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Evolution equations for the probabilistic generalization of the Voigt profile function

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ABSTRACT

The spectrum profile that emerges in molecular spectroscopy and atmospheric radiative transfer as the combined effect of Doppler and pressure broadenings is known as the Voigt profile function. Because of its convolution integral representation, the Voigt profile can be interpreted as the probability density function of the sum of two independent random variables with Gaussian density (due to the Doppler effect) and Lorentzian density (due to the pressure effect). Since these densities belong to the class of symmetric Lévy stable distributions, a probabilistic generalization is proposed as the convolution of two arbitrary symmetric Lévy densities. We study the case when the widths of the distributions considered depend on a scale factor τ that is representative of spatial inhomogeneity or temporal non-stationarity. The evolution equations for this probabilistic generalization of the Voigt function are here introduced and interpreted as generalized diffusion equations containing two Riesz space-fractional derivatives, thus classified as *space-fractional diffusion equations of double order*.

1. Introduction

In molecular spectroscopy and atmospheric radiative transfer, the combined effects of Doppler and pressure broadenings lead to the Voigt profile function, which turns out to be the convolution of the Gaussian (due to the Doppler broadening) and the Lorentzian (due to the pressure broadening) distributions. The study of the Voigt profile is an old issue in the literature and many efforts have been directed to analyzing its mathematical properties and relations with other special functions and to obtaining its numerical computation, e.g. [1–10].

In most papers that have appeared in the literature, the Voigt profile is defined in terms of a single weight parameter, that is the ratio of the Lorentzian to the Gaussian width. In physical applications, this parameter indicates which distribution is the more important. Generally, the weight parameter is considered with a constant value fixed by the process. Here we are interested in studying the Voigt profile function when the widths are not constant but depend on a scale factor with a power law. Physically, the one-dimensional variable of the Voigt function is a wavenumber and this permits one to take into account spatial inhomogeneity or temporal non-stationarity when the scale factor is the distance from an origin or the elapsed time from an initial instant, respectively.

Since in probability theory the Gaussian and the Lorentzian distributions are known to belong to the class of symmetric Lévy stable distributions, in this framework we propose to generalize the Voigt function by adopting the convolution of two arbitrary symmetric Lévy distributions. Moreover, we provide the integro-differential equations with respect to the scale

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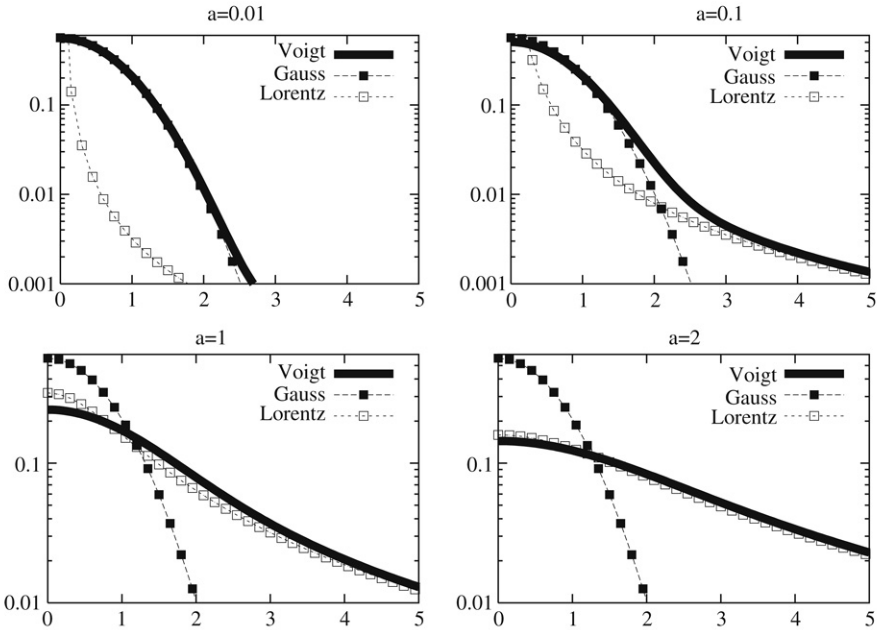

Fig. 1. Comparison between the Voigt, Gauss and Lorentz distributions with weight parameter $a = \omega_L/\omega_G = 0.01, 0.1, 1, 2$.

factor satisfied by the generalized Voigt profiles. These evolution equations can be interpreted as space-fractional diffusion equations of double order.

