Collision-Induced and Multiple Light Scattering by Simple Fluids [and Discussion]

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Collision-induced and multiple light scattering by simple fluids

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Most discussions of light scattering by simple (e.g. classical, atomic) fluids have treated only 'first order' processes, i.e. those where the incident light is scattered only once and the atomic polarizabilities are undistorted by interaction. Correspondingly the scattered intensity is related by Fourier transform to the time- and space- pair correlations. In this paper we describe instead the 'second order' processes of collision-induced scattering (c.i.s.), in which the incident light is scattered only once but the relevant polarizability is that of an interacting cluster of atoms, and multiple light scattering (m.l.s.), in which only undistorted polarizabilities are involved but the incident light is scattered more than once. In both cases the scattered intensity is determined by correlations involving more than two particles. In addition, the c.i.s. experiments provide information about the many-atom polarization while the m.l.s. studies offer new probes of large fluctuations in critical and nucleating fluids. We discuss in particular theoretical and experimental c.i.s. investigations of the two-body polarizability anisotropy induced by collision; it is concluded that the nature and origin of non-point-dipole behaviour has yet to be satisfactorily explained. Similarly, we consider how various depolarization m.l.s. studies suggest improved analyses of pair correlation properties in classical systems.

Introduction

In this paper we present a brief, critical discussion of the present status of theoretical and experimental studies of second order light scattering by classical fluids. The first second order process treated is collision-induced light scattering (c.i.s.) in which the incident light is scattered only once, but by interacting molecules which distort one another's electronic charge clouds (part *a*). The second case (part *b*) considered is multiple light scattering (m.l.s.) in which the light is scattered more than once, but only isolated molecule polarizabilities are involved.

We shall be concerned with classical fluids made up of simple molecules, i.e. molecules whose polarizability anisotropy and internal degrees of freedom can be neglected. Suppose we subject such a fluid to linearly polarized light whose electric field is described by

$$E_0(r, t) = E_0 \exp(i k_0 \cdot r - i\omega_0 t). \tag{1}$$

Denote the instantaneous number density fluctuation at an arbitrary point r in the fluid by

$$\Delta\rho(r, t) = \sum_{i=1}^{N} \delta(r - R_i(t)) - \rho_0, \tag{2}$$

where $R_i(t)$ is the centre-of-mass position of the ith molecule (henceforth called 'atom') at time t, and $\rho_0 = N/V$ is the uniform (average) number density. Let α be the isolated atom

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polarizability. Then, as discussed elsewhere (Gelbart 1974, 1978), the scattered electric field at $1 = R_d$, t can be written, to second order in $\alpha \Delta \rho$, as

$$\Delta E_{\text{scatt}} = \Delta E_s^{(1)} + \Delta E_s^{(2)}, \tag{3}$$

where

$$\Delta E_s^{(1)} = \alpha \int d(2) \; T(1-2) \cdot \Delta \rho(2) \; E_0(2) \tag{4}$$

and

$$\Delta E_s^{(2)} = \alpha^2 \int d(2) \int d(3) \; T(1-2) \cdot \Delta \rho(2) \; T(2-3) \cdot \Delta \rho(3) \; E_0(3). \tag{5}$$

Here, $2 = r'$, t' and $3 = r''$, t'', and $T(1-2)$ is the tensor that acts on the dipole moment at 2 to give the electric field due to it at 1 (and similarly for $T(2-3)$):

$$T(R, \tau) = \frac{c}{2\pi} \int_{-\infty}^{+\infty} dk \exp(-ikc\tau) \; T_k(R), \tag{6}$$

$$T_k(R) = \begin{cases} (\nabla^2 + k^2 I)\,[\exp(ikR)/R], & R > 0^+, \\ 0, & \text{otherwise.} \end{cases} \tag{7}$$

In writing the above equations, and in all the ensuing discussion, we drop multiplicative factors such as n, $(n^2+2)/3$, etc. (where n is the refractive index of the fluid); these can be found in the more rigorous results presented elsewhere (Mazur 1958; Bedeaux & Mazur 1973; Boots et al. 1975 a, b, 1976; Felderhof 1974; Bullough 1965; Oxtoby 1975; Oxtoby & Gelbart 1974 a).

The intensity of light scattered with frequency ω, including first $[\Delta E_s^{(1)}]$ and second $[\Delta E_s^{(2)}]$ order contributions, follows (Gelbart 1974, 1978; Berne & Pecora 1976; Benedek 1968) from:

$$I(\omega) = \int_{-\infty}^{+\infty} dt \exp(i\omega t) \langle \Delta E_s(R_d, t) \; \Delta E_s^*(R_d, 0) \rangle, \tag{8}$$

where R_d describes the position of the detector and $\langle \dots \rangle$ denotes as usual the canonical ensemble average over all fluid configurations $\{R_i\}$. Throughout the remainder of our discussion we shall assume that the sample is centred at the origin of the space-fixed coordinate system and that $R_d = R_d \hat{y}$, $k_0 = (\omega_0/c)\hat{x}$, and $E_0 = E_0\hat{z}$. That is, the incident light is z-polarized and propagates along the x-axis, the scattered light being detected along the y-axis.

In the case where $R_d \gg |r|$ for all r in the illuminated volume, $\Delta E_s^{(1)}$ can easily be evaluated and substituted into equation (8) to give the first order spectrum

$$I^{(1)}(\omega) = (|E_0|/R_d)^2 \, (\omega_0/c)^4 \, V\alpha^2 \, S(K, \Omega), \tag{9}$$

where

$$VS(K, \Omega) = \int_{-\infty}^{+\infty} dt \exp(i\Omega t) \langle \rho_K(t) \, \rho_{-K}(0) \rangle, \tag{10}$$

$$K \equiv (\omega_0/c) \, \hat{R}_d - (\omega_0/c) \, \hat{x} = k - k_0, \tag{11a}$$

$$\Omega \equiv \omega - \omega_0, \tag{11b}$$

and

$$\rho_K(t) = \int dr \exp(-iK \cdot r) \, \Delta \rho(r, t). \tag{12}$$

Equations (9)–(12) comprise the familiar theory (Berne & Pecora 1976) of the Rayleigh–Brillouin spectrum of a simple fluid; they relate the first order polarized light scattering line

shape to the temporal Fourier transform of the pair correlation function of the density fluctuations. The integral $\int_{-\infty}^{+\infty} \mathrm{d}\Omega\, I^{(1)}(\Omega)$ gives the integrated intensity at K; it is the spatial Fourier transform of the equilibrium pair correlation function $g(|\mathbf{r}|) - 1$, where $g(r)$ is the usual radial distribution.

When equation (5) for the second order field is substituted into equation (8) a rather complicated expression for the light scattering spectrum is obtained (see, for example, Boots *et al.* 1975*a*, 1976). Its important characteristics include: (*a*) it is partially depolarized, i.e. it contains an x-, as well as a z-, component; (*b*) it varies with the fourth power of α; and (*c*) it involves the correlation of up to four density fluctuations. This inelastic spectrum was discussed originally as a second order Raman process involving the roton modes of the quantum liquid helium (Halley 1969; Greytak & Yan 1969; Stephen 1969). Mention of the $I^{(2)}(\omega)$ line shape, and its relevance to the analyses of c.i.s. and m.l.s. spectra of classical fluids, will be given later in our discussion.

