The energy of the TLS is $E = \sqrt{A^2 + J^2}$. The TLSs are coupled to phonons or other thermal excitations such that the state of the TLS changes with time. The state of the nth TLS is described by an occupation parameter, $\xi_n(t)$, that is equal to 0 or 1 if the TLS is in its ground or excited state, respectively. The probability for finding the TLS in its upper $\xi = 1$ state, p, is given by the standard Boltzmann form $p = 1/\{1 + \exp[E/(k_b T)]\}$. The transitions between the ground and excited states are described by the up and down transition rates K_u, K_d, which

are related to each other by the standard detailed balance condition.

The excitation of the nth TLS shifts the SM's transition frequency by ν_n. Thus, the SM's transition frequency is

$$\omega(t) = \omega_0 + \sum_{n=1}^{N_{act}} \xi_n(t)\nu_n, \qquad (2)$$

where N_{act} is the number of active TLSs in the system (see details below) and ω_0 is the bare transition frequency that differs from one molecule to the other depending on the local static disorder. We consider a wide class of frequency perturbations

$$\nu = 2\pi\alpha\Psi(\Omega)f(A, J)\frac{1}{r^\delta}, \qquad (3)$$

where α is a coupling constant with units $(Hz\,nm^\delta)$, $\Psi(\Omega)$ is a dimensionless function of order unity, Ω is a vector of angles determined by the orientations of the TLS and molecule (in some simple cases Ω depends on polar angles only), $f(A, J) \geq 0$ is a dimensionless function of the internal degrees of freedom of the fluctuating TLS, and δ is the interaction exponent. The line shape of the SM is given by the complex Laplace transform of the relaxation function

$$I_{SM}(\omega) = \frac{1}{\pi}\text{Re}\left[\int_0^\infty dt\, e^{i\omega t}\Pi_{n=1}^{N_{act}}\Phi_n(t)\right] \qquad (4)$$

provided that the natural lifetime of the SM excited state is long. The relaxation function of a single TLS was evaluated [10] based on methods developed in [9]

$$\Phi(t) = e^{-(\Xi+ip\nu)t}\left[\cosh(\Omega t) + \frac{\Xi}{\Omega}\sinh(\Omega t)\right] \qquad (5)$$

with $\Omega = [K^2/4 - \nu^2/4 - i(p - 1/2)\nu K]^{1/2}$, $\Xi = \frac{K}{2} - i(p - \frac{1}{2})\nu$, and $K = K_u + K_d$. For a bath of TLSs the line shape, Eq. (4), is a formidable function of the random TLS parameters (r, Ω, A, J) as well as the system parameters $(\alpha, T, \text{etc.})$. In the fast modulation limit $K \gg |\nu|$, one finds a simpler behavior: all lines are Lorentzian with half-width

$$\tilde\Gamma = \sum_n^{N_{act}} p_n(1 - p_n)\nu_n^2/K_n, \qquad (6)$$

which varies from one molecule to the other. Equation (6) shows the well known phenomena of motional narrowing. In the slow modulation limit $K \ll |\nu|$ one finds $\Phi(t) = 1 - p + pe^{-i\nu t}$ implying that the line shape of a molecule coupled to a single TLS is composed of two delta peaks, the line shape of a molecule coupled to two TLSs is composed of four delta peaks, etc. (splitting).

The spectral line is characterized by its cumulants κ_j ($j = 1, 2, \ldots$) that vary from one molecule to the other, and we investigate the cumulant probability density $P(\kappa_j)$. We have derived the cumulants of the SM line shape, and the first four cumulants are presented in Table I [15]. We observe that cumulants of order $j \leq 2$ are real while generally cumulants of order $j > 2$ are complex, implying

TABLE I. Cumulants κ_j of the SM line shape.

