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THE SCATTERING OF LIGHT
III†. EXTERNAL SCATTERING FROM A FINITE MOLECULAR FLUID

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We calculate the external incoherent scattering from a finite molecular fluid exposed to a weak, external, coherent electromagnetic field. The scattered field is detected outside the fluid and the system models a real scattering experiment in all its aspects. The analysis is based on a classical all order many-body theory developed in two previous papers. The theory is microscopic, i.e. is developed *ab initio* and in detail in terms of individual scattering processes *in vacuo* at a strictly molecular level. But it is shown that the collective action of these generates all of the macroscopic features expected in the external scattering: for example, the refractive index, as it was calculated previously from the many-body theory, plays much of its expected macroscopic role.

These macroscopic results are reached by showing that the complete scattering process (from a wave incident *in vacuo* on the fluid to a wave *in vacuo* scattered from the fluid) separates into three independent collective processes compactly described by a particular quadrilinear form quadratic in a field $\mathscr{E}$ induced in the fluid by any coherent external field, and quadratic in a 'weight' field $\boldsymbol{\varepsilon}$ describing the scattered field in the fluid. The internal fields $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ couple separately to the external incoming field and to one representing the external scattered field respectively. In each case they account for all collective surface effects. The kernel of the quadrilinear form accounts for all of the internal scattering processes in the fluid.

The weight field $\boldsymbol{\varepsilon}$ and the equations associated with it describe refraction and (multiple) internal reflection of the scattered light at the surface of the medium in all details: these collective surface effects are managed in a very effective way through a new reciprocity principle derived from the microscopic theory and containing a new form of optical extinction theorem for external scattering. The kernel of the quadrilinear form for internal scattering has a natural expansion describing macroscopic single and macroscopic multiple scattering agreeing with phenomenological ideas. The expansion is derived from a relation between the weight field and a propagator for the scattered wave.

We show that macroscopic single scattering contains processes displaying 'back-scattering coherence'. This phenomenon has not been recognized in molecular scattering theory before, and back-scattering enhancement very much like that recently observed in scattering from suspensions of dielectric particles, should be observable near a critical point of phase separation.

We give explicit formulae for macroscopic single scattering from a dilute gas up to two-body contributions with intermolecular correlations determined by a Lennard-Jones potential. We also show how Einstein's phenomenological single scattering formula can be derived from certain microscopic scattering processes of all orders. With a minor qualification the formula is valid in a generalized form up to neglect of terms of order six in the polarizability per unit volume.

1. Introduction

The present paper reports a theory of external light scattering; it is the final part of a series of three papers presenting a classical many-body theory of the optics of molecular fluids. The foundation of the unified theory was laid in the first paper (Hynne & Bullough 1984, to be referred to as part I) in which the problem of the response of a molecular fluid to light was solved. The second paper (Hynne & Bullough 1987, to be referred to as part II) and the present one treat the theories of the complex refractive index and of external light scattering respectively. In part I we demonstrated a close relation between these two theories. We shall utilize this relation here, but the present paper can be read independently of part II; it depends on part I in so far as it starts from results derived there, but otherwise it can be read independently by appealing to the review given in §2 below.

Systematic study of light scattering goes back at least to Tyndall (1869) and its theory to the single-particle work of Rayleigh (1899, 1918) and Cabannes (1921). Smoluchowski (1908) and Einstein (1910) pointed out the significance of fluctuations as a source of light scattering (ideas extended to account for intermolecular correlations in critical opalescence by Ornstein & Zernicke (1914, 1918) and Debye (1959)). Interesting relevant material is in van de Hulst (1957), Landau & Lifshitz (1958) and Chu (1967). We also cite McIntyre & Gormick (1964), Frisch & McKenna (1965), Mountain (1966), Kerker (1963), Rowell & Stein (1967), Cummings & Swinney (1970) and the many hundreds of references in, for example, Cummings & Pike (1974) as some indication of the different further developments of the subject.

Light scattering was first treated on a strictly molecular level by Yvon (1937) in a pioneering paper. The molecular theory was given a new point of view by Hoek (1939) and the molecular theory was then developed in different ways by Rosenfeld (1951), Lax (1951), Fixman (1955), Benoit & Stockmayer (1956), Buckingham & Stephen (1957), Mazur (1958), Kielich (1960, 1963, 1964), Bullough (1962, 1965, 1967), Theimer & Paul (1965), Fulton (1969), Boots *et al.* (1975*a*, *b*, 1976), Hynne (1977, 1980, 1987*a*, *b*), Hynne & Bullough (1982) and many others.

Inelastic scattering was first observed in fluids by Gross (1930) after Brillouin's (1922) prediction, and the central component of the (translational Raman) spectrum was subsequently explained by Landau & Placzek (1934). With the advent of the laser finer details of the spectrum of scattered light have become accessible and have been treated theoretically by Komarov & Fisher (1963), Pecora (1964), Pecora & Steele (1965), Mountain (1966), Tanaka (1968) and Crosignani *et al.* (1975), among others. Some of this work is already referenced above.

These theories are all theories of 'spontaneous' inelastic (or elastic) scattering in the sense introduced by Chiao (1969) (and references by Hopf & Stegeman (1986)). Chiao (1969) then extended to 'stimulated' Raman, Brillouin and other scattering (cf. also Hopf & Stegeman 1986, ch. 20). Here the intensity of the incoming wave plays a fundamental and quantitative role. More generally we refer to relatively simple descriptions of atom or molecule based theories in the very rich and active field of nonlinear optics in Louisell (1964), Chiao (1969), Kaiser & Mailer (1972), Sargent *et al.* (1974), Yariv (1975), Shen (1984) and Hopf & Stegeman (1986). For light scattering concerned with, for example, non-classical effects in resonance fluorescence we refer to Mollow (1969) and Buckingham *et al.* (1979). For related problems associated with transmission of light including self-induced transparency, optical bistability (and the role of the optical extinction theorem there) and the squeezing of light see, for example, Bullough (1971, 1977, 1988) and references therein.

Nevertheless the simpler case of linear elastic external light scattering is experimentally realizable and important; and the problem of constructing a fundamental unified many-body theoretical description of it *ab initio* in classical terms is already enormously complicated. A problem is that the scattering has a strong and complex dependence on the geometry of the scattering sample. Even the simple definition of a valid molecular scattering cross-section offers problems because the scattering is intrinsically non-local.

Solution of the many-body problem with the associated surface effects in the simple (linear, etc.) case therefore applies to an important class of physical phenomena and is a significant (even necessary) step towards a more complete many-body theoretical treatment involving, for example, nonlinear processes. In this paper we therefore complete the task of providing a theory of linear elastic external optical scattering consistent with the refractive index and dielectric theory developed in parts I and II so far. Our aim is to construct (as theory actually dictates) a complete description of a real scattering experiment.

The existence of surface-dependent terms in any such microscopic theory of optical scattering was recognized already by Yvon (1937). Although he did not manage to handle them, he introduced important physical ideas partly to circumvent the problem. Otherwise, surface dependence has been largely ignored in most relevant work on light scattering even though surface dependence in the form of bulk refraction and reflection (at least) has to be intrinsic to the theory.

The existence and importance of surface effects has been emphasized in our work from the beginning (Bullough 1962, 1965, 1967; Bullough *et al.* 1968; Bullough & Hynne 1968) and the problem of deriving techniques to handle the surface terms and to understand their significance has gradually been solved completely (Hynne 1970, 1975, 1977, 1980, 1987*a*, *b*; Hynne & Bullough 1972, 1982). We can now present a synthesis of the various parts of the solution.

The surface problem is a complicated one because there are really four separate surface problems to be solved. One is associated with refraction and reflection of scattered light at the surface of the fluid; another one is associated with macroscopic multiple scattering; a third one is related to back-scattering coherence; and a fourth more technical one remains in 'intermediate propagation in the medium'.

This means that to handle the surface dependence in a meaningful way at the microscopic level we have to transform light scattering in these terms to one in terms of concepts of macroscopic significance: refraction, reflection, macroscopic multiple scattering and back-scattering. In any such microscopic approach to the theory of light scattering all the macroscopic effects just mentioned are obliged to make their appearance. But they emerge first of all mingled with each other and with local scattering in forms which in no way represent their macroscopic significance.

It is the purpose of the present paper to show that the complete scattering process from an incoming wave in vacuum to a scattered wave in vacuum can be decomposed into well defined parts, which can be understood in these macroscopic terms, and that on this basis it is possible to treat all of the geometrical features of external light scattering.

It may be helpful if we briefly indicate how this analysis is achieved. The decomposition is based on a number of relations between 'propagators'. It is justified by the physical contents of these relations and is further supported by the uniformity and simplicity of the expressions and their natural relation to the refractive index theory.

The basic relations were derived in the paper I, and we shall summarize these relations and explain their meaning in §2. We consider the complete scattering process from an incoming wave in vacuum to a scattered wave in vacuum, and in §3 we show how this can be divided into three processes. We first separate it into a scattering process in the medium and the two transitions in and out of the medium at the beginning and end of the scattering process. We then show how the scattering process in the medium can be further analysed into an infinite series of multiple-scattering processes. In this way we may describe macroscopic multiple scattering in the medium in terms of macroscopic single scattering in the medium. In the course of explaining the decomposition of the scattering in §3 we shall indicate the role the various objects will come to play in the developments of the later sections, and in this way we provide an overview of the whole paper and a preparation for the detailed discussions to come.

So §3 already serves the purpose of outlining the argument of the paper, and we need only indicate here the organization of the succeeding sections. In §§4 and 5 we derive and discuss each of the partial processes into which the total scattering process naturally breaks down. The structure of the expression for the scattered flux is such that these partial processes can be treated independently of each other: it is expressed as a functional, equation (5.3) below. The functional, as such, describes scattering in the medium independently of how that process is coupled with the incoming and outgoing waves outside the medium. The particular fields that appear as arguments of the functional (to yield the externally scattered flux) describe the coupling of the scattering process in the medium with the external waves and the associated surface effects. So the partial processes of the total scattering process can be treated independently and then finally combined in a wholly natural, indeed straightforward, way.

Thus in §4 we go on to analyse the fields that appear as arguments of the functional for the scattered flux to show how the scattered light behaves at the surface of the medium. Here we find there exists a reciprocity principle that accounts for a part of the surface dependence of the scattering describable as refraction and reflection of the scattered light, and that the problem consequently can be solved through an argument involving a new form of extinction theorem for the scattered light comparable with that due to Ewald (1912, 1916), Oseen (1915) and Darwin (1924) for the incident light (as described by the response theory developed in the paper I). We demonstrate this way that the microscopic theory exhibits all of the effects one intuitively expects: refraction and reflection with the intuitively correct transmission and reflection coefficients, with intuitively correct transformation of the effective differential solid angle at the surface, and with a natural dependence on the polarization of an analyser, if present. The theory takes proper account of any system of stops used in any real scattering experiment. In short, all geometrical features are quantitatively accounted for. The reciprocity principle introduced also solves the problem of accounting for the contributions from scattering, which has made an arbitrary number of internal reflections inside the scattering medium.

In §5 we consider the form of the functional (5.3) for the scattered flux. This functional can describe the scattering process in the medium independently of the external waves. We develop it into an infinite series of 'macroscopic' multiple scattering. This expansion is the result of an iteration of an integral equation (which though straightforward offers an additional technical problem of convergence to solve). What makes this particular expansion significant is that we can demonstrate that its terms have all the properties we would require from multiple scattering in the macroscopic sense implied by strictly phenomenological theories. We also demonstrate the natural multiple scattering character of the terms by showing explicitly how the simplest multiple scattering terms are associated with damping of propagating waves.

In §5 we briefly discuss macroscopic single scattering. Intuitively an important characteristic of single scattering is that it is spatially localized; we find that macroscopic single scattering is local except for a peculiar class of processes. These non-local (and therefore slightly surface dependent) processes are shown to have a form incompatible with macroscopic ideas of multiple scattering. (Nevertheless they can be viewed as peculiar interference terms associated with multiple scattering, namely terms describing interference between a multiple scattering path and the time-reversed path.) They are shown to be similar to terms that are considered responsible for the phenomenon of back-scattering enhancement in the scattering from suspensions of macroscopic particles (Kuga & Ishimaru 1984; Van Albada & Langendijk 1985; Wolf & Marat 1985).

Section 6 develops the theory of a scattering cross-section per molecule in terms of macroscopic single scattering from a gas or low density fluid. Here we sum all two-body terms in an approximation similar to the one used in the refractive index theory in part II, and we show that (away from resonance) the two results wholly agree.

In §7 we consider Einstein's phenomenological light scattering formula, as modified by Yvon. We prove in detail that this macroscopic single-scattering formula involves microscopic multiple scattering processes of arbitrary order and that it holds (with a minor qualification) up to neglect of specific groups of terms starting at order six in the polarizability density, $n\alpha$. In this case we must neglect terms of relative order $O(k_0^2 l^2)$ with $k_0 = \omega/c$ at frequency ω and l an intermolecular correlation length. So the simple macroscopic formula apparently does not apply to critical opalescence beyond the lowest order in $n\alpha$. In the proof we separately derive exact microscopic expressions for the left and right sides of the phenomenological equation and then compare the two resulting series order by order.

In §8 we summarize the results of the paper and conclude this particular series of three interconnected papers.

2. Review of fundamental results

We shall develop the theory of external light scattering from results of part I, and for easy reference we briefly display and explain the necessary equations. The theory is formulated in terms of a number of propagators and other objects and the three subsections following introduce one by one each of the three quantities that are fundamental to the theory. The three quantities are the scattering kernel, the weight field and the screened radiator.

(a) *Scattering kernel*

We consider a scattering experiment in which a coherent electromagnetic wave, $\boldsymbol{E}(\boldsymbol{x},\omega)$, is incident on a fluid contained in a scattering cell of definite geometry. In response to such external field the system establishes an average polarization of the molecular medium, $\boldsymbol{P}(\boldsymbol{x},\omega)$ and an average electric field inside and outside the medium, $\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega)$. Other features of the response are the external incoherent scattering as well as higher moments of the field. The basic response problem, the determination of $\boldsymbol{P}$ and $\boldsymbol{\mathscr{E}}$ in terms of an external field $\boldsymbol{E}$, was treated in parts I and II by solving the pair of coupled equations (I 3.1) between $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{P}$, namely

$$\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega) + \int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}', \tag{2.1a}$$

$$\boldsymbol{P}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{2.1b}$$

We shall recall the definitions of F and $\boldsymbol{\Lambda}$ shortly. In this paper we are concerned with the incoherent scattering. The total flux per unit solid angle radiated from an instantaneous induced polarization $\boldsymbol{P}^{\mathrm{in}}$ can be obtained from the Poynting vector. The flux in the direction of the vector $\boldsymbol{k}$, detected with polarization $\boldsymbol{v}$, is given by (I 2.27*b*):

$$I^{\mathrm{in}}(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left|\int_V \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)\,\mathrm{d}\boldsymbol{x}\right|^2, \tag{2.2}$$

in which $\boldsymbol{e}$ is defined by

$$\boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{v}\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}), \quad |\boldsymbol{k}| = k_0 = \omega/c, \quad |\boldsymbol{v}| = 1, \quad \boldsymbol{k}\cdot\boldsymbol{v} = 0. \tag{2.3}$$

Equation (2.3) is (I 2.20*b*). (The sign in the exponential is actually wrong in (I 2.20*b*). But it appears correctly everywhere else in part I.)

The coherent scattering is obtained from (2.2) when the instantaneous polarization $\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)$ is replaced by the average polarization $\boldsymbol{P}(\boldsymbol{x},\omega)$; and the incoherent scattering is then the average of the total scattering (2.2) minus the coherent part, i.e.

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left\langle\left|\int_V \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\Delta\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)\,\mathrm{d}\boldsymbol{x}\right|^2\right\rangle, \tag{2.4}$$

in which

$$\Delta\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega) = \boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega) - \boldsymbol{P}(\boldsymbol{x},\omega), \tag{2.5}$$

is the instantaneous fluctuation of the polarization from the average at the point $\boldsymbol{x}$.

Now $\boldsymbol{P}^{\mathrm{in}}$ and $\boldsymbol{P}$ are part of the response of the system to the external field $\boldsymbol{E}$, which has been treated in parts I and II. However, it is preferable to express the scattering in terms of another part of the response to $\boldsymbol{E}$, the average field $\boldsymbol{\mathscr{E}}$, determined by (2.1). The $\boldsymbol{P}$ and $\boldsymbol{P}^{\mathrm{in}}$ are given by (2.1*b*) and (I 3.6):

$$\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{2.6}$$

The kernel $\boldsymbol{\Lambda}^{\mathrm{in}}$ depends on the instantaneous configuration of molecules and has the average $\langle\boldsymbol{\Lambda}^{\mathrm{in}}\rangle = \boldsymbol{\Lambda}$. By use of (2.1*b*) and (2.6) we then get (I 4.27) for the flux of scattered light, namely

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left\langle\left|\int_V\int_V \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\Delta\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'\right|^2\right\rangle, \tag{2.7}$$

in which

$$\Delta\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) - \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega). \tag{2.8}$$

The explicit appearance of configurationally dependent quantities and averages in (2.7) is inconvenient. These features are therefore concealed in a kernel (I 3.33*a*):

$$\boldsymbol{\sigma}_{10} = \int_V\int_V \langle\Delta\boldsymbol{\Lambda}_{12}^{\mathrm{in},\dagger}\cdot[k_0^2\,\boldsymbol{e}_2^*\,\boldsymbol{e}_3]\cdot\Delta\boldsymbol{\Lambda}_{30}^{\mathrm{in}}\rangle\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3, \tag{2.9}$$

which can be expressed in closed form (exhibited below). A superscript † on a kernel denotes the hermitian conjugate kernel. In (2.9) and below we use a concise notation in which variables are indicated by subscripts, thus $\boldsymbol{e}_3 = \boldsymbol{e}(\boldsymbol{x}_3;\boldsymbol{k},\boldsymbol{v})$. The result of using (2.9) in (2.7) is the fundamental form for the flux of scattered light per unit solid angle in the direction of the vector $\boldsymbol{k}$, detected with polarization $\boldsymbol{v}$:

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^2}{8\pi}\int_V\int_V \boldsymbol{\mathscr{E}}^*(\boldsymbol{x},\omega)\cdot\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{2.10}$$

By expressing the scattering by (2.10) together with (2.1) we isolate the problem of finding the behaviour of the incoming wave at the surface of the medium from the rest of the scattering process. The surface dependence associated with, for example, refraction of the incoming wave can therefore be treated separately and is absent from (2.10) when $\boldsymbol{\mathscr{E}}$ is considered a given function (obtained through (2.1)).

This separation of the collective surface effect associated with the incoming field is a significant move. The next, and very important, step towards finding an effective treatment of light scattering in microscopic terms is to find a similar separation for the scattered wave: this is both physically sensible and the only practicable way to handle a strong surface dependence of the scattering process remaining in the kernel $\boldsymbol{\sigma}$ in (2.10).

Thus, the flux of scattered light $J(\boldsymbol{k},\boldsymbol{v})$ is a quadratic form in $\mathcal{E}$, the average field in the medium, and considered as a functional of $\mathcal{E}$ it describes the scattering of a wave $\mathcal{E}$ detected in vacuum outside the medium; so the kernel $\boldsymbol{\sigma}$ may be said to describe this process. We want to separate off the collective surface effect by expressing $\boldsymbol{\sigma}$ itself as a quadratic form in the counterpart of $\mathcal{E}$ for the outgoing field, the weight field ε introduced in the following subsection. We therefore need the explicit form of the scattering kernel, $\boldsymbol{\sigma}$, and that is described most simply if we can refer to an expression for $\boldsymbol{\Lambda}$. We therefore briefly return to (2.1) and explain F and $\boldsymbol{\Lambda}$.

In (2.1) F is the propagator giving the field at $\boldsymbol{x}$ from an oscillatory dipole $\boldsymbol{P}(\omega)$ at $\boldsymbol{x}'$ as $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\omega)$. It can be expressed in any of the several forms (I 2.2), for example

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)=(\nabla\nabla+k_0^2\,\mathsf{U})\frac{\exp(\mathrm{i}k_0 r)}{r},\quad r=|\boldsymbol{x}-\boldsymbol{x}'|,\quad k_0=\frac{\omega}{c},\tag{2.11}$$

where U is the unit tensor. The definition (2.1 *a*) of the average field can now evidently be viewed as the sum of the external field and the field from the average polarization $\boldsymbol{P}$. However, it is necessary to add the interpretation of the integral near the singularity of F as the sum of the conditionally convergent integral over all of the region V except a vanishingly small sphere (denoted v) together with 'the contribution from the small sphere', (I 3.4):

$$\lim_{v\to 0}\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}'=-\tfrac{4}{3}\pi\mathsf{U}.\tag{2.12}$$

The definition (2.1 *a*) with (2.12) is justified by the results of part I, see the discussion in §6 there.

The kernel $\boldsymbol{\Lambda}$ was found in part I as the infinite series expansion

$$\boldsymbol{\Lambda}_{10}=n\alpha\mathsf{U}\delta_{10}+\sum_{p=1}^{\infty}(n\alpha)^{p+1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdots\mathsf{F}_{p0}\,H_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p.\tag{2.13}$$

Here α is the polarizability of an isolated molecule, n is the average density of molecules, and the intermolecular correlation functions H are given in (I 3.18) in general. The first few H functions are

$$H_{12}=G_{12}-1,\quad H_{123}=G_{123}-G_{12}-G_{23}+1,\ldots.\tag{2.14}$$

The generalized distribution function $n^pG_{123\ldots p}$ is defined by (I 3.14) as the averaged product of the instantaneous density of molecules at the points $\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_p$. The functions are generalized in the sense that they include self-correlations represented by delta functions, thus:

$$G_{12}=g_{12}+n^{-1}\delta_{12},\quad G_{123}=g_{123}+n^{-1}(\delta_{12}+\delta_{23})\,g_{13}+\delta_{13}\,g_{12}+n^{-2}\delta_{12}\,\delta_{23},\ldots.\tag{2.15}$$

The functions g are the ordinary correlation functions of the theory of fluids (see, for example, Hill 1956) and $\delta_{12}=\delta(\boldsymbol{x}_1-\boldsymbol{x}_2)$ denotes a delta function. We shall refer to the particular functions G or g as distribution functions.

The use of generalized correlation functions results in a great simplification of the theory once we have introduced the interpretation (I 2.26):

$$\int \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}'=\tfrac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}.\tag{2.16}$$

The self-correlations generate the self-interactions of the theory in the expressions in terms of generalized functions, and by the definition (2.16), in particular, radiation reaction is accounted for. Sometimes it is convenient to conceal the effect of radiation reaction in a complex polarizability (I 2.7),

$$\gamma = \alpha/(1-\tfrac{2}{3}\mathrm{i}k_0^3\alpha). \tag{2.17}$$

In the refractive index theory all self-correlations produce terms involving self-interactions, but in the scattering theory this is not the case. The reason is that a partial process describing radiation to an infinitely distant detector appears in the refractive index theory as the reaction due to that radiation. We shall have occasion to compare the two situations in §5.

The scattering kernel has an expansion of a form very similar to (2.13). We shall quote it once we have introduced a special propagator associated with scattering, namely the factor in square brackets in (2.9),

$$\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\,\boldsymbol{e}^*(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{e}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) \tag{2.18a}$$

together with one for scattering not analysed for polarization,

$$\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = k_0^2(\mathsf{U}-\boldsymbol{k}\boldsymbol{k})\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]. \tag{2.18b}$$

The form (2.18*b*) is obtained from (2.18*a*) by summation over two orthogonal polarization states perpendicular to $\boldsymbol{k}$. We shall call $\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ a 'radiator'. It determines the total scattering per unit solid angle in the direction of $\boldsymbol{k}$ with polarization $\boldsymbol{v}$ from an instantaneous polarization $\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)$ as

$$I^{\mathrm{in}}(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^2}{8\pi}\int_V\int_V \boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)^*\cdot\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{2.19}$$

If the scattering is not analysed for polarization the scattering has the same form (2.19) with $\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ replaced by $\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})$.

The expression for $\boldsymbol{\sigma}$ contains sums of products of a number of propagators F and one S, and to simplify the presentation we need a shorthand notation for such combinations as in (I 3.35). In the expression (2.13) for $\boldsymbol{\Lambda}$ there appears in the integrand a product of propagators F corresponding to an ordered set of points $\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_p, \boldsymbol{x}_0$, in which the points $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ are free whereas the others are integrated. Corresponding to such a product in the expansion of $\boldsymbol{\Lambda}$ there appears in $\boldsymbol{\sigma}$ the combination

$$\mathfrak{S}\{\mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\} = \mathsf{S}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}+\mathsf{F}_{12}^*\cdot\mathsf{S}_{23}\ldots\mathsf{F}_{p0}+\ldots+\mathsf{F}_{12}^*\cdot\mathsf{F}_{23}^*\ldots\mathsf{S}_{p0}. \tag{2.20}$$

Now we are in a position to quote the expansion of the scattering kernel (I 3.34)

$$\boldsymbol{\sigma}(\boldsymbol{x}_1,\boldsymbol{x}_0;\boldsymbol{k},\boldsymbol{v}) = \sum_{p=1}^{\infty}(n\alpha)^{p+1}\int_V\ldots\int_V \mathfrak{S}\{\mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\}\,H_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p. \tag{2.21}$$

In other words, we get the expansion for $\boldsymbol{\sigma}$ from the one for $\boldsymbol{\Lambda}$ by replacing a product of p propagators F by a sum of p terms in which each F in turn is replaced by S, and propagators to the left of S are complex conjugated.

The result (2.21) was derived in part I, and it reveals a close relation between the susceptibility kernel $\boldsymbol{\Lambda}$ and the scattering kernel $\boldsymbol{\sigma}$. Indeed, this can be written

$$\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = \mathfrak{S}\{\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\}, \tag{2.22}$$

if $\mathfrak{S}$ is treated as a linear operator and taken outside integrations and summation. The action of $\mathfrak{S}$ on a term not containing Fs is defined to be zero. The close similarity of the scattering theory and the refractive index theory expressed by (2.22) will be exploited below.

The relation (2.22) also shows that the radiator is a very natural object to use in the scattering theory. It appears on a par with the propagator F in (2.21) (through (2.20)), and S and F are connected by a Bohr–Peierls–Placzek type relation:

$$\int \sum_{j=1,2} \mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j)\,\mathrm{d}\Omega_{\boldsymbol{k}} = 4\pi k_0^{-1}\,\mathrm{Im}\,\{\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\} \tag{2.23}$$

derived in part I below (I 2.14) (cf. Sakurai 1967). And this relation together with (2.22) imply a similar relation between $\boldsymbol{\sigma}$ and $\boldsymbol{\Lambda}$, namely

$$\int \sum_{j=1,2} \boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j)\,\mathrm{d}\Omega_{\boldsymbol{k}} = 4\pi k_0^{-1}\,\mathrm{Im}\,\{\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\} \tag{2.24}$$

proved below (I 3.42). (In (2.23) and (2.24) we sum over two orthogonal polarization states and integrate over all directions of $\boldsymbol{k}$.) Equation (2.24) implies that the extinction coefficient calculated from the total scattering agrees with the one calculated from the imaginary part of the refractive index (see (5.42) below) as we discussed near (I 5.41). But as noted there, there is a paradox associated with the surface dependence of the scattering, which contrasts with the much weaker surface dependence in the corresponding expression for the refractive index. This we shall solve in the present paper.

(b) *Weight field*

We want a formulation of the theory in which the behaviour of the scattered light at the surface of the medium can be treated separately from the scattering process in the medium. We therefore consider the average field at a distant detector at $\boldsymbol{R}$ from an oscillatory dipole probe $\boldsymbol{P}(\omega)$ at $\boldsymbol{x}$ when $|\boldsymbol{R}| \gg |\boldsymbol{x}|$ and $k_0|\boldsymbol{R}-\boldsymbol{x}| \gg 1$ for all $\boldsymbol{x}$ inside the medium. The asymptotic form of that field is (from (I 4.14) with (I 4.18)):

$$R^{-1}\exp\,(\mathrm{i}k_0 R)\,k_0^2\,\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}(\omega), \quad R = |\boldsymbol{R}|, \tag{2.25}$$

for the component with polarization in the direction of $\boldsymbol{v}$; the wave vector $\boldsymbol{k}$ has magnitude $|\boldsymbol{k}| = k_0 = \omega/c$ and the direction of $\boldsymbol{R}$ (approximating $\boldsymbol{R}-\boldsymbol{x}$ for any $\boldsymbol{x}\in V$ in the limit $R\to\infty$; for finite R the origin is chosen inside V). The quantity $\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ in (2.25) satisfies the integral equation (I 4.28), namely

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) + \int_V\int_V \boldsymbol{\varepsilon}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Lambda}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathsf{F}(\boldsymbol{x}'',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}''. \tag{2.26}$$

It must be stressed that although $\boldsymbol{\varepsilon}$ has been defined in terms of dipole probes the result of the theory in no way depends on probes. Only molecular dipoles appear in the theory. The same remark applies to the definition of the propagator $\mathscr{F}$ in (2.33) below. Note also that the 'field' $\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ depends on $\boldsymbol{x}$ which is a source point, so it is not an ordinary field; we call it the weight field for reasons that will become clear. The inhomogeneous term $\boldsymbol{e}$ of the integral equation (2.26) is defined in (2.3): note the minus sign in the exponential. (The definition of $\boldsymbol{e}$ will be generalized in (4.2) below to account for scattering with stops.)

