

The Kubo Line Shape and the q-Gaussian Tsallis Function

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Abstract – Here we consider the Kubo line shape, that is the Fourier transform of the Kubo stochastic time-correlation function, and its q-Gaussian fit. The aim is to further generalize the application of q-Gaussian Tsallis functions in spectroscopy.

Keywords: Raman spectroscopy, q-Gaussian Tsallis lines, Time correlation functions, WolframAlpha by Wolfram Research

In a [previous discussion](#) about the generalization of the Voigt function, which is a function widely used in spectroscopy, we have encountered the “Kubo line shape”, that is the Fourier transform of the Kubo (Gaussian-stochastic) time-correlation function. Here we compare this line shape with the q-Gaussian Tsallis function, which is a function that can be used for fitting band profiles in Raman spectroscopy, as shown by the many examples provided by us (Sparavigna, 2023). The q-Gaussian function is a probability distribution derived in the framework of Tsallis statistics (Tsallis, 1988, 1995, Hanel et al., 2009). It consists in a generalized form of the exponential function (see discussion in Sparavigna, 2022), characterized by a continuous parameter q in the range $1 < q < 3$. As given by Umarov et al., 2008, the q-Gaussian is a function $f(x) = C e_q(-\beta x^2)$, where $e_q(\cdot)$ is the q-exponential function and C a constant. The q-exponential has expression: $exp_q(u) = [1 + (1 - q)u]^{1/(1-q)}$. The function $f(x)$ possesses a bell-shaped profile, and in the case that we have the peak at position x_o , the q-Gaussian is:

$$q\text{-Gaussian} = C exp_q(-\beta(x - x_o)^2) = C [1 - (1 - q)\beta(x - x_o)^2]^{1/(1-q)}$$

For q equal to 2, the q-Gaussian is the Cauchy-Lorentzian distribution (Naudts, 2009). For q close to 1, the q-Gaussian is a Gaussian. Consequently, for the q -parameter between 1 and 2, the shape of the q-Gaussian function is intermediate between Gaussian and Lorentzian profiles.

As [previously shown](#), q-Gaussian functions can be used to mimic the Voigt convolutions, but they are different functions, in particular for what is regarding the behavior of the wings. The Voigt function, as told by Townsend, 2008, “looks like Gaussian for small x (i.e., near line center), and like Lorentzian for large x (i.e., out in line wings)”. We can also appreciate the same by observing the pseudo-Voigt function, which is generally used for approximating the Voigt function. Being the pseudo-Voigt the linear combination of Gaussian and Lorentzian functions, the wings must be necessarily Lorentzian and the kernel Gaussian-like. Consequently, if we use Voigt functions or pseudo-Voigt functions for fitting spectra, the wings of the Raman lines will be always described by a Lorentzian behavior. However, is this always the experimental case? That is, are we always observing Lorentzian wings for the Raman bands? To answer these questions, we started investigation in [ChemRxiv1](#). We observed that a generalization of the pseudo-Voigt functions obtained by means of a linear combination of two q-Gaussians can help us in describing the leading term of the line wings. In this manner, we can quantitatively “measure” the wing power law as well as answering qualitatively whether it is Lorentzian or not. The q-Gaussians are therefore the proper solution for investigation.

For the spectra previously considered (Sparavigna, 2023), the fitted functions are successfully in several cases, for instance graphite [ChemRxiv2](#), anatase [ChemRxiv3](#), SERS spectra [ChemRxiv4](#), and so on, [SSRN](#). In the [discussion previously mentioned](#), we considered deeply the Voigt function, its time-correlation functions, and several other time-correlation functions used for spectroscopy. Among them, let us here remember the time correlation producing the Egelstaff-Schofield line shape. The ES profiles can be obtained from a Fourier transform which is giving an analytical expression (Kirillov, 1999). In [our comparison](#) of ES profiles with q-Gaussians, we noted that the fitted Tsallis function is in good agreement with ES functions.

