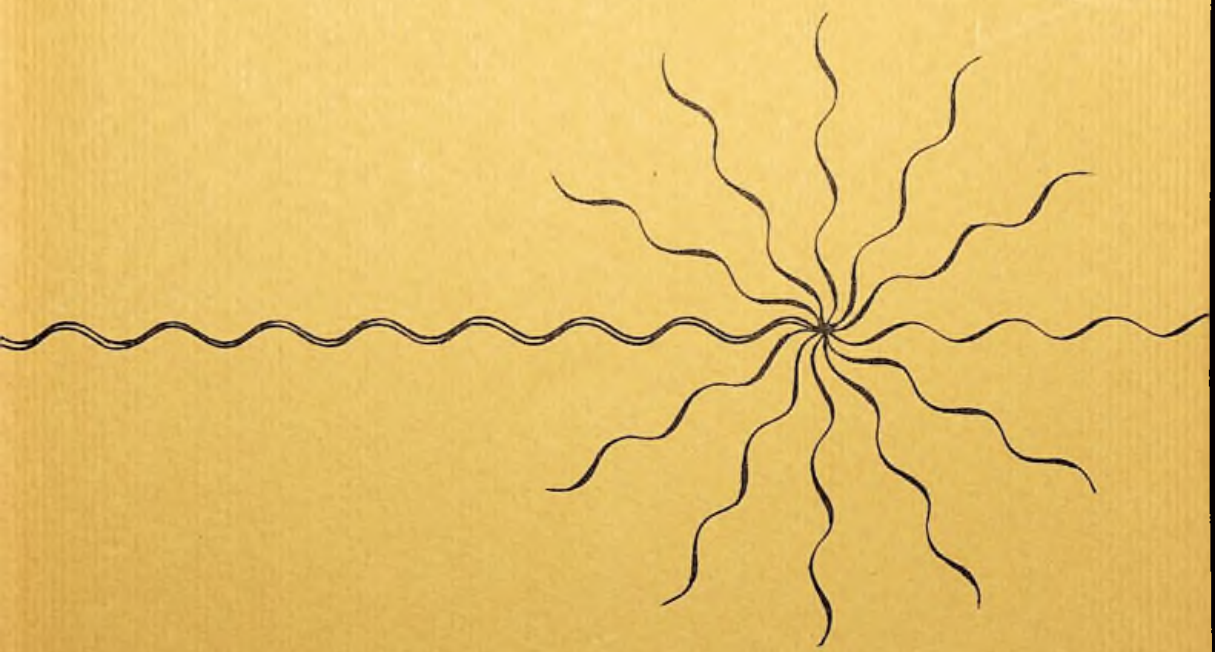
ON THE THEORY OF MULTIPLE SCATTERING



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ON THE THEORY OF MULTIPLE SCATTERING

Proefschrift

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aan mijn ouders

CONTENTS

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Introduction

The modern theory of light scattering from a nonpolar fluid was initiated by Smoluchowski [1] and Einstein [2] in the beginning of this century. In their theories the scattering of light by a fluid is explained in terms of fluctuations of the dielectric constant around its value at the average density. Using the density dependence of the dielectric constant one may then express the scattering intensity in lowest order in terms of the density-fluctuation correlation function. It is precisely this relation (and generalizations thereof) which has made light-scattering experiments such a useful tool to investigate the properties of a wide class of systems. From the frequency-integrated scattering intensity one can deduce equilibrium properties such as the compressibility and from the frequency-dependent scattering intensity one can deduce nonequilibrium properties, such as the viscosity and the thermal conductivity. In particular near the critical point where many of these quantities diverge, light-scattering experiments have played a crucial role in the investigation and therefore in the understanding of the various singularities.

In 1937 Yvon [3] developed a molecular theory for light scattering from a fluid consisting of classical point-dipoles. The incident field, which obeys Maxwell's equations in vacuum, induces dipole-moments in the molecules; these dipole-moments emit secondary fields, which induce other dipole moments, etc.. In this way the singly and multiply scattered fields are generated. The resulting formula for the single-scattering intensity is different from the result of Einstein's phenomenological theory in that it does not contain the so-called "local-field correction factor". For many years this discrepancy was rather controversial until it was finally resolved by Fixman [4] in 1955, who showed that the molecular theory leads to the same expression as the Einstein-Smoluchowski theory, if higher-order

contributions are also taken into account in the molecular theory.

There are several reasons to be interested in multiple scattering. In the first place the multiple-scattering intensities contain information about higher-order correlation functions. In the second place multiple-scattering contributions to the total scattering intensity complicate the interpretation of the data especially in experiments where the scattering intensity is large, for example close to the critical point.

A theory of multiple scattering may in principle be either phenomenological or molecular. In the phenomenological theory the multiply scattered fields are the result of repeated scattering from fluctuations in the dielectric constant and therefore the density. The resulting formulae contain the notorious local-field correction factors, but they have the unpleasant feature that they diverge. This divergence has to be eliminated by the introduction of an ad hoc cut-off of the electromagnetic propagator for wavevectors larger than a typical inverse molecular diameter. In the molecular theory the multiply scattered fields are the result of repeated scattering by the molecules. In that case local-field correction factors may only be obtained by extensive resummations; divergences do not occur. Both theories, however, contain secular (or shadow) terms. These terms do not really correspond to scattering, but they represent the change in the transmitted beam and the scattered fields due to intensity losses by scattering.

It is the aim of this thesis to develop a molecular theory in which the scattering intensity is expanded in correlation functions of fluctuations of the density rather than in correlation functions of the full density as in the conventional molecular theories. In this way one has on the one hand the advantage that, due to its molecular nature, the theory contains no divergences while on the other hand the theory is closely

analogous to the phenomenological theory so that e.g. the local-field correction factors are obtained without resummation. That such a development is possible was suggested by the work of Bedeaux and Mazur [5] who studied the dielectric constant for the same system along similar lines. A further refinement is introduced by expanding the fluctuating dielectric constant around its macroscopic value and not around its value at the average density. As will be shown this leads to the elimination of the secular terms while it introduces attenuation effects in the beam and in the fields between and after scattering events.

In chapter I a simple model of a one-component isotropic nonpolar fluid is considered. The fluid is assumed to consist of point-dipoles with constant polarizability, which is only correct if the electric field varies slowly over distances of the order of the molecular diameter. This model is called the classical point-dipole model and was used by both Yvon and Fixman in their discussion of light scattering. It was also used by Bedeaux and Mazur. Applying their techniques one can derive an explicit form for the fluctuating dielectric constant in terms of the molecular polarizability and the fluctuating molecular density. Furthermore formal expressions are found for the scattered field and the scattering intensity, which contain multiple-scattering effects to all orders. By purely algebraic transformations the scattered field is first expressed in terms of fluctuations of the dielectric constant around its macroscopic value and subsequently in terms of fluctuations of the density around its average value. Finally the scattered field and as a consequence the scattering intensity are expanded in these fluctuations. The term in this expansion which is proportional to the n^{th} power of the density fluctuations is then defined as the n times scattered field. It should be stressed that the precise meaning of "the n times scattered field" depends on the expansion

used and is therefore different in the various theories. This completes the general part of this chapter. The explicit evaluation of the multiple-scattering intensities would imply integrations over higher-order correlation functions, which are not very well known. In view of the application to critical scattering formulae are given for the case that the Gaussian approximation may be used for the higher-order correlation functions. For this case a diagrammatic representation is shortly discussed.

In chapter II the theory is applied to multiple scattering near the gas-liquid critical point. In this chapter the Gaussian approximation is used throughout. Deviations from the Gaussian approximation which may become important very close to the critical point may in principle lead to contributions which are not considered. Using essentially the stationary-phase approximation the scattering formulae are further simplified. It is found, that, due to the long-range nature of the density-fluctuation correlations near the critical point, the most important contributions arise from situations where the successive scattering points are far apart in comparison to the wavelength of the light. As a consequence the multiple-scattering intensity in each order is simply a contraction of consecutive uncorrelated single-scattering events. That this is the case was also conjectured recently by Reith and Swinney [6] on the basis of the work of Oxtoby and Gelbart [7] who also considered multiple scattering near the critical point.

In section (II.5) this result is used to calculate the depolarization factor for an experiment by Trappeniers, Michels and Huijser [8], who measured this factor near the critical point for CO_2. The depolarization factor is in this case in lowest order equal to the ratio of the intensities of depolarized doubly scattered light and polarized singly scattered light.

The theoretical prediction can be calculated analytically and agrees very well with the experimental result. An important consequence of this agreement is the fact that it confirms the conclusion that close to the critical point multiple-scattering is simply a contraction of consecutive uncorrelated single-scattering events.

In section (II.6) we calculate double-scattering corrections to the "Ornstein-Zernike plot", which is the inverse of the scattering intensity as a function of $\sin^2\frac{1}{2}\theta$ with θ the scattering angle. This plot would be a straight line if only single scattering were present. From the extrapolated value for zero scattering-angle one calculates the compressibility, which diverges if the critical point is approached. In this way the critical exponent γ is derived from light-scattering data. Before extrapolating, however, one should subtract the multiple-scattering intensity from the total scattering intensity in order to recover the line that is predicted by the single-scattering theory. It is shown that the multiple-scattering corrections relative to the single-scattering intensity tend to zero for forward and backward scattering. The double scattering intensity is evaluated explicitly for a sample of CO_2 and the scattering geometry used in the experiment by White and Maccabee. [9] It turns out that double scattering becomes important if the temperature distance to the critical point is smaller than $0.01^{\circ}C$ (at the critical density). Since many experiments are performed near the critical point of binary mixtures, it is interesting to develop a similar theory of multiple scattering from critical binary mixtures. This is done in chapter III along the lines of the extension by Kim and Mazur [10] of the theory of Bedeaux and Mazur. It is found again that critical multiple scattering is a contraction of successive uncorrelated single-scattering events.

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I. GENERAL THEORY

Synopsis

A systematic theory of multiple scattering is given for a nonpolar fluid of point dipoles. Local-field correction factors are consistently accounted for to all orders. To first order (single scattering) Einstein's result is obtained; the theory yields, however, automatically to this order the attenuation of the incoming beam before and of the scattered light after scattering. In the usual theories these effects are hidden in secular (shadow) contributions to multiple scattering. The single–triple and double-scattering intensities are briefly discussed.

1. *Introduction.* The theory of light scattering in its present form goes back to the work of Einstein[1]), in which the scattering intensity is related to the fluctuations of the local dielectric constant. Molecular theories of light scattering have subsequently been given by Yvon[2]) and Zimm[3]) and also by Fixman[4,5]), who was able to justify Einstein's result*. Einstein neglects the fluctuations in the polarizing field, his result for this reason contains only single scattering from fluctuations around the average dielectric constant. In the above-mentioned molecular theories on the other hand, multiple-scattering contributions appear in the customary expansions. Single and multiple scattering refer, however, in these theories in general to scattering from particles *in vacuo*. Single scattering from fluctuations, as considered in the phenomenological theory, is in fact a sum over the single- and certain multiple-scattering contributions in the molecular theory.

With the development of laser light sources and better detectors it has in recent years become possible to measure double-scattered light in depolarization experiments. A number of papers deal from a molecular point of view with the theoretical aspects of multiple scattering[6,7]). For an extensive list of references we refer to the review paper on depolarized light scattering by Gelbart[8]). We also

* In the phenomenological theory an additional factor $[(\varepsilon_0 + 2)/3]^2$ appeared compared to the earlier molecular theories. The controversy over this factor was finally resolved by Fixman and we refer to his paper for a discussion of this point.

refer to his paper for a discussion of the relation between multiple scattering and certain "collision induced" phenomena.

In this paper we shall develop a systematic molecular theory of multiple scattering in which multiple scattering is defined, in agreement with the definition of single scattering in the phenomenological theory given by Einstein, consistently as scattering from fluctuations around the macroscopic dielectric tensor. The propagation of the electromagnetic wave before, after and between different scattering events is therefore through the medium described by the full macroscopic dielectric tensor rather than through vacuum.

We consider a nonpolar dielectric consisting of point dipoles with a constant scalar polarizability α_0. We therefore exclude effects due to resonant scattering at molecular frequencies; and furthermore effects related to pair polarizabilities[9]) and certain other collision-induced phenomena[10,11]). In ref. 12 we considered the same system and discussed the behaviour of the dielectric tensor in the critical region.

In section 2 we develop the Maxwell theory in a fluctuating dielectric. An exact expression is given for the scattered field in terms of the fluctuating dielectric tensor, the macroscopic dielectric tensor, the propagator of the electromagnetic field in the medium and the macroscopic field. This expression contains the single- and multiple-scattered fields to all orders.

In section 3 we use the fact that the distance between the observer and the sample is large compared to the diameter of the sample in order to express the total scattered intensity as a function of the frequency in terms of the autocorrelation function of a fluctuating polarization density. The attenuation of the scattered light in the sample is explicit in this formula.

In section 4 we apply the formal theory of the two previous sections to our model. To this end we use a relation between the fluctuating dielectric tensor and the molecular density, which we derived in ref. 12, and which is equivalent to Clausius–Mossotti on the fluctuation level. We use this formula to define a fluctuating and a macroscopic "Clausius–Mossotti" function. The fluctuating polarization density, which is the source of the scattered field, is subsequently expressed in fluctuations of this Clausius–Mossotti function. This automatically introduces local-field correction factors and at the same time modifies the propagator in the medium between scattering events so as to exclude self-polarization effects. The resulting expression for the autocorrelation function of the fluctuating polarization density may then be expanded in powers of the fluctuations in the density. The various terms in this expansion are then defined as the single-, double- *etc.* scattering intensities. In section 5 this expansion is carried out to fourth order. The various terms correspond to the intensities of single- and double-scattered light and to the interference terms between the single- and double- and between the single- and triple-scattered fields. They are expressed in 2-, 3- and 4-point density-fluctuation correlation functions. In the low-density limit our expressions

reduce essentially to the corresponding expressions found by previous authors, *cf.*, ref. 8. In view of a future application to critical scattering[8,13,14]) we use the gaussian approximation in the discussion of the multiple-scattering intensities. A diagrammatic representation of the expansion is introduced and briefly discussed.

In sections 6, 7 and 8 we consider in some detail respectively the single-, single–triple- and double-scattering intensities. The single scattering is found to be the same as the result found by Einstein[1]) with a minor correction related to the attenuation in the sample before and after scattering. This last effect, however, may usually be neglected except very close to the critical point[15]). The single–triple scattering, like the single scattering, is found to contribute only to the polarized-scattering intensity. This contribution is usually not considered[6-8]) although it is in principle of the same order as the double-scattering intensity. This is correct in the study of the depolarized intensity but not for the polarized intensity[7,14]). In both the expressions for the single–triple- and the double-scattering intensities we find the appropriate local-field correction factors similar to those occurring in Einstein's expression for single scattering.

2. *Maxwell theory in a fluctuating dielectric.* The Maxwell equations in a fluctuating dielectric are

$$\begin{aligned} &\operatorname{curl} \boldsymbol{e}(\boldsymbol{r}, t) = -\frac{\partial}{\partial t} \boldsymbol{b}(\boldsymbol{r}, t), \qquad \operatorname{div} \boldsymbol{d}(\boldsymbol{r}, t) = 0, \\ &\operatorname{curl} \boldsymbol{h}(\boldsymbol{r}, t) = \frac{\partial}{\partial t} \boldsymbol{d}(\boldsymbol{r}, t), \qquad \operatorname{div} \boldsymbol{b}(\boldsymbol{r}, t) = 0, \end{aligned} \tag{2.1}$$

where $\boldsymbol{e}(\boldsymbol{r}, t)$ and $\boldsymbol{b}(\boldsymbol{r}, t)$ are respectively the fluctuating electric and magnetic fields, and $\boldsymbol{d}(\boldsymbol{r}, t)$ and $\boldsymbol{h}(\boldsymbol{r}, t)$ the fluctuating inductions; units are chosen such that the velocity of light in vacuum is unity. Neglecting the magnetic properties we have

$$\boldsymbol{h} = \boldsymbol{b}, \qquad \boldsymbol{d} = \boldsymbol{e} + \boldsymbol{p}, \tag{2.2}$$

with $\boldsymbol{p}$ the fluctuating polarization density.

From eqs. (2.1) and (2.2) we obtain the wave equation governing the electric field

$$\operatorname{curl} \operatorname{curl} \boldsymbol{e} + \frac{\partial^2}{\partial t^2} \boldsymbol{e} = -\frac{\partial^2}{\partial t^2} \boldsymbol{p} \tag{2.3}$$

Defining Fourier transforms with respect to $\boldsymbol{r}$ and t of a field f by

$$f(\boldsymbol{k}, \omega) \equiv \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)} f(\boldsymbol{r}, t), \tag{2.4}$$

eq. (2.3) becomes in wavevector–frequency representation

$$(\boldsymbol{kk} - k^2 + \omega^2) \cdot \boldsymbol{e}(\boldsymbol{k}, \omega) = -\omega^2 \boldsymbol{p}(\boldsymbol{k}, \omega). \tag{2.5}$$

The general retarded solution of this equation is

$$\boldsymbol{e}(\boldsymbol{k}, \omega) = \boldsymbol{E}_v(\boldsymbol{k}, \omega) - \mathsf{F}(\boldsymbol{k}, \omega) \cdot \boldsymbol{p}(\boldsymbol{k}, \omega), \tag{2.6}$$

where $\boldsymbol{E}_v$ is a solution of the homogeneous equation and is therefore the incident field in vacuum. We note that in the presence of externally controlled sources the vacuum field due to these sources is also contained in $\boldsymbol{E}_v$. The retarded propagator of the electromagnetic field in vacuum F is given by

$$\mathsf{F}(\boldsymbol{k}, \omega) \equiv [\boldsymbol{kk} - k^2 + (\omega + \mathrm{i}0)^2]^{-1} \omega^2 = [k^2 - (\omega + \mathrm{i}0)^2]^{-1} (\boldsymbol{kk} - \omega^2), \tag{2.7}$$

where i0 is an infinitesimally small positive imaginary number.

Now in order to come to a closed description the polarization is expressed, restricting ourselves to linear optics, in the electric field by a constitutive relation

$$\boldsymbol{p} = (\boldsymbol{\varepsilon}_b - 1) \cdot \boldsymbol{e} = \boldsymbol{\chi}_b \cdot \boldsymbol{e}, \tag{2.8}$$

where $\boldsymbol{\varepsilon}_b$ and $\boldsymbol{\chi}_b$ are the fluctuating (bare) dielectric tensor and susceptibility. These fluctuations are, *e.g.*, caused by the fluctuations in the density. In its most general form $\boldsymbol{\varepsilon}_b$ (and $\boldsymbol{\chi}_b$) is a linear operator, this will become apparent when we give an explicit expression for $\boldsymbol{\varepsilon}_b$.