In part I we showed how J can be expressed by (I 4.36) explicitly in terms of $\boldsymbol{\varepsilon}$ rather than $\boldsymbol{e}$,

$$J(\boldsymbol{k},\boldsymbol{v}) = \sum_{p=2}^{\infty}\sum_{q=1}^{p-1} J_{pq}(\boldsymbol{k},\boldsymbol{v}), \tag{2.27a}$$

$$J_{pq}(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}(n\alpha)^p \int_V \mathrm{d}\boldsymbol{x}_1 \dots \int_V \mathrm{d}\boldsymbol{x}_p \, K^{(q)}_{123\dots p} \times (\boldsymbol{\mathscr{E}}_1\cdot\mathsf{F}_{12}\dots\mathsf{F}_{(q-1)q}\cdot\boldsymbol{\varepsilon}_q)^*\,\boldsymbol{\varepsilon}_{q+1}\cdot\mathsf{F}_{(q+1)(q+2)}\dots\mathsf{F}_{(p-1)p}\cdot\boldsymbol{\mathscr{E}}_p\cdot \tag{2.27b}$$

The general expression for the K functions is given by (I 4.37) in terms of the H functions (2.14). In terms of the Ursell functions (see (I 4.12) and (2.40) below) we have up to fourth order (I 4.38):

$$\left.\begin{aligned} K^{(1)}_{12} &= U_{12}, \quad K^{(1)}_{123} = K^{(2)}_{123} = U_{123},\\ K^{(1)}_{1234} &= U_{1234} + U_{13}\,U_{24} + U_{124},\\ K^{(2)}_{1234} &= U_{1234} + U_{13}\,U_{24} + U_{14}\,U_{23},\\ K^{(3)}_{1234} &= U_{1234} + U_{13}\,U_{24} + U_{134}.\end{aligned}\right\} \tag{2.28}$$

It may be helpful if we discuss a different form of the result (2.27), namely (I 4.29):

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left\langle\left|\int_V\int_V \boldsymbol{\varepsilon}_1\cdot\boldsymbol{\Delta}^{\text{in}}_{10}\cdot\boldsymbol{\mathscr{E}}_0\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_0\right|^2\right\rangle \tag{2.29a}$$

This is an explicit expression for $J(\boldsymbol{k},\boldsymbol{v})$ in so far as the kernel $\boldsymbol{\Delta}^{\text{in}}_{10}$ is given explicitly as (I 4.30):

$$\boldsymbol{\Delta}^{\text{in}}_{10} = \Delta\boldsymbol{\Lambda}^{\text{in}}_{10} - \int_V\int_V \boldsymbol{\Lambda}_{12}\cdot\mathsf{F}_{23}\cdot\Delta\boldsymbol{\Lambda}^{\text{in}}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{2.29b}$$

Here $\Delta\boldsymbol{\Lambda}^{\text{in}}$ denotes the difference (2.8), $\boldsymbol{\Lambda}$ is given explicitly by (2.13), and $\boldsymbol{\Lambda}^{\text{in}}$ can be obtained by straightforward iteration of (I 3.10) with (I 3.12).

The form (2.29) may be easier to understand if less explicit than (2.27). We may think of $\boldsymbol{\Delta}^{\text{in}}$ as representing an instantaneous susceptibility fluctuation, which scatters the incoming wave in the medium, $\boldsymbol{\mathscr{E}}$, into the outgoing wave in the medium represented by $\boldsymbol{\varepsilon}$. The explicit form (2.27) is obtained from (2.29) by writing the absolute square of the double volume integral as a four-fold integral. In this way $\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$ appears between two kernels $\boldsymbol{\Delta}^{\text{in},\dagger}$ and $\boldsymbol{\Delta}^{\text{in}}$. If these kernels are expanded we get the sum of terms in (2.27a) with the averaging producing the correlation functions K.

A comparison of the two forms (2.27) and (2.29) serves to emphasize how the dyadic combination

$$\mathscr{S}'(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\,\boldsymbol{\varepsilon}^*(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{\varepsilon}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) \tag{2.30}$$

of two weight fields appears naturally nested inside a chain of propagators F. We have already seen how the dyadic combination (2.18) of two $\boldsymbol{e}$ appears naturally in a chain of propagators F as in (2.21) with (2.20) and how (2.18) itself has some character of a propagator (see (2.23)). It turns out, that 'nested forms' in which the quantity (2.30) appears inside chains of propagators are by far the simplest formulation of the theory, and that (2.30) is naturally contained in a radiator generalizing (2.18), which has propagator character and other very important properties. It is introduced in the following subsection.

We have now reached an expression in which the collective surface effect associated with the scattering can be treated separately through the weight field $\boldsymbol{\varepsilon}$, and the scattering process in the medium is described explicitly by (2.27) with $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ given functions. The fact that the weight field describes refraction and reflection at the surface will be demonstrated in §4. The following subsection prepares for a necessity of analysing the scattering in the medium still further.

(*c*) *Decomposition of the screened radiator*

We now have two expressions for the scattered flux; one is (2.10) with (2.21), the other is (2.27). Each of these expressions is important in the theory. The first form is used for deductions of theoretical results like (2.24) and for further development of the theory; the form (2.27) is used for an analysis of the Einstein light scattering formula (7.1) and for a description of the low-density behaviour. Nevertheless, even the result (2.27) is still not generally satisfactory because, beyond the third order in $n\alpha$, the integrals of (2.27) depend explicitly on the geometry of the scattering cell (i.e. besides the implicit dependence through the weight field). We shall therefore need to analyse the scattering process still further. To deal with this remaining surface effect we introduce a propagator $\mathscr{S}$ which contains $\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$ and so deals with the collective surface effect as well. We call $\mathscr{S}$ a screened radiator (corresponding to the unscreened radiator $\mathbf{S}$).

Consider a distribution of dipole probes $\{\boldsymbol{P}_s(\omega)\}$ embedded in the many-body system. We define $\mathscr{S}$ to give the average flux per unit solid angle in the direction of $\boldsymbol{k}$ with polarization $\boldsymbol{v}$ from the probes $\{\boldsymbol{P}_s\}$ as

$$\frac{ck_0^2}{8\pi}\sum_{r,s}\boldsymbol{P}_r^*(\omega)\cdot\mathscr{S}(\boldsymbol{x}_r,\boldsymbol{x}_s;\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}_s(\omega). \tag{2.31}$$

The radiator $\mathscr{S}$ is related to the weight field $\boldsymbol{\varepsilon}$: Define an instantaneous weight field $\boldsymbol{\varepsilon}^{\text{in}}$ to give the instantaneous field at a distant point $\boldsymbol{R}$ in the direction of $\boldsymbol{k}$ with polarization $\boldsymbol{v}$ by (2.25) with $\boldsymbol{\varepsilon}$ replaced by $\boldsymbol{\varepsilon}^{\text{in}}$. Then $\mathscr{S}$ is given by (I 4.17), namely

$$\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\langle\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})^*\,\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\rangle. \tag{2.32}$$

Recall that $\boldsymbol{\varepsilon}$ appears in (2.27) in the quadratic combination (2.30). Thus, whereas $\mathscr{S}$ gives the average flux radiated from a collection of dipole probes, $\mathscr{S}'$ gives the flux of the average field. (The instantaneous weight field $\boldsymbol{\varepsilon}^{\text{in}}$ is defined by (I 4.15).)

To see the difference between $\mathscr{S}$ and $\mathscr{S}'$ and to develop the theory in terms of $\mathscr{S}$ we shall need also the screened propagator $\mathscr{F}$ introduced in part I to give the average field at $\boldsymbol{x}$ from a dipole probe $\boldsymbol{P}(\omega)$ at $\boldsymbol{x}'$ as

$$\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\omega). \tag{2.33}$$

(Note the remark below (2.26).) It satisfies the integral equation (I 4.3),

$$\mathscr{F}_{10} = \mathsf{F}_{10} + \int_V\int_V \mathsf{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{2.34}$$

Explicitly it is given by (I 4.13),

$$\mathscr{F}_{10} = \sum_{p=1}^{\infty}(n\alpha)^{p-1}\int_V\ldots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\,G_{23\ldots p}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p \tag{2.35}$$

(where the first term of the series is F_{10}) and it can be approximated by (II 4.13) with (II 4.4),

$$\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega) \approx \tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) + \text{reflections}, \tag{2.36a}$$

$$\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) = (\nabla\nabla + m^2k_0^2\,\mathsf{U})\,\frac{\exp(\mathrm{i}mk_0|\boldsymbol{x}-\boldsymbol{x}'|)}{m^2|\boldsymbol{x}-\boldsymbol{x}'|}. \tag{2.36b}$$

Here $m = m(\omega)$ is the refractive index of the fluid determined in part II. The results (2.35) and (2.36) show that $\mathscr{F}$ is a natural generalization of F to propagation in a medium of refractive index m. The wavenumber is mk_0 rather than the k_0 of (2.11) and for $mk_0|\boldsymbol{x}-\boldsymbol{x}'| \ll 1$ there is the usual static screening with m^2 or the dielectric constant (I 5.27) in the denominator. The propagator $\mathscr{F}$ is surface dependent, but we argued below (II 4.12) (but did not prove) that the surface dependence can be understood in terms of surface reflections of waves radiated from a dipole probe.

It is an interesting and important fact that the screened radiator $\mathscr{S}$ has an expansion very similar to (2.35) for $\mathscr{F}$, namely

$$\mathscr{S}_{10} = \sum_{p=1}^{\infty} (n\alpha)^{p-1} \int_V \dots \int_V \mathfrak{S}\{\mathsf{F}_{12}\cdot\mathsf{F}_{23}\dots\mathsf{F}_{p0}\}\,G_{23\dots p}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\dots\mathrm{d}\boldsymbol{x}_p, \tag{2.37a}$$

or

$$\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = \mathfrak{S}\{\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\}. \tag{2.37b}$$

This result was derived in part I below (I 4.22). Because $\mathscr{F}$ and $\mathscr{S}$ are so closely related, the expression for $\boldsymbol{\sigma}$ in terms of $\mathfrak{S}$ and $\mathscr{S}$ has the very simple form (I 4.25),

$$\boldsymbol{\sigma}_{10} = \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \dots \int_V \mathfrak{S}\{\mathscr{F}_{12}\cdot\mathscr{F}_{23}\dots\mathscr{F}_{p0}\}\,Y_{123\dots p0}\,\mathrm{d}\boldsymbol{x}_2\dots\mathrm{d}\boldsymbol{x}_p, \tag{2.38a}$$

in which the effect of the operator $\mathfrak{S}$ on a product of screened propagators $\mathscr{F}$ is the natural generalization of (2.20), namely (I 4.24) or

$$\mathfrak{S}\{\mathscr{F}_{12}\cdot\mathscr{F}_{23}\dots\mathscr{F}_{p0}\} = \mathscr{S}_{12}\cdot\mathscr{F}_{23}\dots\mathscr{F}_{p0} + \mathscr{F}^*_{12}\cdot\mathscr{S}_{23}\dots\mathscr{F}_{p0} + \dots + \mathscr{F}^*_{12}\cdot\mathscr{F}^*_{23}\dots\mathscr{S}_{p0}. \tag{2.38b}$$

The intermolecular correlation functions Y in (2.38a) are defined by (I 4.11) in general, and the first few functions expressed in terms of generalized Ursell functions are:

$$Y_{12} = U_{12}, \quad Y_{123} = U_{123}, \quad Y_{1234} = U_{1234} + U_{13}\,U_{24}, \dots. \tag{2.39}$$

The Ursell functions can be defined through the recurrence relation (I 4.12a) and the first few functions are (see, for example, Lebowitz & Percus 1961)

$$U_{12} = G_{12} - 1, \quad U_{123} = G_{123} - G_{12} - G_{23} - G_{31} + 2, \dots. \tag{2.40}$$

Recall that the functions are 'generalized' in the sense that they include all self-correlations introduced through the generalized distribution functions (2.15).

Note how naturally the propagators $\mathscr{F}$ and $\mathscr{S}$ fit together. They have similar expansions (2.35) and (2.37a), each in terms of the distribution functions simply; and they are indeed connected by a Bohr–Peierls–Placzek relation (I 4.26) just as S and F are. Note also that each term of the sum (2.38b) generated by the operator $\mathfrak{S}$ is weighted by the same intermolecular correlation function in (2.38a). In contrast the expression (2.27) does not possess this symmetry.

All these simple properties of $\mathscr{S}$ suggests that the screened radiator is an important object; and the weight field certainly is important since it describes the surface behaviour of the scattered wave as we shall show in §4. This raises the question of how $\mathscr{S}$ and $\boldsymbol{\varepsilon}$ (or $\mathscr{S}'$) are related. The answer is (I 4.21)

$$\mathscr{S}_{10} = k_0^2\, \boldsymbol{\varepsilon}_1^*\, \boldsymbol{\varepsilon}_0 + \int_V \int_V \mathscr{F}_{12}^* \cdot \boldsymbol{\sigma}_{23} \cdot \mathscr{F}_{30}\, \mathrm{d}\boldsymbol{x}_2\, \mathrm{d}\boldsymbol{x}_3. \tag{2.41}$$

This relation shows that the screened radiator differs from the quadratic combination (2.30) in the weight field by the term containing a pair of propagators $\mathscr{F}^*$, $\mathscr{F}$ and the scattering kernel. Thus in addition to simple radiation to the detector through the medium from a pair of points $\boldsymbol{x}_1$, $\boldsymbol{x}_0$, the radiator $\mathscr{S}$ contains a term describing propagation through the medium to another pair of points in the medium followed by incoherent scattering from there. This means that $\mathscr{S}$ accounts for scattering of the propagating scattered wave, i.e. multiple scattering.

This fact suggests that (2.41) can be used to obtain a microscopic representation of macroscopic multiple scattering and to develop a systematic theory for it. The details of how this can be done appear in §5. However, we first present an overview of how the complete scattering process can be separated into physically meaningful constituents that can be individually analysed, namely those we have already mentioned, collective surface effect and macroscopic multiple scattering. This we do in the immediately following §3.

3. ANALYSIS OF THE COMPLETE SCATTERING PROCESS

We are considering a situation in which an external electromagnetic wave, $\boldsymbol{E}(\boldsymbol{x}, \omega)$ is incident on a molecular fluid contained in a finite region V, and the incoherent scattering is detected in vacuum outside the medium by a distant detector. The wave is monochromatic (with wavelength large compared with molecular size†) and spatially coherent, but otherwise an arbitrary transverse solution of the free field wave equation (equation (I 5.9)). In figure 1*a* we show a scattering situation in which $\boldsymbol{E}$ is a plane wave restricted by a stop.

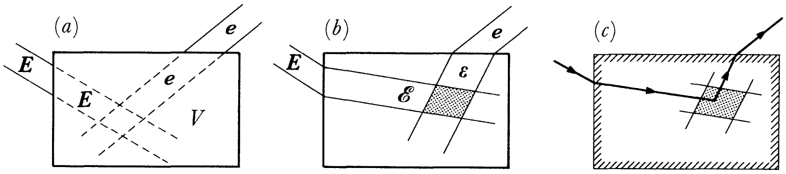

FIGURE 1. The fields $\boldsymbol{E}$ and $\boldsymbol{e}$ and their relation to $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. The region labelled $\boldsymbol{E}$ shows an incident beam of light outside and inside the scattering cell V. The region labelled $\boldsymbol{e}$ shows the part of space that can be seen from the detector through the stops. Inside V the field $\boldsymbol{E}$ is extinguished and replaced by an average field $\mathscr{E}$ non-vanishing in the region labelled $\mathscr{E}$. The weight field $\boldsymbol{\varepsilon}$ is related to $\boldsymbol{e}$ the same way as $\mathscr{E}$ to $\boldsymbol{E}$ and is non-vanishing in the region marked $\boldsymbol{\varepsilon}$. The relation of $\boldsymbol{e}$ and $\boldsymbol{\varepsilon}$ suggests that scattered light is refracted at the surface. This interpretation will be confirmed in §4.

For our purposes the detection system is characterized by the direction from the scattering cell to the detector, by the polarization of an analyser, if present, and by the geometrical arrangement of possible stops for the scattered wave. The effect of these properties of the detection system is accounted for by the 'field' $\boldsymbol{e}(\boldsymbol{x}; \boldsymbol{k}, \boldsymbol{v})$, given by (2.3) when there are no

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† A theory of the same structure arises at X-ray frequencies with a substantial change of details. The smallness of the scattering cross section means that many-body effects are very small, however.

stops for the scattering; and we shall show in §4 how (2.3) can be generalized to cover also the case of scattering restricted by stops.

For illustration we have indicated in figure 1*a* an $\boldsymbol{e}$ for scattering with a stop. The region between the full or dotted lines labelled by $\boldsymbol{e}$ is the part of space where $\boldsymbol{e}$ is non-vanishing. Reference to figure 1 may help in visualizing the scattering process. The figure will be justified in §4; meanwhile we may think of $\boldsymbol{e}$ as given by (2.3) for most of the present discussion. The field $\boldsymbol{e}$ plays a role for the scattered wave similar to the one played by $\boldsymbol{E}$ for the incoming wave, and we may often think of $\boldsymbol{e}$ in figure 1*a* as representing the scattered beam outside the medium just as $\boldsymbol{E}$ is (physically) the incoming beam outside the medium. We shall come back to the question of the way in which $\boldsymbol{e}$ actually represents the scattered wave.

The process we have just indicated is the complete scattering process we want to describe. The process starts with an incoming wave travelling in vacuum outside the material medium and ends with a scattered wave detected in vacuum outside the medium. And to help the reader grasp how this complex process is represented by the mathematics we will list together all the relevant equations distributed throughout §2: $\boldsymbol{E}_1 = \boldsymbol{E}(\boldsymbol{x}_1, \omega)$, is the given externally incident field and

$$\mathscr{E}_1 = \boldsymbol{E}_1 + \int_V \int_V \mathsf{F}_{12} \cdot \boldsymbol{\Lambda}_{23} \cdot \mathscr{E}_3 \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3, \tag{3.1a}$$

$$J = \frac{ck_0^2}{8\pi} \int_V \int_V \mathscr{E}_1^* \cdot \boldsymbol{\sigma}_{10} \cdot \mathscr{E}_0 \, \mathrm{d}\boldsymbol{x}_0 \, \mathrm{d}\boldsymbol{x}_1, \tag{3.1b}$$

$$\boldsymbol{\sigma}_{10} = \sum_{p,\,q} (n\alpha)^{p+1} \int_V \cdots \int_V \mathscr{F}_{12}^* \cdots \mathscr{S}_{q(q+1)} \cdots \mathscr{F}_{p0} \, Y_{12\ldots p0} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_p, \tag{3.1c}$$

$$\mathscr{S}_{10} = k_0^2 \, \boldsymbol{\varepsilon}_1^* \, \boldsymbol{\varepsilon}_0 + \int_V \int_V \mathscr{F}_{12}^* \cdot \boldsymbol{\sigma}_{23} \cdot \mathscr{F}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3, \tag{3.1d}$$

$$\boldsymbol{\varepsilon}_0 = \boldsymbol{e}_0 + \int_V \int_V \boldsymbol{\varepsilon}_1 \cdot \boldsymbol{\Lambda}_{12} \cdot \mathsf{F}_{20} \, \mathrm{d}\boldsymbol{x}_1 \, \mathrm{d}\boldsymbol{x}_2, \tag{3.1e}$$

while $\boldsymbol{e}_0 = \boldsymbol{e}(\boldsymbol{x}_0; \boldsymbol{k}, \boldsymbol{v})$, is given by (2.3) (or by (4.2) below). In the discussion following we shall refer to these equations simply as (*a*)–(*e*); (*a*) is a combination of (2.1*a*) and (2.1*b*), (*b*) is (2.10), (*c*) is (2.38*a*) and (2.38*b*) combined, (*d*) is (2.41), and (*e*) is (2.26).

It is worth noting at this point that the mathematical problem in (*a*)–(*e*) is to calculate the total scattered flux J given by (*b*). To do this we need to calculate $\mathscr{E}_1$ in terms of $\boldsymbol{E}_1$ from (*a*); and we need to calculate $\boldsymbol{\sigma}_{10}$ from equations (*c*)–(*e*). Equation (*e*) allows us to solve for $\boldsymbol{\varepsilon}$, and this allows us to solve the coupled system (*c*) with (*d*) for $\boldsymbol{\sigma}$. Thus the system of relations is complete.

First, it is important to realize that the outgoing wave does not appear as a physical wave in (*a*)–(*e*). The theory gives the flux of scattered light J as a functional of the fields $\boldsymbol{E}$ and $\boldsymbol{e}$ representing the source and detecting systems respectively. The flux J is given by (*b*) and $\boldsymbol{E}$ and $\boldsymbol{e}$ appear in (*b*) through the $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. This means in particular that any conclusion regarding, for example, the behaviour of the scattered wave at the surface of the medium must be inferred from the dependence of J on $\boldsymbol{e}$. Nevertheless we shall see that we are able to deduce all details about the scattered wave from that dependence.

After these preliminary remarks we are now ready to show how the solution to (3.1) in the terms just explained describes the complete scattering process. The interpretations used in the description are substantiated in the following sections.

The entrance of the incident wave into the medium is described by (a), and the exit of the scattered wave from the medium is described by (e). These two similar equations determine the average field in the medium, $\mathscr{E}$, and the weight field, $\boldsymbol{\varepsilon}$. These equations can be treated separately, and they determine the behaviour of the incoming and scattered waves at the surface of the medium: transmission with refraction and attenuation, reflection with loss, polarization dependence, etc. Indeed, (a) has already been solved in parts I and II, and for (e) we can use the same technique and utilize the results obtained in parts I and II. The result is $\mathscr{E}$ in terms of $\boldsymbol{E}$ and $\boldsymbol{\varepsilon}$ in terms of $\boldsymbol{e}$. The general method involving the extinction theorem of Ewald (1912, 1916) and Oseen (1915) and the explicit solution for a parallel-sided slab are described in §4 below and in §6 of part I.

The problem of finding and interpreting the weight field is solved in §4. For the case illustrated in figure 1a we know from parts I and II (and from macroscopic optics as well) that $\mathscr{E}$ has the appearance sketched in figure 1b. Anticipating the results of §4 we have also indicated in figure 1b what $\boldsymbol{\varepsilon}$ may look like in relation to the $\boldsymbol{e}$ shown in figure 1a; it may help our discussion if we can refer to these qualitative results. Roughly $\boldsymbol{\varepsilon}$ may be thought of as representing the scattered wave in the medium.

With (a) and (e) solved for $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ there remains the problem of solving the set of coupled equations (c) and (d) in order to calculate J in terms of $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. Denote the functional dependence J on $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ by $\mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon})$: $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ are then arbitrary. The scattered flux can then be written as

$$J(\boldsymbol{k}, \boldsymbol{v}) = \mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon}), \tag{3.2}$$

when $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ are chosen as solutions to (a) and (e) respectively. Recall that we already have the closed form (2.27) for $\mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon})$. From this result or directly from the equations (3.1) it can be seen that $\mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon})$ is actually quadratic in $\mathscr{E}$ and in $\boldsymbol{\varepsilon}$, or rather it is linear in $\mathscr{E}^*\mathscr{E}$ and $\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$; hence it is determined by a multilinear operator $\mathscr{M}$ describing scattering in the medium, which we shall introduce below. The expression (2.27) is strongly surface-dependent; and to handle the surface dependence and understand what it means physically we must work from the particular set of equations (3.1) rather than (2.27).

In (3.2) $\mathscr{E}$ is the incoming field in the medium and $\boldsymbol{\varepsilon}$ represents the scattered wave in the medium so the functional $\mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon})$ describes the scattering process in the medium. Thus we have obtained the scattering process in the medium either as a part of the complete scattering process (when $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ are solutions to (a) and (e)) or indeed as a more abstract concept (when $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ are considered arbitrary fields in the medium).

We have still to consider (c) and (d), a pair of coupled equations for $\boldsymbol{\sigma}$ in terms of $\boldsymbol{\varepsilon}$. If (d) is substituted for $\mathscr{S}$ in (c) we get a linear integral equation in $\boldsymbol{\sigma}$. The source term of this inhomogeneous equation is given by the right side of (c) when $\mathscr{S}_{q(q+1)}$ is replaced by $\boldsymbol{\varepsilon}_q^*\,\boldsymbol{\varepsilon}_{q+1}$, and it is this term (substituted in (b)) we shall define as macroscopic single scattering. That this is a sensible definition will soon be evident. Then macroscopic multiple scattering is generated by the higher iterates of the linear equation (c) with (d).

To get these iterates and exhibit their structure we rewrite (b)–(d) in terms of two operators $\mathscr{L}$ and $\mathscr{Z}$ as

$$J = (ck_0^2/8\pi)\,\mathscr{E}^*\mathscr{E}:\boldsymbol{\sigma}, \tag{3.3b}$$

$$\boldsymbol{\sigma} = \mathscr{L}:\mathscr{S}, \tag{3.3c}$$

$$\mathscr{S} = k_0^2\,\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon} + \mathscr{Z}:\boldsymbol{\sigma}. \tag{3.3d}$$

Evidently, this transcription of (3.1 *b*–*d*) defines $\mathscr{L}$ and $\mathscr{Z}$. The notation (*b*), (*c*), and (*d*) will now refer equally to either (3.1) or (3.3).

It is preferable to separate the dependence on the outgoing as well as the incoming wave from the scattering process in the medium by introducing a further operator $\mathscr{M}$ representing what is essentially the functional $\mathscr{I}(\boldsymbol{\mathscr{E}}, \boldsymbol{\varepsilon})$ through the definition

$$\boldsymbol{\sigma} = k_0^2 \mathscr{M} : \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}. \tag{3.4}$$

The scattered flux then takes the form

$$J(\boldsymbol{k}, \boldsymbol{v}) = \mathscr{I}(\boldsymbol{\mathscr{E}}, \boldsymbol{\varepsilon}) = (ck_0^4/8\pi)\, \boldsymbol{\mathscr{E}}^* \boldsymbol{\mathscr{E}} : \mathscr{M} : \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}. \tag{3.5}$$

Substitution of (*d*) in (*c*) gives an equation in $\boldsymbol{\sigma}$,

$$\boldsymbol{\sigma} = k_0^2 \mathscr{L} : \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon} + \mathscr{L} : \mathscr{Z} : \boldsymbol{\sigma}, \tag{3.6}$$

and substitution of (3.4) for $\boldsymbol{\sigma}$ then yields the simple equation for $\mathscr{M}$ in terms of $\mathscr{L}$,

$$\mathscr{M} = \mathscr{L} + \mathscr{L} : \mathscr{Z} : \mathscr{M}, \tag{3.7}$$

as $\boldsymbol{\varepsilon}$ can be considered arbitrary. Straightforward iteration of (3.7) now generates the macroscopic multiple scattering expansion

$$\mathscr{M} = \mathscr{L} + \mathscr{L} : \mathscr{Z} : \mathscr{L} + \mathscr{L} : \mathscr{Z} : \mathscr{L} : \mathscr{Z} : \mathscr{L} + \dots. \tag{3.8}$$

In particular, the first term of (3.8) gives macroscopic single scattering

$$J^{(1)} = (ck_0^4/8\pi)\, \boldsymbol{\mathscr{E}}^* \boldsymbol{\mathscr{E}} : \mathscr{L} : \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon} \tag{3.9}$$

upon substitution in (3.5), and the second term of (3.8) similarly gives double scattering

$$J^{(2)} = (ck_0^4/8\pi)\, \boldsymbol{\mathscr{E}}^* \boldsymbol{\mathscr{E}} : \mathscr{L} : \mathscr{Z} : \mathscr{L} : \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}, \text{ etc.} \tag{3.10}$$

Note how operation from the left (right) in equations (3.3)–(3.10) corresponds to multiplication from the inside (outside) in (3.1). We shall be more specific about the form of the operators when we come to treat multiple scattering in §5; thus the operator $\mathscr{L}$ is given explicitly by (5.5) below, and the relations (3.7) and (3.9) are shown in detail in (5.4) and (5.6) respectively.