The ES time-correlation function is (Kirillov, 1999):

$$\Phi(t) = \exp\{-(t^2 + \tau_1^2)^{1/2} - \tau_1\}/\tau_2\} \quad (1).$$

It is containing two relaxation times. According to Kirillov, 1999, we have this function becoming Gaussian for $t \ll \tau_1$ and an exponential for $t \gg \tau_1$. In Kirillov, 1999, 2004, it is stressed that the ES time-correlation function (1) is a function with is able of reproducing the Kubo time-correlation function, in a form possessing an analytic expression of the Fourier transform. And also: the ‘‘Gaussian–Markovian, or Kubo case remains the most common and widely used in spectroscopic practice’’ (Kirillov,2009). The Kubo correlation is given by Kirillov as (M_2 is the second spectral moment and τ_ω a relaxation time):

$$\Phi = \exp\{-M_2\tau_\omega^2[\exp(-t/\tau_\omega) - 1 + t/\tau_\omega]\} \quad (2)$$

Here the frequency is referred to the position of the unshifted frequency. ‘‘When the frequency modulation is a Gaussian Markov stationary process, [that is in the Kubo case] the cumulant beyond the second order vanishes’’ (Dutta et al., 2017). Note please that the time correlation has an exponential factor, which is the Fourier transform of a Lorentzian function:

$$\Phi = \exp\{-M_2\tau_\omega t\} \cdot \exp\{M_2\tau_\omega^2[1 - \exp(-t/\tau_\omega)]\} \quad (3).$$

That is, we have the system subjected to homogeneous broadening mechanisms.

Kirillov’s research considered also the approach defined as Rothschild-Kubo (Rothschild et al., 1987, Feng and Wilde, 1988). ‘‘Efforts to apply a simple Gauss-Markov theory have proven unsuccessful for aqueous ionic solutions, where strong Coulombic and dipolar forces promote vibrational relaxation, and the hydrogen bonding of the water inhibits anion reorientation. An alternate modeling function, the stretched exponential, has been proposed to explain inhomogeneously broadened Raman spectra’’ (Feng & Wilde, 1988). Rothschild et al., 1987, wrote the time correlation related to the stretched exponential as:

$$\Phi = \exp\left(-M_2T^2 \sum_{n=0}^{\infty} \frac{(-1)^n (t/T)^{2+n\alpha}}{n! (1+n\alpha)(2+n\alpha)}\right) \quad (4)$$

Rothschild and coworkers tell the following. ‘‘It has by now been generally accepted that the shapes and widths of band profiles observed by vibrational spectroscopy of condensed-phase systems are, in the vast majority of cases, caused by ‘‘inhomogeneous broadening. ... Although spectral profiles of a large variety of liquid-phase systems have since long been satisfactorily explained by this simple Gauss-Markov process ... , more recent and improved spectral data have led to the realization that the experimental vibrational correlation decay in the intermediate to long time domains is occasionally faster (more ‘‘Gaussian-like’’) than predicted by [the Gauss-Markov approach]’’. In Kirillov, 2004, we can find the Rothschild-Perrot-Guillaume (RPG) model as in Eq.(4), discussed with the Burshtein-Fedorenko-Pusep (BFP) model too.

‘‘Differences in TCFs [time correlation functions] lead to very unlike line profiles. ... the Kubo TCF corresponds to vibrational lines whose profiles vary from Gaussian to Lorentzian. The Rothschild-Perrot-Guillaume TCF corresponds to vibrational lines of quite specific, over-Gaussian form. They are

less sharp than Gaussian in their central part, and much faster fall to zero in the wings. The Burshtein, Fedorenko and Pusep TCF corresponds to over-Lorentzian line profiles. They are sharper than true Lorentzians in their central part, and broader in the wings" (Kirillov, 2004). Therefore, we can tell that Kirillov is proposing a generalization of the Kubo correlation function.

To use (4) in spectroscopy, we need its Fourier transform to determine the corresponding line profile. Being the Fourier transform calculation too heavy for Raman bands deconvolution, Tagliaferro et al., 2020, have proposed a synthetic profile mimicking the line shape. It is a profile named "GauLor", which is a piecewise symmetric function with a Lorentzian central part and wings which are Gaussians; actually, it seems being the opposite of the Voigt profile (Gaussian central part and Lorentzian wings). In GauLors, the onset of the wing happens at a frequency threshold, determined by the overall fitting approach. At the threshold, the Lorentzian and Gaussian piece functions and their derivatives are continuous. Supposing the existence of the threshold within the Raman scan range, the GauLor has the onset of the Gaussian wing which can be very close to the center of the line (in the kernel) or quite far from it (in the far line wings). In fact, we have two families of intermediate functions between Lorentzian and Gaussian line shapes, and they are the q-Gaussians and the GauLors.