The macroscopic electric field is the average of the fluctuating field

$$\boldsymbol{E} = \langle \boldsymbol{e} \rangle, \tag{2.9}$$

where the brackets $\langle \cdots \rangle$ indicate the average over the fluctuations. Similarly the macroscopic polarization field is given by

$$\boldsymbol{P} = \langle \boldsymbol{p} \rangle = \langle \boldsymbol{\chi}_b \cdot \boldsymbol{e} \rangle = \boldsymbol{\chi} \cdot \boldsymbol{E} = (\boldsymbol{\varepsilon} - 1) \cdot \boldsymbol{E}. \tag{2.10}$$

Eq. (2.10) together with eq. (2.9) also defines the macroscopic dielectric tensor $\boldsymbol{\varepsilon}$ and susceptibility $\boldsymbol{\chi}$. In ref. 12 we have used this fact in order to derive explicit expressions for the dielectric tensor close to the critical point (see also the end of section 4).

Adding $\omega^2 \boldsymbol{\chi} \cdot \boldsymbol{e}$ to eq. (2.5) and using eq. (2.8) one obtains the wave equation in the dielectric

$$(\boldsymbol{kk} - k^2 + \omega^2 \boldsymbol{\varepsilon}) \cdot \boldsymbol{e} = -\omega^2 (\boldsymbol{\varepsilon}_b - \boldsymbol{\varepsilon}) \cdot \boldsymbol{e} \equiv -\omega^2 \Delta \boldsymbol{\varepsilon}_b \cdot \boldsymbol{e} \equiv -\omega^2 \Delta \boldsymbol{p}. \tag{2.11}$$

The right-hand side of this equation is the fluctuating source term and has average zero, $\langle \Delta \boldsymbol{p} \rangle = 0$; we note, however, that $\langle \varepsilon_b \rangle \neq \varepsilon$. Eq. (2.11) may formally be solved by

$$\boldsymbol{e} = \boldsymbol{E} - \mathsf{F}_\varepsilon \cdot \Delta \boldsymbol{p} = \boldsymbol{E} - \mathsf{F}_\varepsilon \cdot \Delta \varepsilon_b \cdot \boldsymbol{e}, \tag{2.12}$$

where F_ε is the retarded wave propagator in the medium. Furthermore $\boldsymbol{E}$ is the macroscopic field defined in eq. (2.9) and is therefore the incident field in the medium, which is related to the incident field in vacuum using eq. (2.6) for the averages. Using stationarity and translational invariance, *cf.* ref. 12, one may show that ε is diagonal in $(\boldsymbol{k}, \omega)$ representation; in that case F_ε is also diagonal in this representation and the diagonal elements are given by

$$\mathsf{F}_\varepsilon(\boldsymbol{k}, \omega) = [\boldsymbol{kk} - k^2 + (\omega + \mathrm{i}0)^2 \, \varepsilon(\boldsymbol{k}, \omega)]^{-1} \, \omega^2. \tag{2.13}$$

We find, using eq. (2.12), for the fluctuating field $\boldsymbol{e}$ in terms of the macroscopic field

$$\boldsymbol{e} = (1 + \mathsf{F}_\varepsilon \cdot \Delta \varepsilon_b)^{-1} \cdot \boldsymbol{E}. \tag{2.14}$$

This gives for the fluctuating polarization field $\Delta \boldsymbol{p}$, which is the source of the scattered field,

$$\Delta \boldsymbol{p} = \Delta \varepsilon_b \cdot \boldsymbol{e} = \Delta \varepsilon_b \cdot (1 + \mathsf{F}_\varepsilon \cdot \Delta \varepsilon_b)^{-1} \cdot \boldsymbol{E}. \tag{2.15}$$

Using the fact that $\langle \Delta \boldsymbol{p} \rangle = 0$ one finds the following identity

$$\langle \Delta \varepsilon_b \cdot (1 + \mathsf{F}_\varepsilon \cdot \Delta \varepsilon_b)^{-1} \rangle = 0, \tag{2.16}$$

which we will use to derive an expression for the macroscopic dielectric tensor ε.

The scattered field is given by, *cf.* also eq. (2.12),

$$\boldsymbol{e}_{sc} = \boldsymbol{e} - \boldsymbol{E} = -\mathsf{F}_\varepsilon \cdot \Delta \boldsymbol{p}. \tag{2.17}$$

This equation together with eq. (2.15) will be the starting point of our further discussion. Finally we note that in isotropic systems, to which we will limit ourselves,

$$\varepsilon(\boldsymbol{k}, \omega) = \varepsilon_T(k, \omega)(1 - \boldsymbol{kk}/k^2) + \varepsilon_L(k, \omega)\boldsymbol{kk}/k^2, \tag{2.18}$$

where ε_T and ε_L are the so-called transverse and longitudinal dielectric constants.

3. *Scattering theory.* In this section we derive an expression for the intensity of the scattered light which contains the contributions due to the single- and multiple-scattered light up to all orders. We consider the following, somewhat idealized, scattering experiment. The sample is thought to be embedded in a nonfluctuating medium with a constant dielectric tensor equal to the macroscopic dielectric tensor ε of the sample. This implies that the average field E passes through the sample without refraction at the surface. Though in practice this setup is never realized this is easily corrected for. The scattered field is given by eq. (2.17) which is in (r, ω) representation

$$e_{sc}(r, \omega) = -\int_{V_s} \mathsf{F}_\varepsilon(r - r', \omega) \cdot \Delta p(r', \omega)\, dr', \tag{3.1}$$

where we have used the fact that the fluctuating polarization Δp is zero outside the volume of the sample V_s*. We now use the fact that the distance of the observer to the sample, min $|r - r'|$, is much larger than the wavelength, $2\pi/\omega$. In that case the asymptotic behaviour of F_ε may be used in eq. (3.1) and one obtains, using also isotropy, see appendix A,

$$e_{sc}(r, \omega) = \frac{1}{4\pi}\omega^2 \int_{V_s} dr' \left[1 - \frac{(r - r')(r - r')}{|r - r'|^2}\right] \times |r - r'|^{-1} \exp[i\omega n(\omega)|r - r'|] \cdot \Delta p(r', \omega), \tag{3.2}$$

where the refractive index is related to the transverse dielectric constant by

$$n^2(\omega) = \varepsilon_T(\omega n(\omega), \omega). \tag{3.3}$$

The intensity of the scattered light with polarization u at point r and with frequency ω is now given by

$$\begin{aligned} I_u(r, \omega)\, 2\pi\delta(\omega - \omega') &= u \cdot \langle e_{sc}(r, \omega)\, e_{sc}^*(r, \omega')\rangle \cdot u \\ &= (4\pi)^{-2}\omega^4 u \cdot \int_{V_s} dr'\, dr'' \left[1 - \frac{(r - r')(r - r')}{|r - r'|^2}\right] \\ &\quad \cdot \langle \Delta p(r', \omega)\, \Delta p^*(r'', \omega')\rangle \cdot \left[1 - \frac{(r - r'')(r - r'')}{|r - r''|^2}\right] \\ &\quad \cdot u\, |r - r'|^{-1} |r - r''|^{-1} \\ &\quad \times \exp\{i\omega[n(\omega)|r - r'| - n^*(\omega)|r - r''|]\}. \end{aligned} \tag{3.4}$$

* In case that only a part of the sample is observed V_s should be replaced by the observed volume.

The effect due to correlations in the fluid sample and the nature of the incident beam are still hidden in the correlation function

$$\mathsf{M}(\boldsymbol{r}, \omega \mid \boldsymbol{r}', \omega') \equiv \langle \Delta \boldsymbol{p}(\boldsymbol{r}, \omega) \Delta \boldsymbol{p}^*(\boldsymbol{r}', \omega') \rangle. \tag{3.5}$$

Due to stationarity M contains a delta function $\delta(\omega - \omega')$ as was in fact already anticipated in writing eq. (3.4) both on the left-hand side and on the right-hand side. In order to simplify eq. (3.4) still further we now use the fact that the distance of the observer to the sample is sufficiently large compared to the diameter of the sample. Choosing furthermore the origin of the coordinate system in V_s we may then take the polarization $\boldsymbol{u}$ orthogonal to $\boldsymbol{r}$. One then obtains

$$I_u(\boldsymbol{r}, \omega)\, 2\pi\delta(\omega - \omega') = (4\pi r)^{-2}\, \omega^4 \int_{V_s} \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{r}''\, \boldsymbol{u} \cdot \mathsf{M}(\boldsymbol{r}', \omega \mid \boldsymbol{r}'', \omega') \cdot \boldsymbol{u}\, \mathrm{e}^{-\alpha(\omega) d_s}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_s \cdot (\boldsymbol{r}'' - \boldsymbol{r}')}, \tag{3.6}$$

where α is the extinction coefficient

$$\alpha(\omega) \equiv 2\omega\, \mathrm{Im}\, n(\omega), \tag{3.7}$$

$$d_s \equiv \tfrac{1}{2}(|\boldsymbol{r} - \boldsymbol{r}'| + |\boldsymbol{r} - \boldsymbol{r}''|) \tag{3.8}$$

and

$$\boldsymbol{k}_s \equiv \omega\, \mathrm{Re}\, n(\omega)\, \boldsymbol{r}/r. \tag{3.9}$$

In practice the extinction coefficient is usually very small inside the sample and zero outside the sample in which case the corresponding exponential damping factor may be replaced by unity. Very close to the critical point, however, one may not neglect α inside the sample and one should replace d_s by the average of the distances from $\boldsymbol{r}'$ and $\boldsymbol{r}''$ to the surface of the sample in the direction of the observer, α still being zero outside the sample. We will come back to this in the discussion of single- and multiple-scattering in sections 6 and 7.

4. *The scattering intensity in terms of density-fluctuation correlation functions.* In this section we will relate the scattering intensity to fluctuations in the density. In ref. 12 we have derived on a molecular basis for a fluid consisting of polarizable point dipoles with polarizability α_0 a relation for the fluctuating dielectric tensor $\boldsymbol{\varepsilon}_b$ in terms of the molecular density

$$\varrho(\boldsymbol{r}, t) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i(t)), \tag{4.1}$$

where $\boldsymbol{r}_i(t)$ is the position of particle i at time t. This relation is the following

$$\boldsymbol{\varepsilon}_b = 1 + \alpha_0 \varrho\, (1 - \mathsf{G}\alpha_0 \varrho)^{-1}, \tag{4.2}$$

where G is an operator which is defined in appendix B (*cf.* also ref. 12). For density fields $\varrho(r, t)$ which vary slowly in space and time compared to the molecular diameter, *i.e.* for the long-wavelength small-frequency components of the molecular density, eq. (4.2) reduces to, *cf.* appendix B,

$$\varepsilon_b(r, t) = 1 + \alpha_0 \varrho(r, t)\,[1 - \tfrac{1}{3}\alpha_0 \varrho(r, t)]^{-1}, \tag{4.3}$$

which is the relation of Clausius–Mossotti on the fluctuation level.

For many considerations it is sufficient to use the simpler eq. (4.3) rather than the exact relation eq. (4.2). We will therefore base our further developments in the body of the paper on eq. (4.3) and discuss the modifications arising from the use of eq. (4.2) in appendix B. Whereas ε_b as given in eq. (4.2) is an operator which is neither diagonal in (r, t) nor in (k, ω) representation, ε_b as given in eq. (4.3) is diagonal in (r, t) representation and a scalar.

We now introduce the so-called Clausius–Mossotti tensor γ by

$$\varepsilon \equiv 1 + \gamma \cdot (1 - \tfrac{1}{3}\gamma)^{-1}, \qquad \gamma = 3(\varepsilon - 1) \cdot (\varepsilon + 2)^{-1}. \tag{4.4}$$

Similarly eq. (4.3) defines a fluctuating Clausius–Mossotti function as

$$\gamma_b \equiv \alpha_0 \varrho = 3(\varepsilon_b - 1)(\varepsilon_b + 2)^{-1}. \tag{4.5}$$

We shall also use

$$\Delta\gamma_b \equiv \gamma_b - \gamma = \alpha_0 \varrho - \gamma, \tag{4.6}$$

$$\Delta\varepsilon_b \equiv \varepsilon_b - \varepsilon. \tag{4.7}$$

With some straightforward algebra, see appendix B, one finds the following identity

$$\Delta\varepsilon_b \cdot (1 + \mathsf{F}_\varepsilon \cdot \Delta\varepsilon_b)^{-1} = \tfrac{1}{9}(\varepsilon + 2) \cdot \Delta\gamma_b \cdot (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \cdot (\varepsilon + 2), \tag{4.8}$$

where K is defined by

$$\mathsf{K} \equiv \tfrac{1}{9}(\varepsilon + 2) \cdot [\mathsf{F}_\varepsilon - (\varepsilon + 2)^{-1}] \cdot (\varepsilon + 2). \tag{4.9}$$

We note that in the limit of low densities, when ε reduces to unity, K reduces to $\mathsf{T} \equiv \mathsf{F} - \frac{1}{3}$ which is the familiar propagator used in low-density scattering theory and which excludes self-polarization effects.

The correlation function M appearing in the scattering intensity, eq. (3.6), may now be written in terms of the fluctuations of the Clausius–Mossotti tensor $\Delta\gamma_b$

using eqs. (2.15), (3.5) and (4.8),

$$\mathsf{M}(\boldsymbol{r}, \omega \mid \boldsymbol{r}', \omega') = 3^{-4} \langle [(\varepsilon + 2) \cdot \Delta\gamma_b \cdot (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \cdot (\varepsilon + 2) \cdot \boldsymbol{E}](\boldsymbol{r}, \omega) \times [(\varepsilon + 2) \cdot \Delta\gamma_b \cdot (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \cdot (\varepsilon + 2) \cdot \boldsymbol{E}]^*(\boldsymbol{r}', \omega') \rangle. \tag{4.10}$$

In order to eliminate $\Delta\gamma_b$ in this formula in terms of the density and correlation functions of the density we need an expression for γ in terms of these correlation functions. Such an expression is obtained by substitution of eq. (4.8) into eq. (2.16) which gives

$$\langle \Delta\gamma_b \cdot (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle = 0. \tag{4.11}$$

Using also eq. (4.6) one then obtains for γ

$$\gamma = \langle \alpha_0 \varrho (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle \cdot \langle (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle^{-1} = \alpha_0 \varrho_0 + \langle \alpha_0 \Delta\varrho (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle \cdot \langle (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle^{-1}, \tag{4.12}$$

where

$$\Delta\varrho \equiv \varrho - \langle \varrho \rangle \equiv \varrho - \varrho_0. \tag{4.13}$$

In ref. 12 we found an expression for γ equivalent to eq. (4.12) which was used to calculate ε up to second order in $\Delta\varrho$.

The fluctuation in the Clausius–Mossotti tensor is now given by

$$\Delta\gamma_b = \alpha_0 \Delta\varrho - \langle \alpha_0 \Delta\varrho (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle \cdot \langle (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \rangle^{-1}. \tag{4.14}$$

Solving this equation by iteration one obtains an expression for $\Delta\gamma_b$ in terms of $\Delta\varrho$ and density-fluctuation correlation functions. This then leads, upon substitution in M as given in eq. (4.10), to an expansion of the scattering intensity in terms of density-fluctuation correlation functions. In the next section we will perform this program to fourth order in the density fluctuations, $\alpha_0 \Delta\varrho$.

5. *Expansion of the scattering intensity to fourth order in the density fluctuations.* In order to obtain an expansion to fourth order in the density fluctuations $\Delta\varrho$ it is sufficient to evaluate $\Delta\gamma_b$ up to third order. Eq. (4.14) yields to this order

$$\Delta\gamma_b = \alpha_0 \Delta\varrho + \alpha_0^2 \langle \Delta\varrho \mathsf{K} \Delta\varrho \rangle - \alpha_0^3 \langle \Delta\varrho \mathsf{K} \cdot \Delta\varrho \mathsf{K} \Delta\varrho \rangle. \tag{5.1}$$

The corresponding result for γ is

$$\gamma = \alpha_0 \varrho_0 - \alpha_0^2 \langle \Delta\varrho \mathsf{K} \Delta\varrho \rangle + \alpha_0^3 \langle \Delta\varrho \mathsf{K} \cdot \Delta\varrho \mathsf{K} \Delta\varrho \rangle. \tag{5.2}$$

This yields for ε using eq. (4.4) up to the same order

$$\varepsilon = \varepsilon_0 - \tfrac{1}{9}\alpha_0^2(\varepsilon_0 + 2)^2 \langle \Delta\varrho \mathsf{K} \Delta\varrho \rangle + \tfrac{1}{9}\alpha_0^3(\varepsilon_0 + 2)^2 \langle \Delta\varrho \mathsf{K} \cdot \Delta\varrho \mathsf{K} \Delta\varrho \rangle, \tag{5.3}$$

where

$$\varepsilon_0 = 1 + \alpha_0\varrho_0(1 - \tfrac{1}{3}\alpha_0\varrho_0)^{-1}. \tag{5.4}$$

In fact the third-order term in $\Delta\gamma_b$ in eq. (5.1) does not contribute to M up to fourth order.

Expanding eq. (4.10) for M up to the fourth power in $\Delta\gamma_b$

$$\begin{aligned}
&\mathsf{M}(\boldsymbol{r}, \omega \mid \boldsymbol{r}', \omega') \\
&= 3^{-4}\{\langle [(\varepsilon + 2) \cdot (\Delta\gamma_b - \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b + \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b) \\
&\quad \cdot (\varepsilon + 2) \cdot \boldsymbol{E}](\boldsymbol{r}, \omega) \\
&\quad \times [(\varepsilon + 2) \cdot (\Delta\gamma_b - \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b + \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b \cdot \mathsf{K} \cdot \Delta\gamma_b) \\
&\quad \cdot (\varepsilon + 2) \cdot \boldsymbol{E}]^*(\boldsymbol{r}', \omega') \rangle\}.
\end{aligned} \tag{5.5}$$

An expansion in $\alpha_0 \Delta\varrho$ is now obtained upon substitution of eq. (5.1) for $\Delta\gamma_b$. Up to fourth order M may then be written as

$$\mathsf{M} = \mathsf{M}_{11} + \mathsf{M}_{12} + \mathsf{M}_{21} + \mathsf{M}_{13} + \mathsf{M}_{31} + \mathsf{M}_{22}, \tag{5.6}$$

where M_{ij} contains all contributions with an ith power of $\Delta\varrho$ in the first square bracket and a jth power in the second. M_{ij} is therefore of $(i + j)$th power in $\Delta\varrho$. The intensity corresponding to M_{ij} will be interpreted as due to the interference between the ith-order and the jth-order scattered fields. One thus finds:

single–single (single scattering)

$$\mathsf{M}_{11} = 3^{-4}\alpha_0^2 \langle [(\varepsilon + 2) \cdot \Delta\varrho\,(\varepsilon + 2) \cdot \boldsymbol{E}]\,[(\varepsilon + 2) \cdot \Delta\varrho\,(\varepsilon + 2) \cdot \boldsymbol{E}]^* \rangle, \tag{5.7}$$

single–double

$$\mathsf{M}_{12} = -3^{-4}\alpha_0^3(\varepsilon_0 + 2)^4 \langle (\Delta\varrho \boldsymbol{E})(\Delta\varrho \mathsf{K} \cdot \Delta\varrho \boldsymbol{E})^* \rangle. \tag{5.8}$$

In this term ε has been replaced by the constant ε_0, the difference being of second order in $\alpha_0 \Delta\varrho$, *cf.* eq. (5.3). This would give rise to a fifth-order term in $\alpha_0 \Delta\varrho$ in the scattering intensity and may therefore be neglected. The same approximation may be used in the other higher-order terms. We have also omitted a term which involves the average of $\Delta\varrho$ and is therefore zero. Note that additional local-field corrections are contained in the propagator K, *cf.* eq. (4.9).