We can now see some important features of the total scattering process (up to actual demonstration in detail in the following sections). Note first that each term, whether single scattering or multiple scattering, is linear in $\boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}$ and in $\boldsymbol{\mathscr{E}}^* \boldsymbol{\mathscr{E}}$; and this of course applies as well to each individual term arising from the separate terms contributing to the sum (3.1 *c*) as they appear in single or multiple scattering. This means that each scattering process in the medium, whether single or multiple, has the same collective surface effects and these are solely described by $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ in their relation to $\boldsymbol{E}$ and $\boldsymbol{e}$.

We may exemplify this feature by a simple geometrical consequence. Suppose, for simplicity, that the single scattering process described by $\mathscr{L}$ is spatially local (or consider any local contribution to it). Then note that the fields $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ always appear in the equations (3.1) integrated over the region V. This means that if $\boldsymbol{\mathscr{E}}$ or $\boldsymbol{\varepsilon}$ vanishes in some region of V (for example as an effect of stops) we get no contribution to the (local) single scattering from such region. We get contributions only from regions of V where $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ are both non-vanishing, so single scattering arises from a proper scattering region, shown shaded in figure 1 *b*. For macroscopic double (*n*-tuple) scattering (3.8) shows that there must appear two (*n*) localized scattering processes; and plainly the first one must take place in a region of V where $\boldsymbol{\mathscr{E}}$ is non-vanishing whereas the last one must take place where $\boldsymbol{\varepsilon}$ is non-vanishing. Between such single scattering processes there is propagation in the medium as described by the pair of propagators $\mathscr{F}^*\mathscr{F}$ which is contained in the operator $\mathscr{L}$, as comparison of (3.1*d*) with (3.3*d*) shows. The important point here is that all features of the behaviour of the scattered light at the surface of the medium are determined by $\boldsymbol{\varepsilon}$ and these features are therefore exactly the same for double scattering (for example) as they are for single scattering.

Now that we have seen how the complete scattering process can be separated into physically meaningful partial processes we can proceed to treat each of these partial processes separately. In this way we shall justify, and elaborate on, the assertions we have made in this overview of the complete scattering process given in this section.

4. BEHAVIOUR OF THE SCATTERED LIGHT AT THE SURFACE

In this section we show how the weight field $\boldsymbol{\varepsilon}$ describes the behaviour of the scattered light at the surface of the scattering medium: particularly transmission with refraction and attenuation; reflection with associated loss; dependence on polarization; effect of stops.

We work from equation (2.26) for $\boldsymbol{\varepsilon}$ and note that it can be written in the equivalent form

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) + \int_V \int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\Lambda}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\boldsymbol{\varepsilon}(\boldsymbol{x}'';\boldsymbol{k},\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}'' \tag{4.1}$$

because F and $\boldsymbol{\Lambda}$ are both symmetrical tensor kernels. The integral equation (4.1) has precisely the form of the equation (3.1*a*), which determines the average electric field $\mathscr{E}$ induced in the medium in response to the external field $\boldsymbol{E}$. Hence we may formally view the weight field $\boldsymbol{\varepsilon}$ as the average electric field induced in the medium in response to a fictitious external field $\boldsymbol{e}$, which is a legitimate incident field satisfying a free field wave equation like (I 5.9) and a transversality condition like (I 5.10). We may therefore take over the results of §§5 and 6 of part I with the special choice $\boldsymbol{E}(\boldsymbol{x},\omega) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$, here viewed as a plane electromagnetic wave of unit amplitude, polarization $\boldsymbol{v}$ and wave vector $-\boldsymbol{k}$, incident on the medium from the direction of the detector.

Up to this point we have considered the total scattering from the region V (in a given direction and with a given polarization). On the other hand, the incident field $\boldsymbol{E}$ is quite arbitrary and may in particular be a plane wave restricted by stops as is often the case in light scattering experiments. Usually the scattered wave is also restricted by stops in such experiments, so it is desirable to generalize the theory to cover also the case of stopped scattering.

If we neglect the diffraction of the scattered light by the stops we may calculate the stopped scattering by equation (2.7) when the integration over $\boldsymbol{x}$ is restricted to the intersection V^{o} of V and the cylinder generated by the aperture of the stop with axis along $\boldsymbol{k}$. Figure 2*a* illustrates this situation for scattering emerging from a slab where the cylindrical region is indicated by dashed lines. It is intuitive that neglect of stop diffraction requires the smallest size of the aperture large compared with the wavelength and that the stops are close to the scattering sample.

The stopped scattering is given precisely by (2.7) when $\boldsymbol{e}$ is redefined to vanish outside the cylinder,

$$\boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{v}\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\,\chi(\boldsymbol{x};V^{\mathrm{o}}), \tag{4.2a}$$

in which

$$\chi(\boldsymbol{x};V^{\circ}) = \begin{cases} 1 & \boldsymbol{x}\in V^{\circ}, \\ 0 & \boldsymbol{x}\notin V^{\circ}, \end{cases} \tag{4.2b}$$

is the characteristic function for the region V°. We shall adopt this redefinition of $\boldsymbol{e}$. In this way the theory carries over formally unchanged to the more general case of scattering restricted by stops, expressed in terms of a generalized weight field (which we continue to denote by $\boldsymbol{\varepsilon}$) given by (4.1) in terms of the generalized $\boldsymbol{e}$.

The generalized weight field $\boldsymbol{\varepsilon}$ may still be formally interpreted as the response to an external field $\boldsymbol{e}$ and indeed to a plane wave of unit amplitude coming from the detector with the polarization of the analyser and restricted by the same stops that restrict the scattering, provided we neglect the diffraction from the stops in this inverse response problem (Hynne 1980). Figure 1*b* illustrates this relation between $\boldsymbol{e}$ and $\boldsymbol{\varepsilon}$.

The correspondence between the screening problem for scattering and the inverse response problem establishes a complete characterization of the weight field $\boldsymbol{\varepsilon}$. For we may now use the results of parts I and II to solve equation (4.1). We may even appeal to macroscopic optics, although we shall do so only to illustrate the generality of this reciprocity principle which we shall conveniently refer to as the 'inverse response correspondence'.

It is plain from the discussion of §6 of part I that the weight field will show the same sort of deviation from continuum behaviour as does the average field $\mathscr{E}$ (see the discussion starting on p. 287 of part I). This small deviation can be disregarded if the sample size is large compared with the wavelength. The weight field is then determined completely by the refractive index, which we have already found, and by the geometry of the scattering experiment. So we regard the refractive index as known and neglect the deviations from continuum behaviour through the 'continuum approximation'

$$\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega) \approx ((m^2-1)/4\pi)\,\mathsf{U}\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{4.3}$$

Equation (4.1) then reduces to

$$\tilde{\boldsymbol{e}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) + \frac{m^2-1}{4\pi}\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\tilde{\boldsymbol{e}}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}', \tag{4.4}$$

for the approximation $\tilde{\boldsymbol{e}}$ to $\boldsymbol{\varepsilon}$.

To solve equation (4.4) we note first that the solution is unique up to solutions of the homogeneous equation corresponding to (4.4) in which $\boldsymbol{e} = \boldsymbol{0}$. For given m (given ω) we may disregard the possibility of such normal modes and assume the solution to be strictly unique. This means that if we can find a solution $\tilde{\boldsymbol{e}}$ with wavenumber mk_0 (satisfying a wave equation of the form (I 5.11) then we have both found the solution and shown that it satisfies the wave equation expected for waves in the medium.

As in the response problem we therefore assume that $\tilde{\boldsymbol{e}}$ satisfies the wave equation

$$(\nabla^2 + m^2k_0^2)\,\tilde{\boldsymbol{e}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{0}. \tag{4.5}$$

By use of Green's theorem we then reduce (4.4) to the set of two equations (in concise notation and compare (I 5.15))

$$\boldsymbol{e}(\boldsymbol{x}) + (4\pi k_0^2)^{-1}(\nabla\nabla + k^2\mathsf{U})\cdot\int_{\partial V}\mathrm{d}\boldsymbol{A}'\cdot[(\nabla' G(\boldsymbol{x},\boldsymbol{x}'))\,\tilde{\boldsymbol{e}}(\boldsymbol{x}') - G(\boldsymbol{x},\boldsymbol{x}')\,\nabla'\tilde{\boldsymbol{e}}(\boldsymbol{x}')] = \boldsymbol{0}, \tag{4.6a}$$

$$\nabla\nabla\cdot\tilde{\boldsymbol{e}}(\boldsymbol{x}) = \boldsymbol{0}. \tag{4.6b}$$

Equation (4.6a) with the associated equations (4.5) and (4.6b) may be called the extinction theorem for scattered light. These equations together determine the weight field $\tilde{\boldsymbol{e}}$, given the refractive index (from part II).

We shall actually solve equations (4.5), (4.6) for the special case of a parallel-sided slab. This example will show the significance of the weight field and will allow us to extend the interpretation of $\boldsymbol{\varepsilon}$ to arbitrary geometry. The case of a slab is easy because we can use the results of §§5 and 6 of part I directly, and the solution is convenient for our interpretation of $\boldsymbol{\varepsilon}$ because the solution can be expressed in terms of a set of simple modes.

So we consider the situation shown in figure 2a in which the (infinitely distant) detector is in the direction of $\boldsymbol{k} = (k_t, 0, k_n)$, $k_n = \boldsymbol{n}\cdot\boldsymbol{k} > 0$, where $\boldsymbol{k}$ is the wave vector of the detected radiation. As in part I we take the surfaces of the slab perpendicular to a z-axis at $z = z^+$ and $z = z^-$ with $z^+ > z^-$, and the detector is on the side of the slab where $z > z^+$; $\boldsymbol{n}$ is an outgoing unit normal vector to the surface $z = z^+$ so k_t and k_n denote tangential and normal components of $\boldsymbol{k}$ respectively. For the moment we consider the case where the scattering is not restricted by stops, so the analysis of part I applies immediately. (Figure 2a shows scattering with stops; in this way it is easy to distinguish the different modes.)

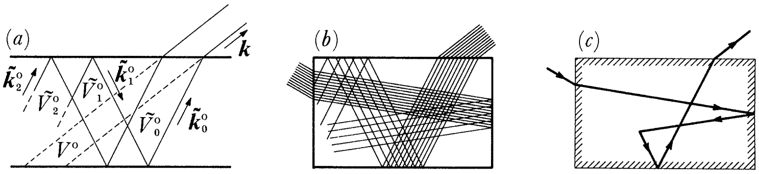


FIGURE 2. Behaviour of scattered light at the surface of the scattering cell. (a) shows wave vectors and regions for a parallel-sided slab as derived in (4.7) and used in (4.11); V^o is the directly observed region whereas $\tilde{V}_j^o$ for $j = 0, 1, 2$, etc., are regions where the jth mode of $\boldsymbol{\varepsilon}$ is non-vanishing. From $\tilde{V}_j^o$ scattering reaches the detector after j internal reflections. (b) and (c) illustrate the role of reflection of scattering for a finite scattering cell with the same scattering geometry as used in figure 1. In (b) the regions $\tilde{V}_l^i$ and $\tilde{V}_j^o$ are shown by sets of parallel lines effectively forming hatchings. The amplitudes of the various reflected modes of $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ are indicated by the degree of 'hatching'. Scattering from a lightly 'cross-hatched' region therefore has low weight W_{jl} in (4.11). (c) shows a 'ray-interpretation' of a contribution to the scattering from a point with one internal reflection of both incoming and scattered wave; the point appears in the integral (4.9b) (with $\boldsymbol{x}$ and $\boldsymbol{x}'$ tied together by the short range of (4.9a)) in the intersection of the observed region $\tilde{V}_1^o$ and the illuminated region $\tilde{V}_1^i$.

The result for the weight field $\boldsymbol{\varepsilon}$ can be written (Hynne 1980)

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) \approx \sum_{j=0}^{\infty} \tilde{\boldsymbol{e}}_j(\boldsymbol{k},\boldsymbol{v}) \exp(-\mathrm{i}\tilde{\boldsymbol{k}}_j^o\cdot\boldsymbol{x}), \tag{4.7a}$$

$$\tilde{\boldsymbol{e}}_j(\boldsymbol{k},\boldsymbol{v}) = (\tilde{e}_j^{\parallel}\tilde{\boldsymbol{v}}_j^{\parallel}\boldsymbol{v}^{\parallel} + \tilde{e}_j^{\perp}\tilde{\boldsymbol{v}}_j^{\perp}\boldsymbol{v}^{\perp})\cdot\boldsymbol{v}, \tag{4.7b}$$

$$\tilde{e}_j^{\parallel,\perp} = T_{\parallel,\perp}(R_{\parallel,\perp})^j \exp\{\mathrm{i}(2[\tfrac{1}{2}j]\,\tilde{k}_n + \tilde{k}_n - k_n)z^+ - \mathrm{i}[\tfrac{1}{2}(j+1)]\,\tilde{k}_n z^-\}, \tag{4.7c}$$

$$\tilde{\boldsymbol{k}}_j^o = (k_t, 0, (-1)^j\tilde{k}_n), \quad \tilde{k}_n = (m^2k_0^2 - k_t^2)^{\frac{1}{2}}. \tag{4.7d}$$

The result (4.7) gives the weight field $\boldsymbol{\varepsilon}$ as an infinite sum of modes. In part I (where $\boldsymbol{\mathscr{E}}$ replaces $\boldsymbol{\varepsilon}$) these were grouped together in two contributions corresponding to the only two wave vectors appearing in (4.7d), namely $\tilde{\boldsymbol{k}}_1 = (k_t, 0, \tilde{k}_n)$ for even j and $\tilde{\boldsymbol{k}}_2 = (k_t, 0 - \tilde{k}_n)$ for odd j. The vector amplitudes (4.7b) with (4.7c) can be obtained by expansion of a relation corresponding to (I 6.20) for even j. For odd j we use in addition the equivalent of (I 6.17a) for fields. In equations (4.7) and figure 2a a superscript o refers to 'outgoing' or 'observed', and indices $\parallel$ and $\perp$ mark polarizations in the plane of incidence and perpendicular to that plane. Quite generally a tilde above a symbol associates that quantity with the medium (in contradistinction to empty space). For example the wave vectors $\tilde{\boldsymbol{k}}_j^{\mathrm{o}}$ of (4.7) have magnitude $|\tilde{\boldsymbol{k}}_j^{\mathrm{o}}| = mk_0$ appropriate for vectors in the medium, whereas a vector like $\boldsymbol{k}$ for waves propagating in vacuum has magnitude k_0.

In (4.7*c*) $[x]$ denotes the largest integer that is smaller than or equal to x, whereas T and R denote Fresnel transmission and reflection coefficients (I 6.19*b*, *c*) and (I 6.17*b*, *c*). The choice for polarization unit vectors is such that $(v^{\parallel}, v^{\perp}, k)$ and $(v_j^{\parallel}, v_j^{\perp}, k_j)$ form right-handed orthogonal systems and

$$v_j^{\perp} = v^{\perp}, \quad j = 0, 1, 2, \dots .$$

To facilitate the graphical representation of the results and extend the theory we shall generalize (4.7) to cover also the case of scattering with stops. It is with a view to this generalization we have expanded results like (I 6.20) to express the weight field as a sum of modes in (4.7). We have not actually solved equations (4.5), (4.6*a*, *b*) for stopped scattering so for this generalization only we must appeal to macroscopic optics through the inverse response correspondence. With neglect of diffraction the weight field has the form

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) \approx \sum_{j=0}^{\infty} \tilde{\boldsymbol{e}}_j(\boldsymbol{k},\boldsymbol{v}) \exp\left(-\mathrm{i}\tilde{\boldsymbol{k}}_j^{\mathrm{o}}\cdot\boldsymbol{x}\right) \chi(\boldsymbol{x};\tilde{V}_j^{\mathrm{o}}), \tag{4.8}$$

in which $\chi(\boldsymbol{x};\tilde{V}_j^{\mathrm{o}})$ is the characteristic function (4.2*b*) for the region $\tilde{V}_j^{\mathrm{o}}$, where the jth reflected mode of the weight field is non-vanishing. The significance of the modes of the weight field and of the associated wave vectors $\tilde{\boldsymbol{k}}_j^{\mathrm{o}}$ and observed regions $\tilde{V}_j^{\mathrm{o}}$ is suggested already by figure 2*a* and it will become clear when we consider the weight field in the context of scattering. This we do next.

At this stage we want to discuss the collective surface effects in association with purely local scattering. Thus we consider only macroscopic single scattering. In §5 we shall show how the description extends naturally to scattering that is non-local because of multiple scattering or for any other reason. The flux J of both macroscopic single and multiple scattered light is expressed in terms of $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ by (3.5) with (3.8) but because we want to consider only local scattering here we may use the explicit expression (2.27) instead and discuss the contribution of its lowest order term as a typical example.

Here the small parameter is $n\alpha$. (Far from an optical resonance $n\alpha < 0.1$ in liquids and is still smaller in gases.) The rate of convergence of (2.27) is unknown, but the analysis carries over to the sum of all local terms. The contribution of the lowest order in $n\alpha$ in (2.27) occurs for $p = 2$ (order $(n\alpha)^2$) and there is only one term in the sum over q, namely J_{21}. For $p = 2$ in (2.27) the intermolecular correlations are described by $K_{12}^{(1)}$, which is simply the two-body generalized Ursell function U_{12}, namely

$$U_{12} = g_{12} - 1 + n^{-1}\delta_{12} = U_2(\boldsymbol{x}_1 - \boldsymbol{x}_2). \tag{4.9a}$$

For later convenience of interpretation we consider the flux into the differential solid angle $\mathrm{d}\Omega$; so we get for $p = 2$ and $q = 1$,

$$J_{21}(\boldsymbol{k},\boldsymbol{v})\,\mathrm{d}\Omega = \left[\frac{c}{8\pi} k_0^4 (n\alpha)^2 \int_V \int_V \mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}' \times \boldsymbol{\mathscr{E}}^*(\boldsymbol{x},\omega)\cdot\boldsymbol{\varepsilon}^*(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{\varepsilon}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,U_2(\boldsymbol{x}-\boldsymbol{x}')\right]\mathrm{d}\Omega. \tag{4.9b}$$

If $\mathscr{E}$ is also a sum of restricted plane wave modes

$$\mathscr{E}(\boldsymbol{x},\omega) \approx \sum_{l=0}^{\infty} \tilde{\boldsymbol{E}}_l \exp(\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{i}}_l\cdot\boldsymbol{x})\,\chi(\boldsymbol{x};\tilde{V}^{\mathrm{i}}_l) \tag{4.10}$$

we then find at lowest, i.e. second, order in $n\alpha$,

$$J_{21}(\boldsymbol{k},\boldsymbol{v})\,\mathrm{d}\Omega = \sum_{j,l} W_{jl}\,\sigma^{(21)}_{jl}(\tilde{\boldsymbol{q}}_{jl})\,\mathrm{d}\tilde{\Omega} + \text{cross-terms}, \tag{4.11a}$$

$$W_{jl} = |\tilde{V}^{\mathrm{o}}_j \cap \tilde{V}^{\mathrm{i}}_l|\,((\tilde{k}^{\mathrm{o}}_{\mathrm{n}}/k_{\mathrm{n}})\,|\tilde{e}_j|^2)\,((c/8\pi)\,m|\tilde{E}_1|^2), \tag{4.11b}$$

$$\sigma^{(21)}_{jl}(\tilde{\boldsymbol{q}}_{jl}) = k_0^4(n\alpha)^2\,(\tilde{\boldsymbol{v}}^{\mathrm{o}}_j\cdot\tilde{\boldsymbol{v}}^{\mathrm{i}}_l)^2\int U_2(\boldsymbol{r})\exp(\mathrm{i}\tilde{\boldsymbol{q}}_{jl}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}, \tag{4.11c}$$

$$\tilde{\boldsymbol{q}}_{jl} = \tilde{\boldsymbol{k}}^{\mathrm{o}}_j - \tilde{\boldsymbol{k}}^{\mathrm{i}}_l, \quad \tilde{\boldsymbol{v}}^{\mathrm{o}}_j = \tilde{\boldsymbol{e}}_j/|\tilde{\boldsymbol{e}}_j|, \quad \tilde{\boldsymbol{v}}^{\mathrm{i}}_l = \tilde{\boldsymbol{E}}_l/|\tilde{\boldsymbol{E}}_l|, \tag{4.11d}$$

$$\mathrm{d}\tilde{\Omega} = (k_{\mathrm{n}}/m\tilde{k}^{\mathrm{o}}_{\mathrm{n}})\,\mathrm{d}\Omega, \quad \tilde{k}^{\mathrm{o}}_{\mathrm{n}} = \boldsymbol{n}\cdot\tilde{\boldsymbol{k}}^{\mathrm{o}}_0. \tag{4.11e}$$

Superscript i refers to 'incoming' or 'illuminated'. Note carefully that (4.11 *a*) contains $\mathrm{d}\Omega$ on the left side but $\mathrm{d}\tilde{\Omega}$ on the right.

If we neglect for a moment the cross-terms in (4.11 *a*) the scattering is the sum over all modes (j,l) of $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ of the differential scattering cross section $\sigma^{(21)}_{jl}$ weighted by W_{jl}. It is natural to view $\sigma^{(21)}_{jl}$ as describing the scattering of an incoming wave in the medium with wave vector and polarization $(\tilde{\boldsymbol{k}}^{\mathrm{i}}_l, \tilde{\boldsymbol{v}}^{\mathrm{i}}_l)$ into an outgoing wave in the medium characterized by $(\tilde{\boldsymbol{k}}^{\mathrm{o}}_j, \tilde{\boldsymbol{v}}^{\mathrm{o}}_j)$. We shall sometimes denote the differential cross-section by $n\,\mathrm{d}\sigma/\mathrm{d}\tilde{\Omega}$ to emphasize its relation to scattering in the medium; note that $\sigma^{(21)}$ is the cross section per unit volume.

The weight W_{jl} is proportional to the volume of the relevant scattering region, which is the intersection of the illuminated region $\tilde{V}^{\mathrm{i}}_l$ and the observed region $\tilde{V}^{\mathrm{o}}_j$. It is also proportional to the intensity of the lth mode of the incoming wave. Finally W_{jl} contains the factor $(\tilde{k}^{\mathrm{o}}_{\mathrm{n}}/k_{\mathrm{n}})\,|\tilde{e}_j|^2$. In the case of a parallel-sided slab and for the special cases of polarization $\boldsymbol{v} = \boldsymbol{v}^{\parallel}$ or $\boldsymbol{v}^{\perp}$ we find from (4.7 *c*) that the factor is

$$(\tilde{k}^{\mathrm{o}}_{\mathrm{n}}/k_{\mathrm{n}})\,|\tilde{\boldsymbol{e}}_j|^2 = \mathscr{T}_{\parallel,\perp}(\mathfrak{R}_{\parallel,\perp})^j. \tag{4.12a}$$

where $\mathscr{T}_{\parallel,\perp}$ is the transmissivity and $\mathfrak{R}_{\parallel,\perp}$ is the reflectivity for parallel, $\parallel$, or perpendicular, $\perp$, polarization,

$$\mathscr{T}_{\parallel,\perp} = \tilde{k}^{\mathrm{o}}_{\mathrm{n}}/k_{\mathrm{n}}\,|T_{\parallel,\perp}|^2, \quad \mathfrak{R}_{\parallel,\perp} = |R_{\parallel,\perp}|^2, \tag{4.12b}$$

in which $T_{\parallel,\perp}$ and $R_{\parallel,\perp}$ are Fresnel transmission and reflection coefficients for light entering the medium (I 6.19 *b*, *c*) and (I 6.17 *b*, *c*) (Born & Wolf 1970, Lekner 1987). Thus, the contribution from the jth mode to the scattering received by the detector equals the scattering in the medium diminished by the loss suffered in j successive internal reflections and in the final transmission from the medium into the vacuum outside the material system.

Figure 2 *b* illustrates the result (4.11) for a more practical geometry. As in figure 1 the incident wave enters from the left and the scattered wave exits at the top. The modes of $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ are shown by parallel lines and the sum in (4.11 *a*) has contributions from all the resulting cross-hatched regions where modes of $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ intersect. The light hatching of reflected modes indicates attenuation due to reflection loss. In this way the degree of cross-hatching indicates the weight W_{jl} of a contribution (j,l) as given by (4.11 *b*).

Figure 2*c* indicates the contribution from one point of the region $\tilde{V}_1^{\mathrm{o}} \cap \tilde{V}_1^{\mathrm{i}}$ with one internal reflection of the incident wave between its entrance into the medium and the local scattering process ($l = 1$) and one internal reflection of the scattered wave between its emergence from the local scattering process and its exit from the medium through the surface ($j = 1$).

It is immediately clear from the construction of the weight field that the wave vectors $\tilde{\boldsymbol{k}}_j^{\mathrm{o}}$ and observed regions $\tilde{V}_j^{\mathrm{o}}$ admit of such interpretation. Snell's law of refraction and the law of reflection are satisfied and the geometry of the regions is correct. We have also just seen in a special case that the weight W_{jl} correctly accounts for the reflection and transmission losses associated with processes as interpreted. Notice how simply the construction of the weight field solves the problem of finding all contributions to the total scattering process.

The result (4.11) gives the flux into the differential solid angle $\mathrm{d}\Omega$ around $\boldsymbol{k}$ and it is essential to the interpretation that the right side of (4.11) contains the corresponding differential solid angle $\mathrm{d}\tilde{\Omega}$ around $\tilde{\boldsymbol{k}}_0^{\mathrm{o}}$ (in the medium rather than in vacuum). In this way the right side of (4.11) presents the flux in vacuum as the flux in the medium corrected by the transmissivity.

The interpretation of (4.11) given above was cavalier as far as the polarization of the scattering is concerned. The point is that the scattering is analysed for polarization in vacuum and not in the medium. Although $\sigma_{lj}^{(21)}$ can naturally be viewed as a cross section for scattering into a wave in the medium of polarization $\tilde{\boldsymbol{v}}_j^{\mathrm{o}}$ such wave is in general not reflected and refracted into a wave with polarization $\boldsymbol{v}$ in vacuum. Rather $\tilde{\boldsymbol{v}}_j^{\mathrm{o}}$ represents the effect of the external polarization analyser referred to the medium.

The correct interpretation of (4.11) or of the more general result (2.29*a*) is as follows. The incoming wave in the medium $\mathscr{E}$ is scattered by a local susceptibility fluctuation represented by $\boldsymbol{\Delta}^{\mathrm{in}}$ into an outgoing wave in the medium. The scattered wave (of whatever polarization) subsequently behaves according to macroscopic optics: It propagates through the medium and crosses the surface, then passes the stop and the analyser and is finally detected. The result (2.29*a*) gives the average flux per unit solid angle in vacuum of the scattering thus described. To be more precise the scattering in the medium referred to in the interpretation is the average radiation from the dipole distribution

$$\boldsymbol{p}^{\mathrm{in}}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Delta}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}', \tag{4.13}$$

embedded in a continuum of refractive index m contained in V; the kernel $\boldsymbol{\Delta}^{\mathrm{in}}$ is (2.29*b*). For a complete proof of the interpretation for any convex polyhedron V we refer to Hynne (1980). The assumption of convexity was made to avoid the complication of reentrance of the scattered wave into the medium. We believe it is unnecessary. Indeed, we believe the interpretation extends to arbitrary geometry.

Note carefully that the construction of the weight field as an inverse response applies independently of any interpretation we might make. It applies to arbitrary geometry. Thus we may infer from macroscopic optics and the mathematical similarity of (4.1) and (3.1*a*) that for curved surfaces we may have a lens effect for the scattered light as indicated in figure 3*a* for a cylindrical cell or qualitatively in figure 3*b* for general geometry.

Notwithstanding the role of the polarization unit vector $\tilde{\boldsymbol{v}}_j^{\mathrm{o}}$ in the interpretation we may of course still use (4.11) to calculate cross sections for scattering into waves polarized in directions $\tilde{\boldsymbol{v}}_j^{\mathrm{o}}$ related to the direction of the external analyser. We also have to correct with the factors prescribed by (4.11). These are well defined though in the general case not all easily

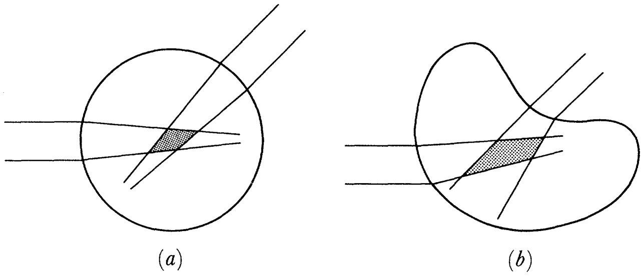


FIGURE 3. Lens effect in scattering through a curved surface as inferred from the inverse response correspondence by appeal to macroscopic optics. The shaded regions in the figures indicate the effective scattering regions for direct scattering from (a) a circular cylindrical cell and (b) some general geometry. Contributions involving internal reflections are not shown.

interpreted. Such a calculation is simple only for simple geometry and it is further complicated by effects of the higher terms of (2.27) to be discussed in §5.