In this framework, with the aim of further generalization to the RPG case, let us consider the q-gaussian fit of Kubo lines.

The Kubo line shape

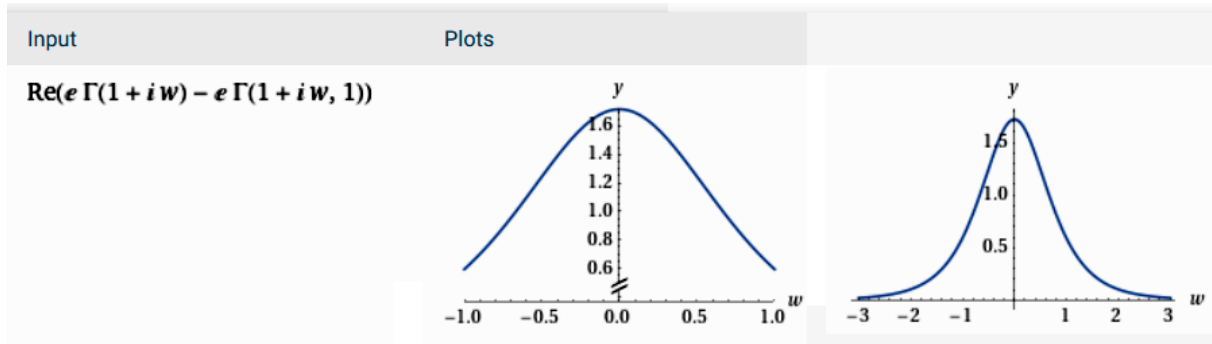
Let us consider specifically the Kubo case in the form (super-exponential):

$$\Phi = \exp\{-[\exp(-t) - 1 + t]\} \quad (5),$$

We use here a dimensionless time. To show the related line shape we need the Fourier transform. To have it, we can pass through the Laplace transform. Here from Wolfram Alpha:

Input interpretation	Result	Alternate form
$\mathcal{L}_t[\exp(-\exp(-\sqrt{t^2}) - \sqrt{t^2} + 1)](s)$	$e(s! - \Gamma(s + 1, 1))$	$e \Gamma(s + 1) - e \Gamma(s + 1, 1)$

Passing from s to $i w$ and evaluating the real part, we have the Fourier transform as:



From the table of values of the function, we find the following line shape in linear and semi log scale.

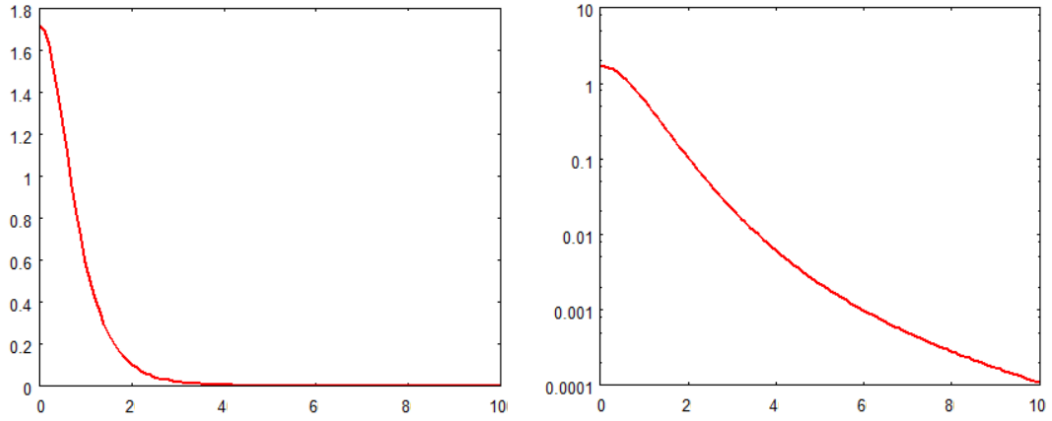


Fig.1: Behavior of the Kubo line shape in linear and semi log scale. Being symmetry only one side of the profile is shown.

