The Voigt Profile as a Sum of a Gaussian and a Lorentzian Functions, when the Weight Coefficient Depends on the Widths Ratio and the Independent Variable

H.O. Di Rocco[a,b,*] and A. Cruzado[c,d]

[a]Instituto de Física Arroyo Seco (IFAS), Universidad Nacional del Centro de la Pcia. de Buenos Aires
Pinto 399, 7000 Tandil, Buenos Aires, Argentina

[b]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)
Rivadavia 1917, C1033AAJ Buenos Aires, Argentina

[c]Facultad de Ciencias Astronómicas y Geofísicas, Universidad Nacional de La Plata, Paseo del Bosque s/n
1900 La Plata, Buenos Aires, Argentina

[d]Instituto de Astrofísica de La Plata (IALP-CONICET), Paseo del Bosque s/n
1900 La Plata, Buenos Aires, Argentina

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Assuming that $V(x) \approx (1-\mu)\ G_1(x) + \mu L_1(x)$ is a very good approximation of the Voigt function, in this work we *analytically* find μ from mathematical properties of $V(x)$. $G_1(x)$ and $L_1(x)$ represent a Gaussian and a Lorentzian function, respectively, with the same height and HWHM as $V(x)$, the Voigt function, x being the distance from the function center. In this paper we extend the analysis that we have done in a previous paper, where μ is only a function of a; a being the ratio of the Lorentz width to the Gaussian width. Using one of the differential equation that $V(x)$ satisfies, in the present paper we obtain μ as a function, not only of a, but also of x. Kielkopf first proposed $\mu(a,x)$ based on numerical arguments. We find that the Voigt function calculated with the expression $\mu(a,x)$ we have obtained in this paper, deviates from the exact value less than $\mu(a)$ does, specially for high $|x|$ values.

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1. Introduction

Let $V_a(x)$ be the Voigt profile obtained by convolution of $G(x)$ with $L(x)$.

Approximating the Voigt profile as

$$V_a(x) \approx (1-\mu)G_1(x) + \mu L_1(x), \tag{1}$$

in a previous paper [1] (PI hereafter), we analytically found μ as a function only on a, using the property of the normalized area.

In PI we did some general considerations showing that, using the expression (1) to represent the Voigt profile, we would rigorously calculate μ for each x value, to obtain μ as a function, not only on a, but also on x, as follows:

$$\mu(a,x) = \frac{V_a(x) - G_1(x)}{L_1(x) - G_1(x)}. \tag{2}$$

Even though the deviations of $V_a(x)$ calculated with $\mu(a)$ from its exact values are smaller than 0.5% relative to the peak value, as it was found in PI, it is useful, theoretically and practically, to calculate $\mu(a,x)$ from Eq. (2).

It is important to emphasize that, although Eq. (2) can be calculated for each x value for every profile $V_a(x)$, there is not a simple analytical expression for the right hand side of this expression. Indeed, if we expand in series, we see that the coefficients of $V_a(x)$ depend complicatedly on a, involving Kummer functions (or confluent hypergeometric functions), as was shown in [2].

The dependence on x was already introduced by Kielkopf [3] based on numerical arguments. In the present paper we find an analytical expression for $\mu(a,x)$ from one of the differential equation that $V(x)$ satisfies, which allow a better fit of $V_a(x)$ than $\mu(a)$ does, specially for high $|x|$ values.

We emphasize that, beyond the usefulness, this semitheoretical approach produces, in our opinion, a certain aesthetic satisfaction.