For the most part, however, we shall concentrate on the intensity integrated over frequency, $\int_{-\infty}^{+\infty} \mathrm{d}\Omega\, I^{(2)}(\Omega)$, given by (Gelbart 1978):

$$I_{fz}^{(2)} = 2\pi \frac{\alpha^4}{R^2} |E_0|^2 \left(\frac{\omega_0}{c}\right)^4 \int_{V_{\mathrm{S}}} \mathrm{d}\mathbf{r}_1 \int_{V_{\mathrm{I}}} \mathrm{d}\mathbf{r}_2 \int_{V_{\mathrm{S}}} \mathrm{d}\mathbf{r}_3 \int_{V_{\mathrm{I}}} \mathrm{d}\mathbf{r}_4\, [T_{k_0}(\mathbf{r}_1 - \mathbf{r}_2)]_{fz}^* \, [T_{k_0}(\mathbf{r}_3 - \mathbf{r}_4)]_{fz}$$
$$\times \langle \Delta\rho(\mathbf{r}_1)\, \Delta\rho(\mathbf{r}_2)\, \Delta\rho(\mathbf{r}_3)\, \Delta\rho(\mathbf{r}_4) \rangle \exp\,(\mathrm{i}\mathbf{k}_0 \cdot \mathbf{r}_2) \exp\,(-\mathrm{i}\mathbf{k} \cdot \mathbf{r}_1)$$
$$\times \exp\,(-\mathrm{i}\mathbf{k}_0 \cdot \mathbf{r}_4) \exp\,(\mathrm{i}\mathbf{k} \cdot \mathbf{r}_3). \tag{13}$$

Here $f = x$ or z denotes the polarization of the scattered light. Recall from equation (7) that:

$$\mathbf{T}_{k_0}(\mathbf{r}) = \exp\,(\mathrm{i}k_0 r) \left[\left(\frac{3}{r^3} - \frac{3\mathrm{i}k_0}{r^2} - \frac{k_0^2}{r} \right) \hat{\mathbf{r}}\hat{\mathbf{r}} + \left(\frac{k_0^2}{r} + \frac{\mathrm{i}k_0}{r^2} - \frac{1}{r^3} \right) \mathbf{I} \right] \tag{14}$$

acts on an oscillating ($\omega_0 = ck_0$) dipole moment to give the resulting electric field at a vector distance $\mathbf{r}$ away. V_{S} denotes the volume of the sample 'seen' by the detector, while V_{I} is the illuminated volume. These integration limits arise from the fact that (see equation (5)) each second order scattered field $\Delta E_{\mathrm{s}}^{(2)}$ corresponds to the incident field E_0 polarizing a density fluctuation at $\mathbf{r}_2 [E_0(\mathbf{r}_2) \neq 0$ if $\mathbf{r}_2 \in V_{\mathrm{I}}]$, followed by this induced moment giving rise [via $\mathbf{T}_{k_0}(\mathbf{r}_1 - \mathbf{r}_2)$] to a field at $\mathbf{r}_1$ which radiates light seen by the detector [if $\mathbf{r}_1 \in V_{\mathrm{S}}$].

(*a*) Collision-induced scattering (c.i.s.)

Suppose all spatial correlations in the fluid are characterized by ranges which are very small compared with the wavelength of light, i.e. the four-point density function $\langle \Delta\rho(\mathbf{r}_1)\, \Delta\rho(\mathbf{r}_2)\, \Delta\rho(\mathbf{r}_3)\, \Delta\rho(\mathbf{r}_4) \rangle \approx 0$ whenever any relative separation becomes comparable with $2\pi/k_0 = \lambda_0$. In this case all exponential phase factors in equation (13) can be replaced by unity and the dipole propagator $\mathbf{T}_{k_0}(\mathbf{r})$ (see equations (7) and (14)) reduces to its $k_0 \to 0$ form:

$$\mathbf{T}_{k_0}(\mathbf{r}) \to \mathbf{T}^{(0)}(\mathbf{r}) = (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I})/r^3. \tag{15}$$

The integrated intensity for $90^\circ\, fz$ scattering then becomes

$$I_{fz}^{(2)}\big|_{\mathrm{eq.\,(13)}} \to 2\pi \frac{\alpha^4}{R_{\mathrm{d}}^2} |E_0|^2 \left(\frac{\omega_0}{c}\right)^4 \left\langle \sum_{i \neq j} T_{fz}^{(0)}(\mathbf{R}_i - \mathbf{R}_j) \sum_{k \neq l} T_{fz}^{(0)}(\mathbf{R}_k - \mathbf{R}_l) \right\rangle. \tag{16}$$

The ensemble average in equation (16) has been evaluated for dense gases and liquids by molecular dynamics computation (Alder *et al.* 1973a) of the two-, three- and four-body positional correlations. In the $\rho \to 0$ limit, on the other hand,

$$I_{xz}^{(2)}\big|_{\text{eq. (16)}} \to \tfrac{2}{15}(\pi)^2 \frac{|E_0|^2}{R_d^2} \left(\frac{\omega_0}{c}\right)^4 \rho^2 \int_0^\infty dR\, R^2\, (6\alpha^2/R^3)^2 \exp\left[-V(R)/k_B T\right], \qquad (17)$$

where $V(R)$ is the interatomic potential. This result can be straight-forwardly evaluated for the noble gases where α and $V(R)$ are both known to high accuracy. It is found that the low density $I_{xz}^{(2)}$ computed in this way (for Ar, say) is roughly 30% larger than that which is observed (Buckingham & Dunmur 1968; Thibeau *et al.* 1970; McTague *et al.* 1972; Lallemand 1972). Similarly, the machine evaluations of equation (16) have established (Alder *et al.* 1973a) that the theoretical values for $I_{xz}^{(2)}$ increasingly overestimate the measured (Thibeau *et al.* 1968) depolarized scattering intensity: by the time liquid densities are reached,

$$I_{xz}^{(2)} \text{ [equation (16)]}/I_{xz}^{(2)} \text{ [measured]}$$

is as large as ten.

The above discrepancy has its origin in the implicit assumption made about the polarization of the fluid by the incident light, namely that the constituent atoms behave as polarizable points. Suppose we consider for the moment a system consisting of an interacting pair of atoms and associate with every point a scalar polarizability density $\alpha(\mathbf{r})$. We demand further that $\alpha(\mathbf{r})$ obey the following equation:

$$\boldsymbol{\mu}(\mathbf{r}) = \alpha(\mathbf{r})\mathbf{E}_0 + \alpha(\mathbf{r})\int d\mathbf{r}'\, \mathbf{T}^{(0)}(\mathbf{r}-\mathbf{r}')\cdot\boldsymbol{\mu}(\mathbf{r}'). \qquad (18)$$

Here $\boldsymbol{\mu}(\mathbf{r})$ is the local polarization (dipole moment density), $\mathbf{T}^{(0)}$ is the static dipole tensor defined by equation (15), and $\mathbf{E}_0$ is the incident electric field (now assumed to be uniform). For our system, we have in mind a pair of noble gas atoms a distance R apart. The induced dipole moment and polarizability tensor associated with this diatom are then given by:

$$\boldsymbol{\mu} = \int d\mathbf{r}\,\boldsymbol{\mu}(\mathbf{r}) = \alpha_{\|,\perp}(R)\mathbf{E}_0, \qquad (19)$$

where $\|$ and $\perp$ refer to $\mathbf{E}_0$ being alternately parallel and perpendicular to the internuclear axis. Approximating the polarizability density by the sum of isolated atom contributions, we write

$$\alpha(\mathbf{r}) = \alpha_A(|\mathbf{r}-\mathbf{R}_A|) + \alpha_B(|\mathbf{r}-\mathbf{R}_B|), \qquad (20)$$

where $\mathbf{R}_A$ and $\mathbf{R}_B$ denote the positions of the nuclei.