We used the WolframAlpha (WA) data given in the Figure 1, to calibrate the numerical Fourier transform of the time correlation function.

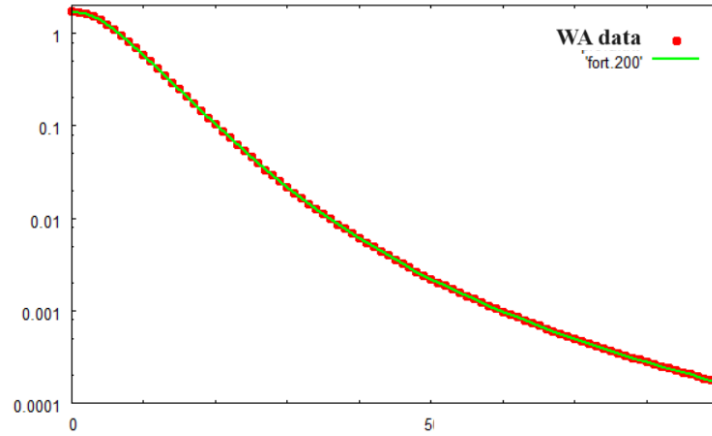


Fig. 2: In red the WolframAlpha data and in green the corresponding numerical Fourier transform.

In the Lecture Notes by Tokmakoff, 2009, the Kubo time correlation function is given as:

$$F(t) = \exp[-\Delta^2 \tau_c^2 (\exp(-t/\tau_c) + t/\tau_c - 1)] \quad (6)$$

where τ_c is the time scale of dynamics. Parameter $\kappa = \Delta \cdot \tau_c$ is introduced, and three cases are given: fast, $\Delta = 1, \tau_c = 0.2, \kappa = 0.2$, mid, $\Delta = 1, \tau_c = 1, \kappa = 1$, and slow $\Delta = 1, \tau_c = 10, \kappa = 10$. The Absorption line shapes are given by Tokmakoff as in the following plot (Fig.3).

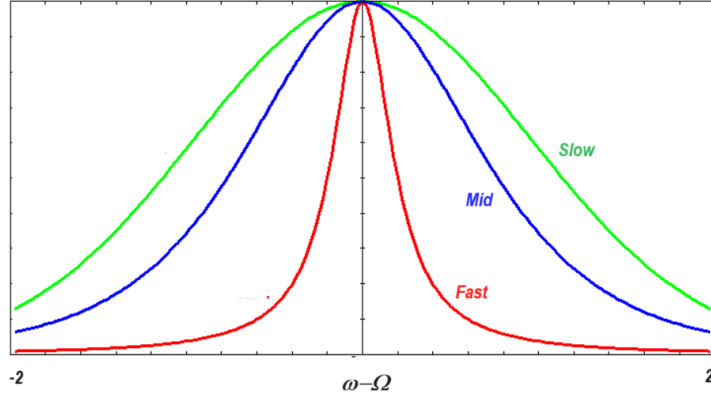


Fig.3.

“We see that for a fixed distribution of frequencies Δ the effect of increasing the time scale of fluctuations through this distribution (decreasing τ_c) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM [Full width at half maximum]) of $2.35 \cdot \Delta$ to a motionally narrowed Lorentzian line shape with width (FWHM) of $\Delta^2 \tau_c / \pi = \Delta \cdot \kappa / \pi$.” (Tokmakoff, 2009). Here again we are facing the problem to find the “intermediate” function between Lorentzian and Gaussian profiles.

We have shown previously that the q-Gaussians are able to mimic the ES line shape. Let us evaluate how they fit the Kubo line shapes. Here in the following plot, five Kubo profiles are given with different τ_c, κ parameters.