2. Analytical deduction of $\mu(a,x)$ using one of the differential equations satisfied by $V_a(x)$

$V_a(x)$ satisfies several differential equations, that can be found in [4] and [5]. Of direct usefulness in our case is the following:

$$V''(x) + \frac{4xV'(x)}{w_{\mathrm{G}}^2} + \left(\frac{4a^2+2}{w_{\mathrm{G}}^2} + \frac{4x^2}{w_{\mathrm{G}}^4}\right)V(x) = \frac{4a}{\pi w_{\mathrm{G}}^3}. \tag{3}$$

If $\mu = \mu(a,x)$ is assumed in Eq. (1), Eq. (3) results very complicated to our purposes, with terms like $\partial\mu/\partial x$ and $\partial^2\mu/\partial x^2$, and other such as $G_1'(x)$, $G_1''(x)$,

* corresponding author; e-mail: hdirocco@exa.unicen.edu.ar

$L_1'(x)$ and $L_1''(x)$. But, if the derivatives like $\partial\mu/\partial x$ and $\partial^2\mu/\partial x^2$ are negligible with respect to the derivatives $G_1'(x)$, $G_1''(x)$, $L_1'(x)$ and $L_1''(x)$, Eq. (3) becomes simple enough to obtain a function $\mu(a,x)$ that permits a better fit as compared with which has been obtained in PI, specially for high $|x|$ values.

Taking into account that the derivatives $G_1'(x)$ and $G_1''(x)$ are proportional to $G_1(x)$ and that $L_1'(x)$ and $L_1''(x)$ are proportional to $L_1(x)$, from Eq. (3) we obtain

$$-\frac{2\ln 2(1-\mu)G_1(x)}{\gamma_{\rm V}^2}+\frac{4(\ln 2)^2(1-\mu)x^2G_1(x)}{\gamma_{\rm V}^4}+\frac{8\mu x^2L_1(x)}{(x^2+\gamma_{\rm V}^2)^2}-\frac{2\mu L_1(x)}{x^2+\gamma_{\rm V}^2}+4x\left[-\frac{2\ln 2(1-\mu)xG_1(x)}{w_{\rm G}^2\gamma_{\rm V}^2}-\frac{2\mu xL_1(x)}{w_{\rm G}^2(x^2+\gamma_{\rm V}^2)}\right]+P(x)[(1-\mu)G_1(x)+\mu L_1(x)]=Q \quad (4)$$

with $P(x)=(4a^2+2)/w_{\rm G}^2+4x^2/w_{\rm G}^4$, $Q=4a/(\pi w_{\rm G}^3)$ and $\mu=\mu(a,x)$. Developing the former expression and collecting terms, we obtain

$$\mu(a,x)=\frac{f_{\rm G}(x)G_1(x)+f_{\rm Q}(x)Q}{f_{\rm L}(x)L_1(x)+f_{\rm G}(x)G_1(x)}, \quad (5)$$

where

$$f_{\rm Q}(x)=\gamma_{\rm V}^8w_{\rm G}^2+2\gamma_{\rm V}^6w_{\rm G}^2x^2+\gamma_{\rm V}^4w_{\rm G}^2x^4, \quad (6)$$

$$f_{\rm G}(x)=-8(\ln 2)^2\gamma_{\rm V}^2w_{\rm G}^2x^4-4(\ln 2)^2\gamma_{\rm V}^4w_{\rm G}^2x^2+2(\ln 2)\gamma_{\rm V}^6w_{\rm G}^2-2P(x)\gamma_{\rm V}^6w_{\rm G}^2x^2-P(x)\gamma_{\rm V}^4w_{\rm G}^2x^4-4(\ln 2)^2w_{\rm G}^2x^6+8(\ln 2)\gamma_{\rm V}^6x^2+16(\ln 2)\gamma_{\rm V}^4x^4+8(\ln 2)\gamma_{\rm V}^2x^6-P(x)\gamma_{\rm V}^8w_{\rm G}^2+4(\ln 2)\gamma_{\rm V}^4w_{\rm G}^2x^2+2(\ln 2)\gamma_{\rm V}^2w_{\rm G}^2x^4 \quad (7)$$

and

$$f_{\rm L}(x)=6\gamma_{\rm V}^4w_{\rm G}^2x^2-2\gamma_{\rm V}^6w_{\rm G}^2+2P(x)\gamma_{\rm V}^6w_{\rm G}^2x^6+P(x)\gamma_{\rm V}^4w_{\rm G}^2x^4+P(x)\gamma_{\rm V}^8w_{\rm G}^2-8\gamma_{\rm V}^6x^2-8\gamma_{\rm V}^4x^4. \quad (8)$$

In spite of neglecting the derivatives $\partial\mu/\partial x$ and $\partial^2\mu/\partial x^2$, the $\mu(a,x)$ values we obtain from Eq. (5) depart very little from those we obtain from Eq. (2).