Note that if we use the point dipole form for the atomic polarizability densities, e.g.

$$\alpha_A(r) = \alpha\delta(\mathbf{r}-\mathbf{R}_A), \qquad (21)$$

then equations (18)–(20) may be solved by iteration to give the familiar classical, dipole–induced-dipole (d.i.d.) result (Felderhof 1974):

$$\beta(R) = \alpha_\|(R) - \alpha_\perp(R) = 6\alpha^2/R^3 + 6\alpha^3/R^6 + O(\alpha^4/R^9). \qquad (22)$$

This is the origin of the $6\alpha^2/R^3$ factor appearing in the integrand of equation (17) and of the $\mathbf{T}^{(0)}$ factors in the general ensemble average of equation (16). Thus we can describe corrections to the point dipole theory by simply introducing a more reasonable distribution than equation

(21) for $\alpha_A(r)$, namely, one in which the polarizability is spread out realistically through the atom. This is the approach suggested by Oxtoby & Gelbart (1975a) (see also Thiemer & Paul (1965)).

Specifically, Oxtoby & Gelbart used atomic, Hartree–Fock, finite electric field charge densities, divided the atom into sperical shells centred at the nucleus, and took the total dipole moment of each shell as a measure of the polarizability density at that distance from the nucleus. This procedure defines the approximation ($z = r \cos \theta$)

$$\alpha_A(r) = (1/E_0) \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \rho(r\theta\phi; E_0) z. \tag{23}$$

Here $\rho(r\theta\phi; E_0)$ is the electron charge density of an atom which sits in a constant electric field $E_0 \hat{z}$. $\alpha_A(r)$ is normalized so that $\int_0^\infty r^2 dr \, \alpha_A(r) = \alpha$. If equation (23) is used in equations (18)–(20), then at large separations the d.i.d. result of equation (22) is recovered while at shorter distances there are corrections due to atomic overlap. More explicitly, a single iteration of equation (18) leads to

$$\beta(R) = 3 \int dr_{1A} \int dr_{2B} \frac{3(\hat{r}_{12})_z (\hat{r}_{12})_z - 1}{r_{12}^3} \alpha_A(r_{1A}) \alpha_B(r_{2B}), \tag{24}$$

where $r_{12} = r_{1A} - r_{2B}$. Evaluations of equation (24) for the light noble gases were carried out by Oxtoby & Gelbart (1975a). The result of a second iteration of equation (18) was similarly investigated (Oxtoby & Gelbart 1975b), leading to contributions to $\beta(R)$ which reduce for large R to the $1/R^6$ d.i.d. terms of equation (22) and which include the appropriate charge cloud overlap corrections at shorter distances. They also estimated the correlation and exchange contributions. Their final results for $\beta(R)$ were found to give good agreement with experimental data on argon (e.g. the low density $I_{xz}^{(2)}$ was reduced by ca. 30% from the point dipole value) and with the much more time-consuming Hartree–Fock calculations on the He—He diatom (O'Brien et al. 1973; Fortune et al. 1974). Finally, B. J. Alder, J. C. Beers, H. L. Strauss & J. J. Weis (1978, personal communication) used the Oxtoby–Gelbart $\beta(R)$ for argon to evaluate $I_{xz}^{(2)}$ for a liquid at a density just above that of the liquid–solid transition (see equation (16)) with $6\alpha^2 T_{xz}^{(0)}(R) = (6\alpha^2/R^3) (3\hat{R}\hat{R} - I)_{xz}$ replaced by $\beta_{calc.}(R) (3\hat{R}\hat{R} - I)_{xz}$; the theoretical values were found to be significantly reduced from that of the point dipole model and gave good agreement with experiment.

The above approach, while providing a simple physical interpretation of the breakdown of d.i.d. theory, involves several questionable assumptions. These assumptions have been discussed critically during this past year, within the context of various rigorous treatments (Sipe & Van Kranendonk 1978; Clarke et al. 1978; Oxtoby 1978) of the polarization of interacting atoms. Sipe & Van Kranendonk (1978) have pointed out that calculations based on an Oxtoby–Gelbart (or Thiemer–Paul) polarizability density give increasingly poorer results for the successively higher multipole moments induced by non-uniform electric fields; the induced dipole moment is, however, correctly described. Clarke et al. (1978) have discussed similar difficulties associated with the Oxtoby–Gelbart choice of polarizability density and internal electric field; they are led to an alternative formulation of the collisional polarizability problem which involves a direct calculation of the Coulomb interaction between a pair of polarized atoms. A convenient way to expose the physical ideas behind these two discussions, and to appreciate

the approximate nature of the earlier Oxtoby–Gelbart theory, is to outline here the most recent work of Oxtoby (1978).

Let us write the energy of two interacting atoms in a uniform electric field as

$$H = H_A + H_B + V, \tag{25}$$

where H_A is the Hamiltonian for atom A in the electric field (similarly for H_B) and V is the sum of Coulomb attractions and repulsions between the electrons and nucleus of A and those of B. Then, treating V as a perturbation, the ground state energy of the diatom in a field can be expressed in the usual way as (Schiff 1969)

$$\epsilon_0^{di} = \epsilon_0(A) + \epsilon_0(B) + \langle \Psi_0(A)\,\Psi_0(B) | V | \Psi_0(A)\,\Psi_0(B) \rangle$$
$$+ \sum_{\substack{\text{all } n,\,m \\ \text{except for} \\ n=m=0}} |\langle \Psi_0(A)\,\Psi_0(B) | V | \Psi_n(A)\Psi_m(B)\rangle|^2 / [\epsilon_0(A) + \epsilon_0(B) - \epsilon_n(A) - \epsilon_m(B)] + \dots \tag{26}$$

Here $\epsilon_n(A)$ and $\Psi_n(A)$ refer to the energy and wavefunction associated with the nth eigenstate of H_A:

$$H_A\Psi_n(A) = \epsilon_n(A)\,\Psi_n(A). \tag{27}$$

Let the charge density associated with the ground state of H_A be expanded in powers of the electric field strength E_0 according to:

$$\rho_A = \rho_A^{(0)} + E_0\rho_A^{(1)} + E_0^2\rho_A^{(2)} \dots . \tag{28}$$

It is easy to show that the first order term $[\langle \Psi_0(A)\Psi_0(B) | V | \Psi_0(A)\,\Psi_0(B)\rangle]$ in equation (26) can be written as (assuming atoms A and B to be identical)

$$\Delta\epsilon_0^{di}(\text{first order in } V) = V_0(R) - \tfrac{1}{2}E_0^2\alpha_{\parallel,\,\perp}(R) + O(E_0^3), \tag{29}$$

where

$$V_0(R) = \int dr \int dr'\, \rho_A^{(0)}(r)\, \rho_B^{(0)}(r')/|r - r'| \tag{30}$$

is the Coulomb interaction between the two zero-field atoms, and

$$\alpha_{\parallel,\,\perp}(R) = \alpha_{\parallel,\,\perp}^{\text{linear}}(R) + \alpha_{\parallel,\,\perp}^{\text{hyper}}(R)$$
$$= -2 \int dr \int dr'\, \frac{\rho_A^{(1)}(r)\,\rho_B^{(1)}(r')}{|r - r'|} - 2 \int dr \int dr'\, \frac{[\rho_A^{(0)}(r)\,\rho_B^{(2)}(r') + \rho_A^{(2)}(r)\,\rho_B^{(0)}(r')]}{|r - r'|} \tag{31}$$

is the interaction (pair) polarizability within the approximation of the above first order perturbation theory. Again, as before, the $\parallel$ and $\perp$ subscripts refer to the electric field being alternately parallel and perpendicular to the diatom axis.