The paper is organized as follows. In Section 2 the basic definitions for the Voigt profile are given. In Section 3 the connection with the class of Lévy stable distributions and the probabilistic generalization are introduced. In Section 4 we derive the integro-differential evolution equations of the generalized Voigt function with respect to the scale factor. In Section 5 the limits of low and high scale factor values are investigated. Finally, Section 6 is devoted to the concluding remarks.

2. The Voigt profile function

The Gaussian $G(x)$ and the Lorentzian $N(x)$ profiles are defined as

$$G(x) = \frac{1}{\sqrt{\pi}\,\omega_G} \exp\left[-\left(\frac{x}{\omega_G}\right)^2\right], \qquad N(x) = \frac{1}{\pi\,\omega_L} \frac{\omega_L^2}{x^2 + \omega_L^2}, \tag{1}$$

where ω_G and ω_L are the corresponding widths. From their convolution we have the ordinary Voigt profile $V(x)$

$$V(x) = \int_{-\infty}^{+\infty} N(x-\xi) G(\xi) \mathrm{d}\xi = \frac{\omega_L/\omega_G}{\pi^{3/2}} \int_{-\infty}^{+\infty} \frac{\mathrm{e}^{-(\xi/\omega_G)^2}}{(x-\xi)^2 + \omega_L^2} \mathrm{d}\xi. \tag{2}$$

The main parameter of the Voigt function is the weight parameter a defined as $a = \omega_L/\omega_G$, which is the ratio of the Lorentzian and Gaussian widths and thus a measure of the relative importance of their influences on the properties of the process. Generally, the $a < 1$ case is important in astrophysics while $a > 1$ for spectroscopy of cold and dense plasma [3]. In particular, two limits can be considered: (i) $a \to 0$; (ii) $a \to \infty$. In the first case, the Lorentzian contribution is negligible with respect to the Gaussian one, while the inverse occurs in the second case; see Fig. 1. Let $\widehat{f}(\kappa)$ be the characteristic function, which is the Fourier transform of $f(x)$, so that

$$\widehat{f}(\kappa) = \int_{-\infty}^{+\infty} \mathrm{e}^{+\mathrm{i}\kappa x} f(x) \mathrm{d}x, \qquad f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}\kappa x} \widehat{f}(\kappa) \mathrm{d}\kappa. \tag{3}$$

Then $\widehat{V}(\kappa) = \widehat{G}(\kappa)\widehat{N}(\kappa) = \mathrm{e}^{-\omega_G^2 \kappa^2/4}\, \mathrm{e}^{-\omega_L|\kappa|}$. These formulae imply the following integral representation for the Voigt profile:

$$V(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}\kappa x} \mathrm{e}^{-\omega_G^2 \kappa^2/4 - \omega_L|\kappa|} \mathrm{d}\kappa = \frac{1}{\pi} \int_0^{+\infty} \mathrm{e}^{-\omega_L \kappa - \omega_G^2 \kappa^2/4} \cos(\kappa x) \mathrm{d}\kappa. \tag{4}$$

3. The probabilistic generalization of the Voigt profile function

It is well known that if X_1 and X_2 are two independent random variables with probability density function (PDF) q_1 and q_2, respectively, then the PDF $p(w)$ of the random variable $W = X_1 + X_2$ is given by the convolution integral

$$p(w) = \int_{-\infty}^{+\infty} q_1(w - x_2)q_2(x_2)\mathrm{d}x_2. \tag{5}$$

From (2) and (5), the Voigt profile can be seen as the resulting PDF of the sum of two independent random variables, one with Gaussian PDF and the other with Lorentzian PDF.