κ_1	$\sum_n p_n\nu_n$
κ_2	$\sum_n p_n(1 - p_n)\nu_n^2$
κ_3	$\sum_n p_n(1 - p_n)(2p_n - 1)\nu_n^3 + ip_n(1 - p_n)K_n\nu_n^2$
κ_4	$\sum_n p_n(-1 + p_n)[K_n^2 + \nu_n^2(-1 + 6p_n - 6p_n^2)]\nu_n^2 - 2i\sum_n K_n(-1 + p_n)p_n(-1 + 2p_n)\nu_n^3$

that the moments of the line shape diverge when $j > 2$. The summation, $\sum_n$, in Table I is over the active TLSs, namely, those TLSs which flip on the time scale of observation τ (i.e., $K_n > 1/\tau$). We consider the slow modulation limit, soon to be justified, which means that we consider the case $K_n \ll \nu_n$. To investigate this limit we set $K_n = 0$ in Table I; then all the cumulants are real and are rewritten as $\kappa_j = \sum_n H_{jn}\nu_n^j$, where H_j are functions of p only and $H_1 = p$, $H_2 = p(1 - p)$, $H_3 = p(1 - p)(2p - 1)$, etc. Note that for κ_1 and κ_2 no approximation is made.

Let $\langle\cdot\rangle_{r\Omega AJ}$ denote an averaging over the random TLS parameters. The characteristic function of the jth cumulant can be written in a form

$$\langle\exp(ik\kappa_j)\rangle_{r\Omega AJ}$$
$$= \exp\left[-\rho_{eff}\left\langle\int d\Omega\int_0^\infty \frac{d(r^d)}{d}(1 - e^{ikB_j/r^{\delta j}})\right\rangle_{AJ}\right], \qquad (7)$$

where ρ_{eff} is the density of the active TLS and $B_j = (2\pi\alpha)^j\Psi^j(\Omega)f^j(A, J)H_j$. To derive Eq. (7) we have used the assumption of independent TLSs uniformly distributed in the system. For odd j cumulants we find

$$\langle\exp(ik\kappa_j)\rangle_{r\Omega AJ} = \hat L_{\gamma,0}(k), \qquad (8)$$

with characteristic exponent $\gamma = d/(\delta j)$ and the scale parameter

$$z_\gamma = \rho_{eff}(2\pi\alpha)^{d/\delta}\langle f^{d/\delta}(A, J)|H_j|^\gamma\rangle_{AJ}c_\gamma$$
$$\times \int d\Omega\,|\Psi^j(\Omega)|^\gamma \qquad (9)$$

with $c_\gamma = \cos(\gamma\pi/2)\Gamma(1 - \gamma)$, $c_1 = \pi/2$. Equation (8) shows that odd cumulants are described by symmetrical Lévy stable density, i.e., $P(\kappa_j) = L_{\gamma,0}(\kappa_j)$. Two conditions must be satisfied for such a behavior, $0 < \gamma < 2$ and $\int d\Omega\sin[\Psi^j(\Omega)] = 0$. The latter condition gives the symmetry condition, $\eta = 0$, which means that negative and positive contributions to κ_j are equally probable.

For even cumulants and $0 < \gamma < 1$ we find

$$\langle\exp(ik\kappa_j)\rangle_{r\Omega AJ} = \hat L_{\gamma,\eta}(k) \qquad (10)$$

with a scale parameter Eq. (9) and with Lévy index of symmetry

$$\eta = \frac{\langle f^{j\gamma}(A, J)|H_j|^\gamma\frac{H_j}{|H_j|}\rangle_{AJ}}{\langle f^{j\gamma}(A, J)|H_j|^\gamma\rangle_{AJ}}. \qquad (11)$$

Equation (10) implies that even cumulants are distributed according to $P(\kappa_j) = L_{\gamma,\eta}(\kappa_j)$. We note that the asymmetrical Lévy functions, with $\eta \neq \pm 1, 0$, only rarely find their applications in the literature. The characteristic exponent γ depends only on the general features of the model (namely, on d and δ). In contrast the Lévy index of symmetry η depends on the details of the model and on system parameters (T, etc.). For $j = 2$ we have $H_j = |H_j|$ and then $\eta = 1$ so the Lévy density is one sided, as is expected since $\kappa_2 > 0$.

As mentioned, in the fast modulation limit, the random linewidth in Eq. (6) characterizes the statistical properties of the spectral lines. Using the approach in Eqs. (7)–(9) one can show that $P(\tilde{\Gamma}) = L_{d/(2\delta),1}(\tilde{\Gamma})$ with the scale parameter $z_{d/(2\delta)}$ given by Eq. (9) with $j = 2$ and $H_2 = p(1 - p)/K$.

