Dispersive Lineshape Theory

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(March 21, 2022)

Motivated by recent experiments we consider a stochastic lineshape theory for the case when
the underlying process obeys power-law statistics, based on a generalized Anderson-Kubo oscillator
model. We derive an analytical expression for the lineshape and find rich type of behaviors when
compared with the standard theory, for example, new type of resonances and narrowing phenomena.
We show that the lineshape is extremely sensitive to the way the system is prepared at time \( t = 0 \)
and discuss the problem of stationarity.

PACS numbers: 33.70.-w, 05.40.Fb, 31.70.Dk

Since its first introduction by Anderson and Kubo(AK)\cite{1,2} lineshape theory based on a stochastic approach has
had wide applications in condensed phase spectroscopy ranging from magnetic resonance spectroscopy \cite{3,4}
to the recently developed single molecule spectroscopy \cite{5,6,7}. The AK approach as well as other standard approaches
(e. g. Bloch equation) is based on the Markovian assumption. These approaches have been applied with great suc-
cess mainly to ensemble averaged measurements. However, single molecule spectroscopy \cite{3,4} has revealed that
in some cases the underlying dynamics in the condensed phase is highly non-Markovian \cite{5,6,7}.

In recent fluorescence intermittency studies on single quantum dot systems \cite{5,6,7} it was found that single quantum dots undergo transitions between bright and
dark states during the measurement, and the sojourn times of both bright and dark states are distributed ac-
cording to power-law, \( t^{-3/2} \), in contrast to an exponential as in the Poisson process. Here we are interested in
the stochastic lineshape theory for such non-Markovian processes with emphasis on power-law behavior of the
underlying dynamics. The introduction of a power-law process in the lineshape problem appears quite naturally.
Consider the following model as an example. The static chromophore \( C \) at the origin interacts with the single
perturber \( P \) via a short range interaction depending on \( r \), the distance between \( C \) and \( P \). \( C \) absorbs light with a
frequency \( \omega_0 \) when \( r < r_c \) and with a frequency \( \omega_0' \neq \omega_0 \) when \( r > r_c \). When \( P \) moves away from \( C \) it performs a
random walk (assumed one dimensional for simplicity).
Since the probability density of the first return time in the one dimensional random walk follows \( t^{-3/2} \) \cite{5,6,9-11},
the chromophore absorbs light at frequency \( \omega_0' \) with times distributed according to a power-law distribution.

An important issue in a power-law stochastic process is stationarity, which is of concern due to a very broad
temporal distribution for underlying processes. The significant difference between stationary and nonstationary
cases has manifested itself in many physical problems, e. g. transport properties in disordered materials \cite{12}
and power-spectra in chaotic systems \cite{13}. We take into ac-
count the stationarity issue fully and show that the line-
shape is a very sensitive measure of stationarity when the underlying dynamics obeys power-law statistics.

The stochastic lineshape theory is based on the equa-
tion of motion for the transition dipole, \( \mu(t) = i\omega(t)\mu(t) \)
where \( \omega(t) \) is the stochastic frequency of the oscillator.
The dynamical quantity which determines the lineshape is the relaxation function \( \Phi(t, t_0) = \langle \mu(t)\mu(t_0)^* \rangle \),
where the average is taken over all the possible real-
izations of the underlying stochastic process and we have set \( \langle \mu(t_0)^2 \rangle = 1 \). From the equation of motion
we can calculate the relaxation function as \( \Phi(t, t_0) = \exp(i\int_{t_0}^t d\tau \omega(\tau)) \).
When the process is assumed to be stationary, \( \Phi(t, t_0) = \Phi(t - t_0) \), then the line-
shape \( I(\omega) \) can be calculated as the Fourier transform of the relaxation function by making use of the Wiener-
Khintchine(WK) theorem \cite{14}:

\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \Phi(t) = \frac{1}{\pi} \text{Re} \hat{\Phi}(i\omega + \epsilon),
\]

where the symmetry of \( \Phi(t) \), \( \Phi(-t) = \Phi^*(t) \), has been used and the Laplace transform of \( z(t) \) denoted by \( \hat{z}(s) = \mathcal{L}\{z(t)\} \) and \( \epsilon \rightarrow 0^+ \).