Double–Single

$$M_{21} = -3^{-4}\alpha_0^3(\varepsilon_0 + 2)^4 \langle(\Delta\varrho K \cdot \Delta\varrho E)(\Delta\varrho E)^*\rangle = M_{12}^\dagger. \tag{5.9}$$

The dagger indicates the hermitian conjugate.

Single–Triple

$$\begin{aligned} M_{13} = {} & 3^{-4}\alpha_0^4(\varepsilon_0 + 2)^4 \\ & \times \langle(\Delta\varrho E)[(\Delta\varrho K \cdot \Delta\varrho K \cdot \Delta\varrho - \Delta\varrho K \cdot \langle\Delta\varrho K \cdot \Delta\varrho\rangle \\ & - \langle\Delta\varrho K \cdot \Delta\varrho\rangle K \cdot \Delta\varrho) E]^*\rangle, \end{aligned} \tag{5.10}$$

where again a term proportional to $\langle\Delta\varrho\rangle = 0$ does not contribute.

Triple–Single

$$M_{31} = M_{13}^\dagger. \tag{5.11}$$

Double–Double (double scattering)

$$\begin{aligned} M_{22} = {} & 3^{-4}\alpha_0^4(\varepsilon_0 + 2)^4 \\ & \times \langle[(\Delta\varrho K \cdot \Delta\varrho - \langle\Delta\varrho K \cdot \Delta\varrho\rangle) E][(\Delta\varrho K \cdot \Delta\varrho - \langle\Delta\varrho K \cdot \Delta\varrho\rangle) E]^*\rangle. \end{aligned} \tag{5.12}$$

The use of the concepts single and double scattering is often confusing. In fact the meaning of these concepts is not the same if one expands in ϱ rather than in $\Delta\varrho$ as is done here. In the conventional theories of multiple scattering terms corresponding to those containing averages between parentheses, in eqs. (5.10) and (5.12), do not occur. These terms originate in the fact that we expanded ε_b in $\Delta\varrho$ around ε rather than around ε_0, the fluctuating dielectric constant at the average density. As a consequence, the so-called shadow or secular contributions*, which represent the renormalization of the dielectric tensor ε and the propagator K in the lower-order intensities, are subtracted from the higher-order intensities right from the start. We will come back to this point at the end of this section. Note furthermore that the contributions corresponding to M_{13} and M_{31} to the intensity, which correspond to the interference between the single- and triple-scattered fields, are in principle of the same order as the double-scattering contribution. It is therefore in principle not correct to neglect these contributions when discussing double scattering. As we will show, they do not contribute, however, to the depolarized scattered intensity.

* The name shadow contribution was suggested to us by professor R. Glauber. These contributions are connected with the attenuation of electromagnetic fields before, between and after scattering events.

In order to evaluate the single-scattering intensity one needs the two-point density-fluctuation correlation function

$$\langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_2, \omega_2)\rangle = (2\pi)^4 \varrho_0^2 S(\boldsymbol{k}_1, \omega_1)\, \delta(\boldsymbol{k}_1 + \boldsymbol{k}_2)\, \delta(\omega_1 + \omega_2). \quad (5.13)$$

For the higher-order terms one needs the three- and four-point correlation functions. In the gaussian approximation

$$\langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_2, \omega_2)\, \Delta\varrho(\boldsymbol{k}_3, \omega_3)\rangle = 0, \quad (5.14)$$

$$\begin{aligned}
&\langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_2, \omega_2)\, \Delta\varrho(\boldsymbol{k}_3, \omega_3)\, \Delta\varrho(\boldsymbol{k}_4, \omega_4)\rangle \\
&\quad = \langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_2, \omega_2)\rangle \langle \Delta\varrho(\boldsymbol{k}_3, \omega_3)\, \Delta\varrho(\boldsymbol{k}_4, \omega_4)\rangle \\
&\qquad + \langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_3, \omega_3)\rangle \langle \Delta\varrho(\boldsymbol{k}_2, \omega_2)\, \Delta\varrho(\boldsymbol{k}_4, \omega_4)\rangle \\
&\qquad + \langle \Delta\varrho(\boldsymbol{k}_1, \omega_1)\, \Delta\varrho(\boldsymbol{k}_4, \omega_4)\rangle \langle \Delta\varrho(\boldsymbol{k}_2, \omega_2)\, \Delta\varrho(\boldsymbol{k}_3, \omega_3)\rangle, \\
&\quad = (2\pi)^8 \varrho_0^4 [S(\boldsymbol{k}_1, \omega_1)\, S(\boldsymbol{k}_3, \omega_3)\, \delta(\boldsymbol{k}_1 + \boldsymbol{k}_2)\, \delta(\boldsymbol{k}_3 + \boldsymbol{k}_4)\, \delta(\omega_1 + \omega_2) \\
&\qquad \times \delta(\omega_3 + \omega_4) + S(\boldsymbol{k}_1, \omega_1)\, S(\boldsymbol{k}_2, \omega_2)\, \delta(\boldsymbol{k}_1 + \boldsymbol{k}_3)\, \delta(\boldsymbol{k}_2 + \boldsymbol{k}_4) \\
&\qquad \times \delta(\omega_1 + \omega_3)\, \delta(\omega_2 + \omega_4) + S(\boldsymbol{k}_1, \omega_1)\, S(\boldsymbol{k}_2, \omega_2)\, \delta(\boldsymbol{k}_1 + \boldsymbol{k}_4)\, \delta(\boldsymbol{k}_2 + \boldsymbol{k}_3) \\
&\qquad \times \delta(\omega_1 + \omega_4)\, \delta(\omega_2 + \omega_3)]. \quad (5.15)
\end{aligned}$$

This approximation is in general only correct for small, hydrodynamic wavevectors and frequencies. For larger wavevectors and frequencies it is not strictly valid and one should in principle substitute the full three- and four-point correlation functions into eqs. (5.8)–(5.12). For the study of critical scattering, however, the gaussian approximation will turn out to be well suited. In our further discussion we shall restrict ourselves to this approximation. Upon substitution of eqs. (5.14) and (5.15) into eqs. (5.8)–(5.12) one obtains

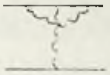
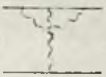
$$\mathsf{M}_{12} = \mathsf{M}_{21} = 0, \quad (5.16)$$

$$\mathsf{M}_{13} = \mathsf{M}_{31}^{\dagger} = 3^{-4}\alpha_0^4 (\varepsilon_0 + 2)^4 \langle \overbrace{[\Delta\varrho E]\, [\Delta\varrho \mathsf{K} \cdot \Delta\varrho \mathsf{K} \cdot \Delta\varrho E]^*}\rangle, \quad (5.17)$$

$$\begin{aligned}
\mathsf{M}_{22} &= 3^{-4}\alpha_0^4 (\varepsilon_0 + 2)^4 \\
&\quad \times (\langle \overbrace{[\Delta\varrho \mathsf{K} \cdot \Delta\varrho E]\, [\Delta\varrho \mathsf{K} \cdot \Delta\varrho E]^*}\rangle + \langle \overbrace{[\Delta\varrho \mathsf{K} \cdot \Delta\varrho E]\, [\Delta\varrho \mathsf{K} \cdot \Delta\varrho E]^*}\rangle),
\end{aligned} \quad (5.18)$$

where the notation implies that only $\Delta\varrho$'s connected by lines are correlated with each other. In the following sections we will study the intensities corresponding to M_{11}, M_{13}, M_{31} and M_{22} in more detail.

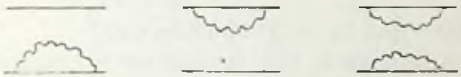
Finally we will shortly discuss a diagrammatic representation of the various contributions to the multiple-scattering intensities. In the diagrams the terms between the square brackets are represented by two straight lines, the $\Delta\varrho$'s by points on these two lines and the propagators K by the line segments connecting these points; the $\Delta\varrho$'s which are correlated are connected by wiggly lines. In terms of diagrams eqs. (5.7), (5.17) and (5.18) become

$M_{11} =$  , $M_{13} =$  , $M_{31} =$  ,

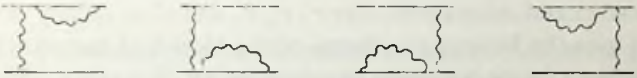
$M_{22} =$  +  . (5.19)

Using the diagrammatic representation it is in fact possible to write M_{ij} down to any order. One may furthermore develop some kind of "Feynman rules" by assigning wavevectors and frequencies to the lines, *etc.*

The shadow or secular contributions, see the discussion after eq. (5.12), may also be represented by diagrams. One may then verify that the following diagrams



have been absorbed in the beam (zeroth-order scattering), whereas the contributions



have been absorbed into the single-scattering intensity.

6. *Single scattering.* If one would replace ε by ε_0 in the single-scattering intensity one would obtain the usual result, which is correct up to the second order in the density fluctuations, and which was first derived by Einstein[1]). In this section we will investigate how these results are affected if one does not replace ε by ε_0. The physical interpretation of the difference is simply that the light passes through the fluctuating medium rather than through the medium at the average density before and after being scattered. We will consider the case that the beam is a plane wave which is given by

$$\boldsymbol{E}(r, \omega) = \boldsymbol{E}_0 \, e^{i\boldsymbol{k}_0 \cdot r} \, 2\pi\delta(\omega - \omega_0)$$

$$\text{with} \quad k_0 = n(\omega_0)\,\omega_0 \quad \text{and} \quad \boldsymbol{E}_0 \cdot \boldsymbol{k}_0 = 0. \tag{6.1}$$

The single-scattering intensity is then obtained by substitution of eq. (6.1) and (5.7) into eq. (3.6) which yields

$$
\begin{aligned}
&I_u^{11}(\boldsymbol{r}, \omega)\, 2\pi\delta(\omega - \omega') \\
&\quad = (4\pi r)^{-2}\, \omega^4 3^{-4} \alpha_0^2 \int_{V_s} \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{r}''\, \mathrm{e}^{-\lambda(\omega) d_s} \\
&\qquad \times \int_{V_s} \mathrm{d}\boldsymbol{r}_1'\, \mathrm{d}\boldsymbol{r}_2'\, \mathrm{d}\boldsymbol{r}_1''\, \mathrm{d}\boldsymbol{r}_2'' \,\langle [\boldsymbol{u}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}_s \cdot \boldsymbol{r}'} \cdot (\varepsilon + 2)(\boldsymbol{r}' - \boldsymbol{r}_1', \omega)\, \Delta\varrho(\boldsymbol{r}_1', \omega - \omega_0) \\
&\qquad \cdot (\varepsilon + 2)(\boldsymbol{r}_1' - \boldsymbol{r}_2', \omega_0) \cdot \boldsymbol{E}_0\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_0 \cdot \boldsymbol{r}_2'}] \\
&\qquad \times [\boldsymbol{u}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}_s \cdot \boldsymbol{r}''} \cdot (\varepsilon + 2)(\boldsymbol{r}'' - \boldsymbol{r}_1'', \omega')\, \Delta\varrho(\boldsymbol{r}_1'', \omega' - \omega_0) \\
&\qquad \cdot (\varepsilon + 2)(\boldsymbol{r}_1'' - \boldsymbol{r}_2'', \omega_0) \cdot \boldsymbol{E}_0\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_0 \cdot \boldsymbol{r}_2''}]^* \rangle .
\end{aligned} \tag{6.2}
$$

In writing this equation we have used the fact that $\Delta\varrho$ is diagonal in $\boldsymbol{r}$ and a convolution operator in ω whereas ε is a convolution operator in $\boldsymbol{r}$ and diagonal in ω. Furthermore we performed two integrations over frequencies using the δ functions in the fields, eq. (6.1). We shall now also use the fact that

$$
\varepsilon(\boldsymbol{r}, \omega) = \varepsilon_0 \delta(\boldsymbol{r}) - \tfrac{1}{9}\alpha_0^2 (\varepsilon_0 + 2)^2\, S(\boldsymbol{r})\, \mathsf{K}(\boldsymbol{r}, \omega) \rho_0^2
$$

will go to zero if $\boldsymbol{r}$ is of the order of the typical fluid correlation length (see also ref. 12 where we calculate ε to the second order in the density fluctuations), which is much smaller than the diameter of the system. Neglecting surface effects one may therefore extend integrations over $\boldsymbol{r}'$, $\boldsymbol{r}''$, $\boldsymbol{r}_2'$ and $\boldsymbol{r}_2''$ to infinity in which case they simply give the Fourier transforms of the local-field factors. Furthermore one may replace ε by its transverse part because $\boldsymbol{u}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}_s \cdot \boldsymbol{r}}$ and $\boldsymbol{E}_0\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_0 \cdot \boldsymbol{r}}$ represent transverse fields. The intensity then becomes

$$
\begin{aligned}
&I_u^{11}(\boldsymbol{r}, \omega)\, 2\pi\delta(\omega - \omega') \\
&\quad = (4\pi r)^{-2}\, \omega^4 3^{-4} \alpha_0^2\, |[n^2(\omega) + 2]\, [n^2(\omega_0) + 2]\, (\boldsymbol{E}_0 \cdot \boldsymbol{u})|^2 \\
&\qquad \times \int_{V_s} \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{r}''\, \exp\{-[\alpha(\omega)\, d_s + \alpha(\omega_0)\, d_0] - \mathrm{i}\,(\boldsymbol{k}_s - \boldsymbol{k}_0') \cdot (\boldsymbol{r}' - \boldsymbol{r}'')\} \\
&\qquad \times \langle \Delta\varrho(\boldsymbol{r}', \omega - \omega_0)\, \Delta\varrho^*(\boldsymbol{r}'', \omega' - \omega_0) \rangle .
\end{aligned} \tag{6.3}
$$

In writing $n^2(\omega)$ instead of $\varepsilon_{\mathrm{tr}}[\mathrm{Re}\, n(\omega)\, \omega, \omega]$ we have used the fact that the resulting difference in the factor $|n^2(\omega) + 2|^2$ is of the fourth order in $\Delta\varrho$. The length d_0 and the wavevector $\boldsymbol{k}_0'$ are defined by

$$
d_0 \equiv \tfrac{1}{2} k_0^{-1} \boldsymbol{k}_0 \cdot (\boldsymbol{r}' + \boldsymbol{r}'') \qquad \text{and} \qquad \boldsymbol{k}_0' \equiv \mathrm{Re}\, \boldsymbol{k}_0 . \tag{6.4}
$$

In the experimental situation there is usually no attenuation outside the sample. In that case it is most convenient to use for E_0 the amplitude of the beam just after entering the sample so that E_0^2 is the intensity of the incident beam; d_0 is in that case the average distance from r' and r'' to the surface pointing backward along the direction of the beam. The factor $\exp[-\alpha(\omega_0)\, d_0]$ accounts for the decrease in the intensity of the incident light between the point where it enters the sample and the point where the scattering takes place. Similarly the factor $\exp[-\alpha(\omega)\, d_s]$ accounts for the decrease in the intensity of the scattered light between the point where the scattering takes place and the point where the scattered light leaves the sample. The density–density fluctuation correlation function is function of $r' - r''$ alone. Its Fourier transform is given in eq. (5.13). For $|r' - r''|$ larger than the typical fluid correlation length the correlation function goes to zero. One may therefore again in eq. (6.3) extend the integration over r' to infinity. Furthermore one may replace r' by r'' in the definition of d_s and d_0 because the attenuation over a typical correlation length is very small, *cf.* ref. 12.

The integrations may then be performed and yield

$$I_u^{11}(r, \omega) = (4\pi r)^{-2}\, \omega^4 3^{-4} \alpha_0^2 \varrho_0^2\, |[n^2(\omega) + 2]\,[n^2(\omega_0) + 2]|^2$$

$$\times\, I_0 \cos^2\theta V_s^{\alpha} S(k_s - k_0, \omega - \omega_0), \tag{6.5}$$

in which I_0 is the intensity of the incident light, θ the angle between E_0 and u and where

$$V_s^{\alpha} \equiv \int_{V_s} \mathrm{d}r \exp[-\alpha(\omega)\, d_s - \alpha(\omega_0)\, d_0], \tag{6.6}$$

where d_s is the distance from r to the surface in the direction of the observer and where d_0 is the distance from r to the surface in the direction of the light source. If only a part of the sample is illuminated and observed one should replace V_s in eq. (6.6) by the cross section of the illuminated and the observed volume of the sample; this should of course not be done in the definition of d_s and d_0. If the attenuation is sufficiently small, *i.e.* not to close to the critical point, V_s^{α} reduces simply to V_s. The difference between V_s^{α} and V_s becomes important, however, and will introduce further angular dependences depending on the geometry of the sample, if one is quite close to the critical point[15]). In practice one may always replace $\alpha(\omega)$ by $\alpha(\omega_0)$ in eq. (6.6) and $n(\omega)$ by $n(\omega_0)$ in eq. (6.5) using the fact that S in eq. (6.5) is very sharply peaked around $\omega = \omega_0$.