2.1. Limit cases

In order to achieve the final analytic expression we are searching, we need to know the behavior of $\mu(a,x)$ near $x=0$ and for $x\to\infty$.

Taking into account that $\mu(a,x)$ is an even function of x, we analyse those limit cases in the following sections.

2.1.1. $\mu(a,x)$ value at $x=0$

Evaluating $f_{\rm G}(x)$, $f_{\rm L}(x)$ and $f_{\rm Q}(x)$ at $x=0$, Eq. (5) can be written as

$$\mu(a,0)=-2.258891354+\frac{6.517782707a^2\gamma_{\rm V}^2}{w_{\rm G}^2}+\frac{3.258891354\gamma_{\rm V}^2}{w_{\rm G}^2}-\frac{2.888117265\times 4a\times\gamma_{\rm V}^3}{\pi w_{\rm G}^3}. \quad (9)$$

Taking into account that $\gamma_{\rm V}/w_{\rm G}=b_{1/2}(a)$, as we see in PI, we finally obtain

$$\mu(a,0)=-2.258891354+6.517782707a^2b_{1/2}^2(a)+3.258891354b_{1/2}^2(a)-\frac{2.888117265\times 4a\times b_{1/2}^3(a)}{\pi}. \quad (10)$$

Comparing $\mu(a,0)$ given by the former expression with $\mu(a)$ obtained in PI and given by

$$\mu(a)=\frac{b_{1/2}(a)\,{\rm e}^{a^2}\varPhi_{\rm c}(a)-\sqrt{\ln(2)}}{b_{1/2}(a)\,{\rm e}^{a^2}\varPhi_{\rm c}(a)\left(1-\sqrt{\pi\ln(2)}\right)}, \quad (11)$$

we conclude that $\mu(a,0)<\mu(a)$ for every a value.

2.1.2. $\mu(a,x)$ value near $x=0$

It is known that a even function can be expanded as an even power series about zero as $f(x)\simeq A_0+A_1x^2+\ldots$ But, since $\mu(a,x)$ is expressed as a quotient (Eq. (5)), we expand numerator and denominator to obtain $\mu(a,x)$ as a quotient of power series about zero.

Then, at $x\simeq 0$ it is verified

$$\mu(a,x\to 0)=\frac{\mu_{\rm app}(a,0)+Ax^2(+Bx^4+\ldots)}{1+Cx^2(+Dx^4+\ldots)}. \quad (12)$$

2.1.3. $\mu(a,x)$ value at $x\to\infty$

Taking into account that $G_1(x)$ tends to zero much faster than Q and $L_1(x)$, from Eq. (5) it is obtained

$$\lim_{x\to\infty}\mu(a,x)\sim\lim_{x\to\infty}\frac{f_{\rm Q}(x)Q}{f_{\rm L}(x)L_1(x)},$$

where

$$\lim_{x\to\infty}f_{\rm Q}(x)\sim\gamma_{\rm V}^4w_{\rm G}^2x^4,$$
$$\lim_{x\to\infty}f_{\rm L}(x)\sim\frac{4\gamma_{\rm V}^4x^6}{w_{\rm G}^2},$$

and

$$\lim_{x\to\infty}L_1(x)\sim\frac{b_{1/2}(a)\exp(a^2)\varPhi_{\rm c}(a)\gamma_{\rm V}}{\sqrt{\pi}x^2}.$$

It would be worthwhile to point out that, both, $\lim_{x\to\infty}(f_{\rm Q}(x)Q)$ and $\lim_{x\to\infty}(f_{\rm L}(x)L_1(x))$ are of fourth degree on x.