In what follows we exhibit our results and compare to simulations based on the standard tunneling model of low temperature glass [14]. We use system parameters which model terrylene in polystryrene [5]. The SM-TLS interaction is dipolar, hence $\delta = 3$, and we consider spatial dimension $d = 3$. The distribution of the asymmetry parameter and tunneling element is $P(A)P(J) = N^{-1}J^{-1}$ for 2.8×10^{-7} K $< J < 18$ K and $0 < A < 17$ K, N denoting a normalization constant. We use $f(A, J) = A/E$ and define a TLS to be active if $K > 1/\tau$; $\tau = 120$ sec is the time of experimental observation. In this way the averaging $\langle \cdots \rangle_{AJ}$ becomes τ independent. The rate of the TLS is given by $K = cJ^2 E \coth(\beta E_n/2)$ and $c = 3.9 \times 10^8$ K^{-3} Hz is the TLS phonon coupling constant. Additional system parameters are the coupling constant $\alpha = 3.75 \times 10^{11}$ nm^3 Hz and the TLS density 1.15×10^{-2} nm^{-3}. According to Eqs. (8)–(11), only the scale parameter z_γ depends on the orientation of the TLS and SM, through $\Psi(\Omega)$. It is therefore reasonable to assume simple forms for $\Psi(\Omega)$. We consider two examples, model 1 (M1) for which $\Psi(\Omega)$ is replaced with a two state variable (i.e., a spin model) $\Psi = 1$ or $\Psi = -1$ with equal probabilities of occurrence and model 2 (M2) $\Psi(\Omega) = \cos(\theta)$, with θ, the standard polar coordinate, distributed uniformly. With these definitions we calculate the symmetry index η and the scaling parameter z_γ and compare between the theory and numerical simulation.

We consider the first two cumulants κ_1 and κ_2 (i.e., the line shape mean and variance). Since $d = \delta$ we find $P(\kappa_1) = L_{1,0}(\kappa_1)$, which is the Lorentzian density, and $P(\kappa_2) = L_{1/2,1}(\kappa_2)$, which is Smirnov's density. We have considered two temperatures for the two models M1 and M2. As shown in Figs. 1 and 2, a scaling behavior is observed and all data collapse on the Lévy densities $L_{1,0}(\kappa_1)$ and $L_{1/2,1}(\kappa_2)$, respectively. In Figs. 1 and 2 we have rejected TLSs within a sphere of radius $r_{\min} = 1$ nm, demonstrating that our results are not sensitive to a short cutoff. Also shown in the inset in Fig. 2 is $P(\mathrm{Re}[\kappa_3])$ which is distributed according to $L_{1/3,0}(\mathrm{Re}[\kappa_3])$ and a scale parameter $z_{1/3}$ given in Eq. (9). The Lévy behavior of
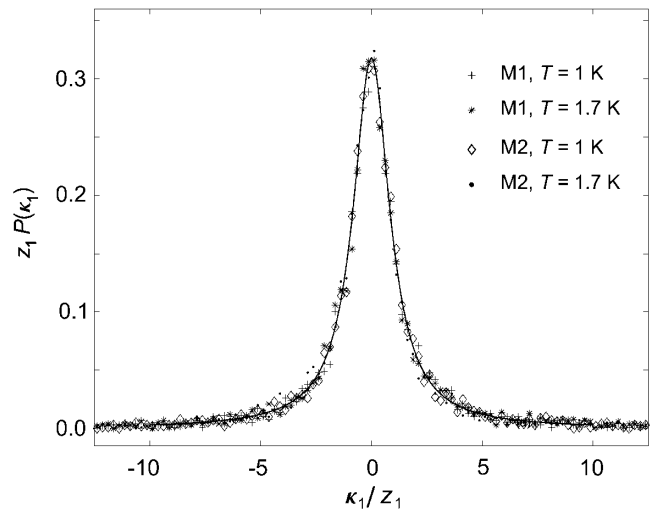

FIG. 1. Scaled probability density of first cumulant $P(\kappa_1)z_1$ versus κ_1/z_1. Symbols are the simulation results obtained from 4000 molecules for different cases indicated in the figure. The theory, plotted as a solid curve, predicts a Lorentzian density $P(\kappa_1) = L_{1,0}(\kappa_1)$ with a scaling parameter z_1 which varies from one set of data to the other.

