Statistical Theory of Pressure Broadening*

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The statistical theory of pressure broadening is developed for any interaction law in which the potential energy is inversely proportional to some power of the distance between the molecules, including cases in which the forces change sign. Markoff's method is used. Special attention is given to the broadening produced by dipoles and by quadrupoles.

I. INTRODUCTION

TO calculate the contour of a spectral line under the most general conditions is a very difficult task. It is customary to use the phase integral method because of its analogy with the classical Lorentz treatment, although this method is sometimes not exact. The statistical theory,[1] on the other hand, has its own major shortcomings, being correct only for slow perturbations among the molecules. However, since it represents a limiting case of both the correct theory and the phase-integral method, its simplicity makes it often a useful guide.

II. THEORY

The statistical theory is based on the following considerations. The distance between the two energy levels involved in a spectral transition is a function, $E_0 + V$, of the position of all perturbing molecules, since the perturbation $V = \sum_i V_i$, which is present in addition to the normal energy difference, E_0, depends on the configuration of all molecules surrounding the radiating one. According to the statistical theory, the intensity of the spectral line at an energy V (i.e., a frequency V/h) to one side of its undisturbed position, E_0, equals the probability of those configurations of perturbers which yield the value V. Our problem is, thus, one of calculating the relative volume of configuration space in which $\sum_{i=1}^{N} V_i$ equals some given V, N being the number of molecules interacting with the emitter.

The potential, V_i, due to the ith molecule depends on r_i, its distance from the radiating molecule, and a set of other variables like angles and spins. Usually the latter, here to be denoted by ξ_i, are separable, and V_i depends on r_i in accordance with a simple power law. We, therefore, set

$$V_i = c r_i^{-m} u(\xi_i).$$

The function $u(\xi)$ has a vanishing mean. When this characteristic is satisfied, the precise form of $u(\xi)$ is relatively unimportant, leading only to different numerical factors than we shall encounter by putting

$$u(\xi) = \begin{cases} -1, & \xi \leqslant 0 \\ +1, & \xi > 0 \end{cases} \qquad -1 \leqslant \xi \leqslant 1.$$

If the volume occupied by the gas is $4\pi R^3/3$, the probability density with respect to r is

$$p(r)dr = 3r^2 dr/R^3,$$

and that with respect to ξ,

$$p(\xi)d\xi = \tfrac{1}{2}d\xi.$$

It is desired to find the probability $W_N(V)$ that, in the presence of N perturbing molecules, the potential energy $\sum_i^N V_i$ shall have the value V. This is most easily determined by the use of Markoff's method.[2] The calculation is analogous to Holtsmark's evaluation of the probability for a given electric field strength at a point in a gas.[3]

According to Markoff's analysis,

$$W_N(V) = (1/2\pi) \int_{-\infty}^{\infty} e^{-i\rho V} A_N(\rho) d\rho, \qquad (1)$$

where

$$A_N(\rho) = \left\{ \int p(\xi)d\xi \int p(r)dr \, \exp[i\rho c r^{-m} u(\xi)] \right\}^N.$$

The last expression can be written

$$A_N(\rho) = [1 - 3B(\rho)/2R^3]^N,$$

provided

$$B(\rho) = \int_{-1}^{1} d\xi \int_{0}^{R} \{1 - \exp[i\rho c r^{-m} u(\xi)]\} r^2 dr.$$

If the number density of molecules is n, so that $N = 4\pi n R^3/3$, the limit of A_N as $R \to \infty$ is

$$A(\rho) = \exp[-2\pi n B(\rho)],$$

and Eq. (1) becomes in this limit

$$W(V) = (1/2\pi) \int_{-\infty}^{\infty} \exp[-i\rho V - 2\pi n B(\rho)]d\rho.$$

We now turn to the evaluation of $B(\rho)$.

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[1] T. Holstein, Phys. Rev. **79**, 744 (1950); H. Margenau and S. Bloom, Phys. Rev. **79**, 213 (1950).

[2] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

[3] J. Holtsmark, Ann. Physik **58**, 577 (1919).

After integrating over ξ,

$$B(\rho) = 2\int_0^\infty (1 - \cos\rho v)r^2 dr, \quad \text{with} \quad v = cr^{-m}. \quad (2)$$

On expressing the volume element in terms of $\rho v \equiv t$, we have

$$B = \tfrac{2}{3}(c|\rho|)^{3/m}\int_0^z (1 - \cos t)d(t^{-3/m})$$

$$= \tfrac{2}{3}(c|\rho|)^{3/m}\int_0^\infty t^{-3/m}\sin t\,dt$$

provided $m > \tfrac{3}{2}$. In fact, B does not exist unless this inequality is satisfied, and W fails to have meaning in that case.

Let

$$\frac{4\pi}{3}c^{3/m}\int_0^\infty t^{-3/m}\sin t\,dt$$

$$= \frac{4\pi}{3}c^{3/m}\sin\left[\left(1 - \frac{3}{m}\right)\frac{\pi}{2}\right]\Gamma\left(1 - \frac{3}{m}\right) = g_m.$$

Then

$$2\pi B(\rho) = g_m|\rho|^{3/m},$$

and

$$W(V) = \frac{1}{\pi}\int_0^\infty \exp(-ng_m\rho^{3/m})\cos\rho V d\rho.$$

For $V = 0$, this integral can be evaluated directly. The probability that the total potential shall be zero, is

$$W(0) = (m/3\pi)\Gamma(m/3)/(ng_m)^{m/3}.$$

The intensity at the center of a "statistically" broadened line, therefore, decreases with $n^{-m/3}$.

