

# Universal relationship between Maxwell's constant and the fine structure in the spectrum of depolarized scattering of light in a dense gas

T. L. Andreeva and A. V. Malyugin

*P. N. Lebedev Physics Institute, Academy of Sciences of the USSR*

(Submitted 5 July 1988)

*Pis'ma Zh. Eksp. Teor. Fiz.* **48**, No. 4, 184–186 (25 August 1988)

The structure of the spectrum for depolarized scattering in a dense molecular gas and inert gas has been studied. The fine structure of the spectrum in each case is determined by the Maxwell gas constant.

The fine structure of the depolarized scattering spectrum of many liquids has recently been detected experimentally as a narrow dip at the center of the scattering line. The contrast of this dip is nearly independent of the shape of the molecule.<sup>1</sup> Such a structure has so far not been detected in gases.

In contrast with liquids, the fine structure of the depolarized spectrum of gases can be calculated microscopically on the basis of the kinetic method.<sup>2</sup> The fine structure can be described by two parameters: the integrated intensity  $J_0$  and the contrast of the dip  $R = (J_0/J_D)(\Delta\nu/\gamma_3)$ , where  $J_D$  and  $\Delta\nu$  are the integrated intensity and the width of the depolarized scattering spectrum;  $\gamma_3 = q^2\eta/\rho$  is the width of the dip, where  $q$  is the wave vector of the scattering of light; and  $\eta/\rho$  is the kinematic viscosity of gas. The parameters  $J_0$  and  $R$  are expressed in terms of the matrix elements and the eigenvalues of the Boltzmann collision operator.

On the other hand, a microscopic expression for Maxwell's constant  $\mu$  in a gas of anisotropic molecules can be found by using the same method. We recall that a flow of a viscous liquid or gas causes a birefringence which is proportional to the macroscopic velocity gradient  $V_{ij} = \frac{1}{2}[(\partial V_i/\partial x_j) + (\partial V_j/\partial x_i)]$ . The proportionality coefficient  $\mu$  in the relation  $\epsilon_{ij} = -2\mu V_{ij}$ , where  $\epsilon_{ij}$  is the dielectric constant of gas, is called Maxwell's constant.

The parameters of the fine structure of the spectrum of the molecular gas and Maxwell's constant are related by a simple relation

$$\frac{J_0}{J_D} = \frac{15}{2} \left( \frac{\mu q v_0}{4\pi N \alpha_2} \right)^2; \quad R = \frac{15}{2} \left( \frac{\mu}{4\pi \alpha_2} \right)^2 \langle v\sigma_{MM} \rangle \langle v\sigma_{VV} \rangle, \quad (1)$$

where  $v_0^2 = T/m$  ( $T$  is the temperature of gas, and  $m$  is the mass of the molecule),  $N$  (in  $\text{cm}^{-3}$ ) is the concentration of molecules, and  $\alpha_2$  is the anisotropic component of the polarizability tensor of the molecule:  $\langle v\sigma_{VV} \rangle = T/\eta$ ,  $\langle v\sigma_{MM} \rangle = \Delta\nu/N$ . Using the familiar expression for  $J_D$  ( $J_D \propto \frac{1}{15} \alpha_2^2 N$ ), we see at once that the relation,  $(J_0/\mu^2) \propto (q^2/2)(T/\rho)$ , in general, depends neither on the shape of the molecules nor on the potential of the interaction between them, i.e., it is universal in nature. A qualitative behavior of the depolarized spectrum of  $VH$  scattering in a molecular gas is shown in

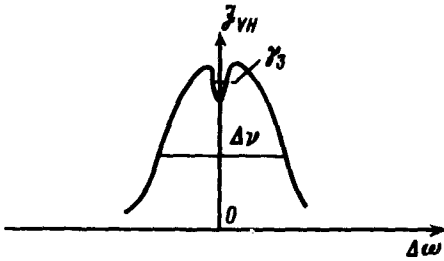


FIG. 1. Spectrum of depolarized  $VH$  scattering in molecular gas.

Fig. 1. We note that the contrast of the gap,  $R$ , and the coefficient  $\mu$  in the molecular gas do not depend on the density.

Since there is no intrinsic polarizability anisotropy of single molecules in inert gases,  $\alpha_2 = 0$ , Maxwell's effect is linked entirely with the anisotropic polarizability  $\Delta\alpha$  produced as a result of the interaction of particles in the collision. The depolarized light scattering which occurs in inert gases at high pressures ( $P > 1$  atm), is also associated with this polarizability. Using the coupled systems of equations for single-particle and two-particle distribution functions, we can show that the general relationship between  $J_0$  and  $\mu^2$  indicated above can also be used for inert gases. The scattering spectrum for inert gases has the following structural features.