We assume that the underlying process is a renewal process as in the AK approach. To make the model as
simple as possible, we consider a two state model. The transition frequency \( \omega(t) \) of the chromophore can take the
value of either \( -\omega_0 \) or \( +\omega_0 \) depending on the perturber state, \( |+\rangle \) or \( |--\rangle \), respectively. Each alternating path be-
tween the states \( |+\rangle \) and \( |--\rangle \) of the perturber leads to a stochastic realization of chromophore frequency mod-
ulation, and it is characterized by a sequence of sojourn times in the states \( |+\rangle \) and \( |--\rangle \). The sojourn times in the states \( |\pm\rangle \), \( t_{\pm} \), are assumed as mutually independent, identically distributed random variables described by the probability density functions(PDFs), \( h_{\pm}(t_{\pm}) \). The original
AK process amounts to the exponential sojourn time PDF. We do not assume any specific functional forms for the
sojourn time probability densities from the beginning, but are mainly interested in the process where the sojourn times are distributed with long time power-law.
tails, \( t^{-(1+\alpha)} \) \((\alpha > 0)\).

Assuming stationarity, which is justified if the process has been going on for long times before the beginning of observation, the sojourn time PDFs for the first transition event is given by \( f_\pm(t_\pm) \) [different than \( h_\pm(t_\pm) \)] by a standard argument, 
\[
\int_{t_\pm} \tau_\pm^{-1} \int_{t_\pm}^{\infty} d\tau h_\pm(\tau),
\]
where the mean sojourn time \( \tau_\pm = \int_0^\infty dt h_\pm(t) \) is assumed to be finite. When \( \tau_\pm \to \infty \) the concept of stationarity breaks down. For the Poissonian case \( h_\pm(t_\pm) = \tau_\pm^{-1} \exp(-t_\pm/\tau_\pm) \), we have \( f_\pm = h_\pm \). Therefore, stationarity is naturally satisfied in the Poissonian process. However, the non-Poissonian process in which we are interested will not be stationary if we simply set \( f_\pm = h_\pm \), and the WK theorem therefore does not hold.

The conditional relaxation functions \( \Phi_{ij}(i,j = +,-) \) are defined over the stochastic paths that start from the state \( |i\rangle \) at time 0 and end with the state \( |j\rangle \) at time \( t \). Here we give a sketch of the derivation for \( \Phi_{++} \) by summing all the possible stochastic paths that start from and end at the state \( |+\rangle \). Along a particular path if no transition is ever made until \( t \), the contribution of this path to \( \Phi_{++} \) is given by \( F_+(t_+) e^{-i\omega_0 t_+} \) in the time domain, where \( F_+(t_+) = \int_0^\infty d\tau f_+(\tau) \) is the survival probability of the states \( \{|\pm\rangle \} \) for the first event. This contribution will amount to \( F_+(s + i\omega_0) \) in the Laplace domain. The next possible paths are those which make the first transition to the state \( |-\rangle \) at \( t_1 + \), jump back to the state \( |+\rangle \) after remaining at the state \( |-\rangle \) for time \( t_2 + \), and stay at the state \( |+\rangle \) until time \( t \). The contribution of these to \( \Phi_{++}(t) \) is given by \( \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \times f_+(t_1+) e^{-i\omega_0 t_1+} h_-(t_2-) e^{i\omega_0 t_2} H_+(t_3+) e^{-i\omega_0 t_3} \) with the constraint \( t_1 + + t_2 + + t_3 + = t \), and \( H_+(t_3+) = \int_0^\infty d\tau h_+(\tau) \) is the survival probability corresponding to \( h_+(t_3+) \). In the Laplace domain this will read as \( \tilde{f}_+(s + i\omega_0) \tilde{h}_-(s - i\omega_0) \tilde{H}_+(s + i\omega_0) \) by the convolution theorem. Summing all the possible stochastic paths, we have
\[
\hat{\Phi}_{++}(s) = \hat{F}_+ + \frac{\tilde{f}_+ \tilde{h}_- \tilde{H}_+}{1 - \tilde{h}_+},
\]
where \( \hat{x}_\pm \equiv \hat{x}(s \pm i\omega_0) \) with \( \hat{x} \) being \( \hat{f}, \hat{h}, \hat{F}, \) or \( \hat{H} \). In a similar way, we have
\[
\hat{\Phi}_{--}(s) = \hat{\Phi}_{+-}(s) = \frac{\tilde{f}_+ \tilde{H}_-}{1 - \tilde{h}_+},
\]
and \( \hat{\Phi}_{-+}(s) \) and \( \hat{\Phi}_{+-}(s) \) are obtained from \( \hat{\Phi}_{++}(s) \) and \( \hat{\Phi}_{--}(s) \) by exchanging \( + \) and \( - \).