We are obliged to discuss also the cross terms of (4.11*a*). They have the form

$$\frac{ck_0^4}{8\pi}(n\alpha)^2\,\mathrm{d}\Omega\sum_{p,q,j,l}(\tilde{\boldsymbol{E}}_q\cdot\tilde{\boldsymbol{e}}_p)^*\,(\tilde{\boldsymbol{e}}_j\cdot\tilde{\boldsymbol{E}}_l)\int_{\tilde{V}_{pq}}\mathrm{d}\boldsymbol{x}\int_{\tilde{V}_{jl}}\mathrm{d}\boldsymbol{x}'\,U_2(\boldsymbol{x}-\boldsymbol{x}')\exp\left[\mathrm{i}(\tilde{\boldsymbol{q}}_{pq}\cdot\boldsymbol{x}-\tilde{\boldsymbol{q}}_{jl}\cdot\boldsymbol{x}')\right] \tag{4.14}$$

in which, for example, $\tilde{V}_{jl} = \tilde{V}_j^{\mathrm{o}} \cap \tilde{V}_l^{\mathrm{i}}$ and the sum is taken over all sets (p,q,j,l) with $(p,q) \neq (j,l)$. Evidently (4.14) represents interference between different modes. A term (p,q,j,l) vanishes unless the regions $\tilde{V}_{pq}$ and $\tilde{V}_{jl}$ overlap (because U_2 is short range) and it is diffraction like and negligible unless $\tilde{\boldsymbol{q}}_{pq} = \tilde{\boldsymbol{q}}_{jl}$. For scattering without stops from an infinite parallel-sided slab one should therefore in practical calculations retain the closed form corresponding to (I 6.20) and work with just two modes for $\boldsymbol{\varepsilon}$.

The scattering is quadratic in the weight field and the quadratic combination $\mathscr{S}'$ is in some ways more expressive than the isolated weight field. It is therefore of interest to see the form of the simple dipole radiator $\mathscr{S}'$ for a region V; we denote it by $\tilde{\mathbf{S}}_V$ in the continuum approximation. In the general case $\mathscr{S}'$ is a sum over all pairs of modes of $\boldsymbol{\varepsilon}^*$ and $\boldsymbol{\varepsilon}$, that is a sum over all modes of $\boldsymbol{\varepsilon}$ plus interference terms. We restrict ourselves to the simple case of a fluid occupying the half-space $z < z^+$. In this case the weight field equals the first term of (4.7*a*) or of (4.8) for scattering restricted by stops. We then find for polarization in one of the principal directions that $\mathscr{S}' \approx \tilde{\mathbf{S}}_V$ with

$$\tilde{\mathbf{S}}_V(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_{\parallel,\perp})\,\mathrm{d}\Omega = \mathscr{T}_{\parallel,\perp}\,\tilde{\mathbf{S}}(\boldsymbol{x},\boldsymbol{x}';\tilde{\boldsymbol{k}}^{\mathrm{o}},\tilde{\boldsymbol{v}}^{\mathrm{o}}_{\parallel,\perp})\,\chi(\boldsymbol{x};\tilde{V}^{\mathrm{o}})\,\chi(\boldsymbol{x}';\tilde{V}^{\mathrm{o}})\,\mathrm{d}\tilde{\Omega}, \tag{4.15a}$$

$$\tilde{\mathbf{S}}(\boldsymbol{x},\boldsymbol{x}';\tilde{\boldsymbol{k}}^{\mathrm{o}},\tilde{\boldsymbol{v}}^{\mathrm{o}}) = mk_0^2\,\tilde{\boldsymbol{v}}^{\mathrm{o}}\tilde{\boldsymbol{v}}^{\mathrm{o}}\exp\left[\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{o}}\cdot(\boldsymbol{x}-\boldsymbol{x}')\right]. \tag{4.15b}$$

The kernel $\tilde{\mathbf{S}}$ may be called a bulk dipole radiator because a quadratic form in a polarization like (2.31) with kernel $\tilde{\mathbf{S}}$ replacing $\mathscr{S}$ gives the flux per unit solid angle radiated from the given polarization in a translationally invariant continuum of refractive index m in the direction of $\tilde{\boldsymbol{k}}$ with polarization $\tilde{\boldsymbol{v}}$. With $\tilde{\mathbf{S}}$ the 'unit solid angle' mentioned refers to the medium, and the radiator for the flux per unit solid angle in vacuum (in the direction of $\boldsymbol{k}$ and with polarization $\boldsymbol{v}$) contains the additional corrections of the transmissivity $\mathscr{T}$ and of the transformation of the differential solid angle $\mathrm{d}\tilde{\Omega}/\mathrm{d}\Omega$ as well as the restrictions of the observed regions for scattering with stops. When the polarization $\boldsymbol{v}$ is not in any of the two principal directions, $\tilde{\mathbf{S}}_V$ does not factorize into a bulk radiator and correction factors. The bulk radiator is associated with an idealized scattering process in the medium. Note that the factor m in (4.15 b) (which comes from the transformation (4.11 e) of the differential solid angle) is transferred in (4.11 b) to the factor in $|\tilde{E}_l|^2$ describing the dependence on the intensity of the incoming wave in the medium.

We have now demonstrated that scattered light as described by the weight field $\boldsymbol{\varepsilon}$ behaves at the surface of the medium in agreement with what one would have inferred from macroscopic optics. This demonstration starts from the microscopic equations in the special case of a parallel-sided slab. And by the inverse response correspondence the proof in terms of reflection and transmission coefficients can be extended to an arbitrary convex polyhedron. Indeed, by appeal to well-known results of macroscopic optics we can infer the behaviour of scattered light at material surfaces for arbitrary geometry, quantitatively (up to neglect of 'surface waves' like those described in part I near (I 6.30)). Our conclusion therefore is that the phenomenologically based corrections for surface effects used in actual experiments as, for example, in Carr & Zimm (1950) (their fig. 2) are well motivated.

However, the relatively simple result (4.11) for the scattered flux represents the lowest contribution to the scattering only. Unfortunately, the term J_{21} is not representative of all higher scattering terms and we cannot immediately generalize the result for a local scattering cross section to all orders. The difficulty is that we have to deal first with macroscopic multiple scattering. We treat this problem in the immediately following section.

5. SCATTERING OF LIGHT IN THE MEDIUM

The flux of scattered light has the form of a functional $\mathscr{I}(\mathscr{E}, \boldsymbol{\varepsilon})$ of the average field in the medium $\mathscr{E}$ and the weight field $\boldsymbol{\varepsilon}$. It can conveniently be expressed in terms of operators just as the expression (3.5) was. The transmission of the incoming and scattered waves across the surface and the associated refraction and reflection are described by the fields $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ in their dependence on $\boldsymbol{E}$ and $\boldsymbol{e}$ as we showed in the preceeding section. Because the fields $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ may be said to represent the incoming and scattered waves in the medium the functional $\mathscr{I}(\boldsymbol{W}, \boldsymbol{w})$ itself represents the scattering process in the medium.

If $\boldsymbol{W}$ and $\boldsymbol{w}$ are solutions to (3.1 a) and (3.1 e) respectively the functional $\mathscr{I}$ describes the scattering process in the medium as a part of a complete scattering process from an incoming wave in vacuum to a scattered wave in vacuum, giving the flux of scattered light at the detector.

It is natural, however, to view the functional $\mathscr{I}(\boldsymbol{W}, \boldsymbol{w})$ with $\boldsymbol{W}$ and $\boldsymbol{w}$ arbitrary transverse waves of wavenumber mk_0 more abstractly as describing a scattering process in the medium, from an incoming wave $\boldsymbol{W}(\boldsymbol{x}, \omega)$ in the medium to a scattered wave in the medium represented by $\boldsymbol{w}(\boldsymbol{x}, \omega)$. So we may conveniently study a prototype of a scattering process in the medium by choosing $\boldsymbol{W}$ and $\boldsymbol{w}$ as simple transverse plane waves of unit amplitude,

$$\boldsymbol{W}(\boldsymbol{x}, \omega) = \tilde{\boldsymbol{v}}^{\mathrm{i}} \exp(\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{i}} \cdot \boldsymbol{x}), \quad \boldsymbol{w}(\boldsymbol{x}, \omega) = \tilde{\boldsymbol{v}}^{\mathrm{o}} \exp(-\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{o}} \cdot \boldsymbol{x}), \tag{5.1 a}$$

$$\tilde{\boldsymbol{v}}^{\mathrm{i}} \cdot \tilde{\boldsymbol{k}}^{\mathrm{i}} = \tilde{\boldsymbol{v}}^{\mathrm{o}} \cdot \tilde{\boldsymbol{k}}^{\mathrm{o}} = 0, \quad |\tilde{\boldsymbol{k}}^{\mathrm{i}}| = |\tilde{\boldsymbol{k}}^{\mathrm{o}}| = mk_0, \quad |\tilde{\boldsymbol{v}}^{\mathrm{i}}| = |\tilde{\boldsymbol{v}}^{\mathrm{o}}| = 1, \tag{5.1 b}$$

where superscripts i and o refer to the incoming and outgoing waves respectively. We shall occasionally use the dyadic combination (I 5.26 a) of two $\boldsymbol{W}$

$$\tilde{\mathbf{I}}(\boldsymbol{x}, \boldsymbol{x}'; \tilde{\boldsymbol{k}}^{\mathrm{i}}, \tilde{\boldsymbol{v}}^{\mathrm{i}}) = \tilde{\boldsymbol{v}}^{\mathrm{i}} \tilde{\boldsymbol{v}}^{\mathrm{i}} \exp[\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{i}} \cdot (\boldsymbol{x} - \boldsymbol{x}')] \tag{5.1 c}$$

and the expression (4.15 b) involving two $\boldsymbol{w}$.

Now it is plain from §3 that apart from the trivial factor $ck_0^4/(8\pi)$ the functional $\mathscr{I}$ is simply given by the operator $\mathscr{M}$, so this is the object we shall study in the present section.

(*a*) *Formal multiple scattering expansion*

We first exhibit the operators $\mathscr{M}$, $\mathscr{L}$, and $\mathscr{Z}$ explicitly; they are all integral operators with fourth-rank tensor kernels depending on four points in space. The kernel of $\mathscr{Z}$ is particularly simple:

$$\mathscr{Z}_{1234} = \mathscr{F}^*_{12}\,\mathscr{F}_{34} = \mathscr{F}^*_{i_1 i_2}(\boldsymbol{x}_1, \boldsymbol{x}_2; \omega)\,\mathscr{F}_{i_3 i_4}(\boldsymbol{x}_3, \boldsymbol{x}_4; \omega). \tag{5.2}$$

It depends on points $\boldsymbol{x}_1$, $\boldsymbol{x}_2$, $\boldsymbol{x}_3$, and $\boldsymbol{x}_4$ and on tensor indices i_1, i_2, i_3, and i_4.

The operators $\mathscr{M}$ and $\mathscr{L}$ are similarly represented by tensor kernels $\mathscr{M}_{1234}$ and $\mathscr{L}_{1234}$ (which form coordinate representations of the operators) and we may write expressions like (3.5) and (3.7) explicitly as

$$J = \frac{ck_0^4}{8\pi}\int_V \dots \int_V \mathscr{E}^*_1\,\mathscr{E}_4\,\mathscr{M}_{1234}\,\boldsymbol{\varepsilon}^*_2\,\boldsymbol{\varepsilon}_3\,\mathrm{d}\boldsymbol{x}_1 \dots \mathrm{d}\boldsymbol{x}_4, \tag{5.3}$$

and

$$\mathscr{M}_{1234} = \mathscr{L}_{1234} + \int_V \dots \int_V \mathscr{L}_{12'3'4}\,\mathscr{Z}_{2'1'4'3'}\,\mathscr{M}_{1'234'}\,\mathrm{d}\boldsymbol{x}'_1 \dots \mathrm{d}\boldsymbol{x}'_4. \tag{5.4}$$

Note how operation to the left (of operators like $\mathscr{M}$ and $\mathscr{L}$) is associated with the exterior (first and last) indices whereas operation to the right involves the interior indices. In (5.3) and (5.4) integration with respect to a variable $\boldsymbol{x}_j$ also sums the corresponding tensor index i_j, and index j in $\mathscr{E}_j$ and $\boldsymbol{\varepsilon}_j$ refers to variables $\boldsymbol{x}_j$ and tensor index i_j.

In association with $\boldsymbol{\varepsilon}^*_2\,\boldsymbol{\varepsilon}_3$ as in (3.9) the kernel $\mathscr{L}_{1234}$ represents macroscopic single scattering (even though $\mathscr{L}$ can also represent the total scattering when it is associated with $\mathscr{S}$ as in (3.3*b*) and (3.3*c*) combined). We can obtain a series expansion for $\mathscr{L}$ from (3.1*c*) by removing $\mathscr{S}_{q(q+1)}$ and the associated integrations. The variables and tensor indices $\boldsymbol{x}_q, i_q$ and $\boldsymbol{x}_{q+1}, i_{q+1}$ then become free and we get:

$$\mathscr{L}_{11'0'0} = \sum_{p=1}^{\infty} (n\alpha)^{p+1} \sum_{q=1}^{p} \int_V \dots \int_V \mathrm{d}\boldsymbol{x}_2 \dots \mathrm{d}\boldsymbol{x}_{q-1}\,\mathrm{d}\boldsymbol{x}_{q+2} \dots \mathrm{d}\boldsymbol{x}_p$$
$$\times\,\mathscr{F}^*_{12}\cdot\mathscr{F}^*_{23}\dots\mathscr{F}^*_{(q-1)1'}\,\mathscr{F}_{0'(q+2)}\dots\mathscr{F}_{p0}\,Y_{123\dots(q-1)1'0'(q+2)\dots p0}. \tag{5.5}$$

In all terms of (5.5) with $q = 1$ the chain of $\mathscr{F}^*$ propagators degenerates to $\mathsf{U}\delta_{11'}$, and in terms with $q = p$ the chain of $\mathscr{F}$ propagators degenerates to $\mathsf{U}\delta_{0'0}$. Indices $1'$ and $0'$ respectively disappear from the Y functions in these cases.

Plainly the expressions quickly get rather complicated so we extend the diagrammatical notation introduced in §4 of the refractive index theory (part II), see figure 4 next. A diagram consists of a set of circles, which may be thought of as representing polarizable molecules. Each circle indicates a factor $n\alpha$ and represents a point in space appearing as one argument of an integrand. Circles carrying a dot represent free variables, the other variables are integrated over the region V.

A line between two circles represents a propagator between the two points; a single line represents F and a double line represents $\mathscr{F}$. A pair of arrows in double line represents the radiator $\mathscr{S}$. It is understood that propagator lines to the left of a pair of arrows in figure 4*b* imply a complex conjugate propagator $\mathscr{F}^*$.

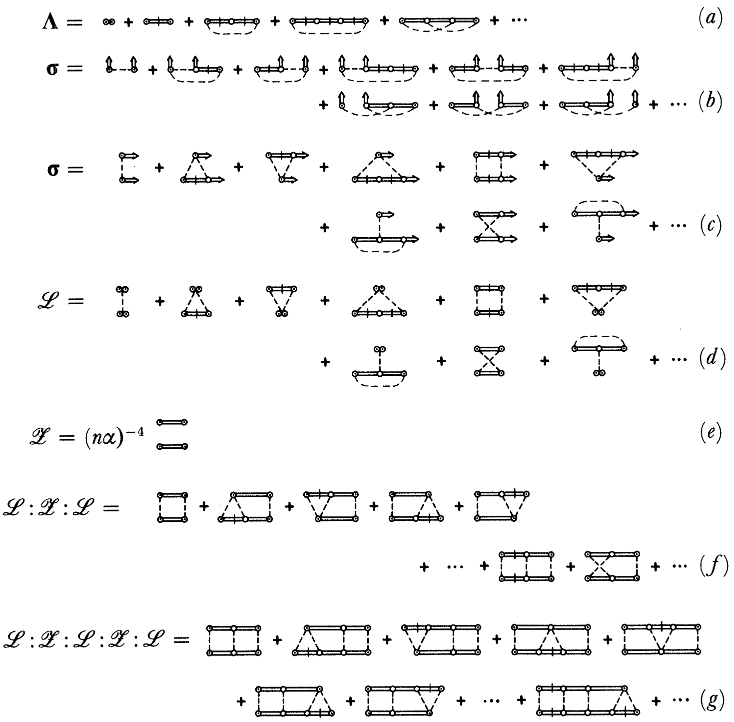


Figure 4. Diagrammatical representation of kernels describing scattering. The scattering kernel $\boldsymbol{\sigma}$ is displayed in two equivalent forms in (*b*) and (*c*). The form (*b*) exhibits the relation (2.22) with (2.38*b*) between $\boldsymbol{\sigma}$ and the polarization kernel $\boldsymbol{\Lambda}$ when compared with (*a*). A term in (*a*) with p propagator double-lines corresponds to p terms in (*b*). The alternative form (*c*) of $\boldsymbol{\sigma}$ exhibits a one to one correspondence between the terms of $\boldsymbol{\sigma}$ and those of (the kernel of) the single scattering operator $\mathscr{L}$, equation (*d*). Equations (*f*) and (*g*) show how two or three operators $\mathscr{L}$ combine to produce operators for double or triple scattering respectively when connected with one or two operators (*e*) representing intermediate propagation in the medium (5.2).

An intermolecular correlation function is represented by a loop of dotted lines, and a dotted line coinciding with a propagator line (full single or double line) adds a cross to that line. A loop degenerates to a (dotted) line when only two circles are involved, and two circles touching each other carry only one factor $n\alpha$ and represent a delta function and a unit tensor U (or a Kronecker delta in tensor components). In this paper we shall use white circles only: loops always represent generalized Ursell functions (2.40) with (2.15), whereas the black circle notation of part II (which indicated distribution functions, not Ursell functions) is not needed here. Note that any generalized Ursell function is symmetrical in all its variables although the representation by a loop of dotted lines does not exhibit the full symmetry.

We shall start by giving the diagrammatical expansions of $\boldsymbol{\Lambda}$ and $\boldsymbol{\sigma}$ in terms of screened propagators to show how $\boldsymbol{\sigma}$ can be formally obtained from $\boldsymbol{\Lambda}$ through (2.22). Figure 4*a* is the series expansion (I 4.10) of $\boldsymbol{\Lambda}$ from figure 2 of part II (except for a small change of notation in the first term introduced for consistency with later extensions).

We note that each diagram contains a chain of circles connected by propagator double lines (representing $\mathscr{F}$). The first and last circles carry a dot because the corresponding variables are free; these are the variables of $\boldsymbol{\Lambda}$. Intermolecular correlations are governed by the Y functions (2.39), expressed in terms of generalized Ursell functions (represented by loops of dotted lines). The first term contains a delta function connecting the two points. The second and third terms are each covered by one Ursell function simply, whereas the fourth-order term (with four circles) gives rise to two diagrams because Y_{1234} contains two terms in Ursell functions as (2.39) shows.

The relation (2.22) works the same way in terms of either screened or unscreened propagators: compare (2.38*b*) with (2.20). Figure 4*b* exhibits the expansion (2.38) of $\boldsymbol{\sigma}$, and by comparison with figure 4*a* we see how (2.22) works in diagramatical notation. We obtain the expansion for $\boldsymbol{\sigma}$ from the one for $\boldsymbol{\Lambda}$ simply by replacing each diagram of $\boldsymbol{\Lambda}$ by a sum of diagrams obtained by replacing each propagator double line in turn by a pair of arrows (in double line). This replacement of lines by pairs of arrows corresponds to (2.38*b*). The first term of $\boldsymbol{\Lambda}$ gives nothing because it does not contain any propagator $\mathscr{F}$. The second term of $\boldsymbol{\Lambda}$ contains one $\mathscr{F}$ and generates one term of $\boldsymbol{\sigma}$ by (2.22). The third term of $\boldsymbol{\Lambda}$ generates two terms of $\boldsymbol{\sigma}$ etc.

The scattering kernel $\boldsymbol{\sigma}$ gives the flux of scattered light J by the quadratic form (3.1*b*) or (3.3*b*). The fields $\mathscr{E}^*$ and $\mathscr{E}$ attach to the free variables of $\boldsymbol{\sigma}$ represented in figure 4*b* by the exterior (first and last) circles, i.e. those carrying dots. By our convention $\mathscr{E}^*\mathscr{E}$ therefore appears to the left of $\boldsymbol{\sigma}$ in (3.3*b*). On the other hand $\boldsymbol{\sigma}$ contains the radiator $\mathscr{S}$ attached to interior variables, appearing inside a chain of propagators $\mathscr{F}$ in (2.38*b*), and the pair of arrows appears inside a chain of lines in each diagram of figure 4*b*. Whereas figure 4*b* expresses the relation of $\boldsymbol{\sigma}$ to $\boldsymbol{\Lambda}$ very clearly it is more convenient for the presentation of the multiple scattering theory to rearrange the diagrams as in figure 4*c*. In this way expressions like (3.8) are represented more simply. We therefore rotate and bend each diagram so that the circles with dots appear to the left and the arrows are to the right. Now it is the upper chain of double lines (say) that represent complex conjugate propagators $\mathscr{F}^*$.

It is straightforward to obtain a diagrammatical representation of the kernel $\mathscr{L}$ from figure 4*c*. Simply remove each arrow and place a dot in the circle to which it was attached (this represents a free variable in $\mathscr{L}$). In the case where an arrow is attached to a circle already carrying a dot in figure 4*c* add another circle (with dot) touching the original one. The new free variable must be connected to the original one by a delta function and a Kronecker delta.

The result for $\mathscr{L}$ is shown in figure 4*d*. And because $\mathscr{Z}$ is represented by a pair of propagator lines essentially (see figure 4*e*) we immediately get the macroscopic multiple scattering expressions shown in lines f and g of figure 4 for double and triple scattering respectively. The flux of macroscopic single, double, triple, etc., scattering is now obtained from the terms of (3.8) substituted in (3.5). In particular, we get macroscopic single scattering from the series figure 4*d* or (5.5) for $\mathscr{L}$ by attaching $\mathscr{E}^*$ and $\mathscr{E}$ to the exterior variables and $\boldsymbol{\varepsilon}^*$ and $\boldsymbol{\varepsilon}$ to the interior ones, integrating all these variables over V and multiplying by $ck_0^4/8\pi$. Thus

$$J^{(1)} = \frac{ck_0^4}{8\pi}\sum_{p=2}^{\infty}(n\alpha)^p\sum_{q=1}^{p-1}\int_V\cdots\int_V \mathrm{d}\boldsymbol{x}_1\ldots\mathrm{d}\boldsymbol{x}_p\,Y_{123\ldots p}$$
$$\times\,\mathscr{E}_1^*\cdot\mathscr{F}_{12}^*\ldots\mathscr{F}_{(q-1)\,q}^*\cdot\boldsymbol{\varepsilon}_q^*\,\boldsymbol{\varepsilon}_{q+1}\cdot\mathscr{F}_{(q+1)\,(q+2)}\ldots\mathscr{F}_{(p-1)\,p}\cdot\mathscr{E}_p. \quad (5.6)$$

We see that each microscopic scattering term contributing to macroscopic single scattering involves a single group of molecules covered by one Y function. A macroscopic double scattering term involves two sets of molecules each covered by Y functions, and these are coupled by propagators $\mathscr{F}^*$ and $\mathscr{F}$ not covered by correlation functions as shown in figure 4*f*. Similarly the macroscopic triple scattering shown in figure 4*g* involves three Y-covered sets of molecules coupled by two pairs of propagators $\mathscr{F}^*\mathscr{F}$, etc.

We now discuss single scattering.

(*b*) *Macroscopic single scattering*

Single scattering is governed by the kernel $\mathscr{L}$, figure 4*d*. Recall that $\mathscr{L}$ also determines the total scattering when $\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$ is replaced by $\mathscr{S}$ in (3.9); but we shall henceforth work in terms of the weight field $\boldsymbol{\varepsilon}$ so that the total scattering is determined by $\mathscr{M}$ through (3.5), and $\mathscr{M}$ is composed of single scattering $\mathscr{L}$, double scattering $\mathscr{L}:\mathscr{X}:\mathscr{L}$, etc.

The simplest single scattering term is the first term of (5.6) coming from the first term of figure 4*d*:

$$\frac{c}{8\pi}k_0^4(n\alpha)^2\int_V\int_V \boldsymbol{\mathscr{E}}_1^*\cdot\boldsymbol{\varepsilon}_1^*\,\boldsymbol{\varepsilon}_2\cdot\boldsymbol{\mathscr{E}}_2\,U_{12}\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2. \tag{5.7}$$

This term has already been discussed in §4 in the context of the complete scattering process from source to detector. As we saw in (4.11) we get a sum over all modes of $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ of a product of a geometrical weight factor W_{jl} and a differential scattering cross-section $\sigma_{jl}(\tilde{\boldsymbol{q}}_{jl})\,\mathrm{d}\tilde{\Omega}/\mathrm{d}\Omega$ for scattering in the medium into the differential solid angle $\mathrm{d}\tilde{\Omega}$ with scattering vector $\tilde{\boldsymbol{q}}_{jl}$.

The weight factor W_{jl} contains the magnitude of the relevant modes of $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ and the volume $|\tilde{V}_{jl}|$ of the proper scattering region $\tilde{V}_{jl}=\tilde{V}_j^{\mathrm{o}}\cap\tilde{V}_l^{\mathrm{i}}$. Here the cross section σ_{jl} depends only on local conditions, the relative orientation of the polarization unit vectors and the scattering vector $\tilde{\boldsymbol{q}}_{jl}$ for waves in the medium.

To study the scattering process in the medium separately we consider single modes (5.1) for $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$:

$$\sigma^{(2)}(\tilde{\boldsymbol{q}})=k_0^4(n\alpha)^2\,(\tilde{\boldsymbol{v}}^{\mathrm{i}}\cdot\tilde{\boldsymbol{v}}^{\mathrm{o}})^2\int U_2(\boldsymbol{r})\exp\,(\mathrm{i}\tilde{\boldsymbol{q}}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}. \tag{5.8}$$

This (second order) contribution to the cross section has a particulary simple form. It is the Fourier transform of the two-body Ursell function

$$U_2(\boldsymbol{x}_1-\boldsymbol{x}_2)=U_{12}=g_{12}-1+n^{-1}\delta_{12}, \tag{5.9}$$

which is the usual pair-correlation function $g_{12}-1$ extended to include also the self-correlation $n^{-1}\delta_{12}=n^{-1}\delta(\boldsymbol{x}_1-\boldsymbol{x}_2)$. This means that $\sigma_{jl}^{(2)}$ also contains a one-body term proportional to n, namely

$$n\alpha^2k_0^4(\tilde{\boldsymbol{v}}_l^{\mathrm{i}}\cdot\tilde{\boldsymbol{v}}_j^{\mathrm{o}})^2, \tag{5.10a}$$

in addition to the two-body term of the form

$$n^2\alpha^2k_0^4(\tilde{\boldsymbol{v}}^{\mathrm{i}}\cdot\tilde{\boldsymbol{v}}^{\mathrm{o}})^2\int[g_{12}(r)-1]\exp\,(\mathrm{i}\tilde{\boldsymbol{q}}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}. \tag{5.10b}$$

The two-body term (5.10*b*) is proportional to n^2 apart from a weak dependence on n through g_{12} and $\tilde{\boldsymbol{q}}$; see the discussion near (II 3.4).

There are two terms at the third order, the second and third terms of figure 4*d*. The contribution to the scattering has the same form as the lowest-order (second-order) term shown in (4.11), except that the simple Fourier transform (5.8) is replaced by a more complicated structure, namely (for single modes)

$$k_0^4(n\alpha)^3\,(\tilde{\boldsymbol{v}}^{\mathrm{i}}\cdot\tilde{\boldsymbol{v}}^{\mathrm{o}})\iint(\tilde{\boldsymbol{v}}^{\mathrm{o}}\cdot\mathscr{F}_{23}\cdot\tilde{\boldsymbol{v}}^{\mathrm{i}})\exp\,\{\mathrm{i}\tilde{\boldsymbol{k}}^{\mathrm{i}}\cdot(\boldsymbol{x}_3-\boldsymbol{x}_1)+i\tilde{\boldsymbol{k}}^{\mathrm{o}}\cdot(\boldsymbol{x}_1-\boldsymbol{x}_2)]\}\,U_{123}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3+\text{c.c.} \tag{5.11}$$

Here c.c. denotes the complex conjugate of the first term.