7. *The intensity due to the interference between the single- and triple-scattered light.* The intensity resulting from the interference between the single- and triple-scattered light is also of fourth order in $\Delta\varrho$ and should in principle therefore be calculated along with the double-scattering intensity. Substitution of M^{31} and E,

as given in eqs. (5.17) and (6.1), into eq. (3.6) yields

$$I_u^{31}(r,\omega)\,2\pi\delta(\omega-\omega')$$

$$= (4\pi r)^{-2}\,\omega^4 3^{-4}\alpha_0^4\,(\varepsilon_0+2)^4 \int_V \mathrm{d}r'\,\mathrm{d}r''\,\mathrm{d}r_1'\,\mathrm{d}r_2'$$

$$\times \int \mathrm{d}\omega_1\,\mathrm{d}\omega_2\,(2\pi)^{-2}\exp\left[-\mathrm{i}k_s\cdot(r'-r'')+\mathrm{i}k_0\cdot(r_2'-r'')\right]$$

$$\times \langle [u\,\Delta\varrho\,(r',\omega-\omega_1)\cdot \mathsf{K}\,(r'-r_1',\omega_1)\,\Delta\varrho\,(r_1',\omega_1-\omega_2)\cdot \mathsf{K}\,(r_1'-r_2',\omega_2)\,\Delta\varrho\,(r_2',\omega_2-\omega_0)\cdot E_0]$$

$$[u\,\Delta\varrho\,(r'',\omega'-\omega_0)\cdot E_0]^*\rangle, \tag{7.1}$$

where we have used the fact that the attenuation α is of second order in $\Delta\varrho$ and may therefore be neglected*. Similarly one may use ε_0 rather than ε in k_s, k_0 and K. Futhermore I_u^{13} is simply given by the complex conjugate

$$I_u^{13}(r,\omega) = [I_u^{31}(r,\omega)]^*. \tag{7.2}$$

Substitution of the density-fluctuation correlation functions gives

$$I_u^{31}(r,\omega) = (4\pi r)^{-2}\,\omega^4 3^{-4}\,(\alpha_0\varrho_0)^4\,(\varepsilon_0+2)^4\cos\theta I_0 \int_{V_s} \mathrm{d}r'\,\mathrm{d}r''\,\mathrm{d}r_1'\,\mathrm{d}r_2'$$

$$\times \int \mathrm{d}\omega_1\,(2\pi)^{-1}\exp\left[-\mathrm{i}k_s\cdot(r'-r'')+\mathrm{i}k_0\cdot(r_2'-r'')\right]$$

$$\times [u\cdot \mathsf{K}\,(r'-r_1',\omega_1)\cdot \mathsf{K}\,(r_1'-r_2',\omega_1+\omega_0-\omega)\cdot u_0]$$

$$\times S\,(r'-r_2',\omega-\omega_1)\,S\,(r_1'-r'',\omega-\omega_0), \tag{7.3}$$

where θ is again the angle between u and E_0 and where u_0 is a unit vector in the direction of E_0. Using furthermore that the correlation functions go to zero if the separation is large compared to the correlation length and the fact that this correlation length is in general much smaller than the diameter of the sample one may extend the integrations over r' and r'' to infinity. One then finds

$$I_u^{31}(r,\omega) = (4\pi r)^{-2}\,\omega^4\,(\varepsilon_0-1)^4\cos\theta I_0 S\,(k_s-k_0,\omega-\omega_0)\,V_s^{31}, \tag{7.4}$$

where V_s^{31} is a factor with the dimension of a volume which is given by

$$V_s^{31} \equiv (2\pi)^{-4}\int \mathrm{d}k\,\mathrm{d}\omega_1 u\cdot \mathsf{K}\,(k,\omega_1)\,S\,(k_s-k,\omega-\omega_1)$$

$$\times \int_{V_s} \mathrm{d}r_1\,\mathrm{d}r_2\exp\left[\mathrm{i}\,(k_0+k-k_s)\cdot(r_2-r_1)\right]$$

$$\cdot \mathsf{K}\,(r_1-r_2,\omega_1+\omega_0-\omega)\cdot u_0 \tag{7.5}$$

* This approximation is not always justified as we shall discuss in our second paper.

and contains through K, *cf.* eq. (4.9), local-field correction factors. In this factor one may use the static approximation for S in the integration

$$S(\boldsymbol{k}, \omega) = S(\boldsymbol{k})\, 2\pi\delta(\omega) \tag{7.6}$$

because the typical fluid velocities are small compared to the velocity of light. This gives

$$V_s^{31} = (2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}\, \boldsymbol{u} \cdot \mathsf{K}(\boldsymbol{k}, \omega)\, S(\boldsymbol{k}_s - \boldsymbol{k}) \cdot \int_{V_s} \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2 \exp\left[\mathrm{i}(\boldsymbol{k}_0 + \boldsymbol{k} - \boldsymbol{k}_s) \cdot (\boldsymbol{r}_2 - \boldsymbol{r}_1)\right] \mathsf{K}(\boldsymbol{r}_1 - \boldsymbol{r}_2, \omega_0) \cdot \boldsymbol{u}_0. \tag{7.7}$$

In a future paper we shall evaluate this contribution to the intensity in detail. We shall now therefore limit ourselves to a few general remarks. In the first place, as a consequence of the cos 0, I_u^{31} (and I_u^{13}) will not contribute to depolarized scattering. Because of this fact it will in general not be possible to separate these small contributions from the single-scattering intensity. These contributions are therefore not very important, except possibly in the critical region. If only a part of the sample is illuminated and observed V_s in eq. (7.7) should be replaced by the cross section of the illuminated and observed volume of the sample.

8. *Double scattering.* The double-scattering intensity contains two contributions. Substituting eqs. (5.13) and (5.18) and (6.1) into eq. (3.6) one obtains similarly to the discussion in section 7

$$I_{u,1}^{22}(\boldsymbol{r}, \omega) = \quad = I_0 (4\pi r)^{-2} \omega^4 (\varepsilon_0 - 1)^4 \times \int_{V_s} \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{r}''\, \mathrm{d}\boldsymbol{r}_1'\, \mathrm{d}\boldsymbol{r}_1'' \int \mathrm{d}\omega_1 (2\pi)^{-1} \times \exp\left[-\mathrm{i}\boldsymbol{k}_s \cdot (\boldsymbol{r}' - \boldsymbol{r}'') + \mathrm{i}\boldsymbol{k}_0 \cdot (\boldsymbol{r}_1' - \boldsymbol{r}_1'')\right] \times \left[\boldsymbol{u} \cdot \mathsf{K}(\boldsymbol{r}' - \boldsymbol{r}_1', \omega_1) \cdot \boldsymbol{u}_0\right] \left[\boldsymbol{u} \cdot \mathsf{K}(\boldsymbol{r}'' - \boldsymbol{r}_1'', \omega_1) \cdot \boldsymbol{u}_0\right]^* \times S(\boldsymbol{r}' - \boldsymbol{r}'', \omega - \omega_1)\, S(\boldsymbol{r}_1' - \boldsymbol{r}_1'', \omega_1 - \omega_0) \tag{8.1}$$

and

$$I_{u,2}^{22}(\boldsymbol{r}, \omega) = \quad = I_0 (4\pi r)^{-2} \omega^4 (\varepsilon_0 - 1)^4 \times \int_{V_s} \mathrm{d}\boldsymbol{r}'\, \mathrm{d}\boldsymbol{r}''\, \mathrm{d}\boldsymbol{r}_1'\, \mathrm{d}\boldsymbol{r}_1'' \int \mathrm{d}\omega_1 (2\pi)^{-1} \times \exp\left[-\mathrm{i}\boldsymbol{k}_s \cdot (\boldsymbol{r}' - \boldsymbol{r}'') + \mathrm{i}\boldsymbol{k}_0 \cdot (\boldsymbol{r}_1' - \boldsymbol{r}_1'')\right] \left[\boldsymbol{u} \cdot \mathsf{K}(\boldsymbol{r}' - \boldsymbol{r}_1', \omega_1) \cdot \boldsymbol{u}_0\right] \times \left[\boldsymbol{u} \cdot \mathsf{K}(\boldsymbol{r}'' - \boldsymbol{r}_1'', \omega - \omega_1 + \omega_0) \cdot \boldsymbol{u}_0\right]^* \times S(\boldsymbol{r}' - \boldsymbol{r}_1'', \omega - \omega_1)\, S(\boldsymbol{r}_1' - \boldsymbol{r}'', \omega_1 - \omega_0). \tag{8.2}$$

Using again the fact that the correlation length is small compared to the diameter of the system two of the integrations over the volume may be extended to infinity so that one obtains

$$I^{22}_{u,1}(r,\omega) = I_0 (4\pi r)^{-2} \omega^4 (\varepsilon_0 - 1)^4 (2\pi)^{-4}$$
$$\times \int \mathrm{d}k \, \mathrm{d}\omega_1 \, [u \cdot \mathsf{K}(k,\omega_1) \cdot u_0] \, S(k_s - k, \omega - \omega_1) \, S(k - k_0, \omega_1 - \omega_0)$$
$$\times \int_{V_s} \mathrm{d}r' \, \mathrm{d}r'' \exp[\mathrm{i}k \cdot (r' - r'')] \, [u \cdot \mathsf{K}(r' - r'', \omega_1) \cdot u_0]^* \qquad (8.3)$$

and

$$I^{22}_{u,2}(r,\omega) = I_0 (4\pi r)^{-2} \omega^4 (\varepsilon_0 - 1)^4 (2\pi)^{-4}$$
$$\times \int \mathrm{d}k \, \mathrm{d}\omega_1 \, [u \cdot \mathsf{K}(k,\omega_1) \cdot u_0] \, S(k_s - k, \omega - \omega_1) \, S(k - k_0, \omega_1 - \omega_0)$$
$$\times \int_{V_s} \mathrm{d}r' \, \mathrm{d}r'' \exp[\mathrm{i}(k_s + k_0 - k) \cdot (r' - r'')]$$
$$\times [u \cdot \mathsf{K}(r' - r'', \omega + \omega_0 - \omega_1) \cdot u_0]^*. \qquad (8.4)$$

In a future paper we shall evaluate these contributions in detail. If only a part of the sample is illuminated or observed one should limit the r' integration in eq. (8.3) to the observed part of the sample and the r'' integration to the illuminated part of the sample. In eq. (8.4), however, both integrations should be over the cross section of the illuminated and the observed part of the sample. Using the fact that S is sharply peaked in frequency compared to the propagators K one may replace the frequency arguments of K in eqs. (8.3) and (8.4) by ω_0. We furthermore recall that K contains local-field corrections, *cf.* eq. (4.9).

APPENDIX A

In this appendix we will derive the asymptotic, long-distance, behaviour of the dipole propagator F_ε in the medium. Substituting eq. (2.18) for an isotropic system into eq. (2.13) one has

$$\mathsf{F}_\varepsilon(k,\omega) = \left[(\omega^2\varepsilon_\mathrm{T} - k^2)\left(1 - \frac{kk}{k^2}\right) + \omega^2\varepsilon_\mathrm{L}\frac{kk}{k^2}\right]^{-1}\omega^2$$
$$= \omega^2(\omega^2\varepsilon_\mathrm{T} - k^2)^{-1}\left(1 - \frac{kk}{k^2}\right) + \varepsilon_\mathrm{L}^{-1}\frac{kk}{k^2}, \qquad (A.1)$$

where ω is supposed to have an infinitesimally small positive imaginary part if ε_T is real. In (r, ω) representation this propagator becomes

$$\begin{aligned} F_\varepsilon(r, \omega) &= (2\pi)^{-3} \int d\boldsymbol{k} \left[\omega^2 (\omega^2 \varepsilon_T - k^2)^{-1} \left(1 - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right) + \varepsilon_L^{-1} \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right] \exp(i\boldsymbol{k} \cdot \boldsymbol{r}) \\ &= (2\pi)^{-3} \int d\boldsymbol{k} k^{-2} \left[\omega^2 (\omega^2 \varepsilon_T - k^2)^{-1} \left(k^2 + \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} \right) \right. \\ &\quad \left. - \varepsilon_L^{-1} \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} \right] \exp(i\boldsymbol{k} \cdot \boldsymbol{r}) \\ &= (4\pi^2 i)^{-1} \int_{-\infty}^{\infty} dk k^{-1} \left[\omega^2 (\omega^2 \varepsilon_T - k^2)^{-1} \left(k^2 + \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} \right) \right. \\ &\quad \left. - \varepsilon_L^{-1} \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} \right] r^{-1} \exp(ikr). \end{aligned} \tag{A.2}$$

The integration over k may now be performed by closing the contour in the upper half plane. The possible singularities are given by the following.

i) $k = 0$: this is only an apparent singularity, because of the fact that $\varepsilon_L - \varepsilon_T = \mathcal{O}(k^2)$, *cf.* refs. 12 and 16, which makes the term between the square brackets proportional to k^2.

ii) $k^2 - \omega^2 \varepsilon_T(k, \omega) = 0$: the solutions of this equation correspond to the transverse excitations of the medium.

iii) $\varepsilon_L(k, \omega) = 0$: the solutions of this equation correspond to the longitudinal excitations. We will restrict ourselves to frequencies for which this equation has no solution, *i.e.* no propagating longitudinal modes are excited in the scattering experiment.

The integration then yields

$$F_\varepsilon(r, \omega) = -\omega^2 \left(1 + [k(\omega)]^{-2} \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} \right) (4\pi r)^{-1} \exp[ik(\omega) r], \tag{A.3}$$

where $k(\omega)$ is defined by

$$k(\omega) \equiv \omega [\varepsilon_T(k(\omega), \omega)]^{\frac{1}{2}} = \omega n(\omega). \tag{A.4}$$

For long distances, $rk(\omega) \gg 1$, only terms in F_ε proportional to $1/r$ survive, so that the propagator reduces to

$$F_\varepsilon(r, \omega) = -\omega^2 (1 - \boldsymbol{r}\boldsymbol{r}/r^2) (4\pi r)^{-1} \exp[i\omega n(\omega) r]. \tag{A.5}$$

Substitution of this equation into eq. (3.1) yields the desired eq. (3.2) for the scattered field.

APPENDIX B

In this appendix we will indicate explicitly, how the various results are affected if one uses Clausius–Mossotti on the molecular level as given in eq. (4.2) instead of the simpler long-wavelength small-frequency form given by eq. (4.3). The operator G in eq. (4.2) is given by, *cf.* ref. 12,

$$\mathsf{G}(rt \mid r't') = \mathsf{G}(r - r', t - t')$$

$$\equiv \begin{cases} 0 & \text{if} \quad |r - r'| > a, \\ \tfrac{1}{2}(\mathsf{F} + \mathsf{F}^{\dagger})(r - r', t - t') & \text{if} \quad |r - r'| < a, \end{cases} \tag{B.1}$$

where a is the molecular diameter. This operator is diagonal in (k, ω) representation. The diagonal elements have been calculated in ref. 12 and are given by

$$\mathsf{G}(k, \omega) = \tfrac{1}{3} + [f(ak, a\omega) - \tfrac{1}{3}](1 - 3\boldsymbol{kk}/k^2)$$

$$+ \omega^2 (k^2 - \omega^2)^{-1} [g(ak, a\omega) - 1](1 - \boldsymbol{kk}/k^2), \tag{B.2}$$

where

$$f(x, y) = (\cos y + y \sin y)(x^{-3} \sin x - x^{-2} \cos x), \tag{B.3}$$

$$g(x, y) = \cos x \cos y + (y/x) \sin x \sin y. \tag{B.4}$$

Note, that $\mathsf{G}(k, \omega)$ is not singular at $k^2 = \omega^2$ because the poles in $(k^2 - \omega^2)^{-1}$ are cancelled by zeros in $[g(ak, a\omega) - 1]$ at $\omega = \pm k$. For small values of k and ω, G reduces to

$$\mathsf{G}(k, \omega) = \tfrac{1}{3} \qquad \text{for} \qquad ak, a\omega \ll 1. \tag{B.5}$$

For the long-wavelength small-frequency components of the density one may therefore substitute $\frac{1}{3}$ instead of G so that eq. (4.2) reduces to eq. (4.3), which is the equation used in the body of the paper.

If one uses the more general equation (4.2) one should define the macroscopic Clausius–Mossotti tensor by

$$\boldsymbol{\varepsilon} \equiv 1 + \boldsymbol{\gamma} \cdot (1 - \mathsf{G} \cdot \boldsymbol{\gamma})^{-1}, \qquad \boldsymbol{\gamma} = (\boldsymbol{\varepsilon} - 1) \cdot [1 + \mathsf{G} \cdot (\boldsymbol{\varepsilon} - 1)]^{-1}, \tag{B.6}$$

rather than by the expression given by eq. (4.4). Similarly eq. (4.5) for the fluctuating Clausius–Mossotti function should be replaced by

$$\gamma_b \equiv \alpha_0 \varrho = (\varepsilon_b - 1) \cdot [1 + \mathsf{G} \cdot (\varepsilon_b - 1)]^{-1}. \tag{B.7}$$

The identity given in eq. (4.8) is replaced by

$$\Delta\varepsilon_b \cdot (1 + \mathsf{F}_\varepsilon \cdot \Delta\varepsilon_b)^{-1}$$

$$= (1 - \boldsymbol{\gamma} \cdot \mathsf{G})^{-1} \cdot \Delta\gamma_b \cdot (1 + \mathsf{K} \cdot \Delta\gamma_b)^{-1} \cdot (1 - \mathsf{G} \cdot \boldsymbol{\gamma})^{-1}, \tag{B.8}$$

where K is now defined by

$$K \equiv (1 - G \cdot \gamma)^{-1} \cdot [F_\varepsilon - G \cdot (1 - \gamma \cdot G)] \cdot (1 - \gamma \cdot G)^{-1}. \tag{B.9}$$

We will now proceed to prove this identity. From eqs. (B.6) and (B.7) follows

$$\begin{aligned} \Delta\varepsilon_b &= \varepsilon_b - \varepsilon = \gamma_b (1 - G\gamma_b)^{-1} - (1 - \gamma \cdot G)^{-1} \cdot \gamma \\ &= (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \cdot (1 - G\gamma_b)^{-1}. \end{aligned} \tag{B.10}$$

One then has

$$\begin{aligned} &\Delta\varepsilon_b \cdot (1 + F_\varepsilon \cdot \Delta\varepsilon_b)^{-1} \\ &= (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \cdot (1 - G\gamma_b)^{-1} \\ &\quad \cdot [1 + F_\varepsilon \cdot (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \cdot (1 - G\gamma_b)^{-1}]^{-1} \\ &= (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \cdot [1 - G\gamma_b + F_\varepsilon \cdot (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b]^{-1} \\ &= (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \\ &\quad \cdot \{1 - G \cdot \gamma + [F_\varepsilon - G \cdot (1 - \gamma \cdot G)] \cdot (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b\}^{-1} \\ &= (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b \cdot \{1 + (1 - G \cdot \gamma)^{-1} \cdot [F_\varepsilon - G \cdot (1 - \gamma \cdot G)] \\ &\quad \cdot (1 - \gamma \cdot G)^{-1} \cdot \Delta\gamma_b\}^{-1} \cdot (1 - G \cdot \gamma)^{-1}, \end{aligned} \tag{B.11}$$

which proves eq. (B.8) together with eq. (B.9). The derivation of the simpler identity given in eq. (4.8) with eq. (4.9) follows if one replaces G in eqs. (B.8) to (B.11) by $\frac{1}{3}$.

We will now show that the operator K is equal to

$$K = H \cdot (1 + \gamma \cdot H)^{-1}, \tag{B.12}$$

where

$$H \equiv F - G. \tag{B.13}$$

For this we need the following relation between the dipole propagator in the medium and in vacuum

$$F_\varepsilon = F \cdot (1 + \chi \cdot F)^{-1}. \tag{B.14}$$

This relation follows immediately from eqs. (2.7) and (2.13). If one uses eqs. (B.6) and (B.14), eq. (B.9) for K becomes

$$\begin{aligned} \mathsf{K} &= (1 - \mathsf{G}\cdot\gamma)^{-1}\cdot\{\mathsf{F}\cdot[1 + (1 - \gamma\cdot\mathsf{G})^{-1}\cdot\gamma\cdot\mathsf{F}]^{-1} \\ &\quad - \mathsf{G}\cdot(1 - \gamma\cdot\mathsf{G})\}\cdot(1 - \gamma\cdot\mathsf{G})^{-1} \\ &= (1 - \mathsf{G}\cdot\gamma)^{-1}\cdot[\mathsf{F}\cdot(1 + \gamma\cdot\mathsf{H})^{-1} - \mathsf{G}] \\ &= (1 - \mathsf{G}\cdot\gamma)^{-1}\cdot[\mathsf{F} - \mathsf{G}\cdot(1 + \gamma\cdot\mathsf{H})]\cdot(1 + \gamma\cdot\mathsf{H})^{-1} \end{aligned}$$

so that eq. (B.12) follows. If one expands in fluctuations of the density it is in many applications sufficient to replace γ in eq. (B.12) by $\alpha_0\varrho_0$. It is this form of the operator K which we used in ref. 12.

