

Neutral Particles Broadening in the Frequency Fluctuation Approach

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ABSTRACT: The dynamics effect on spectral line shape formation is the long standing problem. Various stochastic methods are developed to solve it. The Frequency Fluctuation Model (FFM) is believed to be the most accurate approach of account for thermal motion influence on a spectral profile. The examination of the FFM for van der Waals broadening is presented. Good agreement of the FFM with Chen and Takeo theory is shown. The applicability of the FFM for neutral particles broadening in the impact limit is discussed.

1. INTRODUCTION

The microfield dynamics effect on a spectral line shape is the long standing problem [1, 2]. The best agreement with the results of Molecular Dynamics (MD) simulations provides the Frequency Fluctuation Model (FFM) [3]. There are a lot of applications of the FFM to different Stark Broadening problems (see, e.g., [4, 5, 6, 7, 8, 9]). The Frequency Fluctuation Model procedure was reformulated in terms of simple analytical expression [10]. In the framework of this approach the FFM provides the method of simple and fast spectral line shape calculations.

The FFM was never used for the Stark broadening by neutral particles. Most of the material on the van der Waals broadening accumulated by the end of the 1960s is presented in the famous review of S. Chen and M. Takeo [11]. Moreover, in this paper, the authors present the line shape calculation method (based on the work of P.W. Anderson and J.D. Talman [12]) for arbitrary values of temperatures and densities. The Chen and Takeo results (CT) are very old. Nevertheless, they are in good agreement with experimental data and can be used for the examination of the FFM theory. Moreover, the analytical expressions for the line shape presented in [11] are very cumbersome. The direct use of the CT theory in numerical calculations requires significant computational resources. Therefore, the FFM may provide simple analytical expressions for the description of the van der Waals broadening.

The FFM has a drawback. It does not reproduce the impact width correctly. This circumstance was noted in the original paper [3]. Furthermore, it was directly shown in [8, 13]. However, this problem was solved for the linear Stark effect. The resolution consists of the dependence of the jumping frequency, which characterizes the rate of change of the microfield on the energy shift. This dependence is obtained by comparing the analytical calculations with MD in the paper [8]. The authors of the work [13] overcame this problem in the alternative way. They used the asymptotic expression of the jumping frequency obtained by S. Chandrasekhar and J. von Neumann [14], who derived this for the description of the stellar dynamics.

The detailed analysis of the FFM results for different plasma parameters is presented in the paper [13]. It is demonstrated that the accounting for the dependence of the jumping frequency on the energy shift leads to the correct behaviour of the spectral line width in the impact limit for the linear Stark effect. The difference between the

modified and the original versions of the FFM for moderate values of temperatures and densities is insignificant. Therefore, accounting for the jumping frequency dependence on the electric strength fields the simple analytical theory which provides the correct results for a wide range of plasma parameters. The situation is more complicated for the quadratic Stark effect. In this case, the problem of reproducing the impact width is not solved in this way. However, for realistic plasma parameters, the FFM with the constant jumping frequency provides quite satisfactory results.

Usually, the van der Waals broadening can be described in terms of the impact approximation [15]. Furthermore, there are modern works related to the spectral line broadening by neutral atoms and molecules (see, e.g., [16, 17]). Therefore, the main goal of the present paper is the examination of the FFM for the van der Waals interaction. The second aim of this work is to provide the simple analytical algorithm for the line shape calculations for low temperatures (less than 300K) or high densities.

In the present paper, we focused on the spectral broadening by neutral atoms and molecules. The detailed description of the analytical FFM formulation and the discussion of the dynamics effect on the spectral line formation are given in [13]. For convenience, an abridged version was presented below.

The effect of a multiparticle electric field on molecular and atomic spectra is characterized by the ratio of the jumping frequency and the Stark shift:

$$\nu = \frac{\Omega_J}{\Omega_S^n}, \quad (1)$$

where

$$\Omega_J = N^{1/3} v_T, \quad (2)$$

$$\Omega_S^n = C_n^S N^{n/3}. \quad (3)$$

Here, N and v_T are, respectively, the density and the thermal velocity of interacting particles; C_n^S is the constant of the Stark effect; Ω_J is called the jumping frequency. The potential of binary interacting particles has the following form:

$$V(r) = \frac{C_n^S}{R^n}. \quad (4)$$

In the present paper we considered the case of $n = 6$, which corresponds to a wide class of van der Waals interactions. The interaction between atoms and molecules often differs from 4. However, we focused on the examination of the FFM by the comparison with CT results, which were obtained for the potential 4.