Taking into account that $\gamma_{\rm V}=w_{\rm G}b_{1/2}(a)$, as we see in PI, we obtain

$$\mu(a,\infty)=\lim_{x\to\infty}\mu(a,x)\sim\frac{a}{\sqrt{\pi}\left[b_{1/2}(a)\right]^2\exp(a^2)\varPhi_{\rm c}(a)}, \quad (13)$$

depending on a, as expected.

Comparing the $\mu(a)$ values given by the last expression with that obtained from Eq. (11), $\mu(a,\infty)<\mu(a)$ is verified.

3. On the values of the fitting formula at $x=0$ and $x=\pm\gamma_{\rm V}$

Since $G_1(x)$, $L_1(x)$, and $V_a(x)$ take, all of them, by definition, the same value at $x=0$ and $x=\pm\gamma_{\rm V}$, it is clear that numerator and denominator in Eq. (2) are null at those x values, making it impossible to evaluate μ.

The denominator of expression (5), $f_{\rm L}(x)L_1(x) + f_{\rm G}(x)G_1(x)$, instead, is null at $x \approx \pm\gamma_{\rm L}$; please note the symbol $\approx$. For all those x values for which $f_{\rm L}(x)L_1(x) + f_{\rm G}(x)G_1(x)$ is null, $\mu(a,x)$ must not be calculated from Eq. (5).

All the x values for which $\mu(a,x)$ cannot be calculated from Eq. (5), divided by $a \times \gamma_{\rm G}/\sqrt{\ln 2}$, depend only on $a = w_L/w_{\rm G}$ and are given by the following universal algorithm: we call $\rho(a)$ the function that results after finding the roots of

$$\frac{f_L(x)L_1(x) + f_{\rm G}(x)G_1(x}{a \times \gamma_{\rm G}/\sqrt{\ln 2}}. \tag{14}$$

$\rho(a)$ can be numerically fitted, with a correlation coefficient of $R^2 = 1$, by the following universal function on a:

$$\rho(a) = \frac{a_0 + a_2 a^2 + a_4 a^4 + a_6 a^6}{1 + \beta_2 a^2 + \beta_4 a^4 + \beta_6 a^6}, \tag{15}$$

where $a_0 = 5.9966$, $a_2 = 72.0531$, $a_4 = -37.0930$, $a_6 = 156.6913$, $\beta_2 = 102.8163$, $\beta_4 = -66.6862$, and $\beta_6 = 156.4950$.

Though $a \times \gamma_{\rm G}/\sqrt{\ln 2}$ is exactly $w_{\rm L}$, it is clear that $w_{\rm L}$ is not an independent parameter entering Eq. (14). $w_{\rm L} = a \times w_{\rm G} = a \times \gamma_{\rm G}/\sqrt{\ln 2}$ enter Eq. (14) only through a.

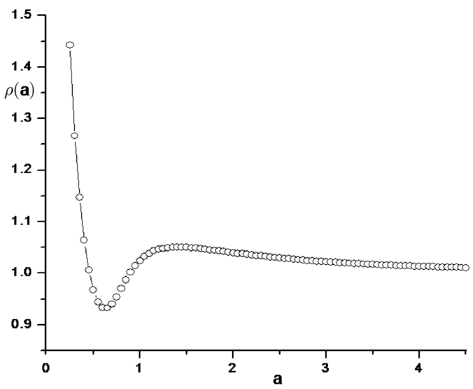

Fig. 1. Roots of $[f_{\rm L}(x)L_1(x) + f_{\rm G}(x)G_1(x)]$ divided by $w_{\rm L} \equiv a\gamma_{\rm G}/\sqrt{\ln 2}$. Points of this plot multiplied by $w_{\rm L}$ should not be used to calculate $\mu(a,x)$ from Eq. (5) (see text).

$\rho(a)$ is represented in Fig. 1 for $0.25 \le a \le 4.5$. For lower or higher a values $V_a(x)$ depart very little from a Gaussian and/or a Lorenztian profile, if the noise is $\ge 1\%$ (easily reached in laboratory experiments).

