Doppler Line Broadening from the Asymptotic Cauchy Distribution

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The half-width of Doppler broadening is derived without assuming Maxwell's distribution for the velocities of the radiating atoms. In the absence of Doppler broadening there is only natural radiation broadening, and by thermalizing the asymptotic Cauchy distribution one obtains asymptotic double exponential distributions for the largest (blue) and smallest (red) values of the frequency shift. These are the relevant extreme value distributions for largest and smallest values. Since the mean values are opposite and equal there is a zero shift in the line, while the standard deviation gives an expression for the half-width to within 2% of the Doppler half-width obtained from the Maxwellian when the damping coefficient is taken as the ratio of the natural radiation damping coefficient to the fine structure constant.

1. Lorentzian versus Maxwellian

Natural broadening, which is governed by a Lorentz distribution, is converted into Doppler broadening, which is assumed to be characterized by a Maxwell distribution, when the atoms are set into motion by placing them in contact with a heat reservoir and, due to the linear relation between velocity and frequency shift, the latter will also be governed by a Maxwell distribution. If, in the absence of Doppler broadening, there is only natural radiation broadening, it is unclear how the contact with a heat reservoir converts a Lorentzian into a Maxwellian distribution.

In fact, the assumption of a Maxwellian distribution is not necessary in order to derive the Doppler line breadth. In this paper we show how the asymptotic Cauchy distribution can be transformed into double exponential distributions for largest and smallest values of the frequency shift by coupling the system to a thermal reservoir. The "thermalization" of the asymptotic Cauchy distribution, leading to the asymptotic double exponential distributions for largest and smallest frequency shift, shows how the red and blue shifts cancel, on the average, and their common standard deviation gives the Doppler half-width to within 2% of the value determined on the assumption that the velocity, and hence frequency, distributions are Maxwellian.

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2. Asymptotic Lorentzian and Extreme Value Distributions

The Cauchy probability density [1],

$$g(x) = \frac{1}{\pi\gamma} \frac{1}{1+(x/\gamma)^2}, \tag{1}$$

is a classic example of a *Häufigkeitsverteilung* or "occurrence distribution": the intensity at the frequency ν is proportional to the probability of the occurrence of this frequency [2]. In spectroscopy, (1) goes under the name of Lorentz, who derived it from a kinetic approach to pressure broadening [3], where $x = \Delta\nu \equiv \nu' - \nu_0$ is the shift from the central frequency ν_0, and γ is the (natural) radiation damping coefficient.

The Cauchy density (1) is an extreme value, or *stable*, density with a characteristic exponent of unity. It separates *strictly stable* distributions, with characteristic exponents in the open interval (0, 1) from *quasi-stable* distributions, with characteristic exponents in the semi-open interval (1, 2], where the upper end point corresponds to the normal distribution. Like all stable distributions, the Cauchy distribution is *infinitely divisible*, meaning that the common distribution of a set of independent random variables and the distribution of their sum differ only by scale and location parameters [4]. The property of infinite divisibility guarantees that the convolution of two Lorentzian line shapes will also be Lorentzian.

Upon integration of (1) we get the cumulative probability distribution

$$G(x) = \frac{1}{2} + \frac{1}{\pi}\arctan(x/\gamma), \tag{2}$$

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which is symmetrical about the median zero, has no moments, and is unlimited in both directions. For large positive values of x, the usual series expansion leads to

$$G(x) = 1 - \gamma/\pi x + O(x^{-3}),$$

or

$$G(x) = e^{-\gamma/\pi x}, \tag{3}$$

as $x \to \infty$.

The Laplace transform of the asymptotic probability density,

$$g(x) = \frac{\gamma}{\pi x^2} e^{-\gamma/\pi x}$$

corresponding to (3), can be expressed in terms of a Basset function:

$$\mathscr{L}(\lambda) = \frac{\gamma}{\pi} \int_0^\infty e^{-\lambda x} \frac{e^{-\gamma/\pi x}}{x^2} \mathrm{d}x = 2\sqrt{\gamma\lambda/\pi}\, K_{-1}(2\sqrt{\gamma\lambda/\pi}),$$

where λ is the Laplace transform variable. Since we are interested in large x, or equivalently small λ, we may approximate the Basset function K_{-1} $(=K_1$ since it is even with respect to its order) by [5]

$$K_1(z) \simeq (1/z) + (z/2)\ln(z/2).$$

We then obtain the logarithm of the generating function as [6]

$$\ln \mathscr{L}(\lambda) = \left(\frac{\gamma\lambda}{\pi}\right) \ln\left(\frac{\gamma\lambda}{\pi}\right). \tag{4}$$

The strict convexity of the logarithm of the generating function, with respect to λ, ensures that its Legendre transform,

$$\Delta S(x) = \ln \mathscr{L}(\lambda) - (\ln \mathscr{L})'\lambda = -\gamma\lambda/\pi, \tag{5}$$

will be a strictly concave function, with respect to x. The prime denotes differentiation with respect to λ. The characterizing property of entropy is its concavity [7], and, apart from an additive constant, it is defined as the Legendre transform of the logarithm of the generating function [8]. For extreme value distributions, ΔS represents the reduction in entropy due to a constraint which takes the system out of its natural, unperturbed state [9]. In the present instance, the reduction in entropy is due to a shift $\Delta\nu = \nu - \nu_0$ in the central frequency, in energy, units where Boltzmann's constant is unity.