κ_1, κ_2 and $\mathrm{Re}[\kappa_3]$ holds generally and is not limited to the slow modulation limit since these random variables do not depend explicitly on the rates K.

Consider the distribution of $\mathrm{Re}[\kappa_4]$, which in the slow modulation limit is distributed according to $L_{1/4,\eta}(\mathrm{Re}[\kappa_4])$, Eq. (10). The question remains if such a slow modulation limit is valid for the standard tunneling model parameters we are considering. The slow modulation limit is expected to work when $K \ll |\nu|$. For large enough r this inequality will fail; however, depending on system parameters, we expect that contributions from TLS situated far from the SM are negligible. We also note that
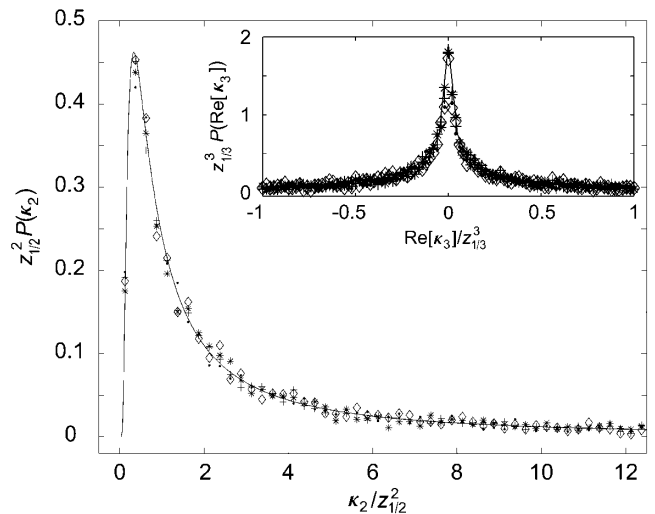

FIG. 2. Same as Fig. 1 for the second cumulant. We show $P(\kappa_2)z_{1/2}^2$ versus $\kappa_2/z_{1/2}^2$. The solid curve is Smirnov's density $L_{1/2,1}(\kappa_2)$. In the inset we show the same as Fig. 1 for $\mathrm{Re}[\kappa_3]$; the solid curve is Lévy density $L_{1/3,0}(\mathrm{Re}[\kappa_{1/3}])$.
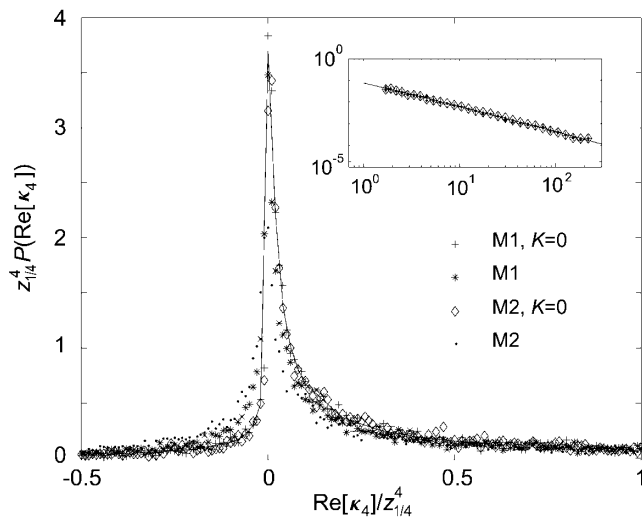
FIG. 3.   Same as Fig. 1 for $\text{Re}[\kappa_4]$ and for temperature $T = 1.7$ K. The symbols are the simulation results obtained for four different cases as indicated in the figure and for 12 000 molecules. The solid curve is $L_{1/4,\eta}[\text{Re}(\kappa_4)]$ with an index of asymmetry $\eta = 0.6104$. In the inset we show the power law tail of the scaled probability density on a log-log plot.