This third order contribution has the same character as the second order term. It has the form (4.11) with the same geometrical weight W_{jl} and with a local cross section σ_{jl}: but the cross section does not depend on a scattering vector $\tilde{\boldsymbol{q}}_{jl}$ alone. It depends on the wave vectors of the incoming and scattered waves independently. This point is worth stressing because the phenomenological theory of Ornstein & Zernicke (1914, 1918) predicts the scattering from fluids near the critical point to be the Fourier transform of some pair-correlation function (which in simplest interpretation is the usual molecular correlation function). Terms like (5.11) make it hard to believe that the Ornstein–Zernicke formula can be supported by the microscopic theory in any simple way when intermolecular correlations are of the order of the wave length or larger, i.e. for critical scattering.

When correlation lengths are short, on the other hand, the phase factors in (5.8) and (5.11) do not matter, and in this case several orders of the expansion of macroscopic single scattering, figure 4*d*, collapse into the simple form of the Einstein light scattering formula as we shall show in §7.

(*c*) *Backscattering coherence*

At fourth order the macroscopic single scattering expansion contains three terms in U_{1234}, which have the same general character as the third order contribution. But the remaining fourth order terms, the last three terms shown in figure 4*d*, contain a product of two Ursell functions, and these terms behave differently. Recall that an Ursell function is short range in the sense that it vanishes whenever the distance between any two of its arguments become large compared with a correlation length. A group of points covered by an Ursell function we shall refer to as a 'cluster'. Thus we are dealing with two-cluster terms here.

The first two of these two-cluster single scattering terms contained in $\mathscr{L}_{1234}$ at the fourth order are

$$(n\alpha)^4 \int_V \mathsf{U}\delta_{12}\, \mathscr{F}_{35}\cdot\mathscr{F}_{54}\, U_{15}\, U_{34}\, \mathrm{d}\boldsymbol{x}_5, \tag{5.12a}$$

and

$$(n\alpha)^4\, \mathscr{F}^*_{12}\, \mathscr{F}_{34}\, U_{13}\, U_{24}. \tag{5.12b}$$

Because we look at these terms one by one we can here use a simpler notation for the variables than in the sum (5.5). The contributions of (5.12*a*, *b*) to the scattered flux are (with variables relabelled)

$$\frac{c}{8\pi} k_0^4 (n\alpha)^4 \int_V \dots \int_V \mathscr{E}^*_1\cdot\boldsymbol{\varepsilon}^*_1\, \boldsymbol{\varepsilon}_2\cdot\mathscr{F}_{23}\cdot\mathscr{F}_{34}\cdot\mathscr{E}_4\, U_{13}\, U_{24}\, \mathrm{d}\boldsymbol{x}_1 \dots \mathrm{d}\boldsymbol{x}_4, \tag{5.13a}$$

and

$$\frac{c}{8\pi} k_0^4 (n\alpha)^4 \int_V \dots \int_V \mathscr{E}^*_1\cdot\mathscr{F}^*_{12}\cdot\boldsymbol{\varepsilon}^*_2\, \boldsymbol{\varepsilon}_3\cdot\mathscr{F}_{34}\cdot\mathscr{E}_4\, U_{13}\, U_{24}\, \mathrm{d}\boldsymbol{x}_1 \dots \mathrm{d}\boldsymbol{x}_4 \tag{5.13b}$$

whereas the contribution from the last term shown in figure 4*d* is the complex conjugate of (5.13*a*).

In each of equations (5.13*a*, *b*) we have two clusters, one consisting of molecules at $\boldsymbol{x}_1$ and $\boldsymbol{x}_3$ the other of molecules at $\boldsymbol{x}_2$ and $\boldsymbol{x}_4$. In the integrals these two pairs of points are uncorrelated, and when the distance between $\boldsymbol{x}_1, \boldsymbol{x}_3$ and $\boldsymbol{x}_2, \boldsymbol{x}_4$ is increased the integrand goes to zero very slowly through the product of two propagators $\mathscr{F}$, that is roughly as r^{-2} with r the distance between the two clusters. (In (5.13*a*) there is an additional oscillatory factor.) Thus the terms (5.12*a*, *b*) are long range and their contribution to the scattering is not of the form

(4.11). Take, for example, a case where $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ are sums of modes (4.10) and (4.8) and consider a single pair of modes j, l contributing to a sum over modes as in (4.11). The integrals of the j, l mode will be effectively restricted to the region $\tilde{V}_{jl} = \tilde{V}_j^{\mathrm{o}} \cap \tilde{V}_l^{\mathrm{i}}$, but in contradistinction to the second order case (4.11) they will not be proportional to the volume $|\tilde{V}_{jl}|$ of the region, and they will not define a local effective scattering cross section. We shall return to these geometrical features of (5.13*a*, *b*) in connection with macroscopic multiple scattering in §5(*d*).

The term (5.13*b*) appears to be the more interesting one so we discuss this one first and return to (5.13*a*) near the end of the present subsection. For simplicity we start by looking at the two-body term contained in (5.13*b*), namely

$$\frac{c}{8\pi}k_0^4 n^2\alpha^4 \int_V\int_V \boldsymbol{\mathscr{E}}_1^*\cdot\boldsymbol{\mathscr{F}}_{12}^*\cdot\boldsymbol{\varepsilon}_2^*\,\boldsymbol{\varepsilon}_1\cdot\boldsymbol{\mathscr{F}}_{12}\cdot\boldsymbol{\mathscr{E}}_2\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2 \tag{5.14}$$

coming from the term $n^{-2}\delta_{13}\,\delta_{24}$ contained in $U_{13}\,U_{24}$. In (5.14) the field at $\boldsymbol{x}_2$ is scattered by a molecule and propagated to another one at $\boldsymbol{x}_1$ and vice versa for the conjugate field; and the two 'exchanged' branches of the wave then create the radiation to the detector.

Non-local exchange terms like (5.13*b*) or (5.14) appear at all orders beyond the third. They give rise to 'coherent backscattering' (Akkermans *et al.* 1986; Stephen 1986). Here the term 'coherent' does not imply coherence with the incoming wave so we shall refer to the phenomenon as 'backscattering coherence'. Terms of a structure similar to (5.14) have been discussed in association with radar backscatter from plasmons (Watson 1969) and with propagation in turbulent atmospheres (De Wolf 1971) as well as in the theory of electrons in impure metals (see, for example, Bergmann 1984).

The phenomenon of backscattering coherence has recently been observed in the laboratory in light scattering from suspensions of dielectric particles (Kuga & Ishimaru 1984; Van Albada & Lagendijk 1985; Wolf & Maret 1985; Kuga *et al.* 1985; compare also Etemad *et al.* (1986) and Kaveh *et al.* (1986)). One observes a narrow peak of scattering in the direction opposite to that of the incoming wave, an effect referred to as 'backscattering enhancement' (Kuga & Ishimaru 1984).

In the context of light scattering from inhomogeneous media it has been discussed theoretically by Tsang & Ishimaru (1984, 1985), Golubentsev (1984), Stephen (1986), Stephen & Cwilich (1986) and Cwilich & Stephen (1987). But backscattering coherence has not previously been recognized in molecular light scattering theory.

To see why (5.14) gives rise to enhanced backscattering choose a pair of plane wave modes for $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ from (4.10) and (4.8) to get

$$\frac{c}{8\pi}k_0^4 n^2\alpha^4 \int_{\tilde{V}}\int_{\tilde{V}} \tilde{\boldsymbol{v}}^{\mathrm{i}}\cdot\boldsymbol{\mathscr{F}}_{12}^*\cdot\tilde{\boldsymbol{v}}^{\mathrm{o}}\tilde{\boldsymbol{v}}^{\mathrm{o}}\cdot\boldsymbol{\mathscr{F}}_{12}\cdot\tilde{\boldsymbol{v}}^{\mathrm{i}}\exp\left[\mathrm{i}(\tilde{\boldsymbol{k}}^{\mathrm{i}}+\tilde{\boldsymbol{k}}^{\mathrm{o}})\cdot(\boldsymbol{x}_2-\boldsymbol{x}_1)\right]\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2. \tag{5.15}$$

Here $\tilde{V}$ denotes the proper scattering region $\tilde{V}^{\mathrm{i}} \cap \tilde{V}^{\mathrm{o}}$ for the modes. The integrand in (5.15) is long range and the phase factor therefore results in a narrow peak for scattering in a direction exactly opposite to that of the incoming wave for which $\mathrm{Re}\,(\tilde{\boldsymbol{k}}^{\mathrm{i}}+\tilde{\boldsymbol{k}}^{\mathrm{o}}) = \boldsymbol{0}$ and the exponential becomes unity apart from a damping factor. Away from the backscattering direction the integral in (5.15) will decrease in magnitude because of the oscillatory exponential. So (5.15) contributes mainly to backscattering where the scattered wave may trace exactly the same path as the incoming wave in the opposite direction, suffering the same reflections and refraction as the incoming wave. We note that it is the longrange (radiation) part of propagators that is important in backscattering. The same remark applies to multiple scattering as we shall see in §5(*e*) below.

In the special case of exact backscattering equation (5.15) equals the corresponding double scattering term coming from (5.21) (below) with single modes. So the contribution from this double scattering term is doubled in the backscattering direction by the contribution of the corresponding exchange term. A similar remark applies to other multiple scattering terms composed of local single scattering and corresponding 'cyclic' exchange terms described below. This means that backscattering enhancement is important when macroscopic multiple scattering is; so it should be detectable in critical scattering, in particular.

The interpretation of the original term (5.13*b*) is now clear from the discussion of the two-body term (5.14) contained in it. The term (5.13*b*) represents exchange scattering with two clusters rather than just two molecules. And there are two-cluster terms of similar structure with larger clusters such as

$$(n\alpha)^5 \int_V \mathscr{F}^*_{12}\,\mathscr{F}_{34}\cdot\mathscr{F}_{45}\,U_{134}\,U_{25}\,\mathrm{d}\boldsymbol{x}_4, \tag{5.16}$$

at order five from (5.5) with variables relabelled. Here the propagation from $\boldsymbol{x}_4$ to $\boldsymbol{x}_3$ described by $\mathscr{F}_{34}$ takes place inside the cluster consisting of molecules at $\boldsymbol{x}_1$, $\boldsymbol{x}_3$ and $\boldsymbol{x}_4$. The common feature of (5.12*b*) and (5.16) is that two clusters are connected by two propagators $\mathscr{F}$ or $\mathscr{F}^*$ that 'exchange' fields between the two clusters. The sum of the infinity of terms of the form of (5.12*b*) or (5.16) corresponds to one term in the scattering from suspensions of macroscopic particles, the one treated by Tsang & Ishimaru (1984).

The Y functions also generate terms corresponding to all of the higher terms called 'cyclical' by Tsang & Ishimaru (1985). (We call them cyclic in this paper.) The simplest contribution to the three-cluster cyclic term is

$$(n\alpha)^6 \int_V \int_V \mathscr{F}^*_{12}\cdot\mathscr{F}^*_{23}\,\mathscr{F}_{45}\cdot\mathscr{F}_{56}\,U_{14}\,U_{25}\,U_{36}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_5, \tag{5.17}$$

at order six or the still simpler three-body term contained in the flux calculated from it, namely

$$\frac{c}{8\pi}k_0^4\,n^3\alpha^6 \int_V \cdots \int_V \mathscr{E}^*_1\cdot\mathscr{F}^*_{12}\cdot\mathscr{F}^*_{23}\cdot\varepsilon^*_3\,\varepsilon_1\cdot\mathscr{F}_{12}\cdot\mathscr{F}_{23}\cdot\mathscr{E}_3\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{5.18}$$

There is an infinity of three-cluster terms of a similar structure making up the equivalent of the cyclic term with three particles in scattering from suspensions.

In addition to the cyclic terms there appear multi-cluster single scattering terms of different character. There are exchange type terms with two clusters connected by more than two propagators. Such terms are not sufficiently long range to give rise to narrow backscattering. And there are terms like (5.13*a*) that are not of exchange type. Although the integrand of (5.13*a*) is long range the product of two propagators $\mathscr{F}$ carries an oscillatory factor in contradistinction to (5.13*b*) (and to double scattering terms) which contain a product $\mathscr{F}^*\mathscr{F}$. Terms like (5.13*a*) are best understood in terms of self-interactions and are conveniently discussed in relation to the corresponding terms in the refractive index theory.

In the refractive index theory (part II) self-interactions can be associated with an effective molecular polarizability β defined by (II 6.9*b*) and (II 6.20*a*). It is natural to ask what role β plays in the theory of external scattering, and we shall briefly comment on that question.

The effective polarizability β was shown in part II to replace the polarizability α of an isolated molecule. This replacement was exact at the lowest order in $n\beta$, but terms corresponding to (5.12) prevented an exact formulation in terms of β beyond the first order in $n\beta$.

From the relation (2.22) connecting the refractive index theory and the external scattering theory it is clear that processes involving β in the refractive index theory produce terms in which a propagator F belonging to β becomes replaced by a radiator S: $\boldsymbol{\beta}$ becomes $\mathfrak{S}\{\boldsymbol{\beta}(\boldsymbol{x},\omega)\}$ which is closely related to $\mathscr{S}(\boldsymbol{x},\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ (connecting a point $\boldsymbol{x}$ with itself) as comparison of (2.37*a*) and (II 6.9*b*) shows. But in $\mathfrak{S}\{\boldsymbol{\beta}(\boldsymbol{x},\omega)\}$ the point $\boldsymbol{x}$ represents the position of a molecule, whereas $\boldsymbol{x}$ in $\mathscr{S}(\boldsymbol{x},\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ is unrelated to molecular configuration. Because the weight field is an absolutely essential part of the scattering theory an effective polarizability would not seem to be a fruitful concept in the scattering theory. However, this conclusion does not exclude the utility of introducing β elsewhere in the expression for the external scattering.

We mention a somewhat crude attempt in this direction (Hynne 1977) leading to a result (equation (7.22) there), which has been obtained before by Yvon (1937, see his equation (333)) and Vuks (1968, equation (13)). Note that the attempted transition to a bulk scattering theory by Hynne (1977) leads to spurious results for the screened radiator corresponding to (4.15*b*) here; but results for the total scattering like equation (7.22) there (referred to above) are independent of the unphysical approximation to the radiator used there. (Of course all of the rigorous results of that paper remain correct as well.)

We shall not attempt a systematic study of the consequences of using the bulk approximation (2.36*b*) to the propagator $\mathscr{F}$. Summation of the contributions from self-correlations and 'small spheres' accounting carefully for various types of terms as we did in the paper II might lead to results useful for numerical work and even to useful concepts. But the complexity caused by the problem of divergences and the lack of immediate physical motivation here has so far made us refrain from undertaking this study.

(*d*) *Macroscopic multiple scattering*

Macroscopic multiple scattering is exemplified by figure 4*f*, *g* exhibiting double and triple scattering. Multiple scattering diagrams are composed of several single scattering diagrams connected by pairs of double lines (representing the pair of propagators $\mathscr{F}^*\mathscr{F}$). For simplicity we shall first describe multiple scattering composed of local single scattering, i.e. of single-cluster single scattering.

Restricted this way multiple scattering agrees wholly with phenomenological ideas as illustrated in figure 5*a*, *c* for double and triple scattering. The first of the double scattering terms of figure 4*f* (contributing to $\mathscr{M}_{1234}$) is

$$(n\alpha)^4\,\mathscr{F}^*_{12}\,\mathscr{F}_{34}\,U_{14}\,U_{23}. \tag{5.19}$$

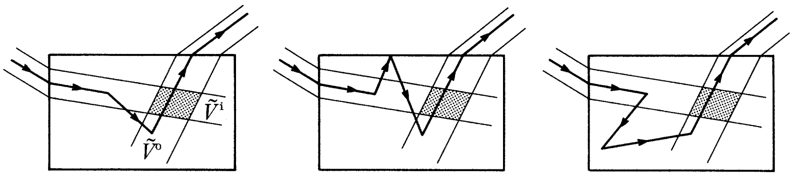
The contribution of (5.19) to the scattered flux through (5.3) is

$$\frac{c}{8\pi}k_0^4(n\alpha)^4\int_V\cdots\int_V \boldsymbol{\mathscr{E}}_1^*\cdot\mathscr{F}^*_{12}\cdot\boldsymbol{\varepsilon}_2^*\,\boldsymbol{\varepsilon}_3\cdot\mathscr{F}_{34}\cdot\boldsymbol{\mathscr{E}}_4\,U_{14}\,U_{23}\,\mathrm{d}\boldsymbol{x}_1\ldots\mathrm{d}\boldsymbol{x}_4. \tag{5.20}$$

In particular (5.20) contains the two-body term

$$\frac{c}{8\pi}k_0^4\,n^2\alpha^4\int_V\int_V \boldsymbol{\mathscr{E}}_1^*\cdot\mathscr{F}^*_{12}\cdot\boldsymbol{\varepsilon}_2^*\,\boldsymbol{\varepsilon}_2\cdot\mathscr{F}_{21}\cdot\boldsymbol{\mathscr{E}}_1\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2, \tag{5.21}$$

which is the simplest of all multiple scattering terms.



(a) (b) (c)

FIGURE 5. Rays indicating contributions to double scattering, (a) and (b), and triple scattering (c) for the same scattering geometry as used in figures 1 and 2b, c. Note that a multiple scattering process is less restricted than a (local) single scattering process, which must take place in the proper scattering region shown shaded (compare with figure 1c). Multiple scattering can start by a scattering event anywhere in $\tilde{V}^{\mathrm{i}}$ and end with one anywhere in $\tilde{V}^{\mathrm{o}}$ with possible intermediate events anywhere in the medium. Note also that propagation between two scattering events is surface dependent because the propagator $\mathscr{F}$ is. Together with a direct contribution to double scattering shown in (a), for example, there are also several in which the intermediate propagation involves one or more reflections in the surface; (b) indicates one contribution with a single intermediate reflection.

Equation (5.21) represents a process of the character depicted in figure 5a. The pair $\mathscr{E}_1^* \mathscr{E}_1$ represents the incoming wave being scattered at a point $\boldsymbol{x}_1$ in the region $\tilde{V}^{\mathrm{i}}$ where $\mathscr{E}_1$ is non-vanishing. (The incoming field in vacuum and the refraction at the surface are represented by the associated equation (3.1a) determining $\mathscr{E}$ from the external field.) The scattered wave propagates from $\boldsymbol{x}_1$ to $\boldsymbol{x}_2$ as described by the pair of propagators $\mathscr{F}_{12}^* \mathscr{F}_{21}$ and is scattered again at $\boldsymbol{x}_2$. The final propagation from $\boldsymbol{x}_2$ to the detector is represented by $\boldsymbol{\varepsilon}_2^* \boldsymbol{\varepsilon}_2$; the outgoing wave outside V and the refraction at the surface are represented by the associated equation (3.1e) for $\boldsymbol{\varepsilon}$. The integration with respect to $\boldsymbol{x}_2$ is effectively restricted to the region $\tilde{V}^{\mathrm{o}}$ where $\boldsymbol{\varepsilon}$ is non-vanishing; so the second scattering process can only take place in $\tilde{V}^{\mathrm{o}}$. The regions $\tilde{V}^{\mathrm{i}}$ and $\tilde{V}^{\mathrm{o}}$ may each correspond to several modes; figure 5 shows only those not associated with internal reflections.

The more general double scattering term (5.20) (in which (5.21) is contained) behaves in the same way as (5.20), but molecules at $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ are each replaced by a cluster of two correlated molecules.

Double scattering depends significantly on the scattering geometry (beyond the dependence through $\mathscr{E}$ and $\boldsymbol{\varepsilon}$). This is so because the product $\mathscr{F}^* \mathscr{F}$ connecting two clusters goes to zero at large distances r essentially as

$$r^{-2} \exp(-\tau r). \tag{5.22}$$

Here τ is the extinction coefficient (I 5.39), namely

$$\tau = 2k_0 \operatorname{Im}(m). \tag{5.23}$$

Usually $\tau|\boldsymbol{x}-\boldsymbol{x}'| \ll 1$ for any pair of points $\boldsymbol{x}, \boldsymbol{x}'$ in V when V has the size of an ordinary laboratory scattering cell. This condition applies as long as the thermodynamical state of the fluid is outside the critical region and the frequency of the light is away from resonances of the molecules.

The range of the propagator $\mathscr{F}$ can be assessed from the form (2.36b) of the translationally invariant approximation to it, derived in §4 of part II. The propagator $\mathscr{F}$ is surface dependent. And as a consequence the intermediate wave can be reflected in the surface on its way from the first to the second scattering event as indicated in figure 5b. Such contributions are also contained in the theory as a result of the reflected parts of $\mathscr{F}$, discussed below (5.39). (In addition there are interference terms between direct and reflected parts.)

The generalization of the interpretation to multiple scattering of higher order is now obvious. At each order multiple scattering is superimposed on the collective effects associated with the incoming and scattered waves. Thus any scattering term contains the establishment of a wave in the medium through $\mathscr{E}$ in terms of $\boldsymbol{E}$ as determined by (3.1 *a*); and similarly it contains all the surface effects associated with the transition of the scattering from the medium into the empty space surrounding V through the weight field $\boldsymbol{\varepsilon}$ as determined by (3.1 *e*) with $\boldsymbol{e}$ defined by (4.2).

Any multiple scattering process must therefore start with a scattering event in a region where $\mathscr{E}$ is non-vanishing and end with one in a region where $\boldsymbol{\varepsilon}$ is non-vanishing as we noted already at the end of §3. Intermediate scattering events appearing in triple and higher-order multiple scattering can occur anywhere in V as indicated for triple scattering in figure 5*c*.

Macroscopic multiple scattering composed of local scattering events is formally very similar to nonlocal single scattering of cyclic type. Compare, for example, (5.21) with (5.14). In each of these terms two uncorrelated points (molecules) are connected by two propagators, $\mathscr{F}^*$ and $\mathscr{F}$. Thus the integrands are long range and each term depends on the scattering geometry in a non-trivial way. Nevertheless only (5.21) has double scattering character. It is independent of the scattering direction (except for a dependence through polarization and through the surface dependent parts of the $\mathscr{F}$s). In contrast the process (5.14) gives rise to narrow backscattering as we have already mentioned. As another difference (5.21) gets contributions from configurations $(\boldsymbol{x}_1, \boldsymbol{x}_2)$ with $\boldsymbol{x}_1$ anywhere in $\tilde{V}^{\mathrm{i}}$ and $\boldsymbol{x}_2$ anywhere in $\tilde{V}^{\mathrm{o}}$, whereas (5.14) can only get contributions from configurations with $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ both in the proper scattering region $\tilde{V}^{\mathrm{i}} \cap \tilde{V}^{\mathrm{o}}$ shown hatched in figure 5*a*. Thus (5.14) certainly does not have double scattering character, and it is physically sensible to distinguish the two classes of terms.

We now briefly discuss multiple scattering composed of multi-cluster single scattering through an example. Look at the last term shown in figure 4*f*. This is a three-cluster double scattering term which contains a three-body term, namely

$$\frac{c}{8\pi} k_0^4 n^3 \alpha^6 \int_V \int_V \int_V \mathscr{E}_1^* \cdot \mathscr{F}_{12}^* \cdot \mathscr{F}_{23}^* \cdot \boldsymbol{\varepsilon}_3^* \, \boldsymbol{\varepsilon}_3 \cdot \mathscr{F}_{31} \cdot \mathscr{F}_{12} \cdot \mathscr{E}_2 \, \mathrm{d}\boldsymbol{x}_1 \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3, \tag{5.24}$$

in which the three molecules are completely uncorrelated. In a term like (5.24) the distinction between macroscopic multiple scattering and multi-cluster single scattering looses some of its significance. The intermediate process involving the pair of propagators $\mathscr{F}_{23}^*$ and $\mathscr{F}_{31}$ does not quite have the characteristics of a double scattering process described above, and the backscattering feature is not so clearly associated with the propagators $\mathscr{F}_{12}^*$ and $\mathscr{F}_{12}$. The existence of such multi-cluster scattering processes certainly demonstrates that light scattering in a molecular fluid is a very complex phenomenon when attention is paid to the details. Note, however, that terms like (5.24) always contain α to a power integral larger than or equal to six and when properly handled this is an indication that even in dense liquids their numerical significance will be small. The problem with (5.24) is that it actually diverges. We therefore look at this problem next.

(*e*) *Solution of the divergence problem*

We have now obtained a macroscopic multiple scattering expansion. Unfortunately there remains a problem of convergence. The terms of the multiple-scattering expansion are not convergent as integrals order by order, although the series is convergent in its totality. This problem is a technical one in the sense that it affects neither the formal structure of the theory nor its interpretation. Nevertheless, it is necessary to deal with the problem to reach a well defined result that can be used for numerical evaluation.

We may illustrate the problem by looking at the two-body terms (5.14) and (5.21) as examples. In each of these terms a product of two propagators $\mathscr{F}$ connects the two points $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. For present purposes we may think of $\mathscr{F}$ in terms of the approximation (2.36) or we may note that $\mathscr{F}$ contains F as the first term of the rigorous expansion (2.35). At short distances $r = |\boldsymbol{r}| = |\boldsymbol{x}_1 - \boldsymbol{x}_2|$, $\mathscr{F}$ is roughly proportional to

$$(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \mathsf{U})\, r^{-3}, \quad \hat{\boldsymbol{r}} = \boldsymbol{r}/r, \tag{5.25}$$

so each of the integrals (5.14) and (5.21) diverges at $\boldsymbol{x}_2 = \boldsymbol{x}_1$.

The terms (5.14) and (5.21) arise from products of delta functions contained in the correlation functions

$$U_{13}\,U_{24} = G_{13}\,G_{24} - G_{13} - G_{24} + 1 \tag{5.26}$$

and

$$U_{14}\,U_{23} = G_{14}\,G_{23} - G_{14} - G_{23} + 1, \tag{5.27}$$

appearing in (5.13*b*) and (5.20). The term (5.26) arises from Y_{1234} (see (2.39)), and $G_{13}\,G_{24}$ is cancelled against a similar term in U_{1234}. This can be seen from the fact that the explicit expression (II 7.13) of Y_{1234} does not contain $G_{13}\,G_{24}$.

This means that the divergence of (5.14) is cancelled, and in fact (5.14) is replaced by the convergent term

$$\frac{c}{8\pi}k_0^4 n^2 \alpha^4 \int_V \int_V \mathscr{E}_1^* \cdot \mathscr{F}_{12}^* \cdot \varepsilon_2^*\, \varepsilon_1 \cdot \mathscr{F}_{12} \cdot \mathscr{E}_2\, g_{12}\, \mathrm{d}\boldsymbol{x}_1\, \mathrm{d}\boldsymbol{x}_2. \tag{5.28}$$

(The factor g_{12} comes from the term $\delta_{13}\,\delta_{24}\,g_{14}$ in G_{1234} (see (II 2.11)), and G_{1234} is contained in Y_{1234} as (II 7.13) shows.) So far as the multiple scattering expansion is concerned the divergence of (5.14) is not a problem, therefore. Even so the divergence of (5.14) should be handled in the same way as we do that of (5.21) below. Only contributions from radiation parts of propagators give rise to proper backscattering. The procedure for backscattering can be inferred from the treatment of the divergence problem associated with macroscopic multiple scattering.

The divergence of (5.21) is a problem in the multiple scattering expansion. Actually the divergence is compensated by one contained in U_{1234} (or in Y_{1234} (II 7.13)). But now the compensating divergences appear at different orders of macroscopic multiple scattering, so each order is not convergent in itself.

It is plainly the Coulomb terms of propagators that cause the divergence problem in the formal multiple-scattering expansion (3.5) with (3.8). (The distinction of Coulomb and radiation parts of propagators was introduced in (II 5.9) and is further discussed below.) Fortunately the Coulomb parts of $\mathscr{F}$ in the operator $\mathscr{L}$ do not generate genuine multiple scattering. As a consequence the Coulomb contributions can (and should) be transferred from higher to lower orders of multiple scattering. In this way macroscopic multiple scattering is directly associated with the radiation parts of propagators.

These facts suggest that we split all propagators into Coulomb and radiation parts and

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transfer the Coulomb parts to the relevant lower order of multiple scattering. To this end we write the operator $\mathscr{X}$ as a sum of two terms

$$\mathscr{X} = \mathscr{X}_{\mathrm{C}} + \mathscr{X}_{\mathrm{R}}, \tag{5.29}$$

with indices C and R referring to 'Coulomb' and 'radiation'. Equation (3.7) then takes the form

$$\mathscr{M} = \mathscr{L} + \mathscr{L}:(\mathscr{X}_{\mathrm{C}} + \mathscr{X}_{\mathrm{R}}):\mathscr{M}. \tag{5.30}$$

This equation may be quite generally rewritten as two nested equations:

$$\mathscr{M} = \mathscr{L}' + \mathscr{L}':\mathscr{X}_{\mathrm{R}}:\mathscr{M}, \tag{5.31a}$$

$$\mathscr{L}' = \mathscr{L} + \mathscr{L}:\mathscr{X}_{\mathrm{C}}:\mathscr{L}', \tag{5.31b}$$

independently of any interpretation of $\mathscr{X}_{\mathrm{C}}$ and $\mathscr{X}_{\mathrm{R}}$. To verify (5.31) substitute (5.31*b*) in (5.31*a*) and use (5.31*a*) itself to get (5.30).