The transition from binary to non-binary type of interactions is often characterized by the number of particles in the Weisskopf sphere h . For $n = 6$ in Expression 4, it equals to [15]

$$h = \left(\frac{3\pi C_6^S}{8 v_T} \right)^{3/5} N. \quad (5)$$

Parameter h also determines the transition from the static theory to the impact limit. The number of particles in the Weisskopf sphere is connected with ν by the simple relation

$$h \sim \nu^{-3/5}. \quad (6)$$

Using the results from [15], we could estimate the parameter ν . For $T \approx 300 - 5000$ K, ν approximately equals to:

$$\nu \approx (10^{35} - 10^{38}) N^{-5/3}, \quad (7)$$

where N is expressed in cm^{-3} .

All over the paper, atomic units were used ($e = m = \hbar = 1$, where: e —the elementary charge; m —the mass of an electron; \hbar is the Planck constant). Furthermore, for the sake of simplicity, we used the reduced detuning: $z = \Delta\omega/\Omega_S^n$.

The FFM procedure is equivalent to the method of the kinetic equation with strong- collision integral, which describes an intensity exchange between different regions of a static profile [10]. The frequency of the exchange equals to ν . The solution of this equation led to the following expression for the resulting profile:

$$I(z) = \frac{1}{\pi} \operatorname{Re} \frac{\int \frac{W(z') dz'}{\nu + i(z-z')}}{1 - \nu \int \frac{W(z') dz'}{\nu + i(z-z')}} \tag{8}$$

where $W(z)$ is the normalized static profile. Note, that when $\nu \rightarrow 0$, $I(z)$ turns into $W(z)$.

The Formula 8 can be rewritten in more convenient form:

$$I(z) = \frac{\nu}{\pi} \frac{J_0(z) J_2(z) - J_1^2(z)}{J_2^2(z) + \nu^2 J_1^2(z)} \tag{9}$$

where

$$J_k(z) = \int_{-\infty}^{+\infty} \frac{W(z')(z-z')^k dz'}{\nu^2 + (z-z')^2} \tag{10}$$

There is a useful relation between the functions $J_0(z)$ and $J_2(z)$:

$$J_2(z) = 1 - \nu^2 J_0(z) \tag{11}$$

S. Chen and M. Takeo presented the analytical expression for the intensity profile for an arbitrary value of ν for the van der Waals broadening [11]:

$$I^{(CT)}(z) = C \cdot \operatorname{Re} \left\{ \int_{-\infty}^{\infty} \exp \left[iz\tau - \frac{1}{\nu^{3/5}} \psi \left(\nu^{6/5} \tau \right) \right] d\tau \right\} \tag{12}$$

where

$$C = \left[\int_{-\infty}^{+\infty} \operatorname{Re} \left\{ \int_{-\infty}^{\infty} \exp \left[iz\tau - \frac{1}{\nu^{3/5}} \psi \left(\nu^{6/5} \tau \right) \right] d\tau \right\} dz \right]^{-1}.$$

The function $\psi(x)$ can be approximated by the simple functions:

$$\left\{ \psi(x \ll 1) = \frac{(2\pi)^{3/2}}{3} \sqrt{x}(1-i), \psi(x \gg 1) = \frac{2\pi}{5} \left(\frac{3\pi}{8} \right)^{-3/5} \Gamma \left(\frac{2}{5} \right) \left(\cos \frac{\pi}{5} - i \sin \frac{\pi}{5} \right) x + 1.91 + 2.63i, \right. \tag{13}$$

where $\Gamma(z)$ is the gamma function.

Expression 12 turned into the static profile $W(z)$ when ν approached zero. In order to derive $W(z)$, it was necessary to use the approximation for $\psi(x)$ for small values of x .

Using the first relation of 13 and the stationary phase approximation, one obtains the following formula for the static profile:

$$W(z) = \begin{cases} 0, & z \geq 0 \\ \frac{2\pi}{3|z|^{3/2}} \exp \left[\frac{4\pi^3}{9z} \right], & z < 0 \end{cases} \tag{14}$$

Result 14 is in agreement with the well-known formula derived by H. Margenau [18].

The examination of the FFM consisted of the comparison of the CT Formula 12 with Expression 9. In the integrand of 10, we substituted the static profile 14. In the impact limit ($\nu \gg 1$), we could perform a simple estimation of the impact width. Namely, for large values of ν , the spectral line shape turned into the Lorentzian:

$$L(z) = \frac{1}{\pi} \frac{\gamma}{\gamma^2 + (z - z_0)^2}, \quad (15)$$

where γ is the width of the profile and z_0 is the coordinate of the centre of the Lorentz profile.

