q-Gaussian Tsallis Functions and Egelstaff-Schofield Spectral Line Shapes

Amelia Carolina Sparavigna[1]✎

[1]Department of Applied Science and Technology, Polytechnic University of Turin, Italy

Abstract: In this article we will discuss the Egelstaff-Schofield line shapes, as used in Raman spectroscopy, and their fit by means of q-Gaussian Tsallis functions. q-Gaussians are probability distributions having their origin in the framework of Tsallis statistics. A continuous real parameter q is characterizing them so that, in the range $1 < q < 3$, q-functions pass from the usual Gaussian form, for q close to 1, to that of a heavy tailed distribution, at q close to 3. The value q=2 corresponds to the Cauchy-Lorentzian distribution. This behavior allows the q-Gaussian function to properly mimicking the Egelstaff-Schofield line shape, which has been introduced to fit the bands of first-order Raman scattering in ionic liquids. This line shape is based on a modified Bessel function of the second kind. Moreover, since the Fourier transform of the Egelstaff-Schofield line shape is given by a simple analytical expression, we can use this expression as an easy substitute for the Fourier transform of the q-Gaussian function.

Keywords: q-Gaussian distribution, Gaussian distribution, Cauchy distribution, Lorentzian distribution, Voigt distribution, Egelstaff-Schofield line-shape, Raman spectroscopy, EPR spectroscopy

1. Introduction

q-Gaussians are probability distributions having their origin in the framework of Tsallis statistics (Tsallis, 1988, Hanel et al., 2009). The relevant functions of Tsallis statistics are the generalized forms of logarithm and exponential functions (see for instance the discussion in Sparavigna, 2022); a continuous real parameter q is characterizing them and when it is going to 1, the q-functions become the usual logarithm and exponential functions. Regarding the q-Gaussian function, in the range $1 < q < 3$ we are passing from the Gaussian distribution, for q close to 1, to a heavy tailed distribution for q close to 3. The value q=2, (Naudts, 2009), corresponds exactly to the Cauchy distribution, also known in physics as the Lorentzian distribution. A change of the q parameter is therefore allowing the q-Gaussian to span the behavior from Gaussian to Lorentzian distribution. The q-Gaussian is therefore an interesting function for rendering the spectral line shape.

In a previous article (Sparavigna, 2023), we have considered the application of q-Gaussian Tsallis line shape to the analysis of Raman spectra. Usually Lorentzian, Gaussian and Voigt profiles are the most commonly used line shapes for modelling Raman spectral bands (see Ferrari and Robertson, 2000, 2004, Ferrari, 2007, Meier, 2005, Naylor et al., 1995, and literature given in Sparavigna, 2023). We have seen that the q-Gaussian is able to fit Voigt line shape, and therefore it can be eligible as substitute in any numerical analysis obtained by means of the above-mentioned functions. We have also reported the role of q-Gaussians in EPR spectroscopy (Howarth et al., 2003). Actually, in Howarth et al., 2003, a "Tsallis lineshape function" has been proposed for describing electron paramagnetic resonance spectra, "and possibly nuclear magnetic resonance (NMR) spectra as well". In the article by Howarth et al., the q-Gaussian is not mentioned in this manner, but as "Tsallis lineshape".

Here we show that the q-Gaussian function is properly mimicking the Egelstaff-Schofield line shape, which has been introduced to fit the bands of first-order Raman scattering in ionic liquids. This line shape is based on a modified Bessel function of the second kind. Since the Fourier transform of the Egelstaff-Schofield line shape is given by an analytical expression, we can use this transform for the q-Gaussian too (the specific Fourier transform of q-Gaussian function has been calculated by Rodrigues and Giraldi, 2016).
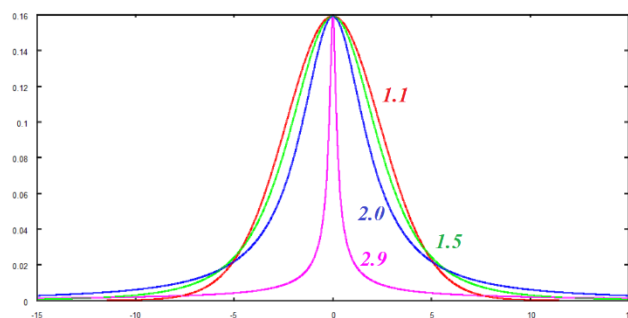

Fig. 1: q-Gaussian functions, for different q indices, from 1.1 (quasi Gaussian) to 2.9 (over-Lorentzian).The blue curve is the Lorentzian line shape.