The Voigt function has been generalized in the literature in different ways; e.g. in [8] the integrand function in formula (4) is multiplied by a polynomial, in [11–13] the cosine function in (4) is replaced with the Bessel function and with the Wright function with one and more variables. In this paper we propose a probabilistic generalization in the framework of Lévy distributions. It is well known that the Gaussian and the Lorentzian distributions are two special cases of the class $\{L_\alpha(x)\}$ of the symmetric Lévy stable distributions, where α, $0 < \alpha \le 2$, is called the characteristic exponent. Writing the characteristic function (3) of the Lévy distributions as $\widehat{L_\alpha}(\kappa) = \mathrm{e}^{-|\kappa|^\alpha}$, the Gaussian and the Lorentzian profiles defined in (1) are recovered with $\alpha = 2$ and $\omega_G = 2$, and with $\alpha = 1$ and $\omega_L = 1$, respectively,

$$G(x) = L_2(x) = \frac{1}{2\sqrt{\pi}}\mathrm{e}^{-x^2/4}, \qquad N(x) = L_1(x) = \frac{1}{\pi}\frac{1}{x^2+1}. \tag{6}$$

The Voigt function can be straightforwardly generalized in a probabilistic sense by considering the sum of two independent random variables with symmetric stable densities. Mathematically, this corresponds to the convolution of two arbitrary symmetric Lévy densities of characteristic exponents α_1 and α_2. Denoting with $\mathcal{V}(x)$ the generalized Voigt function, its integral representation and its characteristic function $\widehat{\mathcal{V}}(\kappa)$ are

$$\mathcal{V}(x) = \int_{-\infty}^{+\infty} L_{\alpha_1}(x-\xi)L_{\alpha_2}(\xi)\mathrm{d}\xi, \qquad \widehat{\mathcal{V}}(\kappa) = \mathrm{e}^{-|\kappa|^{\alpha_1} - |\kappa|^{\alpha_2}}. \tag{7}$$

4. The evolution equations with respect to the scale factor

In the previous sections the widths ω_G and ω_L are considered to be constants and the weight parameter a fixed. However, unlike in the previous papers on the topic, we would like to know what happens when the widths ω_G and ω_L change in space or time with a power law with respect to a scale factor. This analysis is relevant in inhomogeneous or non-stationary cases, for which the scale factor corresponds to the distance from an origin or the elapsed time, respectively. Conversely, constant values of widths can be considered for homogeneous and stationary cases. In the present section we consider a scale factor τ for both spatial inhomogeneity and temporal non-stationarity.

It is well known that the Lévy density functions $L_\alpha(x, \tau)$ are the fundamental solutions of the space-fractional diffusion equation [14–16]

$$\frac{\partial L_\alpha(x,\tau)}{\partial \tau} = D_x^\alpha L_\alpha(x,\tau), \quad L_\alpha(x,0) = \delta(x), \quad 0 < \alpha \le 2, \tag{8}$$

where D_x^α is a pseudo-differential operator known as the Riesz space-fractional derivative of order α. Such a pseudo-differential operator is defined in terms of its symbol $-|\kappa|^\alpha$, i.e. the Fourier transform of $D_x^\alpha f(x)$ is $-|\kappa|^\alpha \widehat{f}(\kappa)$. We recall the explicit representations for $\alpha \neq 2$:

$$D_x^\alpha f(x) = \begin{cases} \dfrac{\Gamma(1+\alpha)}{\pi}\sin\left(\dfrac{\alpha\pi}{2}\right)\displaystyle\int_0^{+\infty}\frac{f(x+\xi) - 2f(x) + f(x-\xi)}{\xi^{1+\alpha}}\mathrm{d}\xi, & \alpha \neq 1 \\ -\dfrac{1}{\pi}\dfrac{\mathrm{d}}{\mathrm{d}x}\displaystyle\int_{-\infty}^{+\infty}\frac{f(\xi)}{x-\xi}\mathrm{d}\xi, & \alpha = 1 \end{cases} \tag{9}$$

and the limit $D_x^\alpha f(x) = \mathrm{d}^2 f/\mathrm{d}x^2$ when $\alpha = 2$. The solutions of (8) have the power law scaling property

$$L_\alpha(x,\tau) = \tau^{-1/\alpha} L_\alpha\left(\frac{x}{\tau^{1/\alpha}}\right). \tag{10}$$