Note, that the CT theory reproduced the impact limit. Indeed, the usage of the second relation from 13 led to Expression 15.

In order to estimate the impact width for the FFM, we used the following property of a wide class of normalized profiles:

$$F(0) \sim \frac{1}{\gamma}. \quad (16)$$

Relation 16 was valid here, because in the impact limit, γ and z_0 always have the same dependence on ν (see, e.g., [15]). Therefore, it was obvious that Property 16 worked for the Lorentz profile 15. Using the asymptotic behaviour of Formula 14, we could estimate $J_k(0)$:

$$\begin{aligned} J_0(0) &\sim \frac{1}{\nu^2}, \\ J_1(0) &\sim \int_{\nu}^{+\infty} dz' \frac{1}{z'^{1/2}(z'^2 + \nu^2)} \sim \frac{1}{\nu^{3/2}}, \\ J_2(0) &\sim \int_{\nu}^{+\infty} dz' \frac{z'^{1/2}}{z'^2 + \nu^2} \sim \frac{1}{\nu^{1/2}}, \\ I(0) &\sim \frac{1}{\nu^{1/2}}. \end{aligned} \quad (17)$$

From Relations 16 and 17, it was easy to see that $\gamma = \gamma_{FFM} \sim \nu^{1/2}$. Thus, the FFM did not reproduce the behaviour of the profile width in the impact limit. Indeed, it was the well-know result of the impact theory [15], which was $\gamma = 8.16\nu^{3/5}$. The difference in the dependence of the impact width on the power of velocity was very small $\gamma_{impact}/\gamma_{FFM} \sim \nu^{1/10}$.

2. THE EXAMINATION OF THE FFM

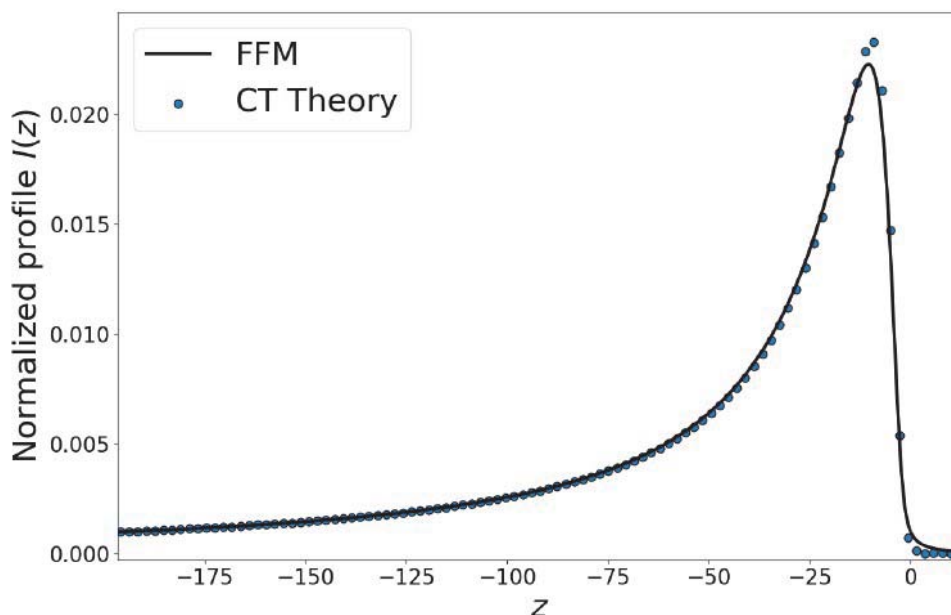


Figure 1. The normalized intensity profile of one spectral component as the function of the reduced energy shift. Comparison of the FFM profile with the Chen and Takeo theory; $\nu = 1:5$.

In order to test the FFM procedure, we compared it with the CT results. The numerical calculations showed that, for $\nu \sim 1$, the FFM was in good agreement with CT. The example of it is demonstrated in Figure 1, where one can see the comparison