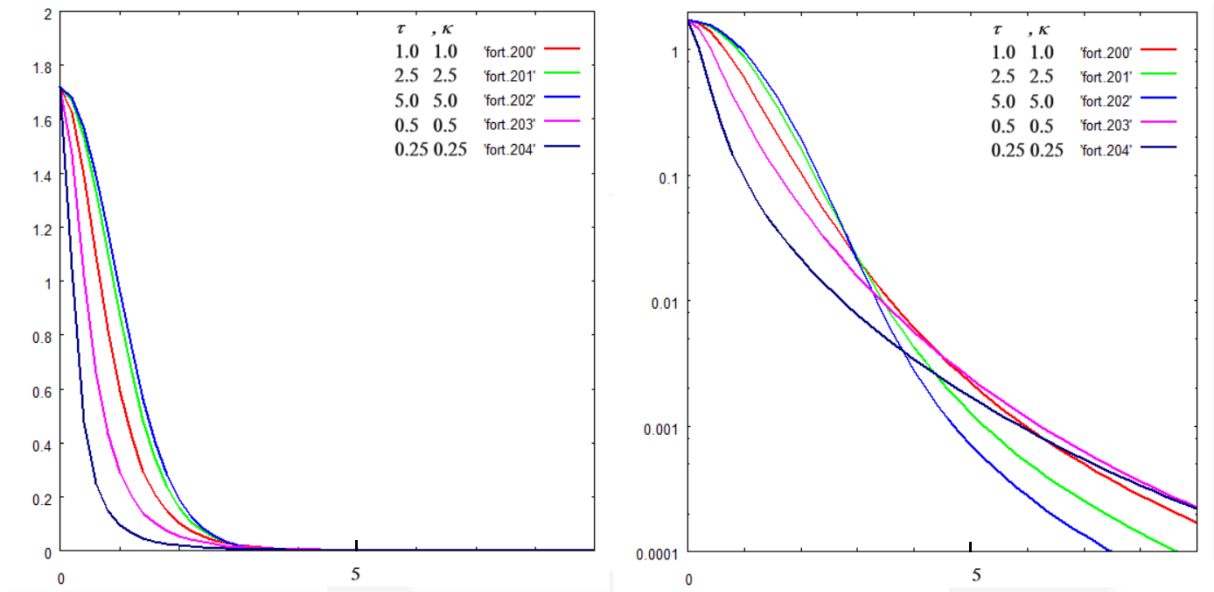


Fig.4: Five Kubo line shapes for different parameters κ, τ_c . In red the mid case $\Delta = 1, \tau_c = 1, \kappa = 1$.

Considering the Kubo line shapes given in the Figure 4, and compare them with q -Gaussian functions. In the following Figure 5, we can see the Kubo data and the fitted q -Gaussians (green).