4. Indicators of the fit quality

As it was set in PI, we can test the quality of our fit by normalizing the deviation of $V(\mu_a, x)$ from the exact value

a) to the peak value, $V_a(0)$

$$\Delta_1 = \frac{V_a(x) - V(\mu(a), x)}{V_a(0)} \quad \text{or}$$

or b) to the value at x, $V_a(x)$

$$\Delta_2 = \frac{V_a(x) - V(\mu(a), x)}{V_a(x)}.$$

Criterion (b) is much more sensitive, since, both, the numerator and the denominator of Δ_2 are increasingly small numbers.

We are going to see in Sect. 6 that the fit obtained using $V[\mu(a,x), x]$ is better than the one obtained in PI using $V[\mu(a), x]$, specially for high $|x|$ values.

5. The recipe to construct $\mu(a,x)$

In order to calculate $\mu(a,x)$, Eqs. (5)-(8) should be used, with $\gamma_{\rm V}$ obtained from the experimental data. For a selected value of a, the needed $w_{\rm G}$ value is determined by considering the relation between $\gamma_{\rm V}$ and $w_{\rm G}$ given by $\gamma_{\rm V} = w_{\rm G} b_{1/2}(a)$, as it is explained in PI.

The calculation must be done taking into account the algorithm (14), that considers the problem of annulment of both, numerator and denominator cited in Sect. 3. Then, in first place, $\rho(a)$ must be obtained from Eq. (15) for the selected value of a, in order to excluded the values $x \approx \pm\rho(a) \times a \times \gamma_{\rm G}/\sqrt{\ln 2}$ ($\equiv \pm w_{\rm L} \times \rho(a)$) from the calculations.

Although at this point we have all that is necessary to carry out the calculation of $V_a(x) \approx (1-\mu(a,x))G_1(x) + \mu(a,x)L_1(x)$, it can be interesting to see the behavior of $\mu(a,x)$, which will be presented in the following section.

6. Results and discussions

In Fig. 2 $\mu(a,x)$ as a function of a, for two different x values, is shown. Note the divergences for $a \approx x/w_{\rm G}$.

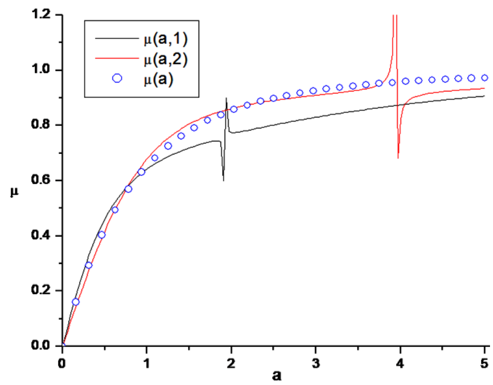

Fig. 2. $\mu(a,x)$ as a function on a for two different x values. $\mu(a,1)$ and $\mu(a,2)$ are displayed as functions on a for $w_{\rm G} = 1$. $\mu(a)$, as obtained in PI, is also shown for comparison.

In Fig. 3 $\mu(a,x)$ as a function of x is shown, for two different a values. In this case, divergences are observed for $x \approx a w_{\rm G} \equiv w_{\rm L}$.

All the curves in Fig. 2 and Fig. 3 have been obtained by adopting $w_{\rm G} = \gamma_{\rm G}/\sqrt{\ln 2} = 1$ in the calculations, but a similar behavior is observed for all $w_{\rm G}$ values. In both figures $\mu(a,x)$ is displayed including the divergences, in order to see its real behaviour. In both figures $\mu(a)$, as obtained in PI, is also shown for comparison.