The total relaxation function can be calculated from the conditional relaxation functions,
\[
\hat{\Phi}(s) = \sum_{i=\pm} \sum_{j=\pm} p_i \hat{\Phi}_{ij}(s),
\]
with the initial distribution of the perturber state given by \( p_\pm = \tau_\pm / \sum_{i=\pm} \tau_i \). Then from Eq. (5) the lineshape is given by
\[
I(\omega) = \frac{1}{\pi} \text{Re} \left[ \frac{\hat{p}_+ (\hat{1} - \hat{h}_+ \hat{1})}{1 - \hat{h}_+ \hat{h}_-} \right],
\]
where \( z_\pm = i\omega \pm i\omega_0 \) and \( \hat{h}_\pm = \hat{h}(z_\pm) \), and we have expressed \( f_\pm, F_\pm, \) and \( H_\pm \) in terms of \( \hat{h}_\pm \). This is the final expression of the lineshape function for the stochastic oscillator undergoing the two state frequency modulation.

It is our aim here to show that the theory exhibits a very strong sensitivity on the choice of PDF for the first event. This becomes important for experimental situations when it is not always clear if the underlying process is stationary or not. For this purpose we define a quasi lineshape \( I_{NS}(\omega) \) by replacing \( f_\pm \) with \( \hat{h}_\pm \) in the derivation of Eq. (4):
\[
I_{NS}(\omega) = \frac{1}{\pi} \text{Re} \left[ \frac{\hat{p}_+ (\hat{1} - \hat{h}_+ \hat{1})}{1 - \hat{h}_+ \hat{h}_-} \right].
\]
Note that for Poissonian case \( I_{NS}(\omega) = I(\omega) \) and for ordinary processes (i.e. when all moments of \( h_\pm(t) \) exist) \( I_{NS}(\omega) \approx I(\omega) \). However, as we show here, strong sensitivity on the first event is recovered for the dispersive case. We emphasize that Eq. (5) is not a lineshape because the underlying process is not stationary. In certain physical situations, however, the underlying process is not an ongoing process, but has been initiated by a measurement itself, for instance, the blinking process in the quantum dot experiment mentioned before. In this case one can calculate the relaxation function \( \Phi_{NS}(t) \equiv \Phi(t,0) \) for the nonstationary stochastic process and \( I_{NS}(\omega) \) is obtained as the complex Laplace transform of a well-defined nonstationary relaxation function, \( \Phi_{NS}(t) \), \( I_{NS}(\omega) \sim \int_0^\infty dt e^{-i\omega t} \Phi_{NS}(t) \).

The original AK model is recovered from Eq. (5) by choosing an exponential sojourn time PDF. [8]. We first consider the sojourn time PDFs which have finite first moments, \( \tau_\pm < \infty \), but divergent second moments. As a representative of this class, we use the following form,
\[
h_\pm(t_\pm) = \left( \frac{\tau_\pm^3}{2\pi t_\pm^3} \right)^{1/2} \exp(-\tau_\pm/2t_\pm).
\]
In this case, \( h_{\pm}(t) \) decays as \( t^{-5/2} \) at long times, thus the first moment exists, but the second moment diverges.

As the next example we consider the one-sided Lévy density as the sojourn time PDF [17]. \( \hat{h}(s) = \hat{L}_{\alpha}(s/r) = \exp(-s/r^\alpha) \), with \( 0 < \alpha < 1 \), and \( r \) being a coefficient with an inverse time dimension. It is well known that the Lévy PDF decays algebraically at long times \( rt \gg 1 \), \( L_{\alpha}(t) \sim t^{-(1+\alpha)} \), and thus all the moments of \( L_{\alpha}(rt) \) including the first moment diverge [17]. Therefore, there is no microscopic timescale for this PDF, and the form of \( f_{\pm}^s(t) \) given in Eq. (2) cannot be applied. However, in realistic situations, it is unlikely to have power-law behavior for an infinitely long time, but rather, it is likely to have a finite cut-off time provided by, for example, the lifetime of a molecule. Therefore, it is natural to introduce a cut-off time \( t_c \) such that the algebraic decay is valid during time interval \( r^{-1} \ll t \ll t_c \). We introduce an exponential cut-off function for the convenience of an analytical treatment. Now the sojourn time PDF is given by \( h_{\pm}(t) = N_{\pm} e^{-t/t_c} L_{\alpha}(r_{\pm} t) \), where \( N_{\pm} \) is the proper normalization constant depending on the cut-off time. Then the Laplace domain expression of \( h_{\pm}(t) \) can be written as

\[
\hat{h}_{\pm}(s) = \exp \left[ \left( r_{\pm} t_c \right)^{-\alpha} \left\{ 1 - (1 + st_c)^{\alpha} \right\} \right] .
\] (9)

Then \( f_{\pm}(t) \) is given from Eq. (3) with the mean being \( \tau_{\pm} = \alpha t_c / (r_{\pm} t_c)^{\alpha} \). Note that in the limit \( t_c \to \infty \) the Lévy PDF without cut-off is recovered as \( \hat{h}_{\pm}(s) = \exp(-s/r_{\pm}) \) and \( \tau_{\pm} \) diverges.