Oxtoby (1978) has shown that the 'linear' contribution to the pair polarizability can be rewritten in the form:

$$\alpha^{\text{linear}} = 2 \int dr \int dr'\, \chi_A(r) \cdot \nabla^2 \frac{1}{|r - r'|} \cdot \chi_B(r'), \tag{32}$$

where $\chi_A(r)$ satisfies the equation:

$$\nabla \cdot \chi_A(r) \cdot E_0 = -E_0\rho_A^{(1)}(r), \tag{33}$$

and that the hyperpolarizability contribution can be similarly expressed as

$$\alpha^{\text{hyper}} = 2 \int dr \int dr'\, [\chi_A^{\text{hyper}}(r)\, \rho_B^{(0)}(r') + \chi_B^{\text{hyper}}(r')\, \rho_A^{(0)}(r)] \frac{(r - r')}{|r - r'|^3}, \tag{34}$$

where

$$E_0\nabla : \chi_A^{\text{hyper}}(r) \cdot E_0 = -E_0^2\, \rho_A^{(2)}(r). \tag{35}$$

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Now recall the classical electrostatics equations relating $\mu(r)$, the local dipole moment, $E(r)$, the total electric field at r, and the linear and lowest order nonlinear susceptibilities $\chi'(r)$ and $\chi''(r)$:

$$\mu(r) = \chi'(r)\,E(r) + \chi''(r) : E(r)\,E(r). \tag{36}$$

The total electric field is defined by

$$E(r) = E_{\text{applied}} + \int dr'\,\rho^{(0)}(r')\,\frac{(r-r')}{|r-r'|^3} + \int dr'\nabla^2\,\frac{1}{|r-r'|}\cdot\mu(r'). \tag{37}$$

A single iteration of equations (36) and (37) leads to a $\alpha(R)$ which is equal to the sum of α^{linear} and α^{hyper} defined by equations (32) and (34). Since equations (32) and (34) follow directly from a 'first principles' quantum mechanical calculation of the response of interacting atoms to an applied electric field, this result establishes the validity of continuum electrostatics theory for local descriptions [see equations (36) and (37)] of molecular systems.

While the above argument of Oxtoby (1978) vindicates the basic starting point of the Oxtoby–Gelbart approach, it also makes explicit several shortcomings:

1. The hyperpolarizability terms given by equations (34) and (35), and discussed also by Clarke et al. (1978), were not considered.

2. Because of the overlap between $\mu_A(r)$ and $\mu_B(r')$, the behaviour of the total electric field at $r = r'$ must be treated more carefully than in the Oxtoby–Gelbart formulation (see Sipe & Van Kranendonk (1978) and Clarke et al. (1978) for a thorough discussion of this point). In particular, the term $-\frac{4}{3}\pi\,\mu(r)$ in equation (37), arising from the second term in

$$\nabla^2(|r-r'|)^{-1} = T_{k_0\to 0}(r-r')|_{\text{eq. (14)}} - \frac{4\pi}{3}\,I\delta(r-r'),$$

must be retained: it provides a non-vanishing contribution to the trace of α^{linear} which was lacking in the original Oxtoby–Gelbart theory.

3. The form of the local susceptibility $\chi(r)$ is found to be different from that postulated by equation (23).

4. A second iteration of the continuum equations (36) and (37) is shown to lead to difficulties associated with the non-uniformity of the first order field. More explicitly, (i) the applied field polarizes the charge distribution of one atom which (ii) induces a quadrupole moment in the other which in turn (iii) induces a dipole moment back in the first. The second step, involving polarization due to a field gradient, cannot be correctly calculated via a local susceptibility description. (See Sipe & Van Kranendonk (1978) and Clarke et al. (1978) for a more complete analysis of this problem.)

The hyperpolarizability contribution to $\beta(R)$ has been evaluated by Clarke et al. (1978) within a scheme equivalent to that outlined by equations (27)–(35) above. In the case of the He—He diatom, they find that the deviations from point dipole behaviour due to α^{linear} charge cloud overlap corrections are largely compensated by those from the α^{hyper} terms. (A similar conclusion is reported by Oxtoby (1978) for the case of two interacting hydrogen atoms.) Thus we must regard as fortuitous the agreement reported earlier in this section between the Oxtoby–Gelbart $\beta(R)$ values (which neglect the hyperpolarizability effects) and those obtained by experiment and Hartree–Fock calculation. A simple explanation of the non-d.i.d. effects remains to be found. In particular, careful additional studies must be carried out on the importance of exchange effects and of second order perturbation theory contributions [see equation (26)] to the interaction polarizabilities.

Until last year all measurements of $I_{xz}^{(2)}(\rho \to 0)$ indicated (Thibeau *et al.* 1970; McTague *et al.* 1972; Lallemand 1972) that $\langle[\beta(R)]^2\rangle_{\rho \to 0}$ (see equation (17)) was *ca.* 30% smaller than the value indicated by $\beta_{\mathrm{d.i.d.}}(R) = 6\alpha^2/R^3$. Thus it was believed that a proper theory must account for a substantial lowering of the interaction anisotropy. Recent data of F. Barocchi (1977, personal communication) however, indicate that $\langle[\beta(R)]^2\rangle_{\mathrm{exp}}$ may actually exceed $\langle[\beta(R)]_{\mathrm{d.i.d.}}^2\rangle$, i.e. that the deviations of $\beta(R)$ from classical point dipole behaviour are not negative. This possibility is also suggested in recent attempts to distinguish between different forms for $\beta(R)$ from analyses of the line shape of the collision-induced spectrum. Alder *et al.* (1973 *b*), for example, have used the molecular dynamics method to evaluate $I_{xz}^{(2)}(\omega)$ for Ar, with several different forms of $\beta(R)$, over a broad range of thermodynamic states. For room temperature and densities less than 500 amagat† the computed spectra are not very sensitive to the choice of $\beta(R)$: for each $\beta(R)$ the exponential wings ($|\Omega| > 15 \mathrm{~cm}^{-1}$) agree with experiment within the uncertainties due to the laboratory measurements and to the limiting statistics of the computer simulation. At higher densities, e.g. for the triple point ($T \approx 90 \mathrm{~K}, \rho \approx 780$ amagat), the differences in short range $\beta(R)$ behaviours appear to give dissimilar high frequency slopes, but further calculations (e.g. at still higher densities) are necessary to establish this more definitely. In any case, the $\beta_{\mathrm{d.i.d.}}(R)$ ($|\Omega| > 15 \mathrm{~cm}^{-1}$) lineshape appears to be closest to experiment, suggesting that the deviations from $1/R^3$ behaviour implied by $\beta(R)$'s which include overlap corrections only must be compensated by other non-point-dipole effects (such as the hyperpolarizability or exchange or second order terms mentioned earlier).

The fact that the depolarized lineshape is relatively insensitive to $\beta(R)$ at low densities is consistent with the fact that the dominant collisional effects in these thermodynamic states involve large R; and, at large R, all of the $\beta(R)$ vary as $6\alpha^2/R^3$. At higher densities the shorter range interactions become important and the calculated scattering shows the differences in the $\beta(R)$ values. The wings are precisely the part of the line shape which is expected (Stuckart *et al.* 1977; Bucaro & Litovitz 1971; Oxtoby 1977) to be most dramatically affected by short range two-body dynamics. (See, however, the calculations and discussion of Berne *et al.* (1973).) However, as mentioned above, even the wings are well accounted for by a d.i.d.–$\beta(R)$. Madden (1977) has shown further that all observed features of the line shape, including both the quasi-elastic ($|\Omega| < 15 \mathrm{~cm}^{-1}$) Lorentzian peak (An *et al.* 1976) and the exponential wings, are well accounted for by a single d.i.d. polarization mechanism. Thus it appears possible that a proper calculation of the collisional anisotropy will reveal $\beta(R) \approx \beta_{\mathrm{d.i.d.}}(R)$ for all R of interest. The question of non-point-dipole $\beta(R)$ behaviour remains unanswered, a challenge to new theoretical and experimental work on the classical atomic fluids. There is also beginning to emerge an analogous set of problems in the study of molten salt solutions (Bounds *et al.* 1977; Woodcock 1975) and superionic conductors (Rahman 1976; Geisel 1978) but there the collisional polarizability effects are much larger and the fluid structure and dynamics much more subtle.