The correlation function appearing in the scattering intensity may now be written in terms of fluctuations of the Clausius–Mossotti tensor $\Delta\gamma_b$ similar to eq. (4.10) as

$$\begin{aligned} &\mathsf{M}(r, \omega \mid r', \omega') \\ &= \langle[(1 + \chi\cdot\mathsf{G})\cdot\Delta\gamma_b\cdot(1 + \mathsf{K}\cdot\Delta\gamma_b)^{-1}\cdot(1 + \mathsf{G}\cdot\chi)\cdot\boldsymbol{E}](r, \omega) \\ &\quad \times [(1 + \chi\cdot\mathsf{G})\cdot\Delta\gamma_b\cdot(1 + \mathsf{K}\cdot\Delta\gamma_b)^{-1}\cdot(1 + \mathsf{G}\cdot\chi)\cdot\boldsymbol{E}]^*(r', \omega), \end{aligned} \tag{B.15}$$

where we have used the fact, that

$$(1 - \gamma\cdot\mathsf{G})^{-1} = 1 + \chi\cdot\mathsf{G} \quad \text{and} \quad (1 - \mathsf{G}\cdot\gamma)^{-1} = 1 + \mathsf{G}\cdot\chi. \tag{B.16}$$

One may now in principle find the equations for single and multiple scattering equivalent to those used in sections 5–8 by the substitution of $(1 + \mathsf{G}\cdot\chi)$ and $(1 + \chi\cdot\mathsf{G})$ instead of the local-field correction factors $(\varepsilon + 2)/3$ used in the body of the paper. In practice, however, one may convince oneself that the factor $(1 + \mathsf{G}\cdot\chi)$ is only needed at the wavevector and frequency of the incident field $\boldsymbol{E}$ and that the factor $(1 + \chi\cdot\mathsf{G})$ is only needed at the wavevector and frequency of the scattered field. See also the discussion of a similar point in section 6. As a consequence of this one finds that eq. (4.10) and all the subsequent equations for single and multiple scattering, which we derived in the body of the paper on the basis of the "phenomenological" Clausius–Mossotti relation, eq. (4.3), are also valid if one uses Clausius–Mossotti on the molecular level, eq. (4.2). The only difference is in fact that the operator K is modified in the molecular theory for molecular wavevectors and frequencies. Using eq. (B.5) it follows that for small values of $\boldsymbol{k}$ and ω ($ak, a\omega \ll 1$) K as given by eq. (B.9) reduces to the simpler form given by eq. (4.9).

If one expands the scattering intensity to fourth order in the density fluctuations one may replace γ in eq. (B.12) for K by $\alpha_0\varrho_0$. The resulting operator is then given by, *cf.* ref. 12,

$$\mathsf{K}(k,\omega) = -(3\alpha_0\varrho_0)^{-1}\left[\theta(ak,a\omega)\left(1-\frac{\theta(ak,a\omega)+3}{\theta(ak,a\omega)+1}\,\frac{\boldsymbol{kk}}{k^2}\right)\right.$$
$$+\,[\Omega(ak,a\omega)-1]\,[\theta(ak,a\omega)+3]$$
$$\left.\times\,\omega^2\,[k^2-(\omega+\mathrm{i}0)^2\,\Omega(ak,a\omega)]^{-1}\left(1-\frac{\boldsymbol{kk}}{k^2}\right)\right], \qquad \text{(B.17)}$$

where

$$\theta(x,y) \equiv 3\alpha_0\varrho_0 f(x,y)\,[1-\alpha_0\varrho_0 f(x,y)]^{-1}, \qquad \text{(B.18)}$$

$$\Omega(x,y) - 1 \equiv \alpha_0\varrho_0 g(x,y)\,[1-\alpha_0\varrho_0 f(x,y)]^{-1}. \qquad \text{(B.19)}$$

For small values of k and ω (B.17) reduces to, *cf.* ref. 12,

$$\mathsf{K}(k,\omega) = \tfrac{1}{9}(\varepsilon_0+2)^2\,[\mathsf{F}_{\varepsilon_0} - (\varepsilon_0+2)^{-1}] \qquad \text{if} \qquad ak, a\omega \ll 1, \qquad \text{(B.20)}$$

in agreement with eq. (4.9). For larger values of k and ω the functions f and g will in general be important in order to ensure on the one hand the convergence of the various integrals occurring in the multiple-scattering intensities, and on the other hand to take the finite size of the particles properly into account.

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II. CRITICAL SCATTERING.

Synopsis

The systematic theory of multiple scattering which we gave in a previous paper is further elaborated for critical scattering. It is shown that in each order the multiple-scattering intensity near the critical point is in essence a contraction of consecutive unrenormalized single-scattering intensities. The anomaly of the critical depolarization factor is calculated and is found to be in quantitative agreement with recent experimental results. Double scattering corrections to the Ornstein-Zernike plot are discussed.

1. Introduction.

In a previous paper [1], referred to as paper I, we have developed a formalism to deal with multiple scattering of light from a non-polar fluid. In this formalism single and multiple scattering refers to single and multiple scattering from fluctuations of the density around its average value. In this way the theory, though developed on a molecular basis, closely parallels the phenomenological theory of Einstein [2] to which it leads in lowest order, i.e. for single scattering. The expansion in fluctuations of the density is obtained by expanding the fluctuating density-dependent dielectric constant around the macroscopic dielectric constant. Due to this procedure the signal propagates from fluctuation to fluctuation through a medium with the macroscopic index of refraction. Formal expressions for higher-order scattering contributions were given in paper I.

In this paper we shall analyze the multiple-scattering contributions in more detail in particular for scattering near the gas-liquid critical point of the fluid. The first satisfactory analysis of double scattering near the critical point was given by Oxtoby and Gelbart [3,4,5] also within the framework of a molecular theory. Though their work predicted many of the qualitative features of critical double scattering they were not able to give an adequate quantitative description. This is due on the one hand to a less satisfactory expansion procedure in multiple-scattering contributions, leading e.g. to an incorrect local-field correction, and on the other hand to the necessity to use an unphysical sample geometry in the evaluation of their final expression. We shall show that the expressions for multiple scattering obtained in paper I may be further simplified in the critical region due to the long-range nature of the density-fluctuation correlations. In this way one obtains more manageable expressions for the explicit evaluation of multiple-scattering contributions for an experimental scattering geometry. Our formulae show that in each order the multiple-scattering intensity near the critical point is in essence a contraction of consecutive

uncorrelated single-scattering intensities. That this is the case was conjectured recently by Reith and Swinney [6,7] on the basis of the results of Oxtoby and Gelbart.

In section 2 we give a survey of scattering formulae for single and multiple scattering near the critical point which are derived in sections 3 and 4.

In section 5 we apply the formula obtained for double scattering to the evaluation of the critical depolarization factor for CO_2 in an experiment performed by Trappeniers, Michels and Huijser. [8] The experimentally measured anomaly agrees within the experimental accuracy with the theoretical prediction. [9]

Finally in section 6 we calculate double-scattering corrections to the Ornstein-Zernike plot. We find that double-scattering corrections are small if one is not too close to the critical point, $T-T_c \gtrsim 0.01\,^{0}C$, but should be taken into account if one comes closer to the critical point. For $T-T_c \lesssim 10^{-4}\,^{0}C$ triple and higher-order scattering should also be accounted for.

2. Survey of scattering formulae for single and multiple scattering near the critical point.

In this section we shall list the formulae for single and multiple scattering which we shall find on the basis of our molecular theory for critical scattering.

i) Single scattering.

In I we derived the following formula for the single-scattering intensity per unit of solid angle in the direction $\vec{\Omega}_s$ with polarization vector $\vec{u}_s$ and frequency ω_s

$$I_s(\vec{\Omega}_s,\vec{u}_s,\omega_s) = I_o\left[(\omega_o/c)^2\alpha_o\rho_o|n^2+2|^2/36\pi\right]^2 S(\vec{k}_s-\vec{k}_o,\omega_s-\omega_o)(\vec{u}_o\cdot\vec{u}_s)^2 \int_{V_S}\exp\left[-\alpha(d_o+d_s)\right]d\vec{r} \qquad (2.1)$$

where I_o, $\vec{k}_o$, $\vec{u}_o$ and ω_o are the intensity, wavevector ($k_o = \omega_o \operatorname{Re} n(\omega_o)/c$, $\vec{k}_o = k_o\,\vec{\Omega}_o$) polarization vector and frequency of the indicent beam respectively; $\vec{k}_s = (\omega_o \operatorname{Re} n(\omega_o)/c)\vec{\Omega}_s$ the wave-vector of the scattered light; c is the velocity of light in vacuum; α_o is the molecular polarizability, ρ_o the average density and n the refractive index (at the frequency ω_o) of the medium; V_S is the so-called scattering volume which is the cross-section of the illuminated volume V_L and the observed volume V_O; $\alpha \equiv 2\omega_o \operatorname{Im} n(\omega_o)$ is the attenuation factor at the frequency ω_o, which accounts for energy losses due to scattering; d_o and d_s are the distances from the point $\vec{r}$, where the scattering takes place, to respectively the point where the incident beam enters the sample and the point where the scattered light leaves the sample in the direction of the observer. $S(\vec{k},\omega)$ is the structure factor of the fluid, i.e. the Fourier transform of the autocorrelation function of the density fluctuations. In most cases one may use in good approximation Clausius-Mossotti (or Lorentz-Lorenz) $\alpha_o\rho_o = 3(n^2-1)/(n^2+2)$ in order to relate $\alpha_o\rho_o$ with n. Deviations from Clausius-Mossotti, even close to the critical point, are very small. [10]

In many cases it is sufficient to consider the integrated intensity

$$I_s(\vec{\Omega}_s,\vec{u}_s) = I_o\left[(\omega_o/c)^2\alpha_o\rho_o|n^2+2|^2/36\pi\right]^2 S(\vec{k}_s-\vec{k}_o)(\vec{u}_s\cdot\vec{u}_o)^2\int_{V_s}\exp\left[-\alpha(d_o+d_s)\right]d\vec{r} \qquad (2.2)$$

The structure factor S is given by

$$S(\vec{k}) \equiv S(\vec{k},t=0) = (2\pi)^{-1}\int d\omega\, S(\vec{k},\omega) = k_B T\kappa f(\xi k) \qquad (2.3)$$

where k_B is Boltzmann's constant, T the temperature, κ the isothermal compressibility, ξ the critical correlation length, and f the appropriate scaling function. For small values of the argument one may use the Ornstein-Zernike form of the scaling function

$$f(x) = (1+x^2)^{-1} \qquad (2.4)$$

In the explicit calculations in this peper we will restrict ourselves to this form of the scaling function, keeping in mind that deviations will occur if the correlation length becomes sufficiently large compared to the wave-longth of the light.

ii) Double scattering.

The double-scattering intensity is given by

$$I_d(\vec{\Omega}_s,\vec{u}_s) = I_o\left[(\omega_o/c)^2\alpha_o\rho_o|n^2+2|^2/36\pi\right]^4\int_{V_0} d\vec{r}_2 \int_{V_L}' d\vec{r}_1 d_{21}^{-2}\exp\left[-\alpha(d_o+d_{21}+d_s)\right]$$

$$S(\vec{k}_s-\vec{k}_{21})S(\vec{k}_{21}-\vec{k}_o)\left[\vec{u}_s\cdot(1-\vec{\Omega}_{21}\vec{\Omega}_{21})\cdot\vec{u}_o\right]^2 \qquad (2.5)$$

where $d_{21} \equiv |\vec{r}_2-\vec{r}_1|$, $\vec{\Omega}_{21} \equiv d_{21}^{-1}(\vec{r}_2-\vec{r}_1)$, $\vec{k}_{21} \equiv (\omega_o \mathrm{Re}\, n/c)\vec{\Omega}_{21}$, d_o is the distance between $\vec{r}_1$ and the point where the incident light enters the sample and d_s the distance between $\vec{r}_2$ and the point where the scattered light leaves the sample. The prime in the integration over V_L indicates that $\vec{r}_1$'s for which the line connecting $\vec{r}_1$ and $\vec{r}_2$ is not completely inside the sample are to be excluded from the integretion.

The formula for the double-scattering intensity may be understood in the following way. Light enters the sample and is scattered twice (in $\vec{r}_1$ and $\vec{r}_2$) using the differential cross-section for single scattering.

Factors are added to account for the attenuation and the distance between $\vec{r}_1$ and $\vec{r}_2$, and the resulting expression is integrated over all possible scattering points $\vec{r}_1$ and $\vec{r}_2$, taking into account the intermediate polarization directions. A formula for the frequency (ω_s) dependent double-scattering intensity is given in section 3.

iii) Multiple scattering.

The m^{th} order scattering intensity is given by

$$I_m(\vec{\Omega}_s,\vec{u}_s) = I_o\left[(\omega_o/c)^2 a_o \rho_o |n^2+2|^2/36\pi\right]^{2m} \int_{V_0} d\vec{r}_m \int_V' d\vec{r}_{m-1} \cdots \int_V' d\vec{r}_2 \int_{V_L}' d\vec{r}_1$$

$$\exp\left[-\alpha(d_o+d_s)\right] \left[\prod_{\ell=1}^{m-1} d_{\ell+1,\ell}^{-2} \exp(-\alpha d_{\ell+1,\ell})\right] \left[\prod_{\ell=1}^{m} S(\vec{k}_{\ell+1,\ell}-\vec{k}_{\ell,\ell-1})\right]$$

$$\left[\vec{u}_s \cdot (1-\vec{\Omega}_{m,m-1}\vec{\Omega}_{m,m-1}) \cdot \ldots \cdot (1-\vec{\Omega}_{21}\vec{\Omega}_{21}) \cdot \vec{u}_o\right] \qquad (2.6)$$

where $d_{\ell+1,\ell} \equiv |\vec{r}_{\ell+1}-\vec{r}_\ell|$, $\vec{\Omega}_{\ell+1,\ell} \equiv d_{\ell+1,\ell}^{-1}(\vec{r}_{\ell+1}-\vec{r}_\ell)$, $\vec{k}_{\ell+1,\ell} \equiv (\omega_o \mathrm{Re}\, n/c)\vec{\Omega}_{\ell+1,\ell}$; $\vec{k}_{m+1,m} \equiv \vec{k}_s$ and $\vec{k}_{1,o} \equiv \vec{k}_o$; d_o is the distance between $\vec{r}_1$ and the point where incident light enters the sample and d_s the distance between $\vec{r}_m$ and the point where the scattered light leaves the sample; V is the volume of the sample. The primes in the integrations indicate that only those points should be integrated over for which all interconnecting lines are completely inside the sample.

The multiple-scattering intensity is again simply the result of m subsequent uncorrelated single-scattering events. The frequency (ω_s) dependent multiple-scattering intensity may be given in the same way.

iv) Scattering formulae for inhomogeneous systems

If one observes light very close to the critical point one must take into account that, owing to gravitational effects, the average density ρ_o is not constant throughout the system. In that case the scattering formulae have to be amended to take this effect into account. Using stationarity, the autocorrelation function of the density fluctuations may be written in the form

$$\langle \Delta\rho(\vec{r}_1,t_1)\Delta\rho(\vec{r}_2,t_2)\rangle = \rho_o^2(\vec{R})S(\vec{R},\vec{r},t) \qquad (2.7)$$

where $\vec{R} \equiv \frac{1}{2}(\vec{r}_1+\vec{r}_2)$, $\vec{r} \equiv \vec{r}_1-\vec{r}_2$ and $t \equiv t_1-t_2$. Furthermore $\rho_o(\vec{R})$ is now the position-dependent avarage density.

We now define the structure factor for the inhomogeneous system by

$$S(\vec{R},\vec{k}) \equiv \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, S(\vec{R},\vec{r},t=0) \qquad (2.8)$$

Assuming that the inhomogeneity is small over distances of the order of the correlation length one may use for $S(\vec{R},\vec{k})$ the form

$$S(\vec{R},\vec{k}) = k_B T\kappa(\vec{R}) f(\xi(\vec{R})k) \qquad (2.9)$$

Extremely close to the critical point, however, this assumption and therefore eq. (2.9) are certainly not correct.

The formulae for single and double scattering may be written, using this inhomogeneous structure factor, as

$$I_s(\vec{\Omega}_s,\vec{u}_s) = I_o\left[(\omega_o/c)^2\alpha_o/36\pi\right]^2(\vec{u}_s\cdot\vec{u}_o)^2\int_{V_s}\rho_o^2(\vec{r})\left|n^2(\vec{r})+2\right|^4 A_s(\vec{r})$$

$$S(\vec{r},\vec{k}_s-\vec{k}_o)\, d\vec{r} \qquad (2.10)$$

$$I_d(\vec{\Omega}_s,\vec{u}_s) = I_o\left[(\omega_o/c)^2\alpha_o/36\pi\right]^4 \int_{V_0} d\vec{r}_2 \int_{V_L} d\vec{r}_1\, d_{21}^{-2}\rho_o^2(\vec{r}_1)\rho_o^2(\vec{r}_2)\left|n^2(\vec{r}_1)+2\right|^4$$

$$\left|n^2(\vec{r}_2)+2\right|^4 A_d(\vec{r}_1,\vec{r}_2)S(\vec{r}_2,\vec{k}_s-\vec{k}_{21})S(\vec{r}_1,\vec{k}_{21}-\vec{k}_o)\left|\vec{u}_s\cdot(1-\vec{\Omega}_{21}\vec{\Omega}_{21})\cdot\vec{u}_o\right|^2 \qquad (2.11)$$

A_s and A_d contain the effects due to attenuation,

$$A_s(\vec{r}) = \exp\left[-\int_{\Gamma_s(\vec{r})} d\Gamma'\alpha(\vec{r}')\right] \qquad (2.12)$$

where for single scattering the integral is along the optical path, $\Gamma_s(\vec{r})$, i.e. from the point where the incident light enters the sample to $\vec{r}$ and then on to the point where the scattered light leaves the sample. Similarly for double scattering

$$A_d(\vec{r}_1,\vec{r}_2) = \exp\left[-\int_{\Gamma_d(\vec{r}_1,\vec{r}_2)} d\Gamma'\alpha(\vec{r}')\right] \qquad (2.13)$$

where $\Gamma_d(\vec{r}_1,\vec{r}_2)$ is the optical path of the double-scattered light.

The position dependence of the refractive index may be calculated in good approximation using Clausius-Mossotti. [10] We note that the finite gradient of $n(\vec{r})$ will lead to curvature of the optical path close to the critical point. [8] In a similar way one may also give expressions for I_n.