according to the standard tunneling model the rates K are distributed over a broad range, albeit with finite cutoffs that ensure that the averaged rate is finite. To check if the slow modulation limit is compatible with the standard tunneling model approach, we compare our slow modulation results with those obtained by simulation in Fig. 3. We also show simulation results in which all rates are set to zero ($K = 0$). For model M1, we find that the deviation between simulation and theory is small so the assumption of slow modulation limit is justified. This implies that it is the static (not dynamic) features of the TLSs that are encoded in the distribution of line shapes. For model M2, we see slightly larger deviations between the theory and numerical results, due to the angular dependence of model M2, $\Psi(\Omega) = \cos(\theta)$, which reduces the typical frequency shift $|\nu|$ compared to model M1. We conclude that the present theory can be used as a criterion for the validity of the slow modulation limit.

Depending on system parameters, Lévy statistics may become sensitive to the finite cutoff $r_{\min}$. Physically, the cutoff can be important since the power law interaction is not supposed to work well for short distances [6]. Our results were derived for $r_{\min} = 0$, while for small though finite $r_{\min}$ one can find intermittency behavior, i.e., the ratio $\langle \kappa_2^2 \rangle / \langle \kappa_2 \rangle^2$ (as well as similar dimensionless ratios) is

very large [16]. When $r_{\min}$ is large one finds a Gaussian behavior. Generally high order cumulants are more sensitive to finite cutoff and for results in Fig. 3 $r_{\min} = 0$ was chosen to see the proper decay laws in the wing.

Besides SM in low temperature glass, our results [Eqs. (8)–(11)] might be applicable to other model systems, for example, SM (or single spin) interacting with independent *identical* slow TLSs randomly distributed in space. Only the scaling z_γ and η are sensitive to the details of the model while the Lévy behavior is universal.

[1] W. E. Moerner and M. Orrit, Science **283**, 1670 (1999); T. Plakhotnik, E. Donley, and U. P. Wild, Annu. Rev. Phys. Chem. **48**, 181 (1997), and references therein.

[2] L. Fleury, A. Zumbusch, M. Orrit, R. Brown, and J. Bernard, J. Lumin. **56**, 15 (1993); M. Vacha, Y. Liv, H. Nakatsuka, and T. Tani, J. Chem. Phys. **106**, 8324 (1997); B. Kozankiewicz, J. Bernard, and M. Orrit, J. Chem. Phys. **101**, 9377 (1994).

[3] P. D. Reilly and J. L. Skinner, Phys. Rev. Lett. **71**, 4257 (1993).

[4] G. Zumofen and J. Klafter, Chem. Phys. Lett. **219**, 303 (1994).

[5] E. Geva and J. L. Skinner, J. Phys. Chem. B **101**, 8920 (1997); E. Geva and J. L. Skinner, Chem. Phys. Lett. **287**, 125 (1998).

[6] W. Pfluegl, F. L. H. Brown, and R. J. Silbey, J. Chem. Phys. **108**, 6876 (1998).

[7] A. M. Boiron, P. Tamarat, B. Lounis, R. Brown, and M. Orrit, J. Chem. Phys. **247**, 119 (1999).

[8] E. Barkai and R. Silbey, Chem. Phys. Lett. **310**, 287 (1999).

[9] P. W. Anderson, J. Phys. Soc. Jpn. **9**, 316 (1954); R. Kubo, *ibid.* **6**, 935 (1954).

[10] P. D. Reilly and J. L. Skinner, J. Chem. Phys. **101**, 959 (1994).

[11] W. Feller, *An Introduction to Probability Theory and Its Applications* (John Wiley and Sons, New York, 1970), Vol. 2.

[12] Y. Furukawa, Y. Nakai, and N. Kunitomi, J. Phys. Soc. Jpn. **62**, 306 (1993).

[13] A. M. Stoneham, Rev. Mod. Phys. **41**, 82 (1969).

[14] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1971); W. A. Philips, J. Low Temp. Phys. **7**, 351 (1972).

[15] In Table I $\omega_0 = 0$, generally $\kappa_1 = \sum_n p_n \nu_n + \omega_0$, while higher order cumulants are ω_0 independent. The distribution of ω_0 depends on the static disorder [13].

[16] J. Wang and P. Wolynes, Phys. Rev. Lett. **74**, 4317 (1995).