(b) *Multiple light scattering (m.l.s.)*

Consider again the starting expression (see equation (13)) for the second order integrated scattering intensity for atomic fluids. Whereas above we discussed the $k_0 \to 0$ limit, we now treat the situation where the range of spatial correlations between particle positions becomes comparable with the wavelength of incident light. In this case (e.g. critical fluids) all the

† 1 amagat unit = 0.0446 mol l^{-1} at unit pressure.

factors in the integrand of equation (13) must be retained without simplification. Recall that $T_{k_0}(r) \cdot \mu$ can be rewritten as

$$\exp\left(ik_0 r\right) \left\{ \frac{k_0^2}{r} \left[(\hat{r} \times \hat{\mu}) \times \hat{r} \right] + \left(\frac{1}{r^3} - \frac{ik_0}{r^2} \right) \left[3\hat{r}(\hat{r} \cdot \hat{\mu}) - \mu \right] \right\}$$

$$= \text{electric field at } r \text{ due to oscillating } (ck_0) \text{ dipole } \mu \text{ at origin,} \quad (38)$$

thereby making explicit the fact that the electric field is transverse only in the far $(k_0 r \gg 1)$ zone. That is, the true radiation term arising from $1/r$ survives only because of the long-range correlations. The $1/r^3$ and $1/r^2$ contributions can henceforth be associated with the collision-induced (short range correlation) effects discussed in part (a). We write:

$$I_{zx}^{(2)} = I_{zx}^{(2)} \text{ (c.i.s.)} + I_{zx}^{(2)} \text{ (d.l.s.)}, \quad (39)$$

where $I_{zx}^{(2)}$ (c.i.s.) is the $k_0 \to 0$ limit of equation (13) and $I_{zx}^{(2)}$ (d.l.s.) is equation (13) with only the $1/r$ terms retained in the $T_{k_0}(r)$ factors.

It is natural at this point to decompose the 4-point correlation function into its disconnected and connected parts (Korenman 1970):

$$\langle \Delta\rho(1)\ \Delta\rho(2)\ \Delta\rho(3)\ \Delta\rho(4) \rangle = \langle \Delta\rho(1)\ \Delta\rho(2) \rangle \langle \Delta\rho(3)\ \Delta\rho(4) \rangle + \langle 1\ 3 \rangle \langle 2\ 4 \rangle$$

$$+ \langle 1\ 4 \rangle \langle 2\ 3 \rangle + \langle \Delta\rho(1)\ \Delta\rho(2)\ \Delta\rho(3)\ \Delta\rho(4) \rangle_c. \quad (40)$$

The connected (c) correlation function is what remains after substracting all possible products of lower order connected correlation functions involving the same density fluctuations. [Since $\langle \Delta\rho \rangle = 0$, the 2- and 3-point correlation functions, $\langle \Delta\rho(1)\ \Delta\rho(2) \rangle$ and $\langle \Delta\rho(1)\ \Delta\rho(2)\ \Delta\rho(3) \rangle$, naturally contain no disconnected contributions.] The importance of this decomposition is that the connected correlation functions are short-ranged, equalling zero when any pair of arguments is separated by a macroscopic distance. Thus $\langle 1\ 2\ 3\ 4 \rangle_c$ will contribute to the depolarized light scattering intensity only when all four atoms are within a correlation length ξ of one another; ξ (to be discussed below) is small compared to the dimensions of V_S and V_I. The disconnected terms in equation (40), on the other hand, will contribute to $I_{xz}^{(2)}$ (d.l.s.) for configurations in which the pairs of atoms are separated by macroscopic distances. They are thus expected to dominate the double light scattering intensity by a factor of V/ξ^3 (Swift 1973); the $\langle 1\ 2\ 3\ 4 \rangle_c$ contribution can be neglected.

The contribution of the disconnected terms in equation (40) to $I_{zx}^{(2)}$ (d.l.s.) was first evaluated analytically for the special case where the illuminated volume V_I is located at the centre of a much larger, approximately spherical observed volume V_S (of radius R_S). Oxtoby & Gelbart (1974a) found in particular that

$$I_{zx}^{(2)} \text{ (d.l.s.)} \approx \frac{\alpha^4}{R_d^2} \left(\frac{\omega_0}{c} \right)^8 |E_0|^2 \frac{64\pi^3}{15} \rho^4 V_I \xi_0^2 R_S \xi^4. \quad (41)$$

Here it has been assumed that the long range part of the pair correlation function can be expressed in the usual Ornstein–Zernicke form:

$$\langle 1\ 2 \rangle_{\text{long range}}(r) \equiv g_{\text{l.r.}}(r) - 1 = (\xi_0/r)(\exp(-r/\xi)), \quad (42)$$

and that $k_0 \xi = 2\pi \xi/\lambda_0 \lesssim 0.3$ as is indeed the case in all of the experiments which we analyse. Note that the right hand side of equation (41) is essentially the square of the first order scattering intensity given by equation (9):

$$\int_{-\infty}^{+\infty} d\Omega\ I^{(1)}(\Omega) \approx k_0^4 \alpha^2 S(K) \approx k_0^4 \alpha^2 \xi_0 \xi^2.$$

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The fact that real double scatterings take place, i.e. that some of the light waves scattered by atoms in V_I do not get out of the cell without being scattered again, means of course that the detector measures contributions to $I_{zx}^{(2)}$ from atoms polarized outside the path of the incident beam. Thus the observed intensities no longer depend only on V_I, but also on the size of part of the sample which would otherwise be 'dark'. In particular we see (equation (41)) that for a spherical V_S with radius R_S, $I_{zx}^{(2)}$ (d.l.s.) is proportional to R_S.

In order to discuss experimental data for Xe it is necessary to approximate $I_{zx}^{(2)}$ (c.i.s.) for Xe near its critical point. As described in detail elsewhere (Oxtoby 1975; Gelbart 1978) we can easily arrive at the following rough estimate of the collision-induced depolarization:

$$I_{zx}^{(2)} \text{ (c.i.s.)} \approx (\alpha^4 k_0^4 |E_0|^2 V_{IS} \rho_{crit}^2 / R_d^2)(6 \times 10^{22} \text{ cm}^{-3}). \tag{43}$$

(Here V_{IS} is the portion of the illuminated volume seen by the detector.) A more accurate estimate can be obtained by measurements carried out at ρ_{crit}, but at temperatures far from T_c. Nevertheless equation (43) suffices nicely for purposes of the present discussion. Recalling equation (39), we now add equations (41) and (43) to obtain

$$I_{(total) zx}^{(2)} \approx \frac{\alpha^4}{R_d^2} k_0^4 |E_0|^2 \rho_c^2 V_I \left\{ (6 \times 10^{22} \text{ cm}^{-3}) + \frac{64\pi^3}{15} \rho_c^2 \xi_0^2 R_S (k_0 \xi)^4 \right\}. \tag{44}$$

Furthermore, as long as $k_0 \xi \lesssim 0.3$, second order scattering remains a small effect compared with first order scattering. Thus the polarized intensity $I_{(total) zz}$ can be well approximated by equation (9) from the introduction:

$$I_{(total) zz} \approx I_{zz}^{(1)} \approx \frac{\alpha^2}{R_d^2} k_0^4 |E_0|^2 V_I S(K) \xrightarrow[\text{critical point}]{K\xi \lesssim 0.3} \frac{\alpha^2 k_0^4}{R_d^2} |E_0|^2 \rho_c^2 V_I 4\pi\xi_0 \xi^2. \tag{45}$$