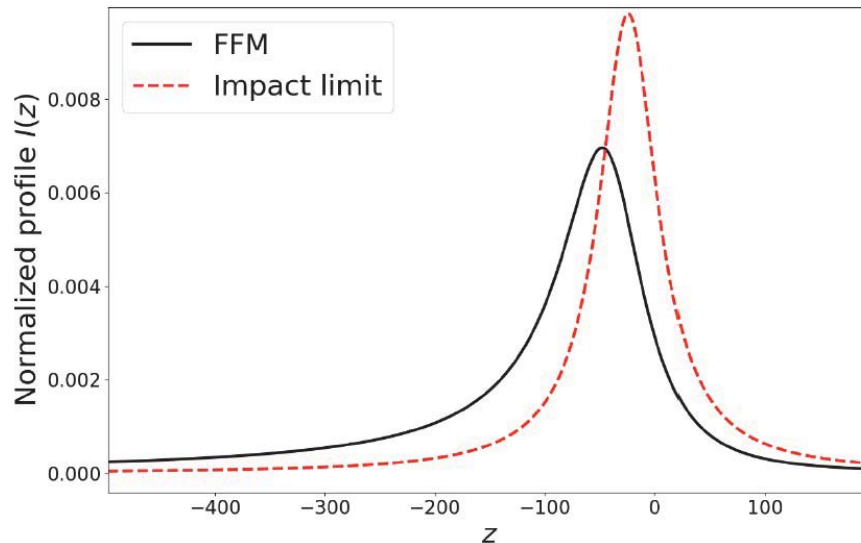


Figure 2. The normalized intensity profile of one spectral component as the function of the reduced energy shift. Comparison of the FFM profile with the impact theory; $\nu = 100$.

of two theories for $\nu = 1:5$. However, the FFM did not reproduce the impact width correctly (Figure 2) as it was shown in the previous section by the analytical estimations. The comparison of the CT theory (in the impact limit) with the FFM profile is presented in Figure 2. The full width at half maximum of the FFM profile was approximately 1.5 as large as the impact width for $\nu = 100$. With an increase in the parameter ν , the FFM profile slowly became wider than the impact line shape. This circumstance was connected with the slow growth of the ratio: $\gamma_{\text{impact}}/\gamma_{\text{FFM}} \sim \nu^{1/10}$. Moreover, we only knew how γ_{FFM} depended on ν . Uncertainty in the value of the prefactor played an important role in the impact width determination. However, the derivation of the certain value of the FFM

impact width prefactor by analytical calculations is a complex problem. It might be determined numerically as in the work of [13], but it is not reasonable to do so until the dependence of the jumping frequency on the detuning is determined. The discrepancy between two graphs became insignificant for $\nu \sim 1000$ (Figure 3). According to Estimation 7, this value of ν for $T = 300 - 5000$ K corresponded to $N = 10^{19} - 10^{21} \text{ cm}^{-3}$.

The discrepancy in the impact limit might have most likely been eliminated by accounting for the dependence of the jumping frequency on the detuning. It was shown that, for the linear Stark effect, it led to the correct result for large values of ν [13]. However, in order to determine this dependence, it was necessary to describe complicated

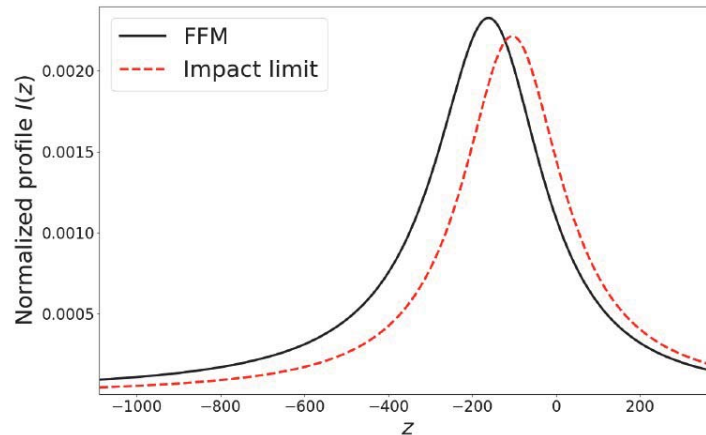


Figure 3. The normalized intensity profile of one spectral component as the function of the reduced energy shift. Comparison of the FFM profile with the impact theory; $\nu = 1200$.

dynamics of the van der Waals forces.

3. CONCLUSIONS

The construction of the general analytical theory, which described the effect of the complicated microfield dynamics on the spectral line shape formation, faced great difficulties. The FFM is simplest method for account such effects. Therefore, it was necessary to examine this theory for different types of interactions. In the present paper, we tested the FFM for the van der Waals forces.

The FFM showed good results for moderate values of temperature and density. In the case of broadening by neutral atoms, it was no exception. The results of the FFM procedure were in agreement with the CT theory (Figure 1).

The FFM did not reproduce the impact width correctly (Figure 2). As it was shown in [13], for the linear Stark effect, this problem could be solved by accounting for the dependence of the jumping frequency on the field strength. Apparently, the resolution of the problem of the broadening by neutral particles consisted of the description of the complicated dynamics of the van der Waals field.

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