The idea is that shorter-range contributions of the formal multiple scattering expansion are summed in the operator $\mathscr{L}'$ by equation (5.31*b*); and the expansion (5.31*a*) then generates each order of macroscopic multiple scattering, physically well motivated and well defined.

We still have to choose a division (5.29) that realizes that goal. Such a division is hardly unique, but we propose a natural one. We first divide $\mathscr{F}$ into Coulomb and radiation parts

$$\mathscr{F} = \mathscr{C} + \mathscr{R} \tag{5.32}$$

working from the expansion (2.35) with each F expressed as a sum $\mathsf{C}+\mathsf{R}$ of a Coulomb part and a radiation part as in (II 5.9*a*). We define $\mathscr{C}$ as the sum of all terms from (2.35) in which the free variables $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ are connected by a chain of Coulomb part propagators C and delta functions. Equation (5.32) then defines $\mathscr{R}$; in other words $\mathscr{R}$ is the sum of all terms from (2.35) containing at least one radiation part propagator R in the direct chain between $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ (i.e. not in a loop). Defined this way $\mathscr{R}$ is long range much like R and $\mathscr{C}$ is shorter range like C. Both $\mathscr{C}$ and $\mathscr{R}$ are surface dependent and both are complex. We shall regard the propagators $\tilde{\mathsf{C}}$ and $\tilde{\mathsf{R}}$ obtained in (II 5.9*b*) as bulk approximations to $\mathscr{C}$ and $\mathscr{R}$ although we have not demonstrated a formal equivalence.

We now define $\mathscr{X}_{\mathrm{R}}$ from $\mathscr{X}$ by replacing the kernel $\mathscr{F}_{12}^{*}\mathscr{F}_{24}$ by $\mathscr{R}_{12}^{*}\mathscr{R}_{34}$ in equation (5.2). The operator $\mathscr{X}_{\mathrm{C}}$ is then defined through (5.29). Notice that $\mathscr{X}_{\mathrm{C}}$ contains two cross terms between $\mathscr{C}$ and $\mathscr{R}$ as well as a term in $\mathscr{C}_{12}^{*}\mathscr{C}_{34}$.

As an example of the use of the machinery described above to eliminate the divergences of the multiple scattering expansion we look at the two-body double scattering term (5.21). As it stands it is clearly divergent at $\boldsymbol{x}_2 = \boldsymbol{x}_1$. Macroscopic single scattering now sums terms included in higher-order multiple scattering in the formal series (3.5) with (3.8). When these terms are transferred from (5.21) to the macroscopic single scattering there remains

$$J_2^{(2)} = \frac{c}{8\pi} k_0^4 n^2 \alpha^4 \int_V \int_V \mathscr{E}_1^{*} \cdot \mathscr{R}_{12}^{*} \cdot \varepsilon_2^{*}\, \varepsilon_2 \cdot \mathscr{R}_{21} \cdot \mathscr{E}_1 \,\mathrm{d}\boldsymbol{x}_1 \,\mathrm{d}\boldsymbol{x}_2. \tag{5.33}$$

The terms removed from (5.21) associate with the single scattering term at fourth order in $n\alpha$. More specifically they go together with the terms coming from the terms in Y_{1234} containing a factor $n^{-2}\delta_{14}\delta_{23}$ and no other delta functions, namely

$$n^{-2}\delta_{14}\delta_{23}(g_{12}-1). \tag{5.34}$$

When the terms transferred from (5.21) are combined with the fourth-order single scattering term from (5.34) the contribution from the '-1' of (5.34) is cancelled for all but the radiation part of the $\mathscr{F}^*_{12}\mathscr{F}_{21}$ pair. So we get:

$$\frac{c}{8\pi}k_0^4 n^2\alpha^4\int_V\int_V \boldsymbol{\mathscr{E}}_1^*\cdot\boldsymbol{\mathscr{F}}^*_{12}\cdot\boldsymbol{\varepsilon}_2^*\,\boldsymbol{\varepsilon}_2\cdot\boldsymbol{\mathscr{F}}_{21}\cdot\boldsymbol{\mathscr{E}}_1\,g_{12}\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2 - J_2^{(2)}. \tag{5.35}$$

This result is obviously convergent at $\boldsymbol{x}_2 = \boldsymbol{x}_1$; and the two integrals of (5.35) combined are also convergent when the integration with respect to $\boldsymbol{x}_2$ is extended to all space (with $\boldsymbol{x}_1$ fixed inside the scattering region). The integration over $\boldsymbol{x}_1$ then gives the scattering volume. The single scattering term (5.35) is therefore well defined and has the character of bulk scattering expressible in terms of an effective scattering cross section of a molecule in the many-body system.

If $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ are plane waves of amplitudes $\tilde{E}_0\tilde{\boldsymbol{u}}$ and $\tilde{e}_0\tilde{\boldsymbol{v}}$ vanishing outside $\tilde{V}^{\mathrm{i}}$ and $\tilde{V}^{\mathrm{o}}$ respectively we find that the most important (pure Coulomb) contribution of (5.35) is

$$\frac{c}{8\pi}|\tilde{E}_0|^2\,|\tilde{e}_0|^2\,|\tilde{V}|\left[m^{-4}\tfrac{4}{5}\pi k_0^4\,n^2\alpha^4[(\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}})^2+3]\int_0^\infty r^{-4}g_2(r)\,\mathrm{d}r\right]. \tag{5.36}$$

This is the contribution to the flux per unit solid angle *in vacuo*, scattered from the region $\tilde{V} = \tilde{V}^{\mathrm{i}} \cap \tilde{V}^{\mathrm{o}}$ with volume $|\tilde{V}|$. If we calculate the scattering per unit solid angle in the medium we may divide by a weight factor as in (4.11) and obtain the factor in curly brackets as the contribution to the differential scattering cross-section.

The simplest double scattering term (5.33), on the other hand, has a significant surface dependence. We see this clearly if we use the bulk approximation $\tilde{\mathsf{R}}$ and look at the asymptotic part,

$$\tilde{\mathsf{R}}(\boldsymbol{x},\boldsymbol{x}';\omega) \sim k_0^2(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\,r^{-1}\exp(\mathrm{i}mk_0 r), \quad r = |\boldsymbol{x}-\boldsymbol{x}'|\to\infty. \tag{5.37}$$

We then get from (5.33)

$$\frac{c}{8\pi}|\tilde{E}_0|^2\,|\tilde{e}_0|^2\,k_0^8\,n^2\alpha^4\int_{\tilde{V}^{\mathrm{o}}}\mathrm{d}\boldsymbol{x}\int_{\tilde{V}^{\mathrm{i}}}\mathrm{d}\boldsymbol{x}'\,\frac{[\tilde{\boldsymbol{u}}\cdot(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\cdot\tilde{\boldsymbol{v}}]^2}{|\boldsymbol{x}-\boldsymbol{x}'|^2}, \tag{5.38}$$

where $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ are chosen as in (5.36). The unit vector $\hat{\boldsymbol{r}}$ points in the direction of $\boldsymbol{x}-\boldsymbol{x}'$. The geometrical features are illustrated in figure 5*a*. The double-scattering process is not a local one and gets contributions from regions outside the proper scattering region, the intersection of the illuminated and observed regions shown shaded in the figure. Because of this property the double scattering process depends explicitly on the shape of V irrespective of any implicit dependence through $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$. Notice, however, that $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{\varepsilon}$ retain their simple physical significance even in connection with complex multiple-scattering processes as figure 5*a* indicates. Calculations (partly numerical) of the dependence of double scattering on the geometry have been made by Reith & Swinney (1975), Beysens & Zalczer (1978), Bray & Chang (1975) and Boots *et al.* (1975*a*).

However, $\mathscr{F}$ itself is surface dependent, and in the continuum approximation described in part II takes the form (II 4.13),

$$\tilde{\mathsf{F}}_V(\boldsymbol{x},\boldsymbol{x}';\omega) = \tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) + \tilde{\mathsf{f}}(\boldsymbol{x},\boldsymbol{x}';\omega), \tag{5.39}$$

with $\tilde{\mathsf{f}}$ containing the surface dependence. When $\tilde{\mathsf{F}}_V$ is split into Coulomb and radiation parts $\tilde{\mathsf{f}}$ must go with $\tilde{\mathsf{R}}$ so that

$$\mathscr{R}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \approx \tilde{\mathsf{R}}(\boldsymbol{x}, \boldsymbol{x}'; \omega) + \tilde{\mathsf{f}}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \tag{5.40}$$

Figure 5*a* illustrates the main contribution to the double scattering (5.33) which comes from the $\tilde{\mathsf{R}}^*_{12}\,\tilde{\mathsf{R}}_{21}$ part of the total kernel (in the continuum approximation)

$$\mathscr{R}^*_{12}\,\mathscr{R}_{21} \approx \tilde{\mathsf{R}}^*_{12}\,\tilde{\mathsf{R}}_{21} + \tilde{\mathsf{R}}^*_{12}\,\tilde{\mathsf{f}}_{21} + \tilde{\mathsf{f}}^*_{12}\,\tilde{\mathsf{R}}_{21} + \tilde{\mathsf{f}}^*_{12}\,\tilde{\mathsf{f}}_{21}. \tag{5.41}$$

Figure 5*b* indicates a contribution of $\tilde{\mathsf{f}}^*_{12}\,\tilde{\mathsf{f}}_{21}$ with the character of an internally reflected (spherical) wave. For a geometry with several plane surfaces, we expect $\tilde{\mathsf{f}}$ to have several modes giving rise to multiple internal reflections in the internal propagation between two elementary scattering events in a double scattering process. We emphasize that the precise interpretation of the contribution $\tilde{\mathsf{f}}^*_{12}\,\tilde{\mathsf{f}}_{21}$ given above rests on an appeal to macroscopic optics for the character of the solution to equation (II 4.12). The cross-terms of (5.41) evidently represent interference between direct and reflected waves.

The characteristic feature of macroscopic multiple scattering is that intensity is thrown between clusters (groups of correlated molecules) as described by the pair $\mathscr{F}^*_{pj}\,\mathscr{F}_{lq}$ in which indices j and l belong to one cluster, whereas p and q belong to another one. It is this property of multiple scattering that makes the intermediate propagation between single scattering processes long range and the multiple scattering processes surface dependent.

The two-body double scattering (5.33) belongs naturally with a four-body term coming from the corrected first term of figure 4*f*. In a first, somewhat intuitive, microscopic treatment of macroscopic multiple scattering Oxtoby & Gelbart (1974*a*, *b*) have already analysed contributions that may be said to be contained in this four-body term. These authors, and subsequently Boots *et al.* (1976) give estimates of the contribution to double scattering. Experimental depolarization studies, which appear to illustrate the behaviour of macroscopic multiple scattering close to the critical point, have been published by Reith & Swiney (1975) for xenon and by Trappeniers *et al.* (1975) for carbon dioxide. We find the theoretical situation close to the critical point so complicated that at most only a qualitative interpretation is possible there.

(*f*) *Multiple scattering and damped propagation*

We have now reached a strictly microscopic description exhibiting the structure of light scattering in macroscopically recognizable form. Transmission of light in and out of the medium and the associated surface effects are isolated from scattering in the medium through the quadrilinear functional (5.3) with separate equations for $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. Scattering in the medium is resolved in macroscopic multiple scattering naturally superimposed on the collective surface effects. Single scattering in the medium includes non-local processes responsible for backscattering and the theory is capable of distinguishing these from genuine multiple scattering.

This structure seems entirely natural, but the presence of macroscopic multiple scattering raises a number of questions.

Can an effective scattering cross section be defined despite the highly non-local character of macroscopic multiple scattering?

How can the appearance of terms like (5.38) in the scattering theory be compatible with the relation to the refractive index theory where all terms have oscillatory integrands?

How does multiple scattering manifest itself in the propagator $\mathscr{F}$ in view of the close relation between $\mathscr{F}$ and $\mathscr{S}$, (2.38) and (I 4.26), and the fact that $\mathscr{S}$ includes the effect of macroscopic multiple scattering through the second term of (2.41).

We shall briefly comment on these questions now. In a sense scattering from single clusters is the smallest unit of macroscopic character. But it is not simple, because such scattering processes must be combined in many different ways. So macroscopic single scattering represented by the corrected operator $\mathscr{L}'$ is the most useful macroscopic unit of scattering in the medium: single scattering events combine to form multiple scattering through pairs of propagators simply.

It would seem natural to define a differential scattering cross section from single scattering in the medium despite the complication of multi-cluster single scattering. Working from $\mathscr{L}'$ substituted for $\mathscr{M}$ in (5.3) we make the steps that lead to (4.11) for the lowest-order term. The multi-cluster terms do not quite take the form (4.11). They are not proportional to a scattering volume, as we have already noted. If they are included we must use an average value over the relevant volume much as in (I 5.40). Light scattering is simply more complicated than one might expect from macroscopic ideas: if and how it is useful to define a cross section is a matter of choice; but we note in §7 that the Einstein light scattering formula does include multi-cluster terms in approximate form.

Leaving aside the problem associated with multi-cluster terms the proposed definition of a differential scattering cross section based on macroscopic single scattering in the medium as determined by (5.31 *b*) raises the important question of the consistency of such a differential cross section with the total cross section defined in (I 5.42). Recall that σ was defined on the basis of the total incoherent scattering from the region V and is related to the extinction coefficient τ calculated from the refractive index by the exact relation

$$n\sigma = \tau = 2k_0 \,\mathrm{Im}\,(m). \tag{5.42}$$

Although we have no formal proof we believe a differential cross section calculated from macroscopic single scattering will be essentially consistent with (I 5.42) in the sense that the total cross section (integrated over all angles in the medium) satisfies (5.42). We shall support this view by a comparison of the two-body contribution to the differential cross section to be derived in §6 with (II 3.17) for τ; and we now explain in physical terms why consistency can be expected.

The scattering process in the medium from some small region well inside the system results in a certain angular distribution of scattering. The effect of the collective surface effects and of macroscopic multiple scattering is to redistribute the scattering. The total scattering is unchanged and can therefore be obtained either from the single scattering process in the medium or from the total scattering from the entire region V.

There is, however, a paradox to resolve: namely the compatibility of multiple scattering of the form (5.38) with extinction due to scattering computed via the refractive index theory in part II. The integrand of (5.38) contains no oscillatory factor. At first sight this makes the scattering theory incompatible with the refractive index theory because all terms there contain oscillatory functions in their integrands and these oscillatory terms are important to the convergence of the integrals. However, the exact relation (5.42) shows that no such incompatibility is possible: and any conflict is resolved by observing that one refractive index term at order p corresponds to $p-1$ scattering terms generated by use of the operator $\mathfrak{S}$.

We shall explain the essential point by an example in the unscreened theory, and for clarity we write the radiation reaction $\frac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}$ as F_{22} (compare (2.16)). To the term

$$n^2\alpha^4|V|^{-1}\,\mathrm{Tr}\int_V\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{22}\cdot\mathsf{F}_{21}\cdot\tilde{\mathsf{I}}_{11}\,g_{12}\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2 \tag{5.43}$$

in the refractive index theory there corresponds the sum of three terms,

$$k_0^2[\mathrm{Re}\,(m)]^{-1}\,n^2\alpha^4|V|^{-1}\,\mathrm{Tr}\int_V \mathrm{d}\boldsymbol{x}_1\int_V \mathrm{d}\boldsymbol{x}_2\,g_{12}[\mathsf{S}_{12}\cdot\mathsf{F}_{22}\cdot\mathsf{F}_{21}+\mathsf{F}^*_{12}\cdot\mathsf{S}_{22}\cdot\mathsf{F}_{21}+\mathsf{F}^*_{12}\cdot\mathsf{F}^*_{22}\cdot\mathsf{S}_{21}]\cdot\tilde{\mathsf{I}}_{11}, \tag{5.44}$$

in the scattering theory. The middle term of (5.44) contains the two-body double scattering term (5.38) essentially. We sum (5.44) over polarization states of the scattering and integrate over all scattering directions using (2.23). From the asymptotic behaviour (I 2.3*b*) of F we then see that the middle term of (5.44) has the non-oscillatory integrand r^{-2} as in (5.38). However, the other two terms of (5.44) together contain an integrand $-2r^{-2}\sin^2(k_0 r)$, and the integrands of the three terms therefore combine in the net oscillatory integrand $r^{-2}\cos(2k_0 r)$; in complete agreement with the imaginary part of (5.43).

The consistency exemplified through the relation of (5.43) and (5.44) demonstrates a connection between multiple scattering and damped propagation in a rather indirect way:

When there is multiple scattering the propagation of scattering radiation in the medium is necessarily damped. The first and last terms of (5.44) contribute to the screening of the one-body scattering term, and they are part of the collective process describable as 'propagation of scattered light in the medium'. They must be associated with damping because they contain a single radiation reaction factor. Thus, only when we include terms representing damping of the scattered light together with multiple scattering terms can we get agreement with the refractive index theory.

We can also see a relation between multiple scattering and damped propagation more directly in the relation between radiators and propagators. Recall that propagation of scattered light to the detector is described either by the weight field ε or by the radiator $\mathscr{S}$. The difference is that $\mathscr{S}$ includes multiple scattering through the second term of (2.41). Furthermore it is related to the propagator $\mathscr{F}$ by a Bohr–Peierls–Placzek relation (I 4.26) so the effect of multiple scattering can be expected to appear in $\mathscr{F}$ as damping. To see how damping is contained in $\mathscr{F}$ we may refer to the approximation (2.36*b*).

The screened propagator $\tilde{\mathsf{F}}$ has wavenumber mk_0 so it gains the damping factor $\exp(-\frac{1}{2}\tau r)$ under the differential operator: τ is the extinction coefficient (5.23). To find the terms associated with damping we therefore compare the expansion of $\tilde{\mathsf{F}}$ as the iterated solution of (II 4.10) with the corresponding expansion of (2.34) for $\mathscr{F}$, namely

$$\mathscr{F}_{10}=\mathsf{F}_{10}+\int_V\int_V \mathsf{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\mathsf{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3+\int_V\cdots\int_V \mathsf{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\mathsf{F}_{34}\cdot\boldsymbol{\Lambda}_{45}\cdot\mathsf{F}_{50}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_5+\ldots \tag{5.45}$$

and conclude that to a good approximation damping is introduced through $\mathrm{Im}\,(\boldsymbol{\Lambda})$. Because of the connection (I 4.26) between $\mathscr{S}$ and $\mathrm{Im}\,(\mathscr{F})$, we can use (5.45) and calculate $\mathrm{Im}\,(\mathscr{F})$ in order to understand the role of damping in this relation.

Up to terms involving only one Im (F) kernel we find from the expansion (5.45)

$$\begin{aligned}\operatorname{Im}(\mathscr{F}_{10}) \approx \operatorname{Im}(\mathsf{F}_{10}) &+ \int_V\int_V \operatorname{Im}(\mathsf{F}_{12})\cdot\boldsymbol{\Lambda}_{23}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 + \int_V\int_V \mathscr{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\operatorname{Im}(\mathsf{F}_{30})\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\\ &+\int_V\cdots\int_V \mathscr{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\operatorname{Im}(\mathsf{F}_{34})\cdot\boldsymbol{\Lambda}_{45}\cdot\mathscr{F}_{50}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_5\\ &+\int_V\int_V \mathscr{F}_{12}\cdot\operatorname{Im}(\boldsymbol{\Lambda}_{23})\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \qquad (5.46)\end{aligned}$$

The last term of (5.46) is the approximate sum of all terms with kernel Im $(\boldsymbol{\Lambda})$ from (5.45). The remaining terms form the sum of terms with Im (F). Note that although the right side of (5.46) is actually complex, its imaginary part is ignored in the approximation.

We may obtain another equation for Im $(\mathscr{F})$ of a form strikingly similar to (5.46) from (2.41) for $\mathscr{S}$ in the following way. We substitute (I 4.19) for ε in (2.41), sum over polarizations and integrate over all angles; then apply the Bohr–Peierls–Placzek relations (2.23) for S and (I 4.26) for $\mathscr{S}$ and use the fact that $\mathscr{F}$ and $\boldsymbol{\Lambda}$ are symmetric as tensor kernels. The result is almost (5.46). Indeed, the similarity is changed to identity if we in (5.46) complex conjugate kernels to the left of Im (F) or Im $(\boldsymbol{\Lambda})$.

The conclusion from this comparison is that to multiple scattering in $\mathscr{S}$ there corresponds to a good approximation the effect of Im $(\boldsymbol{\Lambda})$ in Im $(\mathscr{F})$ and the effect of Im (m) in $\tilde{\mathsf{F}}$. This can be no exact relation because as equation (2.36 *b*) shows the refractive index appears also outside the exponential in $\tilde{\mathsf{F}}$. We take the relation between macroscopic multiple scattering and damped propagation we have just demonstrated as another confirmation that the multiple scattering expansion we have derived in the present section is physically well motivated.

In the analysis of the Einstein equation in §7 we calculate the extinction coefficient τ from the refractive index in the unscreened formulation. There we shall use a modification of the result (5.46): we approximate the first three terms by Im $\{\tilde{\mathsf{F}}\}$ with real m and retain the last term as it is, thus

$$\begin{aligned}\operatorname{Im}\{\mathscr{F}_{10}\} \approx \tfrac{2}{3}\operatorname{Re}\{m\}\,k_0^3[j_0(\xi)\,\mathsf{U}+\tfrac{1}{2}j_2(\xi)\,(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U})]&\\ +\int_V\int_V \mathscr{F}_{12}\cdot\operatorname{Im}\{\boldsymbol{\Lambda}_{23}\}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3,\quad \xi=\operatorname{Re}\{m\}\,k_0|\boldsymbol{x}_1-\boldsymbol{x}_0|.& \qquad (5.47)\end{aligned}$$

Here j_0 and j_2 are spherical Bessel functions. Thus for small distances, $\xi \ll 1$ where $j_p(\xi) = O(\xi^p)$, Im $\{\mathscr{F}_{10}\}$ can be approximated by the constant $\frac{2}{3}\operatorname{Re}\{m\}\,k_0^3\,\mathsf{U}$ apart from the damping terms contained in the last term of (5.47) which must be treated separately. These damping terms play a special role in the proof of the Einstein equation.

6. SCATTERING IN A LOW DENSITY GAS

In this section we shall derive an explicit expression for the scattering in a molecular gas at low densities. We shall derive the first two terms of a density expansion in an approximation similar to the one we used in part II for of the refractive index. These parallel calculations allow us to compare single scattering in the medium with extinction due to scattering.

Recall that the relation (5.42) was proved in part I as an exact relation when σ was defined through (I 5.40) on the basis of the scattering collected outside the material system. Here we shall determine whether (5.42) is still satisfied in terms of the total cross section calculated from single scattering in the medium.

(*a*) *Density expansion*

Because we want a density expansion it is most convenient to work from (2.27) with (2.28) which (implicitly) defines the operator $\mathscr{M}$ in terms of unscreened propagators F. Subsequently we must omit terms corresponding to macroscopic multiple scattering, therefore.

To obtain a scattering cross section from (2.27) we choose single modes for $\mathscr{E}$ and ε throughout the region V, separate off a geometrical factor corresponding to (4.11*b*) and introduce $\tilde{\mathsf{I}}$ and $\tilde{\mathsf{S}}$ by (5.1*c*) and (4.15*b*). We then obtain the differential cross section for scattering in the medium

$$n\frac{\mathrm{d}\sigma}{\mathrm{d}\tilde{\Omega}} = \frac{k_0^2}{|V|\,m}\mathrm{Tr}\sum_{p=2}^{\infty}\sum_{q=1}^{p-1}(n\alpha)^p\int_V\ldots\int_V \mathrm{d}\boldsymbol{x}_1\ldots\mathrm{d}\boldsymbol{x}_p$$
$$\times\,\mathsf{F}^*_{12}\ldots\mathsf{F}^*_{(q-1)q}\cdot\tilde{\mathsf{S}}_{q(q+1)}\cdot\mathsf{F}_{(q+1)(q+2)}\ldots\mathsf{F}_{(p-1)p}\cdot\tilde{\mathsf{I}}_{p1}\,K^{(q)}_{123\ldots p}. \qquad (6.1)$$

The factor $|V|^{-1}$ comes from omitting the geometrical weight while retaining all integrations, and the factor m^{-1} arises when $\tilde{\mathsf{S}}$ is introduced. The refractive index m must be understood as $\mathrm{Re}\{m\}$ in (6.1). The form (6.1) is much more sensible than the rather formal definition (I 5.40), but it is still necessarily defined as a global rather than local quantity because it includes macroscopic multiple scattering. To develop a density expansion we integrate all self-correlations (represented by delta functions). Radiation reaction terms are summed and concealed in the complex polarizability (2.17). We then get the differential scattering cross section up to terms in n^2

$$n\,\mathrm{d}\sigma/\mathrm{d}\tilde{\Omega} = |\gamma|^2\,k_0^2\,m^{-1}\,\mathrm{Tr}\,\{\mathsf{B}_1 n + (\mathsf{B}_2^1+\mathsf{B}_2^d+\mathsf{B}_2^s)\,n^2+\ldots\}, \qquad (6.2a)$$

in which

$$\mathsf{B}_1 = \tilde{\mathsf{S}}_{11}\cdot\tilde{\mathsf{I}}_{11}, \qquad (6.2b)$$

$$\mathsf{B}_2^1 = \frac{8\pi}{3}\mathrm{Re}\,(\gamma)\,\tilde{\mathsf{S}}_{11}\cdot\tilde{\mathsf{I}}_{11}+\int_{-v}[\tilde{\mathsf{S}}_{12}\cdot\tilde{\mathsf{I}}_{21}+(\gamma\tilde{\mathsf{S}}_{12}\cdot\mathsf{F}_{21}+\gamma^*\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{21})\cdot\tilde{\mathsf{I}}_{11}$$
$$+\,(\gamma\tilde{\mathsf{S}}_{11}\cdot\mathsf{F}_{12}+\gamma^*\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{22})\cdot\tilde{\mathsf{I}}_{21}]\,(g_{12}-1)\,\mathrm{d}\boldsymbol{x}_2, \qquad (6.2c)$$

$$\mathsf{B}_2^{\mathrm{d}} = \frac{1}{|V|}\int_V\int_V \mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2[\gamma^2\tilde{\mathsf{S}}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}+|\gamma|^2\,\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{21}\cdot\mathsf{F}_{12}+\gamma^{*2}\mathsf{F}^*_{12}\cdot\mathsf{F}^*_{21}\cdot\tilde{\mathsf{S}}_{12}]\cdot\tilde{\mathsf{I}}_{21}\,g_{12}$$
$$+\int[\gamma^3\tilde{\mathsf{S}}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}\cdot\mathsf{F}_{21}+\gamma^*\gamma^2\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{21}\cdot\mathsf{F}_{12}\cdot\mathsf{F}_{21}+\ldots]\cdot\tilde{\mathsf{I}}_{11}\,g_{12}\,\mathrm{d}\boldsymbol{x}_2+\ldots, \qquad (6.2d)$$

$$\mathsf{B}_2^{\mathrm{s}} = \frac{1}{|V|}\int_V\int_V \mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2[\gamma^2\tilde{\mathsf{S}}_{11}\cdot\mathsf{F}_{12}\cdot\mathsf{F}_{21}+|\gamma|^2\,\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{22}\cdot\mathsf{F}_{21}+\gamma^{*2}\mathsf{F}^*_{12}\cdot\mathsf{F}^*_{21}\cdot\tilde{\mathsf{S}}_{11}]\cdot\tilde{\mathsf{I}}_{11}\,g_{12}$$
$$+\int[\gamma^3\tilde{\mathsf{S}}_{11}\cdot\mathsf{F}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}+\gamma^*\gamma^2\mathsf{F}^*_{12}\cdot\tilde{\mathsf{S}}_{22}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}+\ldots]\cdot\tilde{\mathsf{I}}_{21}\,g_{12}\,\mathrm{d}\boldsymbol{x}_2+\ldots. \qquad (6.2e)$$

The term (6.2*b*) comes from J_{21} of (2.27) through a self-correlation contained in $K^{(1)}_{12}$; the remaining part of J_{21} appears in (6.2*c*) as the first term in square brackets. The other terms of (6.2*c*) come from J_{31} and J_{32}. In particular, the first term of (6.2*c*) (containing $\frac{8}{3}\pi$) arises from a 'small sphere' contribution defined through (2.12). The terms of (6.2*d*) and (6.2*e*) arise from terms of order $p > 3$ in (2.27).