(Note that $k_0 \xi \lesssim 0.3$ implies $K\xi \lesssim 0.3$ since $K \equiv |k - k_0| \approx k_0$ for 90° scattering.) Dividing equation (44) by equation (45) gives, finally:

$$\Delta = \frac{I_{zx}}{I_{zz}} \approx \frac{\alpha^2}{4\pi\xi_0} \left\{ \frac{6 \times 10^{22} \text{ cm}^{-3}}{\xi^2} + \left[\frac{64}{15} \pi^3 \rho_c^2 \xi_0^2 R_S k_0^4 \right] \xi^2 \right\}. \tag{46}$$

ξ is the only quantity in equation (46) which is sensitive to the temperature in the critical region. Consider an experiment in which Xe is prepared at its critical density, and T is lowered towards T_c. Then, as the critical point is approached and ξ becomes larger, Δ will initially decrease. This is because I_{zx} is dominated by $I_{zx}^{(2)}$ (c.i.s.) which stays constant since it involves only contributions from short-range correlations. But in this same region I_{zz} increases with ξ^2, and thus Δ decreases as ξ^{-2}. For temperatures closer to T_c, however, the double scattering term in $I_{zx}^{(2)}$ takes over, increasing as ξ^4. Δ is then expected to increase with ξ^2. The exact position and shape of the minimum will depend of course on the actual values of ρ_c, ξ_0, R_S and k_0.

Reith & Swinney (1975a) have carried out experiments which measure the depolarization ratio for a sample of Xe at its critical density, over the temperature range $0.05 \leqslant T - T_c \leqslant 10°$. Most of the results were obtained with an Ar-ion laser ($\lambda_0 = 4679$ Å),† but at $T - T_c = 0.496°$ an Ar laser (5145 Å) and a He–Ne laser (6328 Å) were also used. The incident light from the laser was linearly polarized perpendicular to the scattering plane and the light scattered at 90° passed through a lens and rotatable linear polarizer. The lens formed an image of the sample on a pair of crossed adjustable slits. The horizontal slit was adjusted so that the observed

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† $1\text{Å} = 10^{-10}\text{ m} = 10^{-1}\text{ nm}$.

sample heights ranged from $S = 0.261$ to 1.490 mm; the vertical slit which determined the width W of sample seen by the detector was held fixed at $W = 0.54$ mm. Light passing through the crossed slit ($S \times W$ rectangle) was imaged by a second lens onto the cathode of a photo-multiplier tube which measured its intensity. The collimated, focused beam passing through the sample had a diameter of 0.21 mm. Although this experimental geometry is quite different from that assumed in the theoretical discussion above, the theory can be tested qualitatively by associating R_S with S. In particular Reith & Swinney (1975a) found a curve of Δ against $T - T_c$ which had the predicted shape, the minimum lying at 1–2° from T_c. Furthermore, Δ was found to increase linearly with S and k_0^4, in agreement with equation (46).

Recall that the dominant contribution to I_{zx} arises from the disconnected term $\langle \Delta\rho(r_1)\,\Delta\rho(r_3)\rangle$ $\langle \Delta\rho(r_2)\,\Delta\rho(r_4)\rangle$ in the 4-point correlation function. This contribution arises from the inter-ference between two doubly scattered waves, the first involving the successive polarization of atoms 1 and 2 [see the $T_{k_0}(r_1 - r_2)$ term in equation (13)] and the second involving 3 and 4 [see $T_{k_0}(r_3 - r_4)$]. $\langle 1\,3\rangle\langle 2\,4\rangle$ forces the initial polarizations at r_1 and r_3 to take place within a correlation length of one another and similarly for the final (second) polarizations at r_2 and r_4. The r_1–r_2 and r_3–r_4 separations can in principle be small (i.e. $\lesssim \xi$) but these configurations are much less likely (by at least the factor of $\xi/V_S^{\frac{1}{3}}$ mentioned earlier) than larger separation ones. Thus the two pairs 1–2 and 3–4 are essentially uncorrelated, and the double scattering event can be regarded as successive (and independent) single scattering.

Reith & Swinney (1975a) have exploited this conclusion by expressing the second order d.l.s. intensity in terms of the familiar single scattering cross sections, $I_{zz}^{(1)}(90°) = \sigma_0(|E_0|^2 V_{\mathrm{IS}}/R_d^2)$; here $\sigma_0 = \alpha^2 k_0^4 S(|k_0 - k|) \approx 4\pi\alpha^2 k_0^4 \rho^2 \xi_0 \xi^2$ for $k_0\xi \lesssim 0.3$. In particular, they show that the depolarization ratio assumes the form

$$\Delta = I_{zx}^{(2)}\ (\text{c.i.s.})/I_{zz} + \sigma_0 g S. \tag{47}$$

g is a constant which is determined completely by the characteristics of the volumes V_I and V_S. In the case of the Reith–Swinney experiment, $g \approx \frac{1}{4}\pi$. Since $I_{zz} \approx \xi^2$ and $\sigma_0 \approx k_0^4\xi^2$ we see that equation (47) predicts the same $\xi(T)$, k_0 and S dependence for Δ as was discussed earlier; when $g = \frac{4}{15}\pi$, equations (47) and (46) are in fact identical. What is significant about the particular form of equation (47) is that Δ is shown to be linear in σ_0, the differential cross section for single scattering. σ_0 is proportional (by a factor of $\alpha^2 k_0^4$) to the all-important static structure factor $S(K)$ which is, in turn, proportional to the isothermal compressibility κ_T, etc. Since $I_{zz}^{(1)}(90°) = \sigma_0(|E_0|^2 V_{\mathrm{IS}}/R_d^2)$, σ_0 has commonly been obtained from absolute intensity determinations of polarized scattering. However, because ratios of scattering intensities are measured more accurately and easily than absolute cross sections, equation (47) suggests a valuable new method for learning about σ_0. Reith & Swinney (1975a, b) have shown that it is indeed feasible to determine σ_0 from the depolarization ratio measured in critical fluids and in solutions of macromolecules whose dimensions are not too small compared with the wave-length of light.

Experimental studies of the critical behaviour of the depolarization ratio have also been pursued by Beysens et al. (1975) and by Garrabos et al. (1976). Their results provide further verification of the temperature dependence discussed above. Also, Beysen & Zalczer (1977) have analysed the frequency dependence of the depolarized intensity in the critical region. They discuss how the experimental lineshape can be expressed as a convolution of $I^{(1)} \approx S(k', \omega')$ with itself (see Boots et al. (1975a, b, 1976) and Reith & Swinney 1975a)), consistent

[159]

with the spectrum being dominated by double scattering events which involve independent and successive single scatterings.

Throughout the above discussion we have neglected the double scattering contributions to the polarized intensity, as is appropriate for $k_0\xi < 0.3$ and $\boldsymbol{k}_0 \perp \boldsymbol{k}$. Nevertheless, even though $I_{zz}^{(2)}$ (d.l.s.) is more than one hundred times smaller than $I_{zz}^{(1)}$ over the temperature range of interest, the angular distribution of $I_{(\text{total})\,zz}$ can be significantly distorted by double scattering contributions. This possibility was first suggested by Oxtoby & Gelbart (1974 b) who showed that small double scattering contributions give rise to easily observable downward curvature in the usual Ornstein–Zernicke–Debye plots of $1/I_{(\text{total})\,zz}$ against $\sin^2(\tfrac{1}{2}\theta_s)$. (Here θ_s is the angle between $\boldsymbol{k}_0$ and $\boldsymbol{k}$.) Neglect of this effect leads to spurious inferences about the pair correlation function for critical fluids. This point has been treated more thoroughly by Boots $et\ al.$ (1975 a, b, 1976), who have developed a general, rigorous theory of multiple light scattering.