3. The double-scattering intensity.

In order to calculate the n^{th} order scattering intensity one needs the n^{th} order density autocorrelation function (cf. I.5), which is defined in $\vec{k},\omega$ representation by

$$S_n(\vec{k}_1,\omega_1;\vec{k}_2,\omega_2;\ldots;\vec{k}_n,\omega_n) \equiv \langle \Delta\rho(\vec{k}_1,\omega_1)\Delta\rho(\vec{k}_2,\omega_2)\ldots\Delta\rho(\vec{k}_n,\omega_n)\rangle \tag{3.1}$$

Close to the critical point the small wavevector and frequency behaviour of these correlation functions becomes important. We shall therefore write S_n as a sum of a "hydrodynamic" (i.e. small wavevectors and frequencies) part S_n^H and a molecular part S_n^M

$$S_n = S_n^H + S_n^M \tag{3.2}$$

We shall now assume that in each order the dominant critical contribution to the scattering intensity may be found using the hydrodynamic part S_n^H alone.

Furthermore we shall make the usual assumption that S_n^H satisfies the Gaussian approximation (cf. eqs. (I. 5.14) and (I. 5.15)). In this approximation S_n^H is expressed in the two-point correlation function:

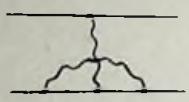
$$S_2^H(\vec{k}_1,\omega_1;\vec{k}_2,\omega_2) = (2\pi)^4 S^H(\vec{k}_1,\omega_1)\delta(\vec{k}_1+\vec{k}_2)\delta(\omega_1+\omega_2) \tag{3.3}$$

for n is even and S_n^H is zero for n is odd. The index H will be dropped from now on.

In paper I we have shown, using the Gaussian approximation, that there are four contributions to the scattering intensity which are quadratic in the structure factor. The sum of these contributions will be called the double-scattering intensity.

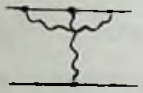
$$I_d = I^{31} + I_1^{22} + I_2^{22} + I^{13} \tag{3.4}$$

Here I^{31} and I^{13} are due to the interference between the single and the triple-scattered light and are given (cf. eqs. (I.7.2), (I.7.4) and (I.7.5)), using as incident field a plane wave $\vec{E}(\vec{r},\omega) = \vec{u}_o I_o^{\frac{1}{2}} 2\pi \exp(i\vec{k}_o\cdot\vec{r} - i\omega\vec{\Omega}_o\cdot\vec{r})\delta(\omega-\omega_o)$, by

$I^{31}(\vec{\Omega}_s,\vec{u}_s,\omega_s) =$  =

$$= I_o\left[\omega_o^2\alpha_o^2\rho_o^2|n^2+2|^2/36\pi\right]^2 S(\vec{k}_s-\vec{k}_o,\omega_s-\omega_o)(\vec{u}_o\cdot\vec{u}_s)(2\pi)^{-4}\int d\vec{k}\int d\omega\ \vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)$$

$$S(\vec{k}_s-\vec{k},\omega_s-\omega)\int_{V_s} d\vec{r}_1\int_{V_s} d\vec{r}_2\ \exp\left[i(\vec{k}_o+\vec{k}-\vec{k}_s)\cdot(\vec{r}_1-\vec{r}_2)-\alpha(d_o'+d_s')\right]\cdot\vec{\vec{K}}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o \qquad (3.5)$$

$I^{13}(\vec{\Omega}_s,\vec{u}_s,\omega_s) =$  $= \left[I^{31}(\vec{\Omega}_s,\vec{u}_s,\omega_s)\right]^*$ (3.6)

In these equations we have used the fact that S is sharply peaked in the frequency so that the prefactor ω_s^4 may be replaced by ω_o^4; a similar approximation has been made in the integrand. Furthermore we have not replaced the dielectric tensor $\vec{\vec{\varepsilon}}$ by the Clausius-Mossotti value ε_o as we did in paper I, but by $n^2(\omega_o)$. The motivation of this alternative and more exact replacement is completely analogous to the same replacement in the single-scattering intensity which was discussed in detail in section 6 of paper I. The factor $\exp\left[-\alpha(d_o'+d_s')\right]$ occurs for the same reason. This factor was taken into account in paper I in the discussion of single scattering whereas in the discussion of double scattering, where $n^2(\omega_o) = \varepsilon_o$ was used in paper I, it was suppressed. Here d_o' is half of the sum of the distances from $\vec{r}_1$ and $\vec{r}_2$ to the surface of the sample in the direction of the incident beam (the $-\vec{\Omega}_o$ direction), similarly d_s' is half the sum of the distance from $\vec{r}_1$ and $\vec{r}_2$ to the surface in the direction of the observer (the $\vec{\Omega}_s$ direction). Units have been chosen such that the velocity of light in vacuum c=1.

Similarly I_1^{22} and I_2^{22} which are due to the double-scattered field are given by (cf. eqs. (I.8.3) and (I.8.4))

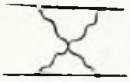
$I_1^{22}(\vec{\Omega}_s,\vec{u}_s,\omega_s)$ =

$$= I_o\left[\omega_o^2\alpha_o^2\rho_o^2|n^2+2|^2/36\pi\right]^2(2\pi)^{-4}\int d\vec{k}\int d\omega\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-\vec{k},\omega_s-\omega)$$

$$S(\vec{k}-\vec{k}_o,\omega-\omega_o)\int_{V_L} d\vec{r}_1\int_{V_0} d\vec{r}_2\ \exp\left[i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)-\alpha(d_o+d_s)\right]\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (3.7)$$

where d_o and d_s have been defined in section 2.

$I_2^{22}(\vec{\Omega}_s,\vec{u}_s,\omega_s)$ =



$$= I_o\left[\omega_o^2\alpha_o^2\rho_o^2|n^2+2|^2/36\pi\right]^2(2\pi)^{-4}\int d\vec{k}\int d\omega\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-\vec{k},\omega_s-\omega)$$

$$S(\vec{k}-\vec{k}_o,\omega-\omega_o)\int_{V_S} d\vec{r}_1\int_{V_S} d\vec{r}_2\ \exp\left[i(\vec{k}_s+\vec{k}_o-\vec{k})\cdot(\vec{r}_2-\vec{r}_1)-\alpha(d_o'+d_s')\right]$$

$$\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (3.8)$$

The propagator $\vec{\vec{K}}$, which propagates light from one density fluctuation to another is diagonal in $(\vec{k},\omega)$ representation and its diagonal elements are, for k and ω small compared to $(2\pi/a)$ where a is the molecular diameter, given by (cf. eqs. (I.4.9) and (I.A.1))

$$\vec{\vec{K}}(\vec{k},\omega) = -\frac{1}{9}(\varepsilon_T+2)^2\{\omega^2(k^2-\varepsilon_T(\omega+i0)^2)^{-1}+(\varepsilon_T+2)^{-1}\}(1-\frac{\vec{k}\vec{k}}{k^2})+\frac{2}{9}\varepsilon_L^{-1}(\varepsilon_L+2)\frac{\vec{k}\vec{k}}{k^2}$$

$$\text{for } k,\omega << (2\pi/a) \qquad (3.9)$$

where ε_T and ε_L are the transverse and the longitudinal parts of the dielectric tensor $\vec{\vec{\varepsilon}}(\vec{k},\omega)$ respectively; i0 is an infinitesimally small positive imaginary constant. The behaviour of $\vec{\vec{K}}$ for k and ω of the order of, or larger than the inverse molecular diameter is discussed in ref. 10 (cf. also I). We shall not need the explicit large k and ω behaviour of $\vec{\vec{K}}$ except for the fact that $\vec{\vec{K}}(\vec{k},\omega)$ goes to zero for $k>(2\pi/a)$. For $r>>a$ and $\omega<<(2\pi/a)$ the propagator $\vec{\vec{K}}(\vec{r},\omega)$ may be evaluated by Fourier

transformation of eq. (3.9). The long distance, i.e. $r \gg 2\pi/\omega$, result may be found analogous to the discussion in appendix A in paper I and is given by

$$\vec{K}(\vec{r},\omega) = -\frac{1}{8}(n^2(\omega)+2)^2\omega^2(4\pi r)^{-1}\exp(i\omega n(\omega)r)(1-\frac{\vec{r}\vec{r}}{r^2}) \qquad \text{for } r \gg 2\pi/\omega \gg a \tag{3.10}$$

We shall first consider I_1^{22} which will be found to give the dominant contribution in the neighbourhood of the cirtical point. In appendix A we show, justifying essentially the method of stationary phase, *) that in the critical region I_1^{22} becomes, except for negligible contributions, equal to

$$I_1^{22}(\vec{\Omega}_s,\vec{u}_s,\omega_s) = I_o\left[\omega_o^2\alpha_o^2\rho_o^2|n^2+2|^2/36\pi\right]^2(2\pi)^{-3}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}dk\ k^2\int_{V_L}d\vec{r}_1\int_{V_o,|\vec{r}_2-\vec{r}_1|>\lambda_o}d\vec{r}_2(ik|\vec{r}_2-\vec{r}_1|)^{-1}$$

$$\exp\left[ik|\vec{r}_2-\vec{r}_1|-a(d_o+d_s)\right]\left[\vec{u}_s\cdot\vec{K}(k\vec{\Omega}_{21},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-k\vec{\Omega}_{21},\omega_s-\omega)S(k\vec{\Omega}_{21}-\vec{k}_o,\omega-\omega_o)$$

$$\left[\vec{u}_s\cdot\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \tag{3.13}$$

where $\vec{\Omega}_{21} \equiv (\vec{r}_2-\vec{r}_1)/|\vec{r}_2-\vec{r}_1|$ and $\lambda_o = 2\pi/k_o$. For an order of magnitude estimate of the correction terms we refer to appendix A.

In appendix B we furthermore show that I^{13}, I^{31} and I_2^{22} are of the same order of magnitude as the terms neglected in deriving eq. (3.13) from eq. (3.7).**) In the critical region one therefore has for all practical purposes

*) In this method one approximates $\int d\vec{\Omega}\ f(k\vec{\Omega})e^{i\vec{k}\cdot\vec{r}} \sim \frac{2\pi}{ikr}\left[e^{ikr}f(k\frac{\vec{r}}{r}) - e^{ikr}f(-k\frac{\vec{r}}{r})\right]$

**) In fact I^{13} and I^{31} both contain an additional term of exactly the same structure as the single-scattering intensity but roughly a factor 10^3 smaller. This term is therefore in practice indistinguishable from the single scattering and may be interpreted as a vertex correction of I_s. [11] See appendix B for a further discussion of this contribution.

$I_d = I_1^{22} =$  (3.14)

except for small corrections.

For $|\vec{r}_2-\vec{r}_1|>>\lambda_o$ eq. (3.10) may be used for $\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)$ in eq. (3.13). The corresponding integrand is proportional to $|\vec{r}_2-\vec{r}_1|^{-2}$ for large values of $|\vec{r}_2-\vec{r}_1|$. In view of this I_d contains a term proportional to the fourth power of the typical diamoter ℓ of the sample. Tho use of eq. (3.10) for all values of $|\vec{r}_2-\vec{r}_1|>\lambda_o$ is correct up to correction terms of the order (λ_o/ℓ). Substituting eq. (3.10) into eq. (3.13), and using also eq. (3.14), one obtains

$$I_d(\vec{\Omega}_s,\vec{u}_s,\omega_s) = i(4\pi)^{-1}I_o\left|\omega_o^3\alpha_o^2\rho_o^2(n^2+2)^*|n^2+2|^2/108\pi\right|^2(2\pi)^{-3}$$

$$\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}dk\ k\int_{V_L}d\vec{r}_1\int_{V_0}d\vec{r}_2|\vec{r}_2-\vec{r}_1|^{-2}\exp\left[i(k-\omega_o n^*(\omega_o))|\vec{r}_2-\vec{r}_1|-\alpha(d_o+d_s)\right]$$

$$\left[\vec{u}_s\cdot\vec{K}(k\vec{\Omega}_{21},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-k\vec{\Omega}_1,\omega_s-\omega)S(k\vec{\Omega}-\vec{k}_o,\omega-\omega_o)\left[\vec{u}_s\cdot(1-\vec{\Omega}_{21}\vec{\Omega}_{21})\cdot\vec{u}_o\right] \quad (3.15)$$

The limitation of the integration $|\vec{r}_2-\vec{r}_1|>\lambda_o$ has been dropped in view of the fact that the difference contributes a term of relative order (λ_o/ℓ) which may be neglected. We now close the integral over k in the upper half plane. The poles of the integrand are due to on the one hand the electromagnetic propagator $\vec{K}$ and on the other hand the correlation functions S. The propagator $\vec{K}$ has a pole for $k = \omega_o n(\omega_o)+io$, cf. eq. (3.9). The residue due to this pole leads to an integrand for the integration over $\omega,\vec{r}_1$ and $\vec{r}_2$ in which the exponential factor merely gives the attenuation of the signal between $\vec{r}_1$ and $\vec{r}_2$. This exponential factor is in general of order unity even over distances of the order ℓ and close to the critical point. The resulting integral over $\vec{r}_1$ and $\vec{r}_2$ then becomes of the order ℓ^4. In the contributions due to the residues of the correlation functions the exponential factor remains, so that the resulting integral becomes at most of the order $\lambda_o\ell^3$ and may therefore be neglected. Performing the integration over k in the above described manner one finally obtains

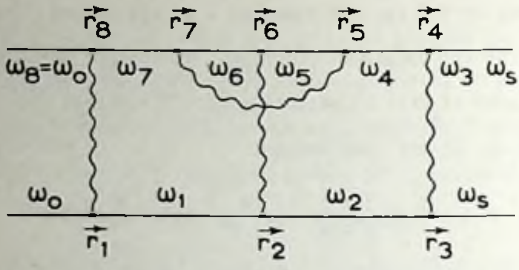


Fig. 1 An example of a fourth-order (m=4) diagram with three dots (j=3) on the lower solid line and five dots (2m-j=5) on the upper solid line.

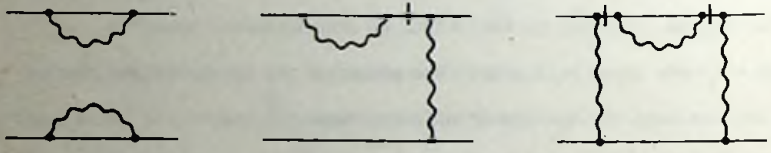


Fig. 2 Examples of "unconnected" diagrams of class i, ii and iii respectively.

$$I_d(\vec{\Omega}_s,\vec{u}_s,\omega_s) = I_o\left[\omega_o^2\alpha_o\rho_o|n^2+2|^2/36\pi\right]^4(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\int_{V_L}d\vec{r}_1\int_{V_0}{}'d\vec{r}_2$$

$$d_{21}^{-2}\exp\left[-\alpha(d_o+d_{21}+d_s)\right]S(\vec{k}_s-k_o\vec{\Omega}_{21},\omega_s-\omega)S(k_o\vec{\Omega}_{21}-\vec{k}_o,\omega-\omega_o)$$

$$\left[\vec{u}_s\cdot(1-\vec{\Omega}_{21}\vec{\Omega}_{21})\cdot\vec{u}_o\right]^2 \qquad (3.16)$$

The prime in the integration over $\vec{r}_2$ restricts the integration to values of $\vec{r}_2$ for which the line connecting $\vec{r}_1$ and $\vec{r}_2$ runs through the sample. This restriction arises as a consequence of absorbing barriers in the experimental geometry and is due to the fact that $\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)$ should really be taken zero for such points in eq. (3.13).

Eq. (3.16) is the general formula for the double-scattering intensity which we set out to derive. Upon integration over ω_s one obtains eq. (2.5).

4. The multiple-scattering intensity.

In this section we shall briefly discuss the derivation of eq. (2.6) for the multiple-scattering intensity. This will be done using the diagrammatic representation of the multiple-scattering intensities given in paper I. The m^{th} order scattering intensity may be written as

$$I_m = \sum_{j=1}^{2m-1}\sum_{\ell=1}^{\ell(m,j)} I_\ell^{j,2m-j} \qquad (4.1)$$

Here $I_\ell^{j,2m-j}$ is the contribution to the intensity from the ℓ^{th} diagram due to interference between the j and the (2m-j) times scattered fields. The corresponding "connected" $\ell(m,j)$ diagrams are constructed in the following way. Draw two parallel solid lines, take j dots on the lower line and (2m-j) dots on the upper line and finally connect the dots two by two by curly lines. A typical example for j=3 and m=4 is drawn in fig. 1. The internal solid lines correspond to propagators $\vec{K}$

whereas the curly lines correspond to density autocorrelation functions S. Not all diagrams which may be constructed in this way are "connected" and contribute to I_m. The following three classes of "unconnected" diagrams do <u>not</u> contribute to the scattering intensity

i) Diagrams with no curly lines connecting the lower and the upper solid lines. This class of (unconnected) diagrams has been taken into account by the renormalization of the vacuum field into the average field in the medium.

ii) Diagrams which become unconnected by cutting one internal solid line. These diagrams correspond to the renormalization of the external solid lines.

iii) Diagrams in which either one or the other solid line may be cut in two places such that the part of the diagram between the cuts is neither connected to the solid line which has been cut nor to the other. These diagrams correspond to the renormalization of the internal solid lines.

Typical examples of these three classes are shown in fig. 2.