The new peaks we observe in Fig. 1(c) and (d) at \( \omega = \pm \omega_0 \) for the stationary lineshape result from the first event in the stochastic process \( \omega(\tau) \). The probability for the perturber remaining at the initial state is governed by the long time tail in the sojourn time PDF. Due to the stationarity condition in Eq. (2) the survival probability for the first event decays more slowly for the stationary case (\( \sim t^{1-\alpha} \)) than for the nonstationary case (\( \sim t^{-\alpha} \)), where \( \alpha = 3/2 \) in this example. Therefore, the stationary case effectively requires the perturber to remain at the initial state until much longer times than the nonstationarity case, resulting in the enhanced peaks at \( \omega = \pm \omega_0 \). This is why we observe new peaks not present in the standard Poissonian case.
In Fig. 3, we have investigated the effect of the cutoff time in the Lévy PDF case both in the stationary and the nonstationary cases. When \( \alpha = 0.3 \) (Fig. 3 (a) and (b)), both the stationary and the nonstationary Lévy lineshapes show distinct peaks at \( \omega = \pm \omega_0 \). As the cutoff time is increased, there is little change in both lineshapes other than becoming narrower. When \( \alpha = 0.8 \) (Fig. 3 (c) and (d)), there appears a new peak near \( \omega = 0 \) in addition to the two resonance peaks. This is a new type of the narrowing behavior which is absent in the Poissonian case and is termed power-law narrowing.

Also, as the cutoff time is increased, the central peak in the lineshape for the stationary case diminishes while it remains in the nonstationary case. This is because in the stationary case, as the cutoff time is increased the first event will dominate the probability weight in the stochastic paths of the perturber dynamics. The difference between the stationary and nonstationary cases is therefore more significant in the Lévy case than in the Poissonian case.

To investigate the power-law narrowing we consider the limit \( t_c \to \infty \). In this limit the stationary lineshape approaches two delta functions, \( I(\omega) = p_+ \delta(\omega + \omega_0) + p_- \delta(\omega - \omega_0) \), since the second term in the Eq. (1) vanishes as \( t_c \to \infty \). The nonstationary case, however, yields in the limit \( r_{\pm} \gg |\omega| \),

\[
\lim_{t_c \to \infty} I_{NS}(\omega) = \frac{\sin(\pi \alpha)}{2 \pi \omega_0} \frac{2 + x + x^{-1}}{\eta x^\alpha + (\eta x^\alpha)^{-1} + 2 \cos(\pi \alpha)}, \tag{10}
\]

for \( |\omega| < \omega_0 \) and vanishes when \( |\omega| > \omega_0 \). This expression has been obtained from Eq. (7) by taking the small frequency limit of the sojourn time PDF, \( \hat{h}_\pm(s) = 1 - (s/r_{\pm})^\alpha + \cdots \). Note that Eq. (10) is not limited to Lévy PDF, but valid for any PDF with \( t^{-1+\alpha} \) tail \((0 < \alpha < 1)\). Here, \( x = (\omega_0 + \omega)/(\omega_0 - \omega) \) is a dimensionless frequency, and \( \eta = \lim_{t \to \infty} (p_+/p_-) = (r_-/r_+)^\alpha \) is the asymmetry parameter. This function shows a very asymmetric power-law singularities at \( \omega = \pm \omega_0 \), \( (\omega_0 \pm \omega)^{1-\alpha} \) depending on \( \alpha \). It is worthwhile to mention that such a strong asymmetric lineshape has been encountered in the problem of the X-ray edge absorption of metals [22]. In the symmetric case \((\eta = 1)\) Eq. (10) reduces to a simpler expression, and in this case there exists a critical value of \( \alpha \) below which the lineshape is concave and above which convex at \( \omega = 0 \), which is given by \( \alpha_c = \cos(\pi \alpha_c/2) = 0.5946 \cdots \).

In Fig. 3 we have confirmed this finding by plotting the nonstationary lineshapes for the Lévy PDF case with \( \eta = 1 \) and finite, large \( r_{\pm} \) and \( t_c \). The nonstationary case in Fig. 3 (b) shows the concave-to-convex transition at the critical value of \( \alpha \) as predicted. For the stationary lineshape, similar kind of behavior can be observed in Fig. 3 (a), however, \( \alpha_c \) now depends on \( t_c \).

In summary, we have generalized the stochastic lineshape theory to arbitrary renewal processes. Compared with the standard theory, we have found a variety of new phenomena in the lineshapes, such as new peaks and narrowing behaviors. The issue of the stationarity has been considered and the strong sensitivity of the lineshape to the first event in the stochastic trajectory was found. One of many extensions of this work is to consider the random frequency modulation of stochastic oscillator among \( N > 2 \) values, and will be published elsewhere. This work was supported by NSF.

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