

# Depolarized light scattering from monatomic fluids \*

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Computer experiments on dense argon are used to evaluate the depolarized spectrum of scattered light. Certain features of the spectrum can be associated with the dynamics of atomic motions in the fluid. The calculations show that the uncorrelated binary collision picture is inadequate since the major time dependence in the variation of the polarizability of the system comes from the correlated reorientation of pairs.

Consider what happens during an atomic collision. At large internuclear distances the electrons are spherically distributed about the atomic centers, whereas at small internuclear distances, the electrons are distributed with axial symmetry about the line drawn between the atomic centers. This axial distribution of electrons gives rise to an axially symmetric polarizability tensor, and thereby to a depolarized component in the light scattering spectrum.<sup>1</sup> It is the purpose of this note to explore the underlying molecular dynamics which contributes to this collision-induced light scattering in dense fluids.

The traceless part of the polarizability tensor of two interacting closed shell atoms  $\beta(\mathbf{R})$  is axially symmetric about the separation  $\mathbf{R}$  with the explicit form

$$\beta(\mathbf{R}) = \beta(R) \{ \hat{\mathbf{R}}\hat{\mathbf{R}} - \frac{1}{3}\mathbf{I} \},$$

where  $\hat{\mathbf{R}}$  is a unit vector along  $\mathbf{R}$ ,  $\mathbf{I}$  is the unit tensor, and  $\beta(R) \equiv \alpha_{||}(R) - \alpha_{\perp}(R)$  is called the optical anisotropy, where  $\alpha_{||}(R)$  and  $\alpha_{\perp}(R)$  are, respectively, the components of the full polarizability tensor parallel and perpendicular to  $\hat{\mathbf{R}}$ . Although the precise dependence of  $\beta(R)$  on  $R$  is unknown,<sup>2</sup> it can be shown that  $\beta(R) \rightarrow R^{-3}$  as  $R \rightarrow \infty$ .

In a dilute gas where only binary collisions are important, the spectrum of depolarized scattering is given by the time Fourier transform of the correlation function

$$C(t) = \langle \beta(0) \beta(t) P_2[\hat{\mathbf{R}}(0) \cdot \hat{\mathbf{R}}(t)] \rangle, \quad (1)$$

where  $P_2(x)$  is the second order Legendre polynomial,  $\beta(t) = \beta[\mathbf{R}(t)]$  is the optical anisotropy at time  $t$  of the colliding pair,  $\langle \dots \rangle$  indicates the proper equilibrium ensemble average, and  $\hat{\mathbf{R}}(0) \cdot \hat{\mathbf{R}}(t)$  is the projection of the interatomic unit vector at  $t$  on its initial orientation.

In dense gases and liquids the situation is more complicated. It has been suggested<sup>3</sup> that even in the high density region the characteristics of depolarized

light scattering can be understood in terms of a binary collision picture corresponding to Eq. (1) above. However, our purpose here is to study the behavior of correlated binary collisions as well as to investigate the validity of Eq. (1) in describing depolarized light scattering from dense systems. It is assumed that binary interactions still dominate in dense systems, but that the binary collisions are not independent. In this case the spectrum is given by the transform of<sup>4</sup>

$$C_1(t) = \langle \sum_{i \neq j} \sum_{l \neq m} \beta[R_{lm}(0)] \beta[R_{ij}(t)] P_2[\mathbf{R}_{lm}(0) \cdot \mathbf{R}_{ij}(t)] \rangle, \quad (2)$$

where  $(ij)$  and  $(lm)$  designate pairs of atoms. Despite the fact that only two body contributions to the polarizability tensor are considered,  $C_1(t)$  contains two, three, and four body correlations. It is almost stating the obvious to say that in dense systems the collision induced polarizability may contain three, four, and many atom contributions and cannot be ascribed entirely to two body interactions as in Eq. (2). Nevertheless, we must understand the nature of the two body terms before we go on to discuss the many body terms which have not yet been explicitly considered (except in the simple dipole-induced-dipole limit).

Although we believe that a strictly two body model of the polarizability anisotropy is inadequate in dense systems, we believe that a study of Eq. (2) would be useful in understanding the phenomenon of the collision-induced spectrum. To go beyond the two body theory would require the enormously complicated quantum mechanical calculation of the many body polarizability.