According to the Legendre transform definition of dual variables, the Legendre duals to $\pm\lambda$ are

$$(\ln \mathscr{L})' = \frac{\gamma}{\pi}\left[\ln\left(\frac{\gamma\lambda}{\pi}\right) + 1\right] = \pm x. \tag{6}$$

Upon introducing (6) into (5) we obtain the expressions

$$\Delta S_{\pm}(x) = -\exp[\pm(\pi x/\gamma \mp 1)] \tag{7}$$

for the reduction in entropy due to line shifts. More specifically, since it will turn out that $\gamma\lambda/\pi \ll 1$ [cf. (10) below], the $+$ sign in (6) corresponds to $x = \nu - \nu_0 < 0$, or a red shift, while the $-$ sign corresponds to a blue shift.

In the latter case, Boltzmann's principle for extreme value distributions [9],

$$G_-(x) = \exp(\Delta S_-(x)) = \exp\{-e^{-(\pi x/\gamma + 1)}\}, \tag{8}$$

converts the asymptotic Cauchy distribution (3) into an asymptotic double exponential distribution of the largest value of the frequency shift. The symmetry principle between the asymptotic distributions of largest and smallest values is [10]

$$G_-(x_-) = 1 - G_+(-x_+),$$

where $G_+(-x_+)$ is the asymptotic distribution of the smallest value. It is expressed in terms of its tail as [9]

$$1 - G_+(x) = \exp(\Delta S_+(x)) = \exp\{-e^{(\pi x/\gamma - 1)}\}. \tag{9}$$

Hence, the Legendre transform (5) together with (6) convert the asymptotic Cauchy distribution (3) for large positive values of the frequency shift into asymptotic double exponential distributions, (8) and (9), corresponding to extreme blue and red shifts, respectively.

Differentiating the expressions for the entropy reduction (7) we get

$$\mp S'_{\pm}(x) = \frac{\pi}{\gamma}\exp\{\pm(\pi x/\gamma \mp 1)\} = \frac{h}{T} = \lambda, \tag{10}$$

where the second and third equalities in (10) follow from the second law and the definition of the Legendre dual variable, respectively. In the expression for the second law, we have used the fact that energy is the product of Planck's constant h and the frequency, and T is the absolute temperature measured in energy units. In order to make the definitions of the Legendre conjugates (6) and (10) compatible with one another, it is necessary to introduce "$\mp$" in the definition of the absolute temperature. The entropy is always a monotonically increasing function of the absolute value of the frequency shift; in other words, the temperature is always positive, independent of whether the shifts are toward the blue or the red. The smaller the frequency shift, the smaller the reduction in entropy. And since we can associate an entropy to every non-vanishing frequency interval, it must also have a well-defined temperature.

3. Doppler Half-Width

Since the averages of the extremes are equal in magnitude and opposite in sign, cf. (6),

$$-\overline{(\Delta\nu)_-} = \overline{(\Delta\nu)_+} = (\ln \mathscr{Z})' = \frac{\gamma}{\pi}\left(\ln \frac{\gamma h}{\pi T} + 1\right),$$

the blue and red shifts cancel each other on the average. On the contrary, the variances of the distributions are equal [1],

$$\overline{(\Delta\nu)^2_-} = \overline{(\Delta\nu)^2_+} = (\ln \mathscr{Z})'' = \gamma T/\pi h\,,$$

and give rise to a finite line width. The half-width is proportional to the standard deviation,

$$\delta \sim \sqrt{\gamma T/\pi h}\,. \tag{11}$$

If the damping coefficient happens to be the ratio of the natural radiation damping constant to the fine structure constant,

$$\gamma = \frac{2}{3}\,\frac{(2\pi)^2 e^2 \nu_0^2}{m c^3}\cdot\frac{hc}{2\pi e^2} = \frac{4\pi}{3}\,\frac{h\nu_0^2}{mc^2}\,,$$

[1] The variances may be calculated by differentiating twice the reduction in the entropies, (7), and using the fact that the Legendre duals satisfy $(\ln \mathscr{Z})''(\lambda) = -1/S''(x)$, where x and λ are related by (6).

where c is the speed of light in vacuum, then the half-width (11) is

$$\delta \sim \frac{\nu_0}{c}\sqrt{4T/3m}\,. \tag{12}$$

We can appreciate the fact that the division of the natural radiation damping constant by the fine structure constant eliminates the electric charge e and expresses the damping constant solely in terms of the central frequency ν_0 and mass m. And with m as the mass of the radiating atom, (12) is within 1.93% of the Doppler half-width,

$$\delta_{\text{Doppler}} = \frac{\nu_0}{c}\sqrt{2T \ln 2/m}\,,$$

which is derived under the assumption that the velocities are governed by a Maxwell distribution and consequently, to lowest order, the frequency shift is also Maxwellian. It is quite remarkable that the variances of entirely different radiation distributions, implying totally different radiative mechanisms, coincide when the damping coefficient undergoes change of the scale, set by the fine structure constant [11].

The fact that the ratio of natural to Doppler broadening is of the order of the fine structure constant strengthens our belief that characteristic phenomena, as well as characteristic dimensions, appear as simple powers of the fine structure constant. Moreover, there is no mysterious transformation of a Lorentzian into a Maxwellian distribution upon thermalization, and no particular assumptions need be made regarding the nature of the motion of the radiating atoms and the law of equipartition of energy which is explicitly contained in Maxwell's velocity distribution.

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