For analytical and graphical representations of stable densities we refer the reader to [15]. We observe that the distributions defined in (10) are self-similar and they obey to the same power law scaling for all values of the scale factor τ. In particular, for $\alpha = 2$ and $\alpha = 1$ the Gaussian and the Lorentzian densities are recovered, respectively, and from (10) we have $\omega_G \propto \tau^{1/2}$ and $\omega_L \propto \tau$.

Following scaling (10), our generalized Voigt function (7) becomes

$$\mathcal{V}(x,\tau) = \tau^{-1/\alpha_1 - 1/\alpha_2}\int_{-\infty}^{+\infty} L_{\alpha_1}\left(\frac{x-\xi}{\tau^{1/\alpha_1}}\right) L_{\alpha_2}\left(\frac{\xi}{\tau^{1/\alpha_2}}\right)\mathrm{d}\xi, \tag{11}$$

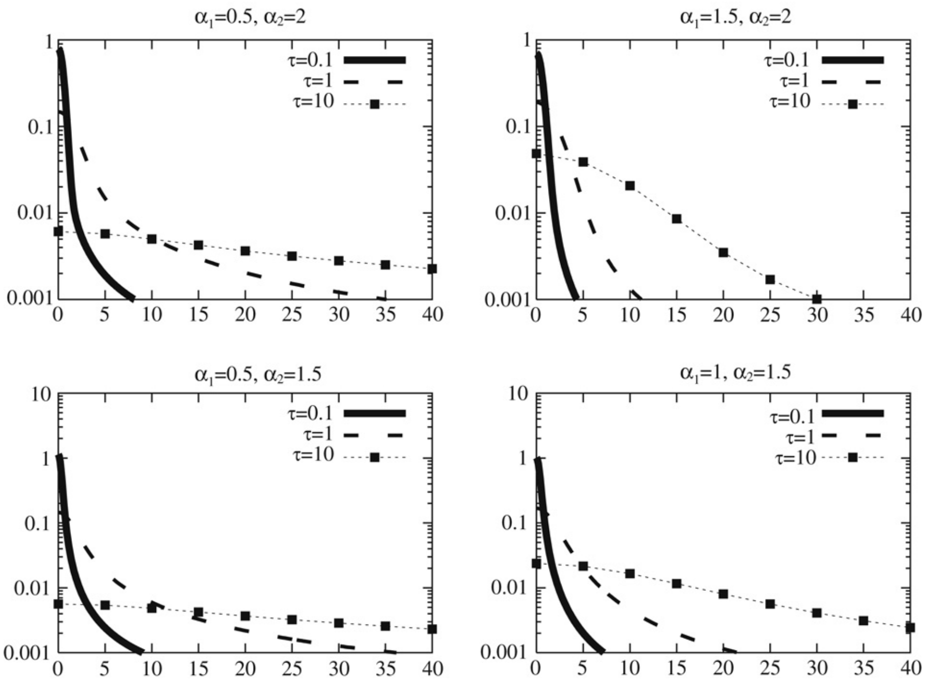

Fig. 2. The evolution of the generalized Voigt function $\mathcal{V}(x, \tau)$ for the pairs $(\alpha_1, \alpha_2) = \{(0.5, 2), (1.5, 2), (0.5, 1.5), (1, 1.5)\}$ with $\tau = 0.1, 1, 10$.

and its characteristic function is

$$\widehat{\mathcal{V}}(\kappa, \tau) = \mathrm{e}^{-|\kappa|^{\alpha_1}\tau - |\kappa|^{\alpha_2}\tau}. \tag{12}$$