In this paper we present a molecular dynamics calculation<sup>5</sup> of  $C_1(t)$  for several suggested models of  $\beta(R)$  for argon. The argon atoms are assumed to interact with a Lennard-Jones (12-6) potential with potential parameters ( $\epsilon/k = 119.9^\circ\text{K}$ ,  $\sigma = 3.405 \text{ \AA}$ ). Two thermo-

dynamic states  $S_1$  (765 amagat, 88.5°K) and  $S_2$  (1000 amagat, 300°K) were studied. Fleury *et al.*<sup>6</sup> have shown that the measured depolarized spectrum of argon can be fitted to a two-branch exponential spectrum

$$I(\omega) = I_0 \exp(-\omega/\Delta_1) \quad \omega \leq \omega_0$$

$$= I_0 A(\omega_0) \exp(-\omega/\Delta_2) \quad \omega \geq \omega_0, \quad (3)$$

where  $A(\omega_0) = \exp[(\Delta_2^{-1} - \Delta_1^{-1})\omega_0]$  and where  $\Delta_1$ ,  $\Delta_2$ ,  $\omega_0$  are parameters which depend on the thermodynamic state. The parameters corresponding to the two states in our computer study are

$$S_1(\Delta_1 = \Delta_2 = 21 \text{ cm}^{-1}, \omega_0 = 0),$$

$$S_2(\Delta_1 = 29.5 \text{ cm}^{-1}, \Delta_2 = 48.3 \text{ cm}^{-1}, \omega_0 = 42 \text{ cm}^{-1}).$$

Equation (3) is easily Fourier inverted to find the experimental time correlation function.

Several models have been suggested<sup>1,7</sup> for  $\beta(R)$ , but its precise form is unknown. In order to ascertain the sensitivity of the computed spectrum to the form of  $\beta(R)$  we have computed the autocorrelation function  $C_1(t)$  for state  $S_2$  for the models indicated in Curves b and d of Fig. 1. Although we have not included error bars, the errors can be estimated on the basis of the analysis of Zwanzig and Ailawadi.<sup>8</sup> This analysis shows that the differences between these models can be ascertained from the decay.

In addition to determining  $C_1(t)$ , we have also determined the following two functions:

$$C_2(t) = \langle \sum_{i \neq j} \sum_{l \neq m} \beta[R_{ij}(0)] \beta[R_{lm}(t)] \rangle,$$

$$C_3(t) = \langle \sum_{i \neq j} \sum_{l \neq m} P_2[\hat{\mathbf{R}}_{ij}(0) \cdot \hat{\mathbf{R}}_{lm}] \rangle \quad (4)$$

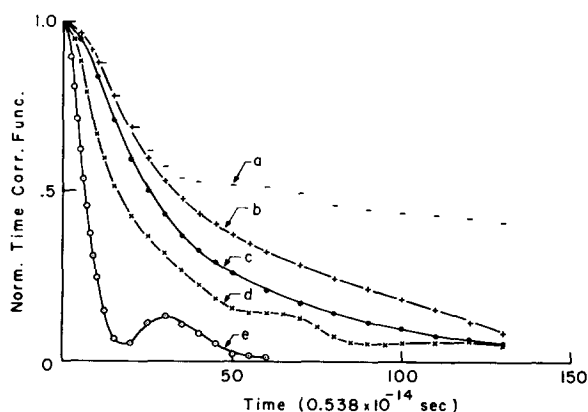


FIG. 1. Normalized time correlation functions for argon in thermodynamic state  $S_2$  (1000 amagat, 300°K). a: Distinct correlation function, Eq. (1), for  $\beta(x) = x^{-3} - 0.473x^{-9.3}$ . b: Total correlation function  $C_1(t)$ , Eq. (2), for  $\beta(x) = x^{-3} - 28.32 \times \exp(-2.72x)$ . c: Experimental correlation function, with  $\Delta_1 = 29.5 \text{ cm}^{-1}$ ,  $\Delta_2 = 48.3 \text{ cm}^{-1}$ ,  $\omega_0 = 42.0 \text{ cm}^{-1}$ . d: Total correlation function  $C_1(t)$ , Eq. (2), for  $\beta(x) = x^{-3} - 0.473x^{-9.3}$ . e: Time correlation function  $\psi(t)$ , Eq. (6).

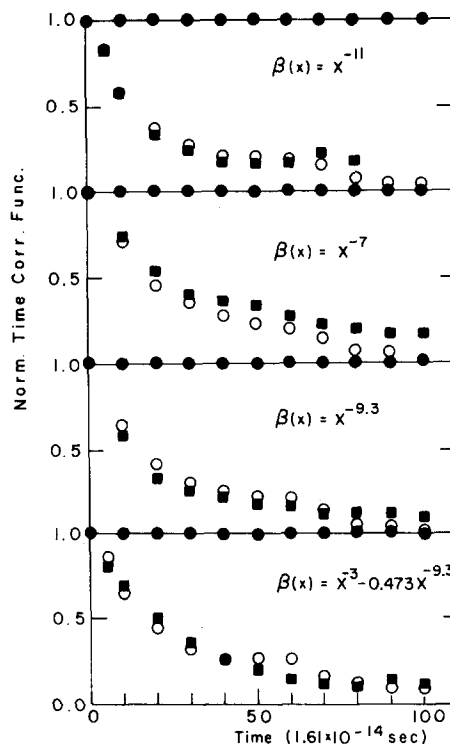


FIG. 2. Comparison between the different normalized time correlation functions  $C_1(t)$ ,  $C_2(t)$ ,  $C_3(t)$  for the indicated models  $\beta(x)$  for argon in thermodynamic state  $S_1$  (765 amagat, 88.5°K). In this figure  $C_1(t)$  is given by  $\circ$ ,  $C_2(t)$  is given by  $\bullet$ , and  $C_3(t)$  is given by  $\blacksquare$ .