In the theory of Boots $et\ al.$ (1975 a, b, 1976) the calculated cross sections contain the various 'local field' correction factors (e.g. powers of n and $(n^2+2)/3$, etc.) which we have dropped in the present discussion, and attenuation of the incoming and outgoing light has been properly treated. By using the critical point parameters and V_S and V_I dimensions appropriate to the depolarization ratio measurements on CO_2 of Trappeniers $et\ al.$ (1975), Boots $et\ al.$ (1975 a, b, 1976) calculated values for Δ which were in excellent agreement with experiment over the temperature range $0.02^\circ \leqslant T - T_c \leqslant 0.7^\circ$. This suggests negligible contributions from collision-induced effects, beam deflection by gravity-induced density gradients, and triple and higher order multiple scattering.

The only published experimental study of higher than double scattering by simple fluids is that of Trappeniers $et\ al.$ (1977). Recall that just as $I_{zx}^{(2)}$ (d.l.s.), involving two successive single scatterings, has been shown to vary as σ_0^2, $I_{xz}^{(3)}$ (t.l.s.) is expected to vary as $\sigma_0^3 \approx \kappa_T^3$. As argued by Trappeniers $et\ al.$ (1977) however, its dependence on V_S should be negligible compared to that of $I_{zx}^{(2)}$ (d.l.s.). This is because the second scattering event can take place anywhere in the sample, rather than only in V_S. Now suppose we approach near enough to T_c, along the critical isochore, so that triple scattering becomes observable. Then since

$$\Delta_{\text{d.l.s.}}^{(2)} \equiv (I_{zx}^{(2)}\ (\text{d.l.s.})/I_{zz}) \approx S \text{ for small } V_S\text{-height } S, \text{ whereas } \Delta_{\text{c.i.s.}}^{(2)} \equiv I_{zx}^{(2)}\ (\text{c.i.s.})/I_{zz}$$

is independent of S, a plot of Δ against S should yield $\Delta_{\text{c.i.s.}}^{(2)} + \Delta_{\text{t.l.s.}}^{(3)}$ when extrapolated to $S = 0$. However, since $\Delta_{\text{c.i.s.}}^{(2)}$ is essentially constant in the critical region, this $S = 0$ intercept should vary with temperature according to $\Delta_{\text{t.l.s.}}^{(3)} \equiv (I_{zx}^{(3)}(\text{t.l.s.})/I_{zz}) \approx \kappa_T^3/\kappa_T \approx (T - T_c)^{-2.46}$. Over the range $0.02^\circ \leqslant T - T_c \leqslant 0.1^\circ$ this is indeed the behaviour found by Trappeniers $et\ al.$ (1977). At temperatures still closer to the critical point, the measurements are disturbed by fluid inhomogeneity due to gravity-induced density gradients and by higher order multiple scattering.

Another interesting application of the multiple scattering theory, recently considered by Metiu (1977, 1978), involves the study of fluid mixtures undergoing phase separation via spinodal decomposition. For systems which are quenched into their spinodal region, thermodynamic instability results in amplification of long wavelength concentration fluctuations (the effective diffusion coefficient is negative). Whereas it is generally believed that the linearized Cahn equation (Langer $et\ al.$ 1975) provides a qualitatively correct description of the concentration fluctuations at short times, the light scattering evidence is still somewhat ambiguous. As

Metiu has pointed out, part of the difficulty may be associated with multiple light scattering contributions which have not been considered in previous analyses. He has shown for example, that whereas the linearized Cahn equation predicts that the intensity of a single scattering interference ring will grow exponentially, the growth associated with double scattering contributions is decidedly non-exponential. Non-exponentiality can also arise, of course, from the breakdown of the linearization of the Cahn equation. In any case, Wong & Krobler (1977) have recently reported significant deviations from exponential behaviour in their study of the growth of interference ring intensity following the quenching of isobutyric acid–water mixtures into their spinodal regions. Further experimental and theoretical work will be of great importance in helping to understand further the dynamics of fluctuations in these thermodynamically unstable systems.

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Discussion

R. K. BULLOUGH (*Department of Mathematics, U.M.I.S.T., PO Box* 88, *Manchester* M60 1QD). I should like to make a general comment on multiple scattering. Professor Gelbart is concerned with microscopic scattering processes between polarizable atoms or molecules. The macroscopic optical properties of his simple classical fluid are built up from these microscopic processes. In this picture, single scattering is not the first Born approximation Dr Pike has mentioned. Single scattering with its proper factors of refractive index (dielectric constant) contains multiple scattering processes of all orders which can be explicitly summed and subsumed in just these refractive index factors (Bullough *et al.* 1968; Bullough & Hynne 1968). In consequence, there is the risk that in isolating one multiple scattering process for particular study its contribution is being counted twice, or at least, not precisely once. This is exactly the situation surrounding collisionally induced three-body scattering: two three-body multiple scattering diagrams arise and the collisionally induced scattering (c.i.s.) in both sums into the macroscopic factor multiplying single scattering. In the four-body scattering two of the three c.i.s. diagrams sum into the macroscopic factor. The third, which I call the four-body depolarization diagram, is concerned with the depolarization discussed by Professor Gelbart, but there are already significant differences of detail between the results of the exact study (Bullough *et al.* 1968; Bullough & Hynne 1968) and Gelbart's apparently more *ad hoc* four-body scattering term. I am not familiar with Professor Gelbart's derivation of this scattering term: thus I would like to ask him first of all to what extent he feels this possibility of overcounting can be discounted.

In the exact study there is also a double infinity of 5, 6, 7, ... -body c.i.s. diagrams which can be summed into the four-body depolarization diagram. This means roughly that there is a refractive index factor on this diagram. My colleague F. Hynne in Copenhagen has explicitly carried out some of this summation in a recent paper (Hynne 1977), in terms of a 'screened' photon propagator and a 'screened' outgoing scattering process. I cannot say that these additional processes can change the estimate of the four-body depolarization diagram by 30 % at the low density of Ar used for the experiments. Certainly, for condensed liquids (refractive index = 1.5) refractive index factors can change the absolute value of the total scattered intensity by a factor of 3. For Xe near the critical point, the factor is about 1.4. However, the all order multiple scattering theory shows that there is yet another feature involved, namely that infinite series of scattering terms involving the same power of atomic number density arise. These terms include dipole–induced-dipole effects of the kind considered by Professor

Gelbart. I think it would be worthwhile looking in detail at the totality of these terms in connection with the d.i.d. effects Professor Gelbart mentions. This is my second point.

Incidentally, I am a bit concerned with the problem of overcounting in the argument Professor Gelbart uses for distributed polarizability within the atoms. The definition of the fundamental polarizable units in classical dielectric theory is always arbitrary. The multipole contributions constituting the finite size corrections to point dipoles are well defined in principle however and in using them overcounting can be avoided. Their important effects in connection with the c.i.s. are static quadrupole and octopole effects depending on $\nabla\nabla\, r^{-1}$ and $\nabla\nabla\nabla\, r^{-1}$, but these effects converge very slowly. Some years ago my colleague B. V. Thompson and myself developed a theory (Bullough *et al.* 1968) of the dielectric properties of a classical fluid from the first principles of quantum mechanics, deriving the propagator $r^{-1} \exp(\mathrm{i}k_0 r)$ of the vector potential rather than the dipole propagator $(\nabla\nabla + k_0^2 U)\, r^{-1} \exp(\mathrm{i}k_0 r)$. The calculation becomes extremely complex without a multipole expansion which is the natural choice for neutral 'classical' atoms. My present opinion is that the all-order summation of polarizability terms at fixed number density referred to already, together with a judicious inclusion of multipole corrections, has the merit of providing a controlled count on contributions and may be the best approach to the d.i.d. problem. As my third point I would therefore like to ask Professor Gelbart for any comments he might have on this remark.