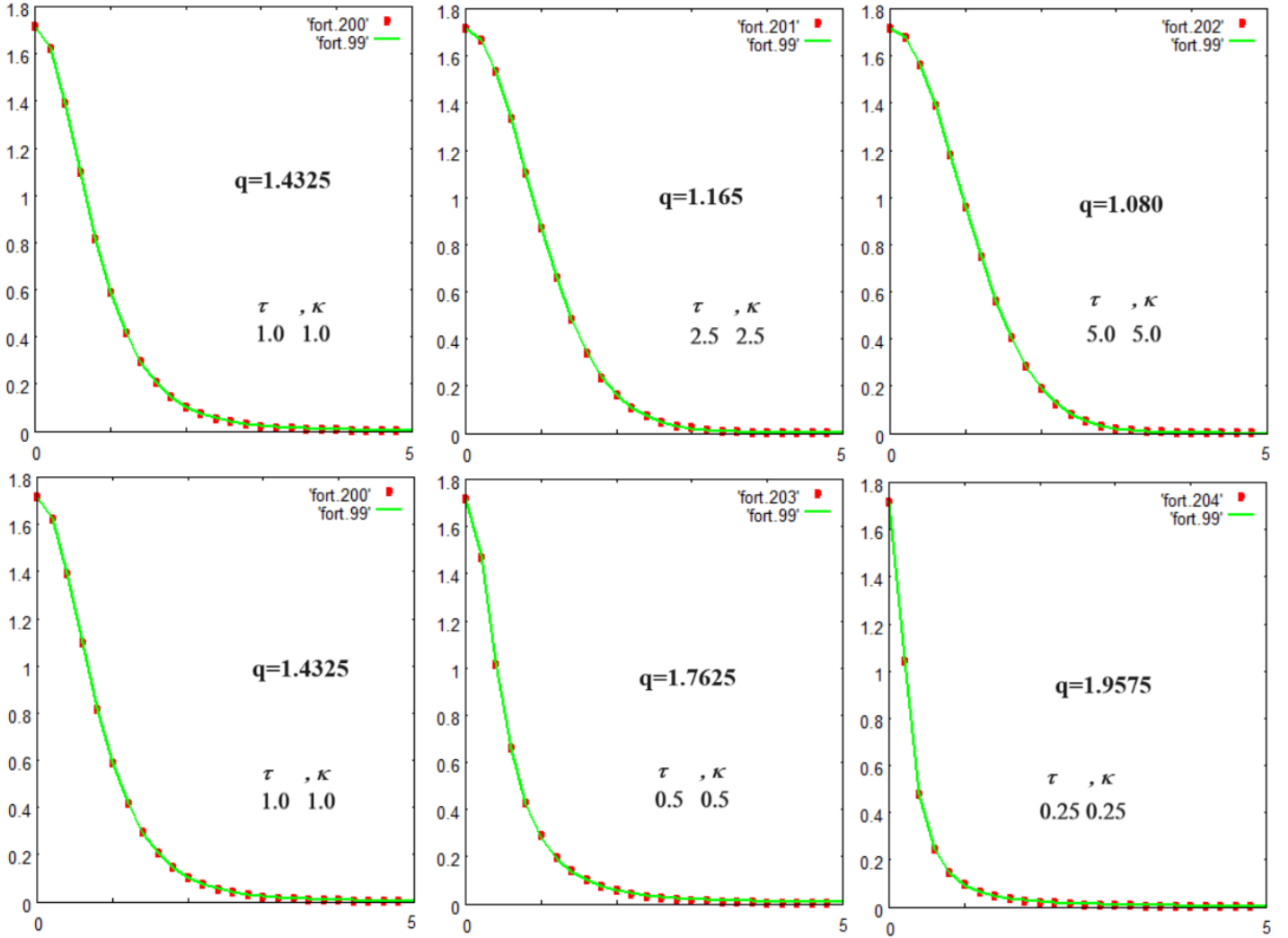


Fig. 5: The Kubo line shapes of the Figure 4 are represented by red dots. The Kubo line shapes are compared with q -Gaussian functions. The best fits are given with green lines. The q parameters are reported in the plots. Note that we pass from a slow Gaussian-like case (q parameter equal to 1.080) to a fast Lorentzian-like case (q parameter equal to 1.9575). The slow and fast cases are compared to the mid case given in the left panels (q parameter 1.4325). Plots are given in the linear scale.

Since the difference is very small, the Kubo and q -Gaussian line shapes are giving the same profile in the Figure 5. To appreciate where these functions differ, let us use the semi log scale (Fig.6).