In this case, it is possible to show that formula (11) is the solution of the following integro-differential equation:

$$\frac{\partial \mathcal{V}}{\partial \tau} = D_x^{\alpha_1}\mathcal{V}(x, \tau) + D_x^{\alpha_2}\mathcal{V}(x, \tau), \qquad \mathcal{V}(x, 0) = \delta(x). \tag{13}$$

In fact, after the Fourier transformation Eq. (13) becomes

$$\frac{\partial \widehat{\mathcal{V}}}{\partial \tau} = -|\kappa|^{\alpha_1}\widehat{\mathcal{V}}(\kappa, \tau) - |\kappa|^{\alpha_2}\widehat{\mathcal{V}}(\kappa, \tau), \qquad \widehat{\mathcal{V}}(\kappa, 0) = 1, \tag{14}$$

which is solved by (12). When $\alpha_1 = 1$ and $\alpha_2 = 2$ the integro-differential equation (13) is the evolution equation of the ordinary Voigt function. Eq. (13) can be classified as a *space-fractional diffusion equation of double order*. The evolution of $\mathcal{V}(x, \tau)$ for different pairs of (α_1, α_2) with $\tau = 0.1, 1, 10$ is shown in Fig. 2.

5. The asymptotic scaling laws for low and high scale factors

The Voigt (2) and the generalized Voigt (7) profiles are derived from the convolutions of two self-similar processes with different scaling laws and, as a consequence, the similarity is lost. However, we ask which are the scaling laws of the Voigt functions in the limits of low and high values of the scale factor τ.

Since for Lévy stable densities with $\alpha \neq 2$ the mean square displacement diverges, the same occurs for the ordinary and the generalized Voigt functions. Then, to analyze the scaling laws when $\tau \to 0$ and $\tau \to \infty$ the variance $\langle x^2 \rangle$ cannot be used. However, the scaling law of a Lévy stable process with characteristic exponent α can be studied by means of the quantity $\langle |x|^q \rangle^{1/q}$, with $0 < q < \alpha$. In this respect, we have

$$\langle |x|^q \rangle = 2\int_0^{+\infty} x^q \mathcal{V}(x, \tau)\mathrm{d}x = 2\,\mathcal{V}^*(q + 1, \tau), \quad 0 < q < \min\{\alpha_1, \alpha_2\}, \tag{15}$$

where $\mathcal{V}^*(s)$ is the Mellin transform of $\mathcal{V}(x)$, $x > 0$, defined as [17]

$$\mathcal{V}^*(s) = \int_0^{+\infty} \mathcal{V}(x)x^{s-1}\mathrm{d}x, \qquad \mathcal{V}(x) = \frac{1}{2\pi \mathrm{i}}\int_{c-\infty i}^{c+\infty i} \mathcal{V}^*(s)x^{-s}\mathrm{d}s. \tag{16}$$

Without loss of generality, let us state $\alpha_1 < \alpha_2$. Starting from (7) and following [7], the Mellin–Barnes integral representation of the generalized Voigt function $\mathcal{V}(x)$ is

$$\mathcal{V}(x,\tau) = \frac{\tau^{-1/\alpha_2}}{\alpha_2\pi}\frac{1}{2\pi \mathrm{i}}\int_{\mathcal{L}_0}\frac{1}{2\pi \mathrm{i}}\int_{\mathcal{L}_1}\Gamma(s_0)\Gamma(s_1)\Gamma\left(\frac{1-s_0-\alpha_1 s_1}{\alpha_2}\right)\tau^{s_0/\alpha_2+(\alpha_1/\alpha_2-1)s_1}\cos(s_0\pi/2)x^{-s_0}\mathrm{d}s_0\mathrm{d}s_1. \quad (17)$$