We shall now give the prescription, which follows from our general theory in paper I, of how to construct the explicit form of $I_\ell^{j,2m-j}$ if the diagram is given. In the first place one ascribes positions $\vec{r}_1,\ldots,\vec{r}_{2m}$ to the vertex points starting with $\vec{r}_1,\ldots,\vec{r}_j$ from left to right on the lower line and then $\vec{r}_{j+1},\ldots,\vec{r}_{2m}$ from right to left on the upper line. Secondly one assigns frequencies $\omega_o,\omega_1,\ldots,\omega_{j-1},\omega_s$ from left to right to the solid line segments on the lower line, this including the external lines, and similarly one assigns frequencies $\omega_j,\omega_{j+1},\ldots,\omega_{2m-1},\omega_o$ to the solid line segments on the upper line from right to left. An example is given in fig. 1. One then has for the corresponding contribution to the intensity

$$I_\ell^{j,2m-j}(\vec{\Omega}_s,\vec{u}_s,\omega_s) = (4\pi)^{-2}\omega_o^4 3^{-4}|n^2+2|^4(\alpha_o\rho_o)^{2m}(2\pi)^{-2m+1}\int_{-\infty}^{\infty}d\omega_1\ldots d\omega_{2m-1}$$

$$\int_{V_L}d\vec{r}_1 d\vec{r}_{2m}\int_{V_0}d\vec{r}_j d\vec{r}_{j+1}\int_{V}d\vec{r}_2\ldots d\vec{r}_{j-1}d\vec{r}_{j+2}\ldots d\vec{r}_{2m-1}\left[\vec{u}_s\cdot\vec{K}(\vec{r}_j-\vec{r}_{j-1},\omega_{j-1})\ldots\vec{K}(\vec{r}_2-\vec{r}_1,\omega_1)\cdot\vec{u}_o\right]$$

$$\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r}_{j+2}-\vec{r}_{j+1},\omega_{j+1})\cdots\vec{\vec{K}}(\vec{r}_{2m}-\vec{r}_{2m-1},\omega_{2m-1})\cdot\vec{u}_o\right]^{*}\exp\left[-i\vec{k}_s\cdot(\vec{r}_j-\vec{r}_{j-1})+\right.$$

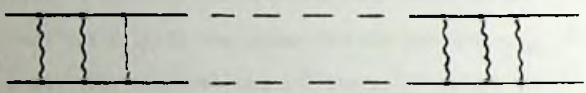
$$\left.i\vec{k}_o\cdot(\vec{r}_1-\vec{r}_{2m})-\alpha(d_o+d_s)\right]\prod_{(a,b)}^{\ell}\left[S(\vec{r}_a-\vec{r}_b,\omega_a-\omega_{a-1})2\pi\delta(\omega_a-\omega_{a-1}+\omega_b-\omega_{b-1})\right] \qquad (4.2)$$

The product is over all pairs (a,b) connected by curly lines in the ℓ^{th} diagram. Furthermore $\omega_{2m}=\omega_o$ and if a or b equals j one should replace ω_j by ω_s in the corresponding δ function; that this is not necessary in the correlation function is due to the fact that, owing to the δ functions, $\omega_s=\omega_j$. The distance d_o is equal to half the sum of the distances from $\vec{r}_1$ and $\vec{r}_{2m}$ to the surface of the sample in the direction of the incident beam. Similarly d_s is equal to half the sum of the distances from $\vec{r}_j$ and $\vec{r}_{j-1}$ to the surface in the direction of the observer. Eq. (4.2) may be found upon substitution of the ℓ^{th} diagram contribution of $\vec{\vec{M}}_{j,2m-j}$ into eq. (I.3.6) using eq. (I.6.1) for the incident field. *) The factor $|n^2(\omega_o)+2|^4$ comes from the four factors $(\vec{\vec{\varepsilon}}+2)$ in $\vec{\vec{M}}$, cf. eq. (I.4.10). Using the fact that $\vec{\vec{\varepsilon}}$ is a convolution operator in $\vec{r}$ representation and goes to zero for $|\vec{r}-\vec{r}'|$ larger than a typical fluid correlation length and the transverse nature of the incident and observed fields the factors $(\vec{\vec{\varepsilon}}+2)$ have been pulled out of the integration and give $|n^2(\omega_o)+2|^2|n^2(\omega_s)+2|^2$. One may then replace $n(\omega_s)$ by $n(\omega_o)$ in view of the fact that $n(\omega)$ varies only very little over the typical variation of ω_s. For a more extensive discussion of the conversion of $(\vec{\vec{\varepsilon}}+2)$ into $(n^2(\omega_o)+2)$ we refer to paper I section 6. The discussion given there also applies to multiple scattering.

Using the fact that S is sharply peaked in the frequency one may replace the frequency arguments of the propagator $\vec{\vec{K}}$ by ω_o. Furthermore we use the fact that S goes to zero if $|\vec{r}_a-\vec{r}_b|$ is larger than a typical fluid correlation length so that the m integrations over $\vec{r}_b$ may be extended to infinite space.

*) Note that $k_o = \omega_o \mathrm{Re}\, n(\omega_o)$ in this paper whereas we used $k_o = \omega_o n(\omega_o)$ in paper I.

If we subsequently write $S(\vec{r}_a-\vec{r}_b,\omega_a-\omega_{a-1})$ as a Fourier integral over $S(\vec{k}_i,\omega_a-\omega_{a-1})$, with i = 1,...,m, one may perform the m integrations over $\vec{r}_b$. In this way one obtains an expression in which m integrations over space-vectors have been replaced by m integrations over wave-vectors. This may be done in such a way that (m-1) propagators $\vec{\vec{K}}$ are still in space representation whereas the remaining (m-1) propagator $\vec{\vec{K}}$ are in wave-vector representation. Furthermore one finds one δ-function in the wavevectors restricting the number of integrations over wavevectors essentially to (m-1). One may now convince oneself that, as in the case of double scattering (cf. section 3 and appendix B), close to the critical point the dominant contributions to each order are given by the socalled ladder diagrams

$I_m \simeq$  (4.3)

with m curly lines in the diagram for I_m.

Using finally what amounts to again essentially the method of stationary phase for the integration over the (m-1) wavevectors one finds that I_m may be approximated close to the critical point by eq. (2.6) if one integrates over ω_s. The ω_s-dependance may also easily be given but is not expected to be of much relevance.

5. The critical depolarization factor.

In a typical depolarization experiment one measures the scattering intensity in a direction orthogonal to both the incident wave- and polarization-vectors ($\vec{k}_o$ and $\vec{u}_o$). The ratio of the two scattering intensities, one with a polarization vector $\vec{u}_s$ orthogonal to $\vec{u}_o$ and the other with $\vec{u}_s = \vec{u}_o$ is called the depolarization factor Δ. Owing to the fact that the single scattering intensity vanishes for $\vec{u}_s \cdot \vec{u}_o = 0$ the first, and usually largest, contribution to the depolarized scattered light is due to double scattering. One therefore has in good approximation

$$\Delta = I_d \text{ (depolarized)}/I_s \text{ (polarized)}, \tag{5.1}$$

if one is not extremely close to the critical point where higher order terms might become important.

In our subsequent discussion we shall apply the theory presented in the previous sections to evaluate the depolarization factor for an experiment by Trappeniers, Michels and Huijser. [8] In their experiment they measured Δ for CO_2 at the critical density for a temperature range between 0.02 and 0.7 degrees above the critical temperature. A similar experiment was recently done by Reith and Swinney for Xenon in a comparable temperature range. [6] A cross-section of the scattering cell (top view) is drawn in fig. 3, details of the geometry, which are not relevant for our discussion, have been left out. The beam is incident from the left and its cross-section has a rectangular shape with a diameter of 4.5 mm in the horizontal direction and a diameter of 0.35 mm in the vertical direction, the polarization is in the vertical direction. The observed volume has the shape of a parallelepiped; the vertical diameter was variable and the experiment was performed with vertical diameters 0.7, 2 and 4 mm respectively. The average vertical position of the illuminated and observed volumes was the same (i.e. they were centered with respect to each other). For other data concerning the geometry see fig. 3.

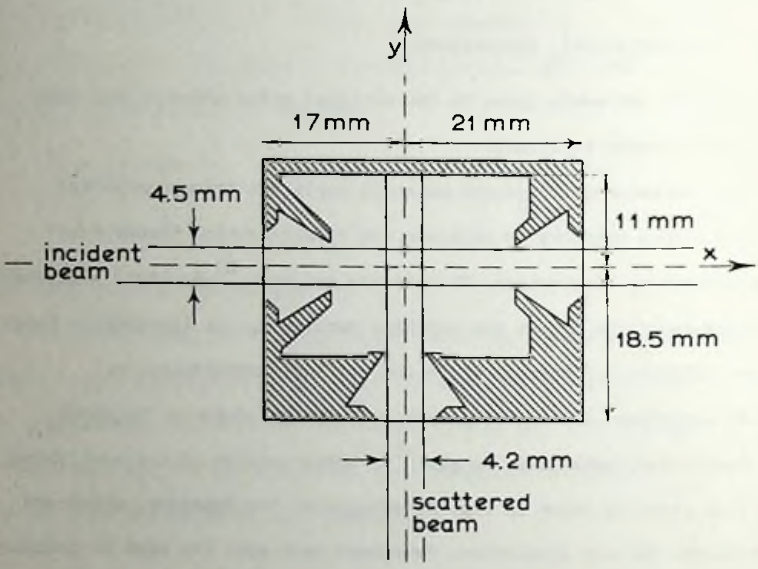


Fig. 3 Top view of the light scattering cell, drawn to scale. Details irrelevant for our computation have been suppressed.

Using eq. (5.1) for Δ and eqs. (2.2) and (2.5) for the single and the double scattering intensities one has, using Clausius-Mossotti for $\alpha_o \rho_o$,

$$\Delta = \left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2\{\int_{V_0}\vec{dr}_2\int_{V_L}\vec{dr}_1\, d_{21}^{-2}\exp\left[-\alpha(d_o+d_{21}+d_s)\right]$$

$$S(\vec{k}_s-\vec{k}_{21})S(\vec{k}_{21}-\vec{k}_o)(\vec{u}_s\cdot\vec{\Omega}_{21})^2(\vec{u}_o\cdot\vec{\Omega}_{21})^2\}$$

$$\{S(\vec{k}_s-\vec{k}_o)\int_{V_S}\exp\left[-\alpha(d_o'+d_s')\right]d\vec{r}'\}^{-1} \qquad (5.2)$$

where we have used the fact that $(\vec{u}_s\cdot\vec{u}_o)$ is zero or one in I_d and I_s respectively. We now choose a coordinate frame with its origin in the center of V_S, the z-axis in the vertical direction and the x-axis in the direction of the beam (cf. fig. 3). Furthermore we assume that the vertical diameter of V_L (and hence $V_S=V_0\cap V_L$) is sufficiently small so that both I_d and I_s are linear in this diameter. This implies that Δ is independent of this diameter so that Δ may be evaluated in the limit that this diameter is zero. Indeed in the experiment [8] no such dependence of Δ was found. Performing the integration in the denominator we then obtain

$$\Delta = \int_{-\frac{1}{2}d}^{\frac{1}{2}d}\Delta_z dz \qquad (5.3)$$

with

$$\Delta_z = \left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2\{S(k_o\sqrt{2})4\alpha^{-2}\sinh(\alpha x_o)\sinh(\alpha y_L)\}^{-1}$$

$$\int_{-x_o^-}^{x_o^+}dx_2\int_{-y_L^-}^{y_L^+}dy_1\int_{-x_L^-}^{x_L^+}dx_1\int_{-y_o^-}^{y_o^+}dy_2\; d_{21}^{-6}z^2(x_1-x_2)^2S(k_o\{2[1-(y_1-y_2)/d_{21}]\}^{\frac{1}{2}})$$

$$S(k_o\{2[1+(x_1-x_2)/d_{21}]\}^{\frac{1}{2}})\exp\left[\alpha(x_1+y_2+d_{21})\right]\,, \qquad (5.4)$$

here $d_{21} = \left[(x_1-x_2)^2 + (y_1-y_2)^2 + z^2\right]^{\frac{1}{2}}$ and d is the vertical diameter of the observed volume. Furthermore $x_o^+, -x_o^-, -y_o^-, y_o^+$ and $x_L^+, -x_L^-, y_L^+, -y_L^-$ are the positions of the boundaries of the observed

and illuminated volumes respectively. The primes in the integrations over x_1 and y_2 indicate as usual that the domain of integration should be further limited by excluding points for which the line connecting (x_1,y_1) with (x_2,y_2) crosses a barrier.

In appendix C we show that

$$\Delta_o \equiv \lim_{z\to 0} \Delta_z \tag{5.5}$$

exists. Furthermore it is shown in this appendix that in the case that the O.Z. form of the structure factor, eq. (2.4), is used Δ_o may be calculated analytically. The result is

$$\Delta_o = \tfrac{1}{3}\pi\left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2 k_B T\kappa\, f(2k_o^2\xi^2/(1+2k_o^2\xi^2)) \tag{5.6}$$

where

$$f(a) = 8a^{-4}(1-a)\left(\frac{\pi}{2} - 1 - 2\,\mathrm{arctg}\sqrt{1-a^2} + \sqrt{1-a^2}\right) \tag{5.7}$$

For small values of a

$$f(a) = 1-a + \mathcal{O}(a^2) \tag{5.8}$$

For the special case $k_o\xi=0$, when $f=1$, eq. (5.6) was also found in refs. 6 and 7. According to eq. (5.6) Δ_o depends neither on the size of the system nor on the value of the attenuation α; Δ_o does depend, however, on $k_o\xi$ an effect which will be important close to T_c. In fact for CO_2 one has $k_o\xi \simeq 0.65$ for $T-T_c \simeq 0.02$, so that $f \simeq 0.63$. Extremely close to T_c when $\xi\to\infty$, so that $a\to 1$, $f(a)$ goes to zero as

$$f(a) \simeq 2(k_o\xi)^{-2}(\pi-2), \qquad k_o\xi \gg 1 \tag{5.9}$$

As a consequence Δ_o approaches a finite value if T goes to T_c.

If the attenuation in the sample is sufficiently small, i.e. when $\alpha R \ll 1$ where R is a typical horizontal diameter of the sample, it may be shown, see also Appendix C, that

$$\Delta_z = \Delta_o\left[1+\mathcal{O}(z^2/R^2)\right] \qquad \text{if } \alpha R \ll 1 \tag{5.10}$$

This implies that Δ satisfies

$$\Delta = \Delta_o d\left[1+\mathcal{O}(d^2/R^2)\right] \qquad \text{if } \alpha R \ll 1 \tag{5.11}$$

The depolarization factor is therefore linear in the vertical diameter of the observed volume if $d \ll R$ and $\alpha R \ll 1$. Such a linearity is confirmed by the experimental results [6,8] and was first predicted by Oxtoby and Gelbart [4] on the basis of a molecular theory for a rather idealized geometry.

If the attenuation is non-negligible, $\alpha R \gtrsim 1$, Δ_z and therefore Δ cannot be calculated analytically. This is related to the fact that for finite values of α the expansion in z/R does not converge (cf. Appendix C). In that case we have integrated eq. (5.4) for Δ_z numerically using a four-dimensional Monte Carlo integral procedure. *) In this calculation we have used the following critical parameters for CO_2: [12,13]

critical pressure:	$p_c = 7.37$ MPa
critical temperature:	$T_c = 304$ K
compressibility:	$\kappa = p_c^{-1}\,\Gamma(\Delta T)^{-\gamma}$
with:	$\Delta T \equiv T - T_c \quad (T > T_c)$
	$\gamma = 1.199$
	$\Gamma = 0.650$
critical correlation length	$\xi = 63(T-T_c)^{-\gamma/2} \quad \text{Å}\ \kappa^{\gamma/2}$
refractive index:	$n = 1.106$

Furthermore we have used for the attenuation [10,14]

$$\alpha = (54\pi)^{-1}(\omega_o/c)^4(\varepsilon-1)^2(\varepsilon+2)^2 k_B T \kappa g(2k_o^2\xi^2/(1+2k_o^2\xi^2)) \qquad (5.13)$$

with

$$g(a) = \frac{3}{8}a^{-3}(1-a)\{-2a+(1+a^2)\ln[(1+a)/(1-a)]\} = 1-a+\mathcal{O}(a^2) \qquad (5.14)$$

The resulting values for Δ_z as a function of z are plotted in fig. 4 for a number of temperatures. The variation of Δ_z between zero and two millimetres is about 14% for the temperature closest to T_c; this

*) In this integration it is most convenient to replace x_1, y_2 as integration variables by the variables t and ϕ introduced in appendix C.

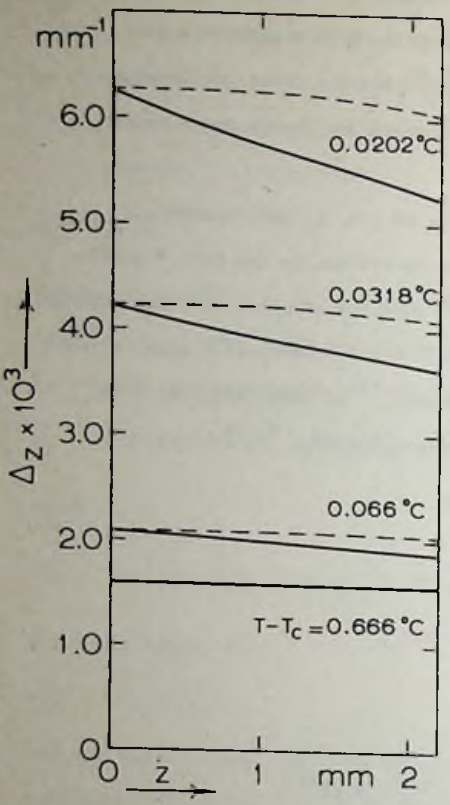
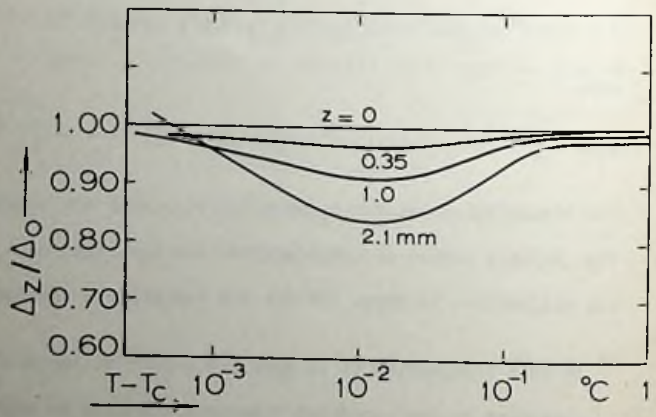


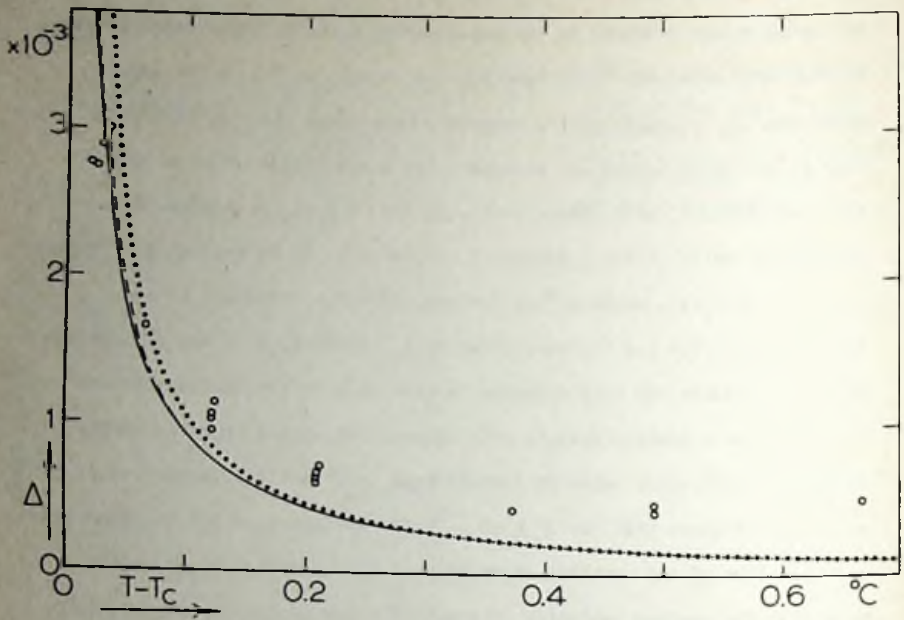
Fig. 4 Δ_z as a function of z for some temperatures used in the experiment. The solid and broken lines are calculated for the actual value of α and for α=0 resp..