Concerning the multiple scattering (m.l.s.) Professor Gelbart considers, it is perhaps useful to point out that Fixman (1955) first wrote down the four-body expression which leads to depolarization of the scattered light. Since that time F. Hynne and myself have developed the general theories of multiple scattering which treat all orders of multiple scattering in terms of 'unscreened' (Bullough & Hynne 1968) and 'screened' (Hynne 1977) propagators, and include all orders of depolarization diagrams. The true m.l.s. parts are apparently not summable into refractive index factors and do not seem to represent any of the macroscopic multiple scattering processes we once conjectured (Bullough *et al.* 1968; Bullough & Hynne 1968).

In the theory in terms of unscreened propagators, a principal problem which emerged was the effects of finite volume. The key to these is a development of the multiple scattering terms in terms of generalized Ursell functions or in terms of the Y-functions due to F. Hynne (1975). The Ursell functions cover the connected parts of a multiple scattering integral to which Gelbart refers. The terms which remain are disconnected, do not quite agree with those Gelbart quotes at four-body, and play two roles: one is to provide vital factors, in terms of refractive index, to the single scattering; the other is to provide specific terms which are of m.l.s. type. These are surface dependent and represent in some way transmission and reflexion coefficients for multiple scattering leaving the scattering volume. In the 'bulk scattering theory' (Hynne 1977) in terms of screened photon propagators, these surface terms do not arise. The bulk theory is concerned with an infinite scattering medium so that surface terms should indeed be absent.

We have examined these surface terms for the integrated three-body scattering (Bullough *et al.* 1968; Bullough & Hynne 1968) and for four-body scattering. The latter contribute terms to the depolarized intensity $I_{zx}^{(2)}$ (d.l.s.) (in Gelbart's notation). We have assumed that the scattering volume is an infinite parallel-sided slab with light normally incident upon it because this is the scattering geometry for which it is easiest to calculate the behaviour of the coherently transmitted light (more precisely we consider a flat cylinder of very large radius and a plane wave axially incident upon it). For the integrated intensity, or more specifically for the optical extinction or turbidity, we have found no term linear in the slab width d. Typically,

the oscillatory terms $\exp(ik_0 r)$ in the propagators $r^{-1}\exp(ik_0 r)$ of the radiation field are always together sufficient to convert an integral linear in d to one which is, at most, finitely oscillating at the surface of the slab. These terms represent the diffraction and transmission of the multiply scattered light induced by the finite geometry. We have concluded from this that these terms are weakly geometry dependent, that they depend on k_0^8 for four-body scattering, and that they can become important close enough (but very close) to the critical point.

For the scattered intensity at fixed scattering angle, however, there are also terms which throw intensity from atomic group to atomic group of the scattering medium. These terms are, roughly speaking, linear in the dimensions of the scattering region, and would diverge for an infinite region (much as in Olber's paradox in cosmology). In the particular geometry considered by Professor Gelbart (a small spherical illuminated region inside a larger spherical scattering region), I can see that such terms could have the linear dependence on the radius R_s of the scattering region he reports. We have not considered any spherical geometry in detail because we are not able to handle the coherent and incoherent parts of the scattering consistently for it.† My fourth question to Professor Gelbart is, however, to ask him if he has also looked at the non-depolarizing four-body m.l.s. and whether he considers that this scattering might also have observable effects. In our view, the paradox between finite optical extinction and divergent four-body depolarized m.l.s. can be resolved only because all four-body m.l.s. processes combine together in the integrated scattering and we have proved quite generally that the integrated scattering at whatever order properly determines the extinction. Plainly, if terms linear in the size of the scattering cell arise in the expression for the extinction, it is no longer possible to define a complex refractive index for a scattering medium which is independent of its geometry, although other problems arise in the theory of complex refractive index when the scattering is large.

Finally, I would like to remark that in an unscreened theory the wavevector of the incident light takes on the refractive index of the scattering medium while the scattered wavevector does not do so without further consideration of multiple scattering processes. If the distinction between these two forms of wavevector is not made initially, it is not easy to disentangle the coherent and incoherent parts of the scattering. Indeed, a linear term in the scattering dimension arises in the connection between the external field amplitude and the induced dipole density, although this is not relevant to the R_s dependence that Professor Gelbart finds in four-body depolarized scattering. Since, as I understand it, he does not place the refractive index of the medium in either the incident or scattered wavevector, I should like his opinion on the correct form of these wavevectors, and whether he is certain he isolates correctly the incoherent four-body scattering from the coherent scattering. This latter point has some bearing on the relation between multiple scattering and single scattering, but without detailed analysis I cannot see how numerically significant the details here might be.

References

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Bullough, R. K. & Hynne, F. 1968 *Chem. Phys. Lett.* **2**, 307–311. (This unscreened theory has not yet been reported in complete detail but should appear in such detail in the *K. danske Vidensk. Selsk. Skr.*, late in 1978.)

† In spoken discussion I mistakenly gave the impression that I had earlier derived exactly the expression $I_{xx}^{(2)}$ (d.l.s.) reported by Professor Gelbart. I meant only to state that Hynne and myself have studied all comparable three-body and four-body surface terms in our particular geometry. It is particularly nice to see the use both Professor Gelbart and Reith and Swinney have made of the special features of four-body m.l.s.

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W. M. GELBART. Professor Bullough's first, second, fourth and fifth questions are all related to the same fundamental problem, namely that of separating 'real' multiple scattering contributions from refractive index corrections (macroscopic factors). In our published work on depolarized light scattering at the gas-liquid critical point, we did not attempt to sum systematically the multiple scattering diagrams to arbitrary order in the interparticle correlations. Thus, for example, we did not obtain a depolarization ratio which contains the appropriate factors of $n^2 - 1$, $2n^2 + 1$, etc. Nor did we include explicitly the attenuation of light in the sample. Instead, our purpose was to characterize the functional form of the 'real' double scattering contributions to the depolarization and to estimate their approximate dependence on wavelength, temperature and sample dimensions. As discussed in the above paper, these predictions have been unambiguously confirmed by the experiments of Reith & Swinney and of others (see references in text).

As for the non-depolarizing higher order effects about which Professor Bullough enquires, we have again treated them only approximately. In particular, we estimated the effects of the four-body contributions [$I_{zz}^{(2)}$ (d.l.s.)] to the angular asymmetry of the polarized intensity. These effects were found to give Ornstein–Zernicke–Debye plots with significant downward curvature at small angles. F. Hynne (1977, see Bullough's references), has most recently derived two-body corrections which partially offset these four-body contributions and which were not included in our original formulation; their relative importance can only be determined by a consistent treatment of the coherent and incoherent multiple scattering effects. Hynne discusses this general problem by means of the screening transformations (of the dipole propagator) which describe the correct form for the incident and scattered wavevectors (see also Ladanyi & Keyes (1976) and references in text).

The inclusion of multipole corrections to the polarizability of a pair of interacting atoms, suggested by Professor Bullough in his remaining (third) question, has been considered by several investigators during this past year. While I did not have a chance to describe this work in my talk, it has been discussed critically in the above paper. The original Oxtoby–Gelbart approach to collisional polarizabilities can be derived as an approximation to the first order perturbation description of a pair of atoms in an external electric field; their assumption of a local continuum electrostatics is consistent with a first order treatment of the Coulomb interaction between the electrons and nuclei of the two atoms. A second iteration of the continuum equations (see equations (36) and (37) in the text), however, brings in electric field nonuniformities and hence induced polarization effects associated with quadrupole and higher order multipole moments. These corrections do indeed change significantly the collisional polarizability, as do the hyperpolarization and exchange effects also mentioned in the text. As stressed there, the complete *a priori* calculation of interaction anisotropy remains an open problem, even for the most simple of the noble gas systems.

Reference

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