The term in B_1, namely

$$n|\gamma|^2\,k_0^4(\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}})^2, \qquad (6.3)$$

is the complete one-body term. It is proportional to n and describes scattering from independent molecules. All interactions in (6.3) are self-interactions through the all order radiation reaction contained in γ.

The term of (6.2) containing $\mathsf{B}_2^1+\mathsf{B}_2^{\mathrm{d}}+\mathsf{B}_2^{\mathrm{s}}$ gives the complete two-body contribution to the scattering. In this we substitute the density expansions (II 3.4) and (II 3.5) for g_{12} and $\tilde{\mathsf{I}}_{12}$ and the expansion of m in the wave vector $\tilde{\boldsymbol{k}}$ of $\tilde{\mathsf{S}}$. Only the lowest-order term of each of these expansions contributes to the true two-body term, which is proportional to n^2. The term B_2^1 is a finite sum of local contributions each containing the short range function $(g_{12}-1)$ in the integrand. The terms $\mathbf{B}_2^{\mathrm{d}}$ and $\mathbf{B}_2^{\mathrm{s}}$ are infinite series. Corresponding terms of these differ essentially only in that $\tilde{\mathsf{S}}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ in $\mathsf{B}_2^{\mathrm{d}}$ connects 'distinct' points, $\boldsymbol{x}\neq\boldsymbol{x}'$, whereas $\boldsymbol{x}$ and $\boldsymbol{x}'$ represent the 'same' point in $\mathsf{B}_2^{\mathrm{s}}$.

The first term of each of the series $\mathsf{B}_2^{\mathrm{d}}$ and $\mathsf{B}_2^{\mathrm{s}}$ contains an integral of three terms (in square brackets). These first terms are surface dependent, whereas all the other terms of (6.2d) and (6.2e) are not. In the surface independent terms the integration with respect to $\boldsymbol{x}_2$ has been extended to all space (assuming $\boldsymbol{x}_1$ well inside V), and the subsequent integration with respect to $\boldsymbol{x}_1$ has provided a factor $|V|$ entering a geometrical weight W as in (4.11).

The surface dependent parts of $\mathsf{B}_2^{\mathrm{d}}$ and $\mathsf{B}_2^{\mathrm{s}}$ contain backscattering and double scattering respectively. Because a differential scattering cross section must be defined in terms of single scattering in the medium, we must omit the multiple scattering term from (6.2). Arguably we should also omit the backscattering term. Both of these omissions are accomplished if we simply omit all radiation parts of propagators as an approximation. We therefore now consider the contribution to two-body scattering arising from the Coulomb parts of propagators F, $\nabla\nabla|\boldsymbol{x}-\boldsymbol{x}'|^{-1}$. We want to sum the series $\mathsf{B}_2^{\mathrm{d}}$ and $\mathsf{B}_2^{\mathrm{s}}$, and to further simplify the summation we neglect the phase factors arising from $\tilde{\mathsf{S}}$ and $\tilde{\mathsf{I}}$, that is we replace $\tilde{\mathsf{S}}_{12}$ and $\tilde{\mathsf{I}}_{12}$ by the constant tensors $\tilde{\mathsf{S}}_{11}$ and $\tilde{\mathsf{I}}_{11}$. In this way the two series $\mathsf{B}_2^{\mathrm{d}}$ and $\mathsf{B}_2^{\mathrm{s}}$ become equal but any dependence of the scattering on the scattering directions (other than through polarizations) is lost.

The sum of the terms with a factor $\tilde{\mathsf{S}}$ to the extreme left or right can evidently be expressed in terms of the function h_2 defined by (II 3.9b) (Hynne 1974),

$$h_2(\omega,T)=\tfrac{8}{3}\pi\int_0^{\infty}\left[\frac{1}{r^3-2\gamma(\omega)}-\frac{1}{r^3+\gamma(\omega)}\right]\exp\left[-\phi(r)/k_{\mathrm{B}}T\right]r^2\,\mathrm{d}r. \tag{6.4}$$

The remaining terms can be written as an integral of a product of $\tilde{\mathsf{S}}$ and two sums. The result may be expressed partly in terms of the imaginary part of h_2. We then find the differential scattering cross section up to terms in n^2:

$$n\,\mathrm{d}\sigma/\mathrm{d}\tilde{\Omega}=n^2|\gamma|^2k_0^4\{|\gamma|\,d_2+(\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}})^2\,[n^{-1}-2B_2(T)+\tfrac{8}{3}\pi\,\mathrm{Re}\,(\gamma)+4\,\mathrm{Re}\,(\gamma h_2)$$
$$+3k_0^{-3}\,\mathrm{Im}\,(h_2)-3|\gamma|\,d_2]\}. \tag{6.5}$$

Here $B_2(T)$ is the second virial coefficient of the theory of fluids (II 3.8b), whereas $\tilde{\boldsymbol{u}}$ and $\tilde{\boldsymbol{v}}$ are polarization unit vectors of the incoming and scattered waves respectively. The function d_2 is defined as

$$d_2(\omega,T)=\tfrac{2}{15}|\gamma|\int_0^{\infty}\left|\frac{2}{r^3-2\gamma}+\frac{1}{r^3+\gamma}\right|^2\exp\left[-\phi(r)/k_{\mathrm{B}}T\right]4\pi r^2\,\mathrm{d}r. \tag{6.6}$$

If we choose a Lennard-Jones potential (II 3.12) for $\phi(r)$ then $h_2(\omega,T)$ and $d_2(\omega,T)$ become functions of the reduced variables a^3/γ and T_0/T, in which a and $k_{\mathrm{B}}T_0$ denote the intermolecular separation and the energy, each taken at the minimum of the potential curve. Thus h_2 takes the form (II 3.13) with (II 3.14), namely

$$h_2(\omega, T) = B\left(\frac{a^3}{\gamma}, \frac{T_0}{T}\right) - B\left(-\frac{a^3}{2\gamma}, \frac{T_0}{T}\right), \tag{6.7a}$$

$$B(z, w) = \int_0^\infty \frac{\exp\left[w(2t^2 - t^4)\right]}{t+z}\,\mathrm{d}t, \tag{6.7b}$$

whereas $d_2(\omega, T)$ may be written as

$$d_2(\omega, T) = D\left(\frac{a^3}{\gamma}, \frac{T_0}{T}\right) \tag{6.8a}$$

$$D(z, w) = \tfrac{8}{5}\pi|z|^3 \int_0^\infty \frac{\exp\left[w(2t^2 - t^4)\right]}{|(2t-z)\,(t+z)|^2}\,\mathrm{d}t. \tag{6.8b}$$

The function D is a numerical function of the complex variable z and the real variable w. It is shown in figure 6. Notice the scaling by $|z|$ in figure 6*b*, which is made to exhibit its asymptotic behaviour.

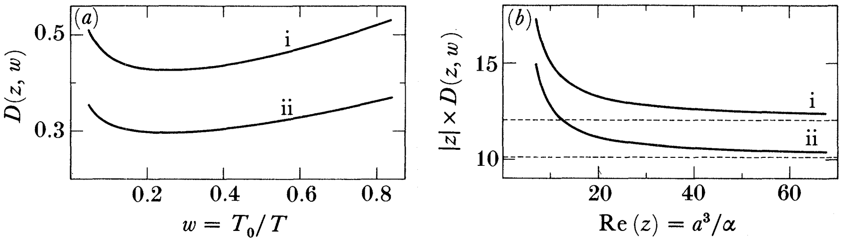

FIGURE 6. The function $D(z, w)$ describing the lowest-order contribution to the depolarization ratio (6.11) from single scattering. Note the scaling in (*b*). (*a*) i, $\mathrm{Re}\,(z) = a^3/\alpha = 25$; ii, $\mathrm{Re}\,(z) = 35$. (*b*) i, $w = T_0/T = 0.8$; ii, $w = 0.4$.

The result (6.5) agrees with (II 3.17) in the sense that the identity (5.42) is satisfied (despite the approximations made to reach (II 3.17) and (6.5)) provided the frequency is well off resonance (i.e. outside the line wings region defined below equation (II 3.24)). To see this we sum (6.5) over two orthogonal polarization states and integrate the result over all scattering directions. Note that the two terms in d_2 cancel. Then recall from §3 of part II that the last term in (II 3.17) equals the term in square brackets there when the frequency is well off resonance.

We view the satisfaction of (5.42) as (weak) support of the idea that the total scattering cross section can be correctly calculated either from the surface-dependent total scattering from the region V as in §5 of part I or from the differential scattering cross section based on macroscopic single scattering in the medium. We believe that the inconsistency in the line wings region must stem from differences in the approximations that underlie (II 3.17) and (6.5).

The terms $(n^{-1} - 2B_2(T))$ in the square brackets in (6.5) form the beginning of an expansion (II 3.18) of the isothermal compressibility κ_T of the fluid, as we noted in part II. These terms are contained in the simplest single scattering term (5.8); the n^{-1} comes from the one-body term (5.10*a*), the $-2B_2$ comes from the two-body term (5.10*b*). For small correlation lengths the exponential phase factor can be ignored in (5.8). The integral then reduces to (see, for example, Hill 1956, p. 236)

$$\int U_2(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \kappa_T k_\mathrm{B} T. \tag{6.9}$$

The $\kappa_T k_\mathrm{B} T$ appears as a factor in the Einstein phenomenological light scattering equation. By virtue of (6.9) it also appears in a microscopic expression for the scattering, valid for small correlation lengths and for not too high densities. This we show in the following section, which is devoted to a proof that the Einstein equation is consistent with the microscopic theory away from the critical point of phase separation.

The relation (6.9) applies when the correlation function is defined from a grand canonical ensemble, i.e. for an open, isothermal system (see, for example, Hill 1956, p. 263). Actually the present theory specifies a closed isothermal system so a canonical ensemble would be more appropriate.

Unfortunately the integral in (6.9) is identically zero when U_2 is defined from a canonical ensemble (see, for example, Hill 1956, p. 185). So the theory seems to depend crucially on the choice of statistical ensemble. Of course, incoherent light scattering is caused by fluctuations which obviously depend on the ensemble, i.e. on the precise specifications of the system. Nevertheless, in so far as light scattering is a local process it must be largely independent on whether the entire material system in open or closed, and the subtle problem can be explained in terms of an analysis of the asymptotic behaviour of the distribution functions due to de Boer (1940). The analysis is based on a modified cluster expansion (see Hill 1956, Appendix 7). According to de Boer (1940), the pair distribution function $g_2(r)$ behaves asymptotically as

$$g_2(r) \to 1 - n\kappa_T k_\mathrm{B} T N^{-1}. \tag{6.10}$$

The deviation from unity is $O(N^{-1})$, which is extremely small compared to unity and entirely without thermodynamical significance. When the phase factor is restored in the integral (6.9) the tail of the canonical correlation function (6.10) yields a contribution to the coherent scattering. But the contribution is of relative order $O(N^{-1})$ and so is small compared with the statistical variation of thermodynamical variables that fluctuate. This means that it is legitimate to ignore the phase factor if we use the grand canonical distribution functions (which have asymptotic values of unity). We get the same results as if we use canonical distribution functions and retain the phase factor. So we shall continue to use grand canonical distribution functions.

(*b*) *Depolarization*

The first term in curly brackets in (6.5) is independent of $\tilde{\boldsymbol{u}}$ and $\tilde{\boldsymbol{v}}$, the polarizations of the incoming and scattered waves in the medium. It gives rise to depolarized scattering. The degree of depolarization is conveniently characterized by the depolarization ratio ρ which is defined as the ratio of the scattering at right angles with polarization $\tilde{\boldsymbol{v}}$ perpendicular to $\tilde{\boldsymbol{u}}$ and with polarization parallel to $\tilde{\boldsymbol{u}}$.

At low densities ρ is governed by two-body depolarized scattering proportional to n^2 in relation to one-body non-depolarized scattering proportional to n. The limiting form at vanishingly low densities is therefore proportional to n and we have

$$\rho \approx \rho_0 = n \lim_{n\to 0} \rho/n \tag{6.11a}$$

at low densities.

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Two-body depolarized scattering may also get a significant contribution from real double scattering (5.38). This term depends on the shape of the region as we discussed in §5. Its effect may be minimized by suitable choice of scattering geometry, and we consider only depolarized single scattering here.

In the approximation (6.5) we immediately find the depolarization ratio

$$\rho_0 = n|\gamma|\, d_2(\omega, T) = \tfrac{8}{15}\pi n|\gamma|^2 \int_0^\infty \left|\frac{3r^3}{r^6-\gamma r^3-2\gamma^2}\right|^2 \exp\left[\frac{-\phi(r)}{k_B\, T}\right] r^2\, \mathrm{d}r, \tag{6.11\,b}$$

which agrees with the result of a direct classical argument involving the polarizability of a pair of molecules (Silberstein 1917; Buckingham & Pople 1955*a*, *b*; Buckingham & Stephen 1957; Fromhold *et al.* 1978; Oksengorn 1983). When the pair potential is approximated by a Lennard-Jones potential this result becomes

$$\rho_0 = n|\gamma|\, D(a^3/\gamma,\, T_0/T). \tag{6.11\,c}$$

For argon at room temperature and for radiation of wavelength 633 nm (for which $z = 33.5-\mathrm{i}3.64\ 10^{-8}$ and $w = 0.402$) we find $D = 0.319$, and hence

$$\rho_0 = (5.32\times 10^{-25}\ \mathrm{cm}^3)\cdot n. \tag{6.12}$$

This gives $\rho_0 = 1.31\times 10^{-5}$ at atmospheric pressure. The result (6.12) is 25% larger than the experimental value (at $\lambda = 514.5$ nm) of Oksengorn (1983) and 6% larger than the first term of its expansion in α/a^3. Further experimental and theoretical results are summarized in table 1. Related experimental results on the spectrum of depolarized scattering have been given by Fromhold *et al.* (1978), Fromhold & Proffitt (1978), Barocchi & Zoppi (1978) and by Shelton & Tabisz (1980). See also the model studies of Ladanyi *et al.* (1986) and the reviews by Gelbart (1974) and Fromhold (1981) and references therein. Comparison of results from integrated spectra and discussion of experimental discrepancies have been made by Oksengorn (1983), Fromhold (1981) and others.

The temperature dependence of $D(z, w)$ is shown in figure 6*a*. The function has a minimum at $w = 0.245$ for $a^3/\alpha = 33.5$. This case applies to argon at optical frequencies and it corresponds to $T = 489$ K or 216 °C. The temperature coefficient is

$$\frac{\partial\rho_0}{\partial T} = -\frac{n|\gamma|}{T_0}\, w^2\, \frac{\partial D}{\partial w}, \tag{6.13}$$

and table 1 gives $w^2\,\partial D/\partial w$ for a few substances.

TABLE 1. THE TWO-BODY CONTRIBUTIONS TO THE DEPOLARIZATION RATIO; EXPERIMENTAL AND THEORETICAL VALUES AND THEORETICAL TEMPERATURE COEFFICIENTS

	argon	krypton	xenon	methane
$\alpha/(10^{-30}\ \mathrm{m}^3)$	1.668	2.484	4.045	2.616
$a/(10^{-10}\ \mathrm{m})$	3.822	4.04	4.60	4.285
$\mathrm{Re}\{z\} = a^3/\alpha$	33.5	26.6	24.1	30.1
T_0/K	119.8	171	221	148.2
$w = T_0/T$	0.402	0.574	0.741	0.497
$(\rho_0/n)/(10^{-30}\ \mathrm{m}^3)$	0.532	1.081	2.120	0.966
experimental	0.46[a]			0.73[b]
$(w^2\,\partial D/\partial w)/10^{-2}$	1.527	6.205	14.65	3.495

[a] Oksengorn (1983), $2\pi/\omega = 514.5$ nm, room temperature.
[b] Thibeau *et al.* (1970), $2\pi/\omega = 633$ nm, $T = 293$ K.

The dependence on z is best presented by rewriting equation (6.8) as

$$\rho_0 = |z|\, D(z, w)\, n|\gamma|^2/a^3. \tag{6.14}$$

Figure 6*a* shows $zD(z, w)$ as a function of $\mathrm{Re}\,(z) = a^3/\alpha$ for $w = 0.4$ and $w = 0.8$. The horizontal lines are asymptotes for $a^3/\alpha \rightarrow \infty$. They represent the first-order approximations referred to above.

Preparatory to the analysis of Einstein's light-scattering formula in §7 we now discuss depolarized scattering more generally. We first classify terms according to their dependence on polarization. This allows us to account for a class of complicated terms through a correction factor of Cabannes (1921) type in an approximate way. Such a correction factor was first used in the present context by Yvon (1937). We shall generalize Yvon's argument in a straightforward way to an infinite class of terms and stress the approximations involved.

We consider single scattering in the medium and omit also backscattering. Thus, the effect of the surface and the contribution of real multiple scattering should be taken into consideration separately or minimized by the choice of geometry. We use (2.27) and continue to denote the polarization unit vectors of the incoming and scattered waves in the medium by $\tilde{\boldsymbol{u}}$ and $\tilde{\boldsymbol{v}}$ respectively (but note the discussion of $\tilde{\boldsymbol{v}}$ well below (4.12)).

The terms of the double series (2.27) with $q = 1$ and $q = p-1$ all contain a factor $\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}}$. Such terms cannot give rise to depolarization; and if the correlation length is small compared with the wavelength, single cluster terms of the type considered will have the form

$$A(\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}})^2, \tag{6.15}$$

in which A is a constant. However, multi-cluster terms may give rise to a dependence on the scattering vector even at small correlation lengths and will not be of the form (6.15). Such terms appear at fourth and all higher orders in $n\alpha$.

Next we consider the terms of (2.27) with $q = 2$ or $q = p-2$. Such terms contain an 'isolated' propagator F or F^* to the right or left of $\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$. The small-sphere contribution associated with the isolated F or F^* gives rise to terms of the form (6.15) (with the same qualifications as discussed above). For small correlation lengths the Coulomb part of the isolated F or F^* gives rise to scattering of the form

$$B[(\tilde{\boldsymbol{u}}\cdot\tilde{\boldsymbol{v}})^2+3], \tag{6.16}$$

in which B is a constant. Again we make reservations as regards a possible small dependence on the scattering vector which may arise from exchange type terms at fourth and higher orders even if proper backscattering arising from radiaton parts of propagators is omitted.

To derive (6.16) we first integrate over all orientations of the whole cluster under rotations around $\boldsymbol{r} = \boldsymbol{x}-\boldsymbol{x}'$ in which $\boldsymbol{x}$ and $\boldsymbol{x}'$ are the arguments of the isolated F or F^*. In a subsequent integration over all orientations of $\boldsymbol{r}$ we come to deal with the average of $(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U})\,\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}$ (because the average of $3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U}$ vanishes), and the result is (6.16).

Terms of (2.27) with $3 \leqslant q \leqslant p-3$ (that appear at $p \geqslant 6$) are not of the form of either (6.15) or (6.16). The same applies to the multi-cluster terms which appear at orders $p \geqslant 4$. Now suppose that the contribution of all such terms can be neglected. Then we may express the depolarization ratio ρ in terms of A and B or alternatively express B in terms of A and ρ:

$$\rho = 3B/(A+4B), \quad B = \rho A/(3-4\rho). \tag{6.17}$$

We may therefore express the scattering and in particular the total scattering cross-section in terms of A and ρ:

$$\sigma_{\text{tot}} = \tfrac{8}{3}\pi A(3+6\rho)/(3-4\rho) = \tfrac{8}{3}\pi AC(\rho). \tag{6.18}$$

The correction factor $C(\rho)$ accounts for the contributions of the terms of the form (6.16). We shall refer to $C(\rho)$ as the Cabannes factor and we call terms of the form (6.16) Cabannes terms.

Note that (6.18) differs slightly from the original factor introduced by Cabannes (1921) who considered the scattering from a thin gas of anisotropical molecules.

By introducing a Cabannes factor all the infinity of Cabannes terms, that is all terms with $q = 2$ or $q = p-2$ in (2.27) are summed by expressing them in terms of the sum of all the infinity of non-depolarizing terms. We sum the non-depolarizing terms in §7. Unfortunately no such device expressing microscopic terms in terms of macroscopic quantities seems available for the remaining (infinite) sets of scattering terms with $3 \leqslant q \leqslant p-3$; but these remaining terms are $O(n^6\alpha^6)$ and therefore typically small.

7. The Einstein light scattering formula

We now use the microscopic theory to analyse the validity of the macroscopic light scattering formula of Einstein (1910),

$$\tau \approx \tau_{\mathrm{E}} = \frac{k_0^4}{6\pi}\left(n\frac{\partial m^2}{\partial n}\right)^2 \kappa_T k_{\mathrm{B}} T. \tag{7.1}$$

This analysis has already been reported in brief (Bullough *et al.* 1968; Bullough & Hynne 1968). But we are now in a position to state the result with greater precision, and to give the details of the argument.

We compare the exact microscopic expression for the extinction coefficient τ with the exact microscopic expression for Einstein's approximation τ_{E} to τ. We work from the expression (I 5.25) with (2.13) for the refractive index, namely

$$\frac{m^2-1}{4\pi} = \sum_{p=1}^{\infty} M_p(n\alpha)^p, \tag{7.2a}$$

$$M_p = |V|^{-1}\,\mathrm{Tr}\int_V \dots \int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\dots\mathsf{F}_{(p-1)p}\cdot\tilde{\mathsf{I}}_{p1}\,H_{123\dots p}\,\mathrm{d}\boldsymbol{x}_1\dots\mathrm{d}\boldsymbol{x}_p. \tag{7.2b}$$

So we calculate τ by taking the imaginary part of (7.2*a*) using

$$\tau = \frac{4\pi k_0}{\mathrm{Re}\{m\}}\,\mathrm{Im}\left\{\frac{m^2-1}{4\pi}\right\}, \tag{7.2c}$$

and we calculate τ_{E} from the same equation (7.2*a*, *b*) by differentiation with respect to density.

The result is given in diagrammatic notation in figure 7. Here and in figure 8 a row of dots symbolizes a factor $\tfrac{3}{2}m^{-1}k_0^{-3}\,\mathrm{Im}\,(\mathsf{F})$ and terms with a coefficient of 2 are to be understood as a sum of two equivalent terms in an obvious way. The series (*b*) and (*c*) of figure 7 should actually be understood as their real parts. (In the following we shall refer to the equations of figure 7 by the letters marking them.) Originally the expansion (*a*) is governed by the H functions (2.14). But in the second form of (*a*) we have screened the single imaginary part propagator

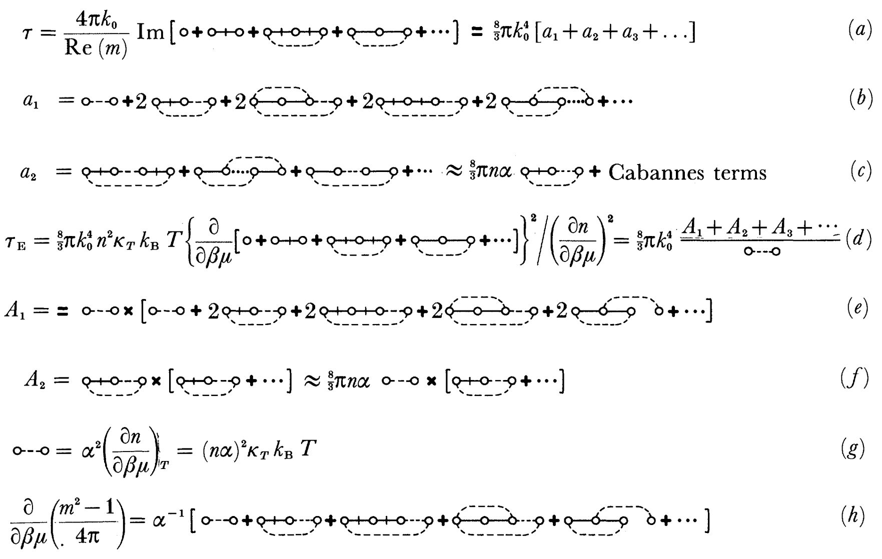

FIGURE 7. Diagrammatical representation of the exact series for the extinction coefficient (a) and Einstein's approximation to it (d), used to determine the accuracy of the Einstein formula.

in each of the terms shown. As a result the factor $1/\mathrm{Re}\,(m)$ is cancelled by a factor $\mathrm{Re}\,(m)$ from $\mathrm{Im}\,(\tilde{\mathsf{F}})$, and the correlation functions remaining are precisely the K functions (2.28). (We shall give the details below.)

The result (a) with (b) and (c) is an expression for the extinction coefficient up to the fourth order, and before we compare it with Einstein's approximation to it (equation (d) with (e) and (f)) we shall show that it is consistent with scattering in the medium, (6.1). We can get the total scattering cross section per unit volume for scattering in the medium by summing (6.1) over two orthogonal polarization unit vectors $\tilde{\boldsymbol{v}}$ (contained in $\tilde{\mathsf{S}}$ as defined by (4.15b)) and integrating over all directions of $\tilde{\boldsymbol{k}}$. The radiator $\tilde{\mathsf{S}}$ is then replaced by

$$\int \sum_{j=1,2} \tilde{\mathsf{S}}(\boldsymbol{x},\boldsymbol{x}';\tilde{\boldsymbol{k}},\tilde{\boldsymbol{v}}_j)\,\mathrm{d}\tilde{\Omega} = 4\pi k_0^{-1}\,\mathrm{Im}\,\{\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)\}. \tag{7.3}$$

Equation (a) (second form) with (b) and (c) then follows. (The result (7.3) is a straightforward generalization of (2.23) and is valid if and only if the refractive index is real; compare (5.47) and the direct argument for (a) with (b) and (c) given below.)

We now come back to the proof of the Einstein equation (7.1) and we first compare the results (a) and (d). Subsequently we explain how these results are derived and describe the qualifications on the formula (7.1) and its extension, equation (7.5) below.

In (a) and (d) τ and τ_{E} are rewritten in terms of a common factor $\frac{8}{3}\pi k_0^4$ so we must compare the series $a_1+a_2+a_3+\ldots$ in (a) with the ratio with numerator $A_1+A_2+A_3+\ldots$ in (d). Equations (e) and (f) show that the denominator is a factor of each of the terms A_1 and A_2 of the numerator, and apart from the Cabannes terms the ratios are equal to a_1 and a_2 respectively provided we ignore the row of dots in one diagram (times two) of (b); we come back to this problem shortly. Thus we have up to fourth order in $n\alpha$

$$a_1 = A_1/a_{11}, \tag{7.4a}$$

$$a_2 = A_2/a_{11} + \text{Cabannes terms}, \tag{7.4b}$$

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in which a_{11} denotes the diagram in the denominator of (d). This result immediately proves the simple Einstein formula (7.1) up to neglect of terms of fourth order in the small parameter $n\alpha$; the Cabannes terms start at fourth order and a_3 starts at sixth order.

Recall from §6 that the Cabannes terms are so called because the corresponding scattering terms have the dependence on polarizations $(\tilde{\boldsymbol{u}}, \tilde{\boldsymbol{v}})$ given by equation (6.16); in contrast, all others terms from (7.2) correspond to scattering terms of the form (6.15). We can therefore include the Cabannes terms in the Einstein formula up to fourth order in $n\alpha$ simply by correcting equation (7.1) by the Cabannes factor $C(\rho)$ defined in (6.18), to get

$$\tau \approx \frac{k_0^4}{6\pi}\left(n\frac{\partial m^2}{\partial n}\right)^2 \kappa_T k_B T \frac{3+6\rho}{3-4\rho}. \tag{7.5}$$

In this step we have used the argument leading to (6.18).

We now discuss the the derivations of (a)–(f). To obtain (a) with (b) and (c) we ignore terms with more than one imaginary part propagator, $\mathrm{Im}\{\mathsf{F}\}$. The single $\mathrm{Im}\{\mathsf{F}\}$ in each bulk term is now screened by summing all its non-damping screening terms and using (5.47). As a result the factor $1/\mathrm{Re}\{m\}$ of the first form of (a) is eliminated by the factor $\mathrm{Re}\{m\}$ of the first term of (5.47). This elimination applies to all terms where the screened $\mathrm{Im}\{\mathsf{F}\}$ is covered by an Ursell function, which is short range: here the first term of (5.47) can be approximated by the constant $\frac{2}{3}\mathrm{Re}\{m\}k_0^3$ up to terms of relative order $O((k_0 l)^2)$. This approximation is good when the correlation length l is small compared with a wavelength, i.e. when $k_0 l \ll 1$. It does not apply to fluids near the critical point of phase separation.

Note that in the last term of (b) the $\mathrm{Im}\{\tilde{\mathsf{F}}\}$ cannot be replaced by a constant because it is not covered by an Ursell function; and as a factor $\frac{2}{3}\mathrm{Re}\{m\}k_0^3$ has been extracted from the term the reciprocal of this factor must appear explicitly, concealed in an *ad hoc* diagrammatical element, a row of dots.