✎ **Amelia Carolina Sparavigna (Correspondence)**
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2. The q-Gaussians

Before giving the q-function expression, it is necessary to stress that the term "q-Gaussian" is regarding the deformation of the Gaussian probability distribution function according to Tsallis generalized statistics. It is not a function of the "q-calculus", that is the quantum calculus (about q-calculus, Sparavigna, 2021). As given by Umarov et al., 2008, the q-Gaussian is:

$$f(x) = C e_q(-\beta x^2) \quad (1),$$

where $e_q(.)$ is the q-exponential function and C a constant based on Γ function. In the exponent, in the discussion proposed here, we use $\beta = 4/\gamma^2$, where γ is the parameter of Lorentzian curves. The q-exponential has the expression:

$$exp_q(u) = [1 + (1-q)u]^{1/(1-q)} \quad (2).$$

Plots in the Figure 1 (see also Figure 2 in Sparavigna, 2023, 10.18483/ijSci.2671) are showing the behaviour of q-Gaussians.

3. The Egelstaff-Schofield model

In Sparavigna, 2023, we have considered the Lorentz model of absorption and emission of light, leading to the Lorentzian profile of spectral lines. Due to Doppler and instrumentation broadening, the profile assumes a Voigt shape (Meier, 2005). We have also seen that q-Gaussian functions are fitting the Voigt functions, and therefore can be interesting alternatives for numerical analyses of Raman bands.

Let us now consider another approach to the fit of Raman spectra, based on Egelstaff-Schofield line shapes. The use of these lines had been proposed by Bunten et al., 1984, for the study of ionic liquids. The researchers assumed that the first-order Raman scattering was coming from large currents and that the widths of the lines had been depending "on the disordering motions in the melt which will range from Brownian at short times to diffusive (conductive) at long times" (Bunten et al., 1984). For molten salts, the light scattering has a timescale which is including both processes "and the form of the damping must range from Gaussian at short times to exponential at long times" (Bunten et al., 1984). The researchers had therefore used the proposal by Egelstaff and Schofield (1962) of the following time correlation function:

$$G(t) = exp\{-[(t^2 + \tau_1^2)^{1/2} - \tau_1]/\tau_2\} \quad (3)$$

This function becomes a Gaussian for $t \ll \tau_1$, and an exponential for $t \gg \tau_1$. Moreover, it is possessing an analytically tractable Fourier transform. In (3) we can find two different relaxation times.

The Egelstaff and Schofield model was also discussed in Kirillov, 2004. Section 2.2 of Kirillov's article provides the existing models for the vibrational relaxation and therefore for the vibrational spectroscopy (Raman spectroscopy). The first model addressed is the Kubo-Rothschild one, about vibrational dephasing according to the Kubo time correlation function (TCF). Let us introduce τ_ω as the "characteristic time of the frequency modulation process (perturbation correlation time)" (Kirillov, 2004). When $\tau_\omega \to \infty$, the Kubo TCF "tends to be Gaussian and predicts the Gaussian form of the entire vibrational line" (Kirillov, 2004). In the other extreme with $\tau_\omega \to 0$, we have the Lorentzian profile. For finite relaxation time, the line is Lorentzian in its central part. Consequently, the Kubo-type TCF corresponds to a line which "is characterized by a Lorentzian central part and Gaussian wings" (Kirillov, 2004).

The other two mentioned models are the Rothschild Perrot Guillaume model and the Burshtein Fedorenko Pusep model. Of these models, we find in the Figure 1 given by Kirillov, the TCFs in reduced coordinates. For the following Figure 2, it is observed that different TCFs are producing "very unlike line profiles". The Kubo TCF corresponds to vibrational lines whose profiles vary from Gaussian to Lorentzian. The Rothschild Perrot Guillaume TCF gives lines that Kirillov defines of over-Gaussian form. The lines "are less sharp than Gaussian in their central part, and much faster fall to zero in the wings" (Kirillov, 2004). The Burshtein Fedorenko Pusep TCF has instead an over-Lorentzian line profile, sharper than true Lorentzian in the kernel and broader in the wings (Kirillov, 2004).