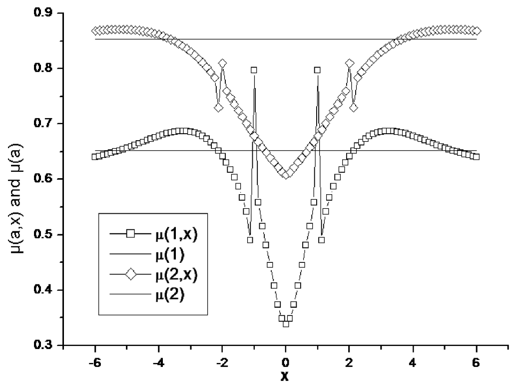

Fig. 3. $\mu(a,x)$ as a function on x for two different a values. $\mu(1,x)$ and $\mu(2,x)$ are displayed as functions on x for $w_{\mathrm{G}} = 1$. $\mu(1)$ and $\mu(2)$, as obtained in PI, are also shown for comparison.

In Fig. 1 all x values for which $f_{\mathrm{L}}(x)L_1(x) + f_{\mathrm{G}}(x)G_1(x)$ is null, and, therefore, for which $\mu(a,x)$ cannot be calculated from Eq. (5), are represented (divided by $a \times \gamma_{\mathrm{G}}/\sqrt{\ln 2}$) for $0.25 \le a \le 4.5$.

In Figs. 4 and 5 we show $\Delta_1 = [V_a(x) - V(\mu(a,x),x)] / V_a(0)$ and $\Delta_2 = [V_a(x) - V(\mu(a,x),x)]/V_a(x)$ for μ as a function only on a, as we have obtained in PI, and for μ as a function on a and x, as we have obtained in the present paper. It is clear from these figures that an improved fit is obtained when μ as a function, not only on a, but also on x, is considered. A good fit is also obtained for high $|x|$ values, which is not obtained by us in PI, nor by other authors in [3] and Liu [6], when μ as a function only on a is considered.

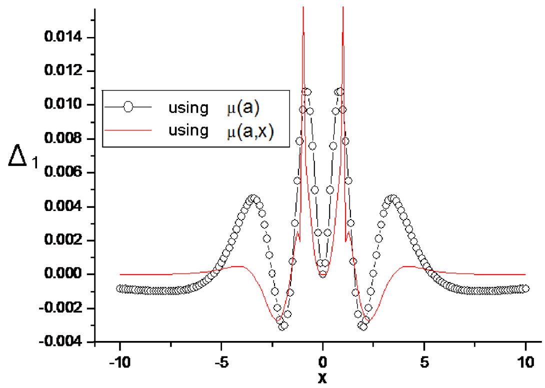

Fig. 4. Δ_1 as a function on $|x|$ using $\mu(a)$, as obtained in PI, and $\mu(a,x)$, as obtained at the present paper. The numerical divergences can be observed.

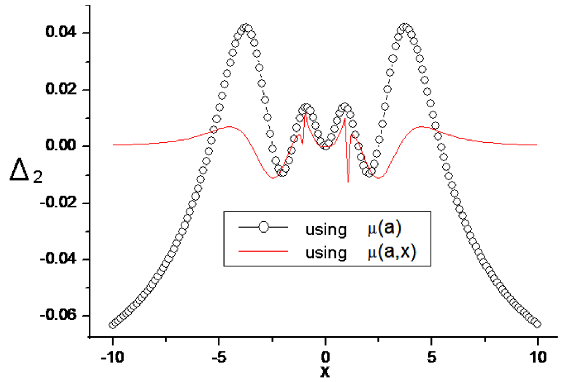

Fig. 5. As in Fig. 4, but for Δ_2.

7. Conclusions

At the present paper we let μ to be a function, not only on a, but also on x. Using one of the differential equations that $V(x)$ satisfies, and neglecting the derivatives $\partial\mu/\partial x$ and $\partial^2\mu/\partial x^2$ with respect to the derivatives $G_1'(x)$, $G_1''(x)$, $L_1'(x)$, and $L_1''(x)$, we have been able to obtain: (i) an analytic expression for $\mu(a,x)$, (ii) relative fits, Δ_1 and Δ_2, better than those we have obtained in PI, (iii) a universal table of values, so that, if we multiply them by $w_{\mathrm{L}} \equiv a \times \gamma_{\mathrm{G}}/\sqrt{\ln 2}$, we obtain the x values for which $\mu(a,x)$ cannot be calculated with the expression we have found.

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