Hence its Mellin transform is

$$\mathcal{V}^*(s_1,\tau) = \frac{\tau^{(s_0-1)/\alpha_2}}{\alpha_2\pi}\Gamma(s_0)\cos(s_0\pi/2)\frac{1}{2\pi \mathrm{i}}\int_{\mathcal{L}_1}\Gamma(s_1)\Gamma\left(\frac{1-s_0-\alpha_1 s_1}{\alpha_2}\right)\tau^{(\alpha_1/\alpha_2-1)s_1}\mathrm{d}s_1, \quad (18)$$

and, finally,

$$\begin{aligned}\langle|x|^q\rangle &= 2\mathcal{V}^*(q+1,\tau)\\ &= -\frac{2\,\tau^{q/\alpha_2}}{\alpha_2\pi}\Gamma(q+1)\sin(q\pi/2)\frac{1}{2\pi \mathrm{i}}\int_{\mathcal{L}_1}\Gamma(s_1)\Gamma\left(\frac{-q-\alpha_1 s_1}{\alpha_2}\right)\tau^{(\alpha_1/\alpha_2-1)s_1}\mathrm{d}s_1. \end{aligned}\quad (19)$$

Applying the residue theorem to $\Gamma\left(\frac{-q-\alpha_1 s_1}{\alpha_2}\right)$, we obtain the convergent series for $\tau \to \infty$:

$$\langle|x|^q\rangle = -\frac{2\tau^{q/\alpha_1}}{\alpha_1\pi}\Gamma(q+1)\sin(q\pi/2)\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\Gamma\left(\frac{\alpha_2 n-q}{\alpha_1}\right)\tau^{-n(\alpha_2/\alpha_1-1)}. \quad (20)$$

Applying the residue theorem to $\Gamma(s_1)$, we obtain the convergent series for $\tau \to 0$:

$$\langle|x|^q\rangle = -\frac{2\,\tau^{q/\alpha_2}}{\alpha_2\pi}\Gamma(q+1)\sin(q\pi/2)\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\Gamma\left(\frac{\alpha_1 n-q}{\alpha_2}\right)\tau^{n(1-\alpha_1/\alpha_2)}. \quad (21)$$

In papers [14,16] the limits ($\tau \to 0$, $\tau \to \infty$) are computed using a different method but with the same results. Then the two limits under consideration give

$$\begin{cases}\langle x^q\rangle^{1/q} \propto \tau^{1/\alpha_2}, & \tau \to 0\\ \langle x^q\rangle^{1/q} \propto \tau^{1/\alpha_1}, & \tau \to \infty.\end{cases} \quad (22)$$

In the limit $\tau \to 0$, the corresponding scaling law of the generalized Voigt profile is governed by the Lévy density with the higher value of the characteristic exponent, while in the limit $\tau \to \infty$ it is governed by the one with the lower value. In particular, for the ordinary Voigt profile ($\alpha_1 = 1$, $\alpha_2 = 2$) the process scales as $\tau^{1/2}$ and τ for low and high values of the scale factor, respectively. This means that if the power law represents inhomogeneity, or non-stationarity, the resulting profile is approximated by a Gaussian for small distances from an origin, or small elapsed times, and it is approximated by a Lorentzian for large distances, or large elapsed times. This result is consistent with the usual limits $a \to 0$ and $a \to \infty$; see Fig. 1.

6. Conclusions

In the present paper we have considered the Voigt profile function and proposed a probabilistic generalization as the convolution of two arbitrary symmetric Lévy densities. Generally, the Voigt profile characteristics are studied with respect to a weight parameter a that is the ratio of Lorentzian to Gaussian widths, $a = \omega_L/\omega_G$, and it is assumed to be a constant property of the process. Conversely, here we have considered both widths depending on a scale factor τ that is representative of inhomogeneity or non-stationarity. We have introduced parametric integro-differential equations for the ordinary and the generalized Voigt functions. These integro-differential equations can be classified as *space-fractional diffusion equations of double order* because they include two Riesz space-fractional derivatives of different orders. In this respect, the present paper shows an application in physics of the distributed fractional derivatives formalism.

Finally, the limits of the Voigt function for low and high values of the scale factor are considered. The Voigt function turns out to be not self-similar, even if it is expressed as the convolution of two self-similar Lévy processes. Its scaling law is dominated by the Lévy density with the higher value of the characteristic exponent when $\tau \to 0$ and by that with the lower value when $\tau \to \infty$.

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