After discussing the above-mentioned models, Kirillov considers Egelstaff and Schofield model. In his work of 1999, about the time-correlation functions obtained from a band-shape fit without involving any Fourier transform, Kirillov proposed "to model real line profiles intermediate between Lorentzian and Gaussian by an analytical function, which has an analytical counterpart in the time domain" (Kirillov, 2004). The model TCF is precisely the Egelstaff-Schofield $G(t)$ in Eq.3. The corresponding line shape is:

$$I(v) = C \; exp(\tau_1/\tau_2)(\tau_1^2/\tau_2) \, K_1(x)/x \quad (4)$$
$$x = \tau_1[4\pi^2 c^2(v - v_0)^2 + 1/\tau_2^2]^{1/2} \quad (5)$$

$K_1(x)$ is the modified Bessel function of the second kind, v_0 is the peak wavenumber. C is a proper dimensioned constant. The Eq.(4) given above is also the line shape given by Eq.22 in Kirillov, 2004. In this equation we can find two relaxation times: considering their values "as empirical parameters, one can completely reproduce any kind of TCF described by the Kubo, Rothschild-Perrot-Guillaume, or Burshtein theory" (Kirillov, 2004).

Let us write (4) and (5) in the following form for comparison with q-Gaussian functions:

$$I(x) = C K_1(y)/y \quad ; \quad y = A[Bx^2 + 1] \quad (6)$$

Here, in the following Figure 2, the behavior of (6) is given according to values of A and B. Since the line shape is symmetric, only the right part of it is proposed. In the Figure 3, the same curves given in Fig.2 are compared with the q-Gaussians.
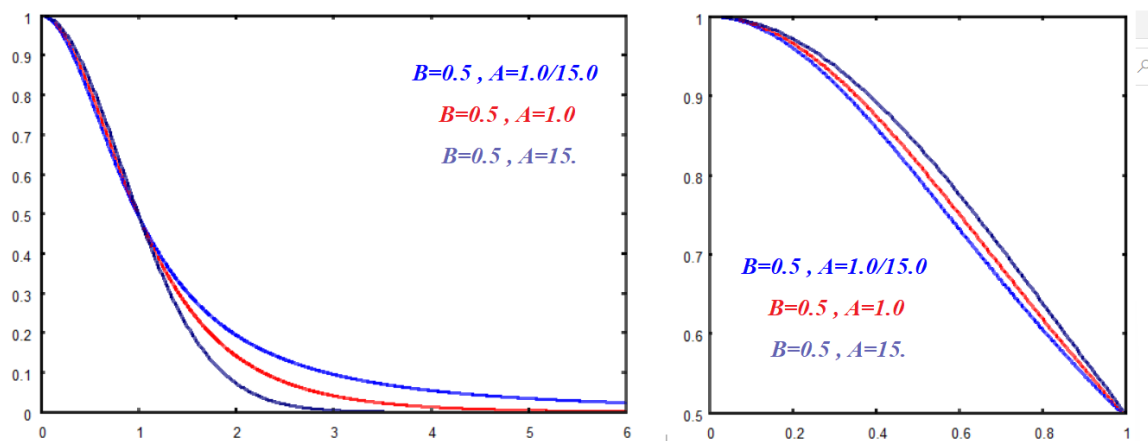
Fig. 2. Line profiles corresponding to Eq.6, for three different choices of parameter A, with B fixed. Abscissa is given in half width at the half-height (HWHH) units. At the line wings, the profile with A=15 is the lower one, that with A=1/15 is located higher. At the central part (kernel) of the line (right panel) the order of lines is opposite. However, they are rather close.
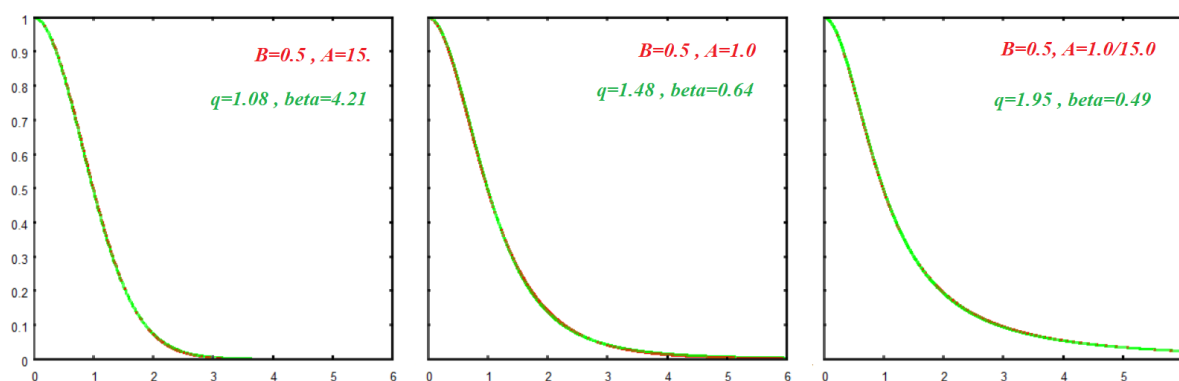