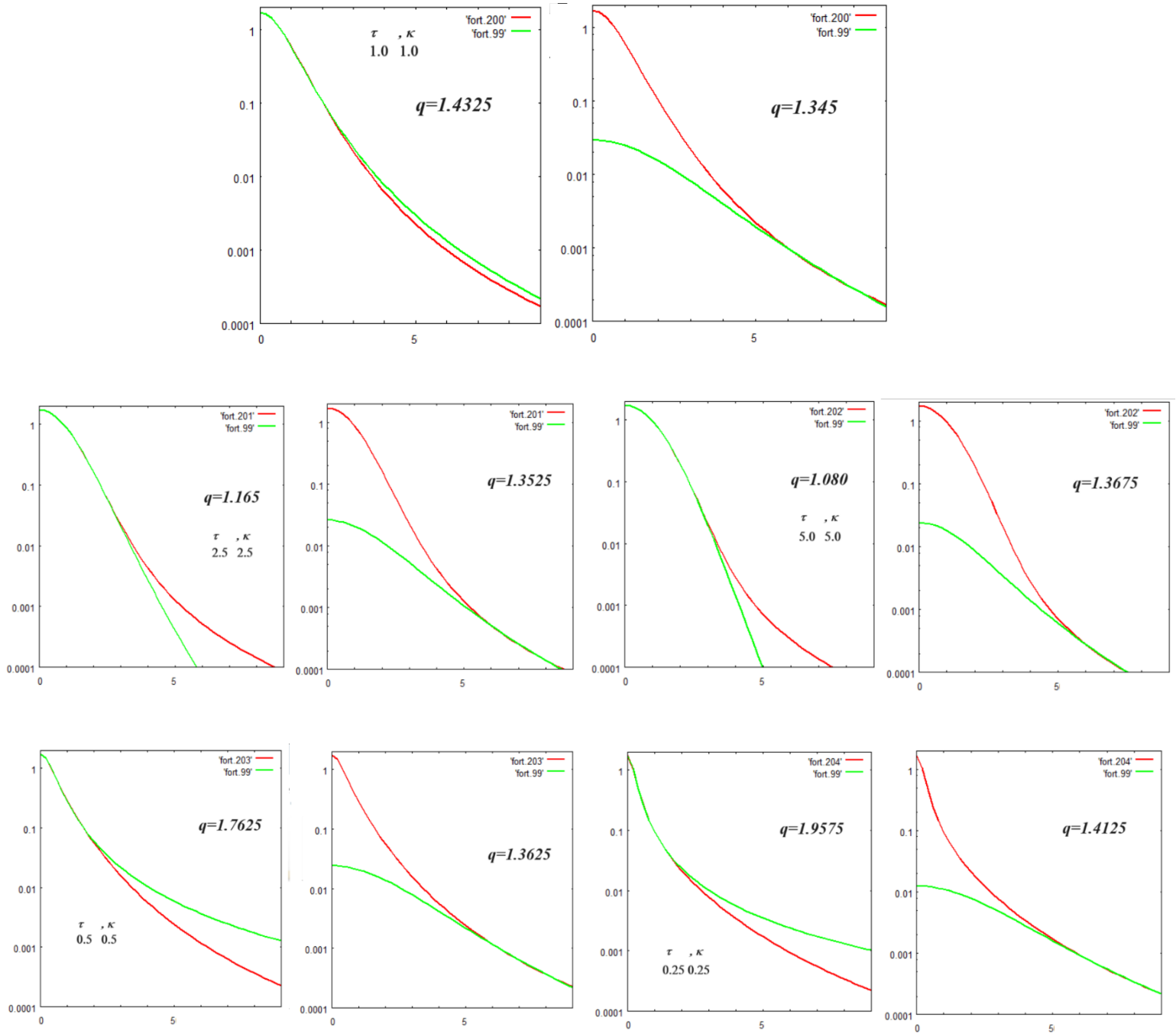


Fig.6: Kubo line shapes in red. The green lines are representing q -Gaussians. For each of the five cases in the Figure 5, we consider on the left the q -Gaussians as given by the best fit (Figure 5) and on the right the fitted q -Gaussians for the far wings. The Kubo and the q -Gaussian are differing in their far wings.

From the Figure 6, where the functions are given in the semi log scale (Kubo line shapes in red and q-Gaussians in green), it is evident that Kubo and q-Gaussians are differing in their far wings. In the five cases here given, the far wings are characterized by q-parameter values ranging from 1.34 to 1.41. It seems that the far wing has a q-parameter increasing its value, when the dynamics is becoming faster. As shown by the following Fig.7, in the fast case $\tau_c = 0.05, \kappa = 0.05$, the q-parameter is equal to 2 and the Kubo line shape is almost equal to a Lorentzian function. However, the slow case $\tau_c = 20, \kappa = 20$ does not become a Gaussian profile.

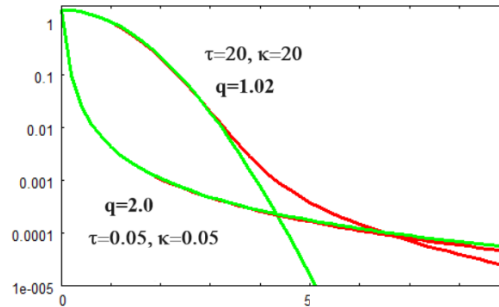


Fig. 7: Kubo line shapes in red and q-Gaussian in green.

Conclusion

The q-Gaussians are able of mimicking the Kubo line shapes. Only the far-wings are different. The Figures 5-7 are representing how a Kubo lines is passing from a Gaussian-like (slow dynamic) to a Lorentzian-like (fast dynamic) case. However, please note that the far wings have a behavior which is not Gaussian. When processes are very fast, the profile is Lorentzian.

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