First, the fluctuations of the two-particle distribution function lead to the appearance of the well-known broad depolarized scattering contour, whose width is proportional to the reciprocal of the scattering time  $1/\tau_s$ . Secondly, incorporation of the relationship between the fluctuations of the two-particle and single-particle distribution functions gives rise to the appearance in the spectrum of a new contour with an integrated intensity  $J_\nu$  and spectral width  $\nu$ , where  $\nu$  is the frequency of the gaskinetic collisions. The fluctuations of the single-particle distribution function in turn give rise in the spectrum, through the coupling with the hydrodynamic modes, to the fine structure  $J_0 \approx (q\nu_0/\nu)^2 J_\nu$  with a width  $\gamma_3$ . The spectrum is shown in Fig. 2. The parameters of the fine structure of the spectrum of inert gas are related to Maxwell's

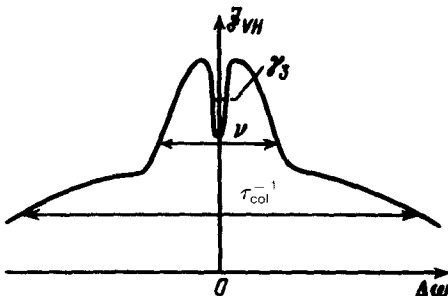


FIG. 2. Spectrum of depolarized  $VH$  scattering in inert gas.

coefficient by the relation

$$(J_0/J_D)^{\text{inert}} = \frac{15}{2} \left( \frac{\mu q v_0}{4\pi N \Delta\alpha} \right)^2 \frac{2}{Nd^3}; \quad J_D^{\text{inert}} \propto \frac{1}{15} \frac{N^2}{2} \Delta\alpha^2 d^3, \\ R \sim \frac{\frac{15}{(4\pi)^2} \frac{1}{(N\Delta\alpha)^2} \left( \frac{\mu}{\tau_{\text{col}}} \right)^2}{1 + \frac{15}{(4\pi)^2} \frac{1}{(N\Delta\alpha)^2} \left( \frac{\mu}{\tau_{\text{col}}} \right)^2}, \quad (2)$$

where  $d^3$  is the volume of the interaction region [more exactly,  $\int \Delta\alpha^2(\mathbf{r}) d\mathbf{r} \equiv \Delta\alpha^2 d^3$ ].

Since  $\mu \propto N$  in the inert gas, the gap contrast  $R$  does not depend on the density. Using the explicit expression for  $\mu^3$ , we can show that  $[15/(4\pi)^2][1/(N\Delta\alpha)^2](\mu/\tau_{\text{col}})^2 \sim \theta^2$ , where  $\theta$  is the characteristic scattering angle in the collision of particles. Consequently,  $R \sim (\theta^2/1 + \theta^2)$ .

Experimental data on the measurement of Maxwell's constant  $\mu$  in gases consisting of anisotropic molecules ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , etc.) have recently been published in the literature.<sup>4</sup> The corresponding values of  $\mu$  for liquids were studied experimentally some time ago.<sup>5</sup> These values are generally higher than those for gases by a factor of 3 or 4. At low pressures the coefficient  $\mu$  of anisotropic gases, as we know, does not depend on the density. In our view, the value of  $\mu$  of a gas differs from that of a liquid because this value depends on the density a gas would have as a result of the presence of a collision-induced anisotropic polarizability of particle pairs. Such an appreciable difference in the values of  $\mu$  in this case is attributable to the small value of the ratio  $(\sigma_{MV}/\sigma_{MM})^2 \sim 10^{-3}$ , which is included in the value of  $\mu$  of the gas at low densities. This ratio was measured experimentally in Refs. 3 and 4.

It can be concluded from the relationship between Maxwell's constant  $\mu$  and the parameters of the light-scattering spectrum that at high pressures the light-scattering spectrum of any gas behaves in a manner similar to that of a dense inert gas.<sup>2</sup> As can be seen from Fig. 2, a depolarized  $VH$  spectrum consists of two contours, whose widths differ markedly ( $\tau_{\text{col}}^{-1}$ ,  $\nu$  and  $\nu \ll \tau_{\text{col}}^{-1}$ ), and a narrow dip at the center. Experiments carried out in dense inert gases have shown that depolarized scattering spectrum has two contours of different widths. The spectrum for liquids behaves in a similar manner.<sup>6</sup>

In conclusion we note that direct experimental measurements of the coefficient  $\mu$  in a gas are restricted by rather low gas pressures ( $p < 1$  atm) because of the onset of turbulence. The established link between  $\mu$  and the parameters of the light-scattering spectrum makes it possible to extend considerably the pressure range to hundreds of atmospheres, making use of the depolarized light-scattering spectrum to measure the value of  $\mu$ .

<sup>1</sup>D. Kivelson and P. A. Madden, *Ann. Rev. Phys. Chem.* **31**, 523 (1980).

<sup>2</sup>T. L. Andreeva and A. V. Malyugin, *Usp. Fiz. Nauk* **150**, 525 (1986) [*Sov. Phys. Usp.* **29**, 1097 (1986)].

<sup>3</sup>T. L. Andreeva and A. V. Malyugin, Zh. Eksp. Teor. Fiz. **94**, 130 (Sic.) (1988).

<sup>4</sup>H. Van Houten, L. I. F. Hermans, and J. J. M. Beenakker, Physica **A131**, 64 (1985).

<sup>5</sup>M. V. Vol'kenshteĭn, *Molecular Optics*, Gostekhizdat, Moscow-Leningrad, 1951, p. 531.

<sup>6</sup>A. De Lorenzi, A. De Santis, R. Frattini, and M. Sampoli, Phys. Rev. **A33**, 3900 (1986).

Translated by S. J. Amoretty