Fig. 3. The line profiles of the Fig.2 are here given in red. The best fit by means of q-Gaussian functions is given in green. The values of q and β are reported in the panels. Abscissa is given in half width at the half-height (HWHH) units. The q-Gaussian line corresponding to profile with A=15 has a q value indicating a Gaussian nature; the q-function corresponding to A=1/15 has a q index indicating a Lorentzian value.
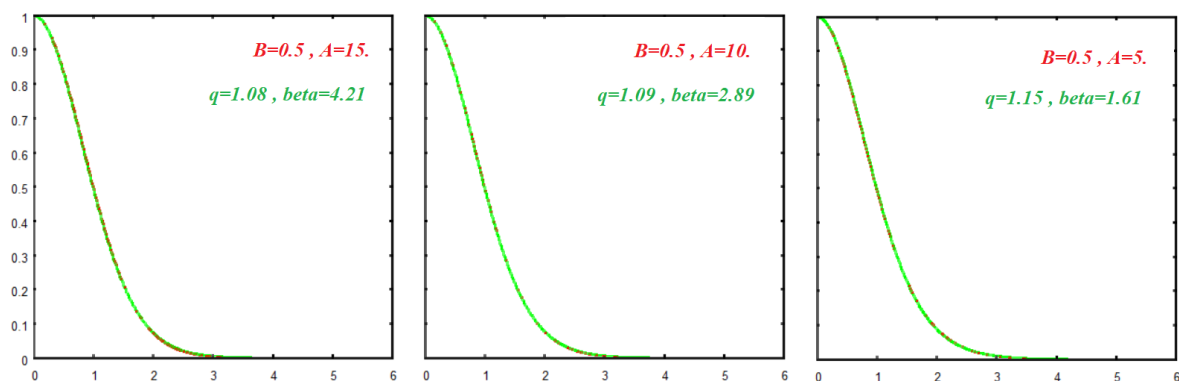

Fig. 4. The panels are proposing the fit by means of q-Gaussian functions, characterized by a Gaussian behavior (in red the lines from Eq.(6) and in green q-Gaussian best fits). The values of q and β are reported in the panels. Abscissa is given in half width at the half-height (HWHH) units. Note that we are changing the value of A. The corresponding q-Gaussian function has values of q and β changing accordingly.

4. Conclusion

In this article we have considered the Egelstaff-Schofield line shape, as used in Raman spectroscopy and discussed by Kirillov (1999, 2004). We have proposed its fit by means of q-Gaussian Tsallis functions. According to the examples proposed above, the q-Gaussian function is properly mimicking the Egelstaff-Schofield line shape. Let us stress that this profile has been introduced to fit the bands of first-order Raman scattering in ionic liquids. Since the Fourier transform of the Egelstaff-Schofield line shape (4),(5) is given by an analytical simple expression (3), we can use this expression in the evaluation of the Fourier transform of the q-Gaussian function. That is, the q-Gaussian function can be fitted by means of the function given in Eq.(6). Of Eq.(6), the Fourier transform is available analytically, according to Eq.(3). The expression (3) is therefore turning into a

good substitute of the Fourier transform of the q-Gaussian, which has been calculated by Rodrigues and Giraldi, 2016.

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