Note also the last term to the left of (c). This is a screening term of the second term on the left side of (a), but because it is a damping term it does not contribute to the elimination of the factor $1/\mathrm{Re}\{m\}$; it must therefore appear explicitly, accounted for by the second term of (5.47).

Neglect of terms of relative order $O((k_0 l)^2)$ is sufficient to prove the simple Einstein equation (7.1) up to the third order in $n\alpha$. Proof of the extended version (7.5) requires replacement of $\mathrm{Im}\,(\tilde{\mathsf{F}})$ by a constant also where the propagator is not covered by an Ursell function. This is therefore represented diagrammatically by the neglect of a row of dots.

In the step to the second form of (c) we extract small-sphere contributions from one of the two F propagators because these correspond to non-depolarizing scattering terms of the type (6.15), and we want to isolate all contributions corresponding to depolarized scattering in the form (6.16) to apply the argument of Cabannes and Yvon. Note that the small-sphere contributions of the second and third terms of (c) containing a product of two two-body Ursell functions are cancelled by a similar term from the first term on the left side of (c). We still have to omit the radiation part of the one F propagator for which we extracted the small sphere contribution since these terms correspond to depolarized scattering in non-Cabannes combination. This means neglect of real double scattering and backscattering. Thus, the Einstein formula describes macroscopic single scattering. This concludes the derivation of (a) with (b) and (c) for the extinction coefficient.

For the Einstein expression we first rewrite the differentiation with respect to n as a differentiation through $\beta\mu = \mu/(k_B T)$ in which μ is the chemical potential a molecule in the fluid. (In the present context β always appear in the combination $\beta\mu$ so there is no risk of confusion with the effective polarizability.)

In the step to the second form of (d) we first use the relations (g) to cancel the factor $n^2\kappa_T k_B T$ and to introduce the two-body diagram. The first of the relations (g) is a special case of (7.6) below, whereas the second equality is a well known thermodynamical relation.

The numerator in the second form of (d) is obtained by doing the indicated differentiation with the use of the recurrence relation for generalized Ursell functions $\mathcal{U}_{123\ldots p} = n^p U_{123\ldots p}$,

$$\left(\frac{\partial \mathcal{U}_{123\ldots p}}{\partial \beta\mu}\right)_T = \int \mathcal{U}_{123\ldots p(p+1)}\,\mathrm{d}\boldsymbol{x}_{p+1}. \tag{7.6}$$

The relation (7.6) can be derived from the recurrence relation for generalized Ursell functions in terms of generalized distribution functions, $\mathcal{G}_{123\ldots p} = n^p G_{123\ldots p} = \mathcal{G}_{[p]}$,

$$\mathcal{G}_{[p]} = \sum_{\mathscr{P}} \prod_{Q\in\mathscr{P}} \mathcal{U}_Q, \tag{7.7}$$

together with the recurrence relation

$$\left(\frac{\partial \mathcal{G}_{[p]}}{\partial \beta\mu}\right)_T = \int [\mathcal{G}_{[p+1]} - n\mathcal{G}_{[p]}]\,\mathrm{d}\boldsymbol{x}_{p+1}, \tag{7.8}$$

which can be derived from the definition of the generalized distribution functions in the grand canonical ensemble, compare with Percus (1964). The sum of equation (7.7) is taken over all partitions $\mathscr{P}$ of the index set $[p] = (1, 2, 3, \ldots, p)$. The recurrence relations (7.6) and (7.8) have been obtained by Lebowitz & Percus (1963) in the form of functional differential relations.

The derivative of the $(m^2-1)/4\pi$ to be squared in (d) is given by (h). Notice in particular that the three-body surface term (the last term in square brackets in (d)) contains the product of a one-body and a two-body Ursell function and hence gives rise to two terms upon differentiation.

The square of the series (h) can be arranged as a sum of series each containing a single square plus an infinity of double products, all with a common factor as in equations (e) and (f). In the step to the second form of (f) we extract the small-sphere contribution from the common factor, and ignore the remaining part, which is of relative order $O((k_0 l)^2)$.

This completes the transformation of the Einstein expression, and the proof of equations (7.1) and (7.5) up to third and fourth order in $n\alpha$ respectively. For simplicity we have only displayed the terms actually needed up to fourth order; but the proof of equation (7.5) extends to including the fifth order in $n\alpha$ within the same type of approximations. Figure 8 exemplifies the terms referred to in the following summary of the proof.

The series a_1 has 24 terms in $(n\alpha)^5$ as 2×6 bulk terms plus 2×6 surface terms. Figure 8*a* shows examples. These 24 terms are one to one identical with 24 terms contained in A_1. The series a_2 contains 22 terms (exemplified in figure 8*b*) as 2×6 bulk terms plus 2×5 surface terms, of which the 2×3 terms shown in brackets in figure 8*c* are damping terms discussed in §5 (f). Up to neglect of $O((k_0 l)^2)$, these 22 terms of a_2 can be written as a sum of Cabannes terms and six fourth-order terms, all multiplied by $\frac{8}{3}\pi n\alpha$. These six terms are also contained in A_2. (They are in fact the fourth-order terms shown within brackets in A_1 in figure 7*e*).

There is an interesting problem associated with the damping terms: initially the two terms of figure 8*d* also remained uneliminated by the factor $1/\mathrm{Re}\,(m)$ together with the six damping

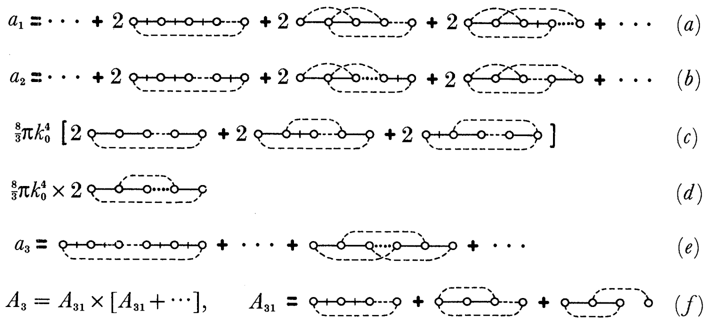

FIGURE 8. Higher terms of the series for τ and τ_E shown in figure 8.

terms of figure 8*c*. Moreover, all damping terms are really screening terms, and hence not automatically screened themselves. Thus, they should appear with a factor $1/\mathrm{Re}\,(m)$ in figure 7*c* (and also in figure 8*c*, *d* if we are concerned about orders higher than five).

Notice, however, that the two terms in surplus at order five (figure 8*d*) have a structure that lets them serve as screening terms for the fourth-order damping term. (They participate in the screening of $\mathrm{Im}\,(\mathbf{F})$.) Therefore these spare terms contribute to the elimination of the factor $1/\mathrm{Re}\,(m)$ in the fourth-order damping term and for the same reason they are themselves eliminated after all.

The terms at order six contribute to the series a_3 and A_3 as well as to a_1, a_2, A_1 and A_2, see figure 8*e*, *f*. The terms of a_3 contain non-Cabannes depolarization even from the Coulomb parts of the propagators (or rather the corresponding scattering terms do). These contributions, therefore, cannot be accounted for by a Cabannes correction factor; and because they are not contained in the Einstein scattering formula itself, we conclude that even the extended formula (7.5) fails at order six in $n\alpha$. Although the agreement thus breaks down elsewhere at order six, it is significant that the relation (7.4*a*) holds at all orders in $n\alpha$ when $\mathrm{Im}\,(\mathbf{F})$ is replaced by $\frac{2}{3}\mathrm{Re}\,(m)\,k_0^3$. The proof of this result is rather complicated so we omit it. This concludes the derivation of the generalized Einstein light scattering formula.

There are three uncertain steps in the preceding evaluation of the Einstein equations. First, there is the substitution of $\frac{2}{3}\mathrm{Re}\,(m)\,k_0^3\,\mathbf{U}$ for $\mathrm{Im}\,(\tilde{\mathbf{F}})$ when this propagator is not Ursell covered. Secondly, we had to replace one propagator $\mathbf{F}$ by its Coulomb part $\nabla\nabla r^{-1}$ in the depolarizing terms. Thirdly, the elimination of the factor $1/\mathrm{Re}\,(m)$ took no account of the possible contribution of the eliminated screening terms to the depolarization (although the main contribution probably comes from the damping terms which remain). Finally, we must admit an uncertainty of the precise numerical significance of the various terms. The complexity of the multiple integrals containing higher-order correlation functions has restricted us to an evaluation in terms of orders of magnitude in the small parameters $n\alpha$ and $k_0 l$.

Nevertheless, the matching of the multitude of terms of distinctly different origin in the series for τ and τ_E is certainly striking, even regarded as a formal relation. From this (real and formal) agreement we conclude that the Einstein light scattering equation (7.1) and its extension (7.5) are well founded in microscopic theory. Note, in particular, that even the simple Einstein equation correctly includes all the infinity of terms a_1 as well as all other non-depolarizing terms up to neglect of $O((n\alpha)^6)$. It is significant here that experiments show the depolarization ratio to be small in general, compare with §6.

It would seem natural to extend the analysis to the phenonological theories of the differential scattering cross section initiated by the work of Ornstein & Zernike (1914, 1918). But recall that we had to neglect terms $O(k_0 l)^2)$ in the analysis of the extinction. This fact implies that the Ornstein–Zernike result can hardly be proved beyond the lowest order, in the interesting case where the cross section depends on the scattering direction.

8. Summary and conclusion

The paper provides a comprehensive microscopic theory of the incoherent light scattered from a molecular fluid. It is based on previous work in which a classical many-body theory of the refractive index and dielectric constant is developed. The theory is therefore linear, classical in terms of molecular polarizabilities and correlation functions, and quasistatic. Within these terms an essentially exact analysis is given.

The theory generates classes of microscopic multiple scattering processes of arbitrary order. From these microscopic processes all of the expected macroscopic features of external optical scattering are derived. Because subtle surface effects appear inevitably in the theory anyway, the model system is deliberately chosen to approximate as closely as possible to the physical situation in a realizable scattering experiment. Thus an external (weak) coherent field is incident upon a spatial region V containing the homogeneous molecular fluid of particle density n and temperature T: V is finite but otherwise arbitrary. The scattered field is analysed at a collector outside V. All macroscopic features expected at the surface of V, namely refraction and reflection of the incident light, and its attenuation inside V, as well as refraction, reflection and attenuation of the scattered field emerges naturally, but non-trivially, from the microscopic theory.

The boundary conditions adopted are simply outgoing boundary conditions at infinity on each individual scattering process. The collective action of these produces the different macroscopic features mentioned: no phenomenological features or boundary conditions at the surface of V are imposed. The following are particularly significant results.

1. A complete theory of macroscopic single scattering derived from all-order microscopic multiple scattering.
2. Sufficiently detailed analysis of macroscopic single scattering at low density from which it should be possible to make quantitative comparison with experiments: comparison is made for the depolarization ratio.
3. Summation of certain microscopic multiple scattering processes, in part to all orders, in part to lower orders, to produce a generalized form of Einstein's phenomenological results for macroscopic single scattering; demonstration that the result cannot be applicable to critical scattering.
4. Identification of certain 'backscattering coherence' within the microscopic theory. This should give rise to back-scattering enhancement observable in an experiment done close enough to a critical point of phase separation.
5. A theory of macroscopic multiple scattering which emerges naturally from the complex of multiple scattering in the microscopic theory.
6. Demonstration that the geometrical corrections that sometimes are made when experimental light scattering results are interpreted to provide 'absolute measurements' rest on a firm theoretical basis: the theory provides a precise interpretation.

These many results all emerge from the unified molecular scattering theory. They are achieved by showing that the total scattering process can be naturally and rigorously divided into a scattering process in the medium plus two transition processes, which account for the coupling of waves in the medium with external waves in vacuum. Thus the scattered flux is expressed (equation (5.3)) as a functional of two fields $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ (describing the scattering process in the medium) together with two equations (3.1 *a*) and (4.1) (separately determining $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ and describing the two transition processes).

The field $\mathscr{E}$ is the average field of the incoming wave in the medium whereas $\boldsymbol{\varepsilon}$, called a weight field, may be said to represent the outgoing wave in the medium, and the scattered flux (5.3) is quadratic in both $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. Equation (3.1 *a*) then relates $\mathscr{E}$ to the actual incoming (weak, coherent) field $\boldsymbol{E}$ incident on V. Similarly, the other equation associated with (5.3), equation (4.1), relates $\boldsymbol{\varepsilon}$ to a field $\boldsymbol{e}$, defined by (4.2), which accounts for the analysis of the scattered light in terms of its direction, its polarization, and in terms of externally imposed stops, which in any real experiment will restrict its aperture. Thus the procedure allows a fairly detailed analysis of the scattered light. (However, if the scattering is not analysed for polarization and the scattering from the entire region V is observed, for example, one must simply replace the quadratic combination $k_0^2\boldsymbol{e}^*\boldsymbol{e}$ by the 'radiator' (2.18 *b*) to get the scattered flux as a function of scattering direction.)

The kernel of the functional (5.3), or the operator $\mathscr{M}$ that it defines, describe all of the internal scattering. Equation (3.8) with the definitions (5.2) and (5.5) show how $\mathscr{M}$ generates all macroscopic multiple scattering (through iteration of (5.4)) from the internal microscopic scattering. In particular the first term of the multiple scattering expansion (3.8) of $\mathscr{M}$ describes macroscopic single scattering represented by the operator $\mathscr{L}$ with kernel (5.5). In this way the theory allows a separate study of macroscopic single scattering.

Note that $\mathscr{M}$ is entirely independent of the arrangement of the source and the detector. And it is independent of the scattering geometry: except for an explicit dependence on the geometry of the region V containing the fluid. Thus (5.3) shows how the scattering process in the medium has been isolated from those describing the incoming and outgoing waves.

Equation (3.1 *a*) describing the entrance of the incoming wave into the medium and (4.1) describing the exit of the outgoing (scattered) wave from the medium have exactly the same mathematical form. Equation (3.1 *a*) is the linear response relation (I 3.2) for the average field $\mathscr{E}$ induced in the medium by the external field $\boldsymbol{E}$. It was solved in part I by an argument involving the 'extinction theorem' of Ewald (1912, 1916) and Oseen (1915). Equation (4.1) differs from (3.1 *a*) only by the form of the source terms. In (3.1 *a*) $\boldsymbol{E}$ can be any free transverse electromagnetic field of wavenumber $k_0 = \omega/c$. But the source term $\boldsymbol{e}$ of equation (4.1) must have the form (4.2) of a free transverse plane wave coming from the direction of the detector (possibly restricted by stops). Nevertheless the weight field $\boldsymbol{\varepsilon}$ can be viewed as the response to a fictitious wave $\boldsymbol{e}$ from the detector: an 'inverse' response.

Such formal similarity expresses a kind of reciprocity principle, and because of it the behaviour of the scattered wave at the surface can be handled by familiar techniques. Thus a version of the extinction theorem applies to the scattered light that can be seen to refract and exhibit (multiple) internal reflection at the surface of V (as illustrated in figures 1 and 2). All of this is demonstrated explicitly in §4 solely on the basis of the microscopic theory. All collective surface effects are accounted for and even quantitatively. Thus we find loss of intensity in transmission and reflection, specific dependence on polarization, and a transformation of the effective differential scattering solid angle between that in the medium and that in the vacuum. Thus for example equation (4.11) (and the discussion following it) shows up all of these features. Only the simplest term of $\mathscr{M}$ is actually considered in (4.11) but the results are not limited by this simplification. And all of these macroscopic behaviours have come from the microscopic theory: the refractive index m in (4.11) is that calculated in part II in a consistent use of the microscopic theory.

Although it is the microscopic theory itself that generates all of these results it is helpful to interpret them in particular cases by appeal to the ideas of macroscopic optics through the inverse response idea. This way arbitrary geometry can be handled. For example, we infer the existence of a lens effect for scattered light in the situations described in figure 3. Most aspects of the collective surface effects associated with the scattering agree exactly with what one would intuitively expect but one must not of course identify the weight field $\boldsymbol{\varepsilon}$ or the field $\boldsymbol{e}$ as in any sense scattered fields.

The scattering of light in the medium is described by the operator $\mathscr{M}$ defined (implicitly) by the representation (2.27) of the relation (5.3). This depends on the geometry of V and a significant part of this dependence is explained in terms of the macroscopic multiple scattering. The macroscopic multiple scattering consists of processes by which intensity is thrown between clusters of molecules, a result of the expansion (3.8) of the operator $\mathscr{M}$ obtained by iterating (5.4). That expression (5.4) explains how our operators are used: the operator $\mathscr{Z}$ there is the pair of propagators (5.2), whereas $\mathscr{L}$ is given explicitly by (5.5) (the Y functions are given by (2.39) or by (I 4.11) more generally).

The resulting series (3.8) is evidently a sensible multiple scattering expansion. Each term of it has the character of scattering processes $\mathscr{L}$ connected with propagations $\mathscr{Z}$. Propagations are long range (though note the discussion in §5 (e)) whereas the processes $\mathscr{L}$ are short range (up to back scattering and generalizations). The series expansion successfully distinguishes multiple scattering from backscattering (which is reviewed below): this is also long range but does not otherwise have evident multiple scattering character. These differences were analysed in §5 (d).

The series (3.8) is based on the relation (2.41) between the special propagator $\mathscr{S}$ (called a radiator) and the quantity $\mathscr{S}' = k_0^2\,\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$, and its status as a macroscopic multiple scattering expansion derives from this relation. Each of $\mathscr{S}$ and $\mathscr{S}'$ describes a radiated flux (as in (2.31)); but $\mathscr{S}$ describes an average flux, whereas $\mathscr{S}'$ describes the corresponding flux of an average field. The relation (2.41) shows that $\mathscr{S}$ differs from $\mathscr{S}'$ by a term containing the scattering kernel $\boldsymbol{\sigma}$, and this implies that $\mathscr{S}$ includes multiple scattering in a natural way. Macroscopic multiple scattering is therefore generated by iteration of equations (3.1 c) and (3.1 d) or of the resulting equation (5.4) for scattering in the medium. Each of $\mathscr{S}$ and $\mathscr{S}'$ plays a vital role in the theory, whereas the multiple scattering expansion appears in an entirely natural way: it is certainly not constructed *ad hoc*. We return to this below.

The theory contains processes exhibiting back-scattering coherence, which give rise to a sharp peak of scattering in a direction opposite to that of the incoming wave. Such processes are analogous to those appearing in theories of scattering from suspensions of dielectric particles where back-scattering enhancement has been demonstrated experimentally (Kuga & Ishimaru 1984). But the phenomenon has not previously been recognized in microscopic scattering theory, and back-scattering enhancement from homogeneous media has not been observed experimentally. We suggest in §5 (d) that it should be possible to detect it experimentally in critical scattering from simple fluids; or (by generalization) from binary mixtures.

The multiple-scattering expansion (3.8) treats back scattering as part of macroscopic single scattering and hence automatically distinguishes it from macroscopic multiple scattering. Despite their close similarity of form (compare 5.12*b*) with (5.19) or compare (5.14) with (5.21)) the two classes of scattering are physically very different in their dependence on the scattering direction and on the scattering geometry; §5(*d*) explains this.

Scattering of light in the medium, totally described by the operator $\mathscr{M}$, is a very complex process exhibiting macroscopic multiple scattering and back scattering. Despite this complexity the collective surface effects described through $\mathscr{E}$ and $\boldsymbol{\varepsilon}$ keep their particular (and simple) significance for all parts of the scattering process. For example, scattering reaching the detector from a multiple scattering process exhibits refraction at the surface in exactly the same way as does a contribution to single scattering. Macroscopic multiple scattering and backscattering processes are simply superimposed on the multi-mode pattern established by $\mathscr{E}$ and $\boldsymbol{\varepsilon}$. Figures 1*c* and 5*a*, 5*c* illustrate this fact by showing contributions from single, double and triple scattering for the same scattering geometry.

When we come to numerical evaluation and to a comparison with experiments and with macroscopic models it has been necessary for sufficient simplicity to limit the scope to local macroscopic single scattering only. Thus in §6 we expand the scattering cross section in a low density series (6.2*a*) and calculate the coefficients up to the second order. The one-body term is trivial, but the two-body term is not. The result (6.5) with (6.4) and (6.6) is obtained in an approximation where propagators are replaced by their Coulomb parts and phase factors are ignored.

Two-body terms involve only pair correlations and up to the second order in the density these are completely determined by the pair potential. We have calculated the two-body terms for a Lennard-Jones potential. The result is (6.5) with the functions h_2 and d_2 given by (6.7) and (6.8) respectively. This result is shown to agree with the extinction coefficient calculated in part II from the refractve index in a similar approximation. The resulting low density form of the depolarization ratio, (6.11), is a function of the complex polarizability (2.17) and the temperature T through the two reduced variables a^3/γ and T_0/T, where a and $k_B T_0$ are Lennard-Jones parameters specifying the minimum of the intermolecular potential curve (II 3.12). Figure 6 shows the function D and table 1 compares with experiments.

As another specific application of the microscopic theory we have analysed in §7 the phenomenological light scattering formulae of Einstein (1910). The conclusion is that the Einstein formula is an approximation to macroscopic single scattering without back scattering. It is correct, as such, up to neglect of terms of order four in $n\alpha$ and order two in $k_0 l$. So it is most applicable to the scattering from fluids of low density and small correlation lengths.

If the formulae are corrected by a Cabannes factor expressed in terms of the depolarization ratio (as first suggested by Yvon (1937)) the generalized formulae are valid to neglect of terms of order six in the polarizability density $n\alpha$: apart from a small discrepancy. (The phenomenological formulae lack one propagator in terms related to the omitted backscattering terms.)

The specific conclusions summarized above in the present section depend on more technical results expressed in terms of a number of quantities: scattering operators $\mathscr{M}$ and $\mathscr{L}$; fields $\mathscr{E}$ and $\boldsymbol{\varepsilon}$; propagators $\mathscr{F}$ and $\mathscr{S}$ (together with their unscreened counterparts F and S); and kernels $\boldsymbol{\Lambda}$ and $\boldsymbol{\sigma}$. It has been necessary to introduce all these objects because of the complexity of the problem; but it is also because it is instructive to exhibit, and indeed exploit, the close relations that exist between the theory of refractive index and the theory of scattering as derived from the same unified microscopic theory. Because the interpretation of the theory in terms of macroscopic ideas partly derives from relations among the objects mentioned it may be useful if we summarize here these relations as well as the meaning of the objects involved. We review them from the standpoint of the final theory so the line of argument here is partly the reverse of the one presented in the derivation given in the text.

The most important new objects of the scattering theory are the weight field, $\boldsymbol{\varepsilon}$, and the single scattering operator, $\mathscr{L}$. The weight field describes the behaviour of scattered light at the surface and is essential to the theory. The single scattering operator describes macroscopic single scattering in the medium from which multiple scattering can be obtained by combining several $\mathscr{L}$ with pairs of propagators $\mathscr{F}^*\mathscr{F}$. In this way the entire scattering in the medium, $\mathscr{M}$, can be built as in (3.8) where $\mathscr{Z}$ denotes $\mathscr{F}^*\mathscr{F}$.

The single scattering operator $\mathscr{L}$ has a simple structure (5.5), and plays a more fundamental role in the theory than the operator $\mathscr{M}$ for the complete scattering. Thus it is an interesting fact that $\mathscr{L}$ (and not $\mathscr{M}$) is closely related to the susceptibility kernel $\boldsymbol{\Lambda}$ of the refractive index theory. (In the series expansion (5.5) of $\mathscr{L}$ each of the p terms at order $p+1$ (in $n\alpha$) are governed by the same $(p+1)$-particle correlation function Y, and this common correlation function is identical to the one appearing at the same order in the expansion (II 4.2) of $\boldsymbol{\Lambda}$).

The reason for the status of $\mathscr{L}$ is the following. Although $\mathscr{L}$ describes single scattering when combined with $\boldsymbol{\varepsilon}$ as in (3.9) or (5.6) it can also describe the complete scattering in a very natural way when it is combined with $\mathscr{S}$. The radiator $\mathscr{S}$ has some character of a propagator, so it is possible to focus on a 'field description' in terms of $\boldsymbol{\varepsilon}$ or a 'propagator description' in terms of $\mathscr{S}$. And because the refractive index theory contains no field analogous to $\boldsymbol{\varepsilon}$ it is the propagator point of view that is the more fruitful one in a comparison between the two theories. We summarize that comparison now.

The weight field $\boldsymbol{\varepsilon}$ appears in the scattering theory in the combination $\mathscr{S}' = k_0^2\boldsymbol{\varepsilon}^*\boldsymbol{\varepsilon}$. Superficially this might be thought of as a propagator. (Recall that it differs from $\mathscr{S}$ by a decorrelation, $\mathscr{S}$ being the average of a product (2.32) whereas $\mathscr{S}'$ is the corresponding product of averages (2.30).) The important point, however, is that although $\boldsymbol{\varepsilon}$ is an important object and the natural counterpart of the incoming field $\mathscr{E}$, it is $\mathscr{S}$ (rather than $\mathscr{S}'$) that is the more natural propagator and counterpart of $\mathscr{F}$. This fact is evidenced by the similarity of their expansions, (2.37*a*) with (2.20) for $\mathscr{S}$ against (2.35) for $\mathscr{F}$, and also by the fact that $\mathscr{S}$ and $\mathscr{F}$ are connected by a Bohr–Peierls–Placzek type relation analogous to (2.23). When $\mathscr{L}$, (5.5), is combined with $\mathscr{S}$ to give the scattering kernel $\boldsymbol{\sigma}$, (3.1*c*), the radiator $\mathscr{S}$ fits naturally into the gap in the chain of propagators $\mathscr{F}^*$ or $\mathscr{F}$ in $\mathscr{L}$, and as a result $\boldsymbol{\sigma}$ expressed in terms of $\mathscr{F}$ and $\mathscr{S}$ has a strucure very similar to that of the susceptibility kernel $\boldsymbol{\Lambda}$.

This close relation is expressed by the formal relation (2.22). It represents (2.21) with (2.20) in the unscreened formulation or (2.38*a*) with (2.38*b*) in the screened one. (Compare these expressions with (2.13) and (II 4.2) respectively for $\boldsymbol{\Lambda}$. Equation (II 4.2) for $\boldsymbol{\Lambda}$ is exhibited in a diagrammatical notation in figure 4*a* which should be compared with figure 4*b* for $\boldsymbol{\sigma}$.) The close relation between $\boldsymbol{\sigma}$ and $\boldsymbol{\Lambda}$ (and hence between $\mathscr{L}$ and $\boldsymbol{\Lambda}$) manifests itself in the Bohr–Peierls–Placzek type relation (2.24) between $\boldsymbol{\sigma}$ and $\boldsymbol{\Lambda}$ and this is analogous to (2.23) between S and F or to (I 4.26) between $\mathscr{S}$ and $\mathscr{F}$.

All these technical results confirm the significance of the radiator $\mathscr{S}$ and the uniqueness of the expansion (3.8), and hence substantiate the interpretation of (3.8) as a macroscopic multiple scattering expansion. (See also the discussion of damped propagation in §5(*f*).)

Thus in summary of the two alternative formulations: our formulation of the scattering theory in terms of the weight field wholly solves the problem of deriving the collective refraction and reflection of the scattered light from the microscopic theory. But the alternative formulation in terms of the specific propagator $\mathscr{S}$ emphasizes the close relation between the refractive index theory developed earlier and the scattering theory. The two formulations together generate a complete and wholly satisfactory description of macroscopic multiple scattering in terms of microscopic scattering events. And the natural way every part fits in the unified theory strengthen our confidence in the interpretations in macroscopic terms we have made.

The conclusion is that the microscopic theory is shown to generate all of the macroscopic aspects of external scattering to be expected. A theoretical structure has been created to make the transition from microscopic scattering events to macroscopic scattering, which models a real experiment. It thus seems to be possible now to embark on particular numerical simulations in the confidence that 'what is going on' (at whatever level of understanding) can completely be determined by a consistent application of the theory.

Future extensions of the theory can go in several directions, particularly to nonlinear and quantum mechanical descriptions. Thus the quantum theoretical basis of the theory, as it was briefly sketched by Bullough *et al.* (1968), is now developed to a point (Bullough & Hynne 1990) where it shows specific quantum (rather than only classical) features. In recent jargon this is a detailed many-body theoretical treatment of the linear 'attenuator' defined as such by Louisell (1964) (and cf. Sargent *et al.* 1974; Lamb 1971). The same formalism describes equally well the linear 'phase insensitive amplifier' (Louisell 1964; Sargent *et al.* 1974); and, for example, the papers by Glauber and others in Tombesi & Pike (1989). There is a rich field for further many-body theoretical endeavour, necessarily quantum based, in these various problems.

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