For finite V, our result can be written in the form

$$W(V) = (1/\pi|V|)I_m(V/V_0), \quad (3)$$

the function I_m being defined by

$$I_m(x) = \int_0^\infty \exp[-(u/x)^{3/m}]\cos u du,$$

and $V_0 = (ng_m)^{m/3}$ represents a convenient unit for measuring the energy; it is a measure of the potential energy of two molecules at their mean distance of separation.

III. APPLICATIONS

Interesting cases are, (a) broadening by permanent dipoles ($m = 3$, e.g., ammonia) and, (b) broadening by quadrupoles ($m = 5$; e.g., oxygen). These have usually been considered from the point of view of impact
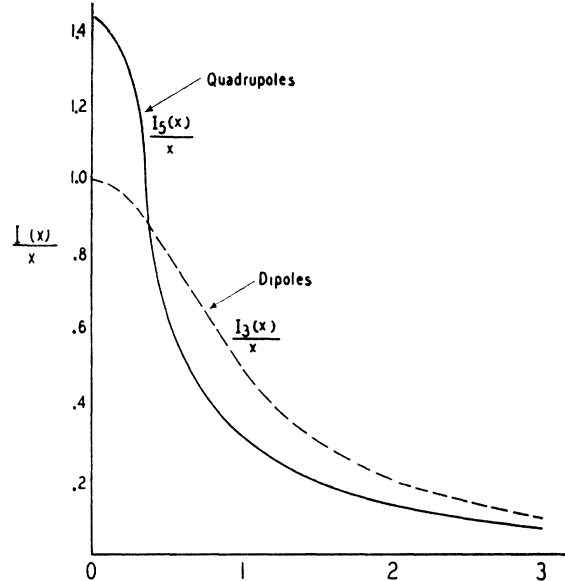

FIG. 1. Line contours for dipoles and quadrupoles. The ordinates are proportional to the intensities, and x is proportional to the frequency displacement.

theories.[4] The present considerations become applicable to these cases at high pressures and, possibly, at low temperatures. But since the statistical effect is always basically present and yields a lower limit for all observations on the broadening of lines, these results may not be without interest.

For $m = 3$ (dipole broadening)

$$V_0 = \tfrac{2}{3}\pi^2 nc, \quad I_3(x) = x/(1 + x^2),$$

and

$$W(V) = V_0/\pi(V^2 + V_0^2).$$

This represents the usual dispersion curve with half-width V_0. In an earlier publication[5] the fact that the statistical theory yields a distribution of this form when many perturbers cooperate was merely stated, but the statement was met with some doubt.[6]

For other values of m the integrals must be evaluated by numerical computation or series expansion. This has been done for a number of instances. As an example, $I_5(x)/x$ is plotted, together with $I_3(x)/x$, in Fig. 1. Note that $x = V/V_0 = \Delta\nu/\Delta\nu_0$ in terms of frequencies, where $\Delta\nu_0$ is the frequency displacement at the mean distance of separation of the molecules.

For large values of V, $W(V)$ becomes proportional to $V^{-1-3/m}$. If one considers only binary interactions, $W(V) \propto d\tau_i/dV_i$, where $\tau_i = 4\pi r_i^3/3$. This also leads to $V^{-1-3/m}$, but with a somewhat different factor than that

[4] W. V. Smith and R. Howard, Phys. Rev. 79, 132 (1950); R. Beringer and J. G. Castle, Phys. Rev. 81, 82 (1950); M. Mizushima, unpublished work. More general considerations may be found in P. Anderson, Phys. Rev. 76, 647 (1949).

[5] H. Margenau, Phys. Rev. 76, 121 (1949).

[6] See the comments relating to this point by Smith and Howard, reference 4.

appearing in the asymptotic expansion of Eq. (3). This is in agreement with expectations, since the large energies are predominantly caused by single impacts of the molecules.

A wholly different physical situation arises if the forces do not change sign, as in the interaction between nonpolar molecules. We then take $u=1$. Equation (2) is replaced by

$$B(\rho)=2\int_0^\infty (1-e^{-i\rho v})r^2 dr$$

$$=i\tfrac{2}{3}(c|\rho|)^{3/m}\int_0^\infty t^{-3/m}e^{it}dt$$

$$=\tfrac{2}{3}\exp[i\tfrac{1}{2}\pi(2-3/m)](c|\rho|)^{3/m}\Gamma(1-3/m).$$

The last step involves a partial integration which is possible only if $m>3$. For smaller values of m the distribution does not exist. This condition is more drastic than in the case of forces which change sign.

Now define

$$g\equiv g'+ig''\equiv (i4\pi/3)c^{3/m}\int_0^\infty t^{-3/m}e^{it}dt.$$

Then, since $B(-\rho)=B^*(\rho)$, we have

$$W(V)=\frac{1}{\pi}\int_0^\infty \exp(-ng'\rho^{3/m})\cdot\cos(\rho V+g''\rho^{3/m})d\rho.\quad(4)$$

This distribution is not symmetric and has a mean different from zero. Indeed, as might have been expected,

$$\int W(V)VdV=4\pi n\int V_i r_i^2 dr_i.$$

The most interesting case for an application of Eq. (4) is to the broadening caused by Van der Waals forces, for which $m=6$ and $g'=g''$. The details of this problem have been worked out already[7] in a manner less compact than the present.

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[7] H. Margenau, Phys. Rev. 48, 755 (1935).