for different models of  $\beta(R)$ . These functions are presented in Fig. 2.  $C_1(t)$  depends on the relative radial motion of pairs through  $\beta(R)$  and on the reorientational motion of pairs through the Legendre polynomials, whereas  $C_2(t)$  depends only on the radial motion, and  $C_3(t)$  depends only on the reorientations. From Fig. 2 it should be noted that  $C_2(t)$  decays much more slowly than either  $C_1(t)$  or  $C_3(t)$ . Moreover,  $C_1(t)$  and  $C_3(t)$  closely resemble each other. This seems to be true for all models of  $\beta(R)$  studied. It can be concluded that the time scale for the decay of  $C_1(t)$  in dense systems is determined by the correlated reorientations of pairs.

To ascertain what the effects of correlated collisions were we compared the foregoing three functions to analogous functions reflecting only independent pair correlations [as in Eq. (1)]. These functions reflect pure pair correlations and do not reflect correlated collisions. For all models of  $\beta(R)$  we found that the independent pair theory [based on Eq. (1)] does not agree at all with the full calculation. In curves a and d of Fig. 1 we present a comparison of Eq. (2) for state  $S_2$ . It can be concluded that correlated collisions are important and, moreover, calculations of liquid state spectra based only on independent binary collisions and/or head-on collisions should be avoided. Any cor-

respondence between such theories and experiment is purely fortuitous.

Two models have been suggested for  $\beta(R)$ : one by Levine and Birnbaum<sup>7</sup>:

$$\beta(x) = [x^{-3} - 0.473x^{-9.3}], \quad (5a)$$

and one by McTague *et al.*<sup>9</sup>:

$$\beta(x) = [x^{-3} - 28.38 \exp(-2.72x)], \quad (5b)$$

where  $x=R/\sigma$  and  $\beta$  is in reduced units. These forms are based on fitting assumed functional forms of  $\beta(R)$  to the observed moments of the depolarized spectra. In curves b, c, and d of Fig. 1 we present a comparison between these two models and experiment for  $S_2$ . The difference between computer and real experiments may be due either to the inadequacy of the models or the failure of a strictly two body theory to account for the phenomenon.

The collision-induced spectrum seems to be related to the density fluctuations in a fluid that destroy spherical symmetry around given atoms. Since the force on a particle is zero if the distribution around it

is spherical, it might be thought that the induced spectrum is related to

$$\psi(t) = \langle P_2[\hat{\mathbf{F}}(0) \cdot \hat{\mathbf{F}}(t)] \rangle, \quad (6)$$

where  $\hat{\mathbf{F}}$  is a unit vector specifying the orientation of a given force on a typical atom. This idea has surfaced many times in connection with collision-induced spectroscopy. From curves e, b, and d of Fig. 1 we see that there is no similarity between  $\psi(t)$  and  $C_1(t)$ , thus negating this idea.

We have not yet found a model consistent with all of our results. We present these results in the hope that they will stimulate a more active search for a workable model.

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<sup>1</sup>See, for example, J. P. McTague and G. Birnbaum, *Phys. Rev. A* **3**, 1376 (1971).

<sup>2</sup>There have been several attempts to compute  $\beta(R)$  for some gases. See, for example, D. B. DuPré and J. P. McTague, *J. Chem. Phys.* **30**, 2024 (1969), and V. McKoy (private communication).

<sup>3</sup>J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.* **54**, 3846 (1971); *J. Chem. Phys.* **55**, 5146 (1971).

<sup>4</sup>Equation (16) of Ref. 1.

<sup>5</sup>For a description and review of the methods used in these computer experiments, see B. J. Berne and D. Forster, *Annu. Rev. Phys. Chem.* **22**, 563 (1971).

<sup>6</sup>P. A. Fleury, W. B. Daniels, and J. M. Worlock, *Phys. Rev. Lett.* **27**, 1493 (1971).

<sup>7</sup>H. Levine and G. Birnbaum, *J. Chem. Phys.* **55**, 2914 (1971).

<sup>8</sup>R. Zwanzig and N. K. Ailwadi, *Phys. Rev.* **182**, 280 (1969).

<sup>9</sup>J. McTague (private communication).