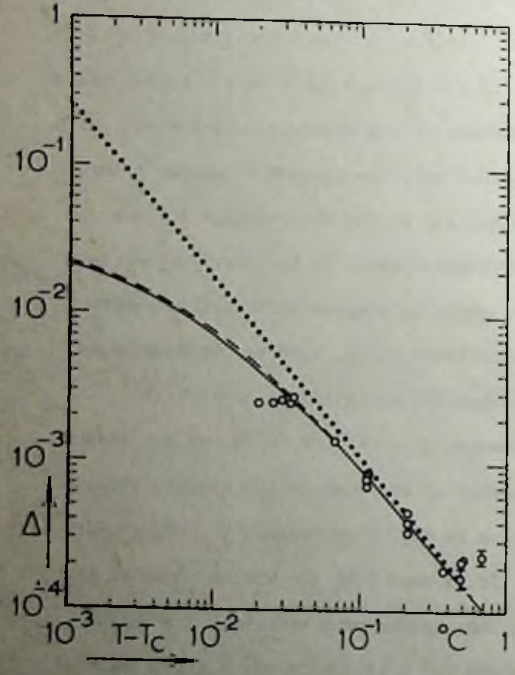
Fig. 5

Δ_z/Δ_o as a function of T-T$_c$ for four values of z.



results in a deviation from linearity for Δ of less than 7% which is not large enough compared to the experimental error at those temperatures to have been observed. [8] We have also plotted Δ_z in fig. 4 for $\alpha=0$, in which case Δ_z is indeed nearly constant. This shows that the $\mathcal{O}(z^2/R^2)$ term in eq. (5.8) is not yet important for these values of z. We have also calculated Δ_z much closer to T_c. In fig. 5 Δ_z/Δ_o is plotted as a function of $\ell n(T-T_c)$ for a number of values of z. As is seen in this figure the value of Δ_z/Δ_o, which is one far away from T_c, decreases if one approaches T_c (for $z \neq 0$); very close to T_c, however, this ratio increases again. The reason for this increase is that some of the double-scattered light follows a shorter optical path through the sample than the single-scattered light which makes it increasingly important for larger values of α. It also follows that for $\Delta T \gtrsim 10^{-4}$ °C the deviation of Δ from linearity as a function of the vertical diameter d of the observed volume is not more than the maximum deviation of about 7% which occurs for $\Delta T \simeq 0.02$ °C. Our results for Δ are compared with the experimental results obtained by Trappeniers, Michels and Huijser [8] in fig. 6. The theoretical prediction (solid line) given in the figure is the average value of the three values for Δ obtained for the three diameters of the observed volume scaled with respect to the smallest diameter (0.7 mm). The agreement between theory and experiment is rather good especially in the peak, except for the value $\Delta T = 0.02$ °C where the experimental value is too low. Further away from T_c the difference may be explained by various contributions which have been neglected close to the critical point, such as the molecular contributions to I_d and the contributions discussed in appendix A and B. The reason for the disagreement at $\Delta T = 0.02$ °C is not yet clear but is possibly related to deflection of the beam in the gravity-induced density profile. [8] The broken line in fig. 6 represents the values for $\alpha=0$ which follow from eq. (5.6). It is seen that the finite value of the attenuation is negligible within the experimental accuracy. The dotted line in fig. 6 represents the values for Δ if both α and $k_o\xi$ are taken





Figs. 6 and 7

The depolarization factor Δ as a function of $T-T_c$ scaled with respect to the diameter 0.7 mm. Circles represent the experimental values from ref. 8. The solid line is the theoretical prediction. The broken and dotted lines are obtained from the theory by putting $\alpha=0$ and ($\alpha=0$, $k_o\xi=0$) resp..

zero which follow using again eq. (5.6) with f(a)=1. Fig. 7 is a double-logarithmic version of fig. 6, in which the theoretical values are also given for temperatures much closer to T_c and where the background has been subtracted from the experimental data. We see that Δ increases as the compressibility for $\Delta T \gtrsim 0.03\ ^{o}C$, for smaller values of ΔT, where $k_o \xi \gtrsim 1$. Δ increases slowly and stabilizes at a value of about 3 parts in a hundred (for d = 0.7 mm) at $\Delta T \simeq 10^{-4}\ ^{o}C$. It should be noted that triple and higher-order scattering have not been considered, which may affect our conclusions very close to T_c. Because of the agreement between the experimental results with the theoretical values obtained on the basis of double scattering alone we conclude that triple and higher-order scattering are not yet large enough, for $\Delta T \gtrsim 0.02\ ^{o}C$, to have any measurable consequences.

In the experiment done on Xenon by Reith and Swinney [6] the smallest value of ΔT is roughly $0.05\ ^{o}C$. In their case the finite value of the attenuation is not yet important. They find a downward curvature in the log-log plot of their data which, as we have seen, is a consequence of the increase of the correlation length. We do not expect triple and higher-order scattering to be important in the temperature range which they consider. Moreover since such contributions would be positive they certainly would not explain the downward curvature of the log-log plot as was suggested in ref. 6.

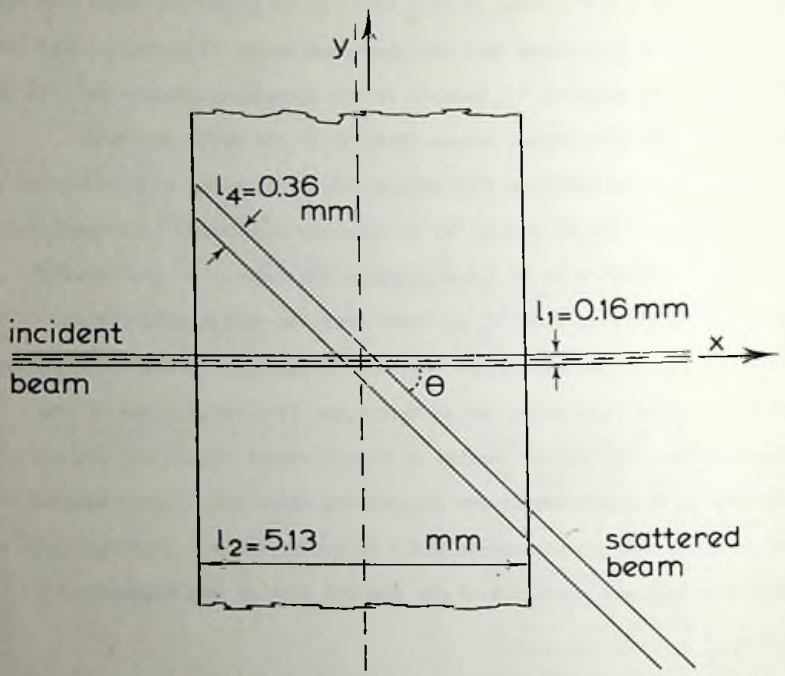


Fig. 8 Top view of the light scattering cell, drawn to scale. Details irrelevant for our computation have been suppressed.

8. Corrections to the Ornstein-Zernike plot.

In the interpretation of scattering data close to the critical point the so-called Ornstein-Zernike plot plays a crucial role. In this plot the inverse of the scattering intensity (per unit of V_s) is plotted as a function of $|\vec{k}_s - \vec{k}_o|^2/k_o^2 = \sin^2 \frac{1}{2}\theta$ where θ is the angle between the direction of the incident beam and the scattered light. Not too close to T_c this plot is a straight line, as is of course predicted by the Einstein theory (single scattering) together with the Ornstein-Zernike form for the correlation function. The extrapolated value for $\theta=0$ is then used as a measure for the compressibility. If one comes closer to the critical point, however, deviations from linear behaviour occur. One reason for this is the increasing value of the attenuation, an effect which one usually corrects for [13]. A derivation of the appropriate formula, eq. (2.1), for this correction on the basis of the molecular theory was presented in paper I. A second reason, which we shall discuss in this section, is multiple scattering. Since we are primarily interested in the influence of multiple scattering we shall not consider two other possible sources of the deviation from linearity, namely a finite value of the critical exponent η in the structure factor *) and a gravity-induced density profile.

We shall now evaluate double scattering corrections to the Ornstein-Zernike plot. In the calculation we again consider CO_2. The experimental details used in the explicit calculation are taken from the experiment on CO_2 by White and Maccabee. [13] In fig. 8 a top view of their scattering experiment is drawn; details of the geometry which are not relevant for

*) As long as I_d is not too large it is sufficient to account for a finite value of η only in I_s.

our discussion have been left out. The beam is incident from the left and its cross section is circular with a diameter $\ell_1 = 0.16$ mm. The polarization $\vec{u}_o$ of the incident beam is in the vertical direction. The illuminated volume is therefore a cylinder with this diameter and a length $\ell_2 = 5.13$ mm. In view of the small size of this diameter we will assume that the double-scattering intensity is a linear function of the corresponding cross section $\frac{1}{4}\pi\ell_1^2$, reducing the illuminated volume in essence to a line segment for the purpose of the integration. The observed volume has the shape of a parallelepiped with a vertical diameter $\ell_3 = 0.144$ mm. The average vertical positions of V_0 and V_L were centered with respect to each other. The resulting cross section of $V_S = V_0 \cap V_L$ is somewhat peculiar in shape, in view of the fact that $\ell_3 < \ell_1$; it is easy, however, to calculate the surface area which is $O_S = 0.019$ (mm)^2. The single-scattering intensity is linear in this cross-section. We note that the assumption of linearity is only correct if attenuation may be neglected over distances of the order of a few tenths of a millimetre.

Using eq. (2.2) for the single scattering one finds upon integration over V_S, substituting the Ornstein-Zernike form for S, the Clausius-Mossotti value for $\alpha_o\rho_o$ and taking the sum over the possible directions of the polarization vector $\vec{u}_s$,

$$I_s(\theta) = I_o\left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2 k_B T\kappa (1+2\xi^2 k_o^2 \sin^2\tfrac{1}{2}\theta)^{-1} V_S(\theta) A(\theta) \qquad (6.1)$$

in which the scattering volume is given by *)

$$V_S(\theta) = O_S \ell_4 / \sin\theta \qquad (6.2)$$

where $\ell_4 = 0.36$ mm, cf. fig. 8. The factor $A(\theta)$ accounts for attenuation

*) For $|\theta|$ or $|\pi-\theta|$ smaller than $\operatorname{arctg}\left((\ell_1+\ell_4|\cos\theta|^{-1})/\ell_2\right) \simeq 0.051$ eq. (6.2) is no longer correct. The divergence of $V_S(\theta)$ in the forward and backward directions is therefore only apparent and levels off and goes to a finite value for $\theta=0$ and π.

and is given by, neglecting $\alpha\ell_4$,

$$A(\theta) = \exp\left[-\tfrac{1}{2}\alpha\ell_2(1+1/\cos\theta)\right] \tag{6.3}$$

For $\alpha=0$ this factor is equal to one. Very close to T_c the attenuation effects should be taken into account, however.

Similarly one finds for the double-scattering intensity from eq. (2.5)

$$I_d(\theta) = I_o\left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^4(k_B T\kappa)^2(\tfrac{1}{4}\pi\ell_1^2)\ell_4 A(\theta)\int_{-\ell_2/2}^{\ell_2/2}dx_1dx_2\int_{-\ell_3/2}^{\ell_3/2}dz_2\, d_{21}^{-6}$$

$$\exp\left[-\alpha(x_1+r-x_2/\cos\theta)\right]\left\{r^4+z_2^2\left[(x_2-x_1)\sin\theta+y_2\cos\theta\right]^2\right\}$$

$$(1+2k_o^2\xi^2\left[1-(x_2-x_1)/d_{21}\right])^{-1}(1+2k_o^2\xi^2\left[1-((x_2-x_1)\cos\theta-y_2\sin\theta)/d_{21}\right])^{-1} \tag{6.4}$$

where $r \equiv ((x_2-x_1)^2+y_2^2)^{\frac{1}{2}}$, $d_{21} = (r^2+z_2^2)^{\frac{1}{2}}$ and $y_2 = x_2\mathrm{tg}\theta$. The integrals are evaluated in appendix D for the case that α may be neglected in the exponential factor in the integrand and under the assumption that $k_o\xi$ is sufficiently small compared to $\ell_2/\ell_3 \simeq 36$.

$$I_d(\theta) = I_o\left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^4(k_B T\kappa)^2(1+2\xi^2k_o^2)^{-2}\tfrac{1}{4}\pi^2\ell_1^2\ell_4\ell_3 A(\theta)$$

$$\left\{\left[1-a^2\cos^2(\theta/2)\right]^{-1}(1-a^2)^{-\frac{1}{2}}\ell n(\ell_2/\ell_3)+f_1(\theta,a)+f_2(\theta,a)\right\} \tag{6.5}$$

where

$$f_1(\theta,a) = a^{-4}(1+\cos\theta)(1-\sqrt{1-a^2})-\tfrac{1}{2}a^{-2}\cos\theta+\left[1-a^2\cos^2(\theta/2)\right]^{-1}$$

$$(1-a^2)^{-\frac{1}{2}}\left\{1+\tfrac{1}{2}\ell n\left[4(a^{-2}-1)(1-\sqrt{1-a^2})(1+\sqrt{1-a^2})^{-1}\right]\right\}$$

$$+\left[1-a^2\cos^2(\theta/2)\right]^{-1}a^{-4}(\sin\theta)^{-1}\left[1+a^2\sin^2(\theta/2)\right]\left[\theta-2\mathrm{arcotg}(\sqrt{1-a^2}\cot g(\theta/2))\right] \tag{6.6}$$

$$f_2(\theta,a) = -\frac{1}{2\pi}\int_0^{2\pi}d\phi\ \ell n\Phi\ (1+a\cos\phi)^{-1}\left[1+a\cos(\theta-\phi)\right]^{-1} \tag{6.7}$$

and

$$a \equiv 2\xi^2k_o^2(1+2\xi^2k_o^2)^{-1} \tag{6.8}$$

The last integral f_2 takes account of the precise position of the

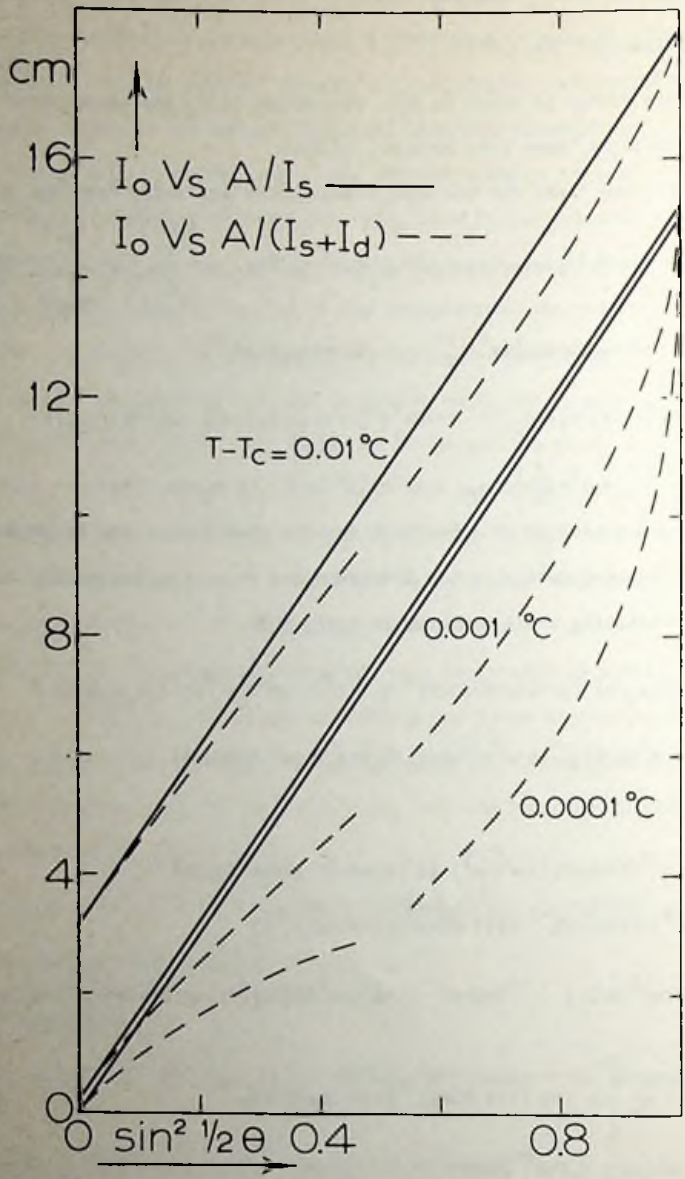


Fig. 9 The Ornstein-Zernike plot. The inverse of the single-scattering (solid line) and of the single- plus double-scattering intensity (broken line) per unit of volume and of incident intensity and corrected for attenuation as a function of $\sin^2\frac{1}{2}\theta$.

boundary through

$$\Phi \equiv |\sin\theta|^{-1} \max\left[\, |\sin\phi|,\ |\cos\theta \sin(\theta-\phi)| \,\right] \tag{6.9}$$

The formula for $I_d(\theta)$ given in eq. (6.5) contains a term proportional to $\ell_3 \ln(\ell_2/\ell_3)$. For ℓ_3 sufficiently small compared to ℓ_2 this term gives the dominant contribution. In fact for the values of ℓ_3 and ℓ_2 used in the experiment this term gives roughly 80% of the double scattering intensity depending somewhat on θ and the temperature, however. In earlier discussions [5]*) the occurrence of the logarithm was not noticed. If one approaches the critical point the finite size of a will become important first of course in $A(\theta)$ which accounts for attenuation over the longest distances and then by changing the value of the integral in eq. (6.4). It is shown in appendix D that the finite size of a will only affect $f_1(\theta,a)$ and $f_2(\theta,a)$ but not the term containing the logarithm. In view of the fact that this logarithmic term is dominant the effects due to the finite value of a on the integral are in general very small until rather close to the critical point. The logarithmic dependence is affected, however, if $k_o\xi \gtrsim \ell_2/\ell_3$, cf. appendix D. For $k_o\xi \gg \ell_2/\ell_3$ the logarithm will in fact vanish. We have also computer-integrated eq. (6.4) for $I_d(\theta)$. It turns out that even for $\Delta T = 10^{-4}$°C eq. (6.5) is at most 8% of. In the plots we have therefore always used the results of eq. (6.5).

In fig. 9 we have plotted the inverse single-scattering intensity and the inverse "total" scattering intensity per unit of volume and incident intensity, and corrected for the attenuation factor $A(\theta)$, $I_o V_S(\theta) A(\theta)/I_s(\theta)$ and $I_o V_S(\theta) A(\theta)[I_s(\theta)+I_d(\theta)]^{-1}$ respectively, for a number of temperatures at the critical density as a function of $\sin^2\frac{1}{2}\theta$, the Ornstein-Zernike plot. In fig. 10 we plot the corresponding ratios of the single scattering over the single plus double scattering intensity. As is to be expected I_d is negligible for $\Delta T = 0.1$ °C and is relatively

*) In ref. 5 a spherical sample was used. In that case one has no logarithmic dependence as may in fact be seen by taking ℓ_2 and ℓ_3 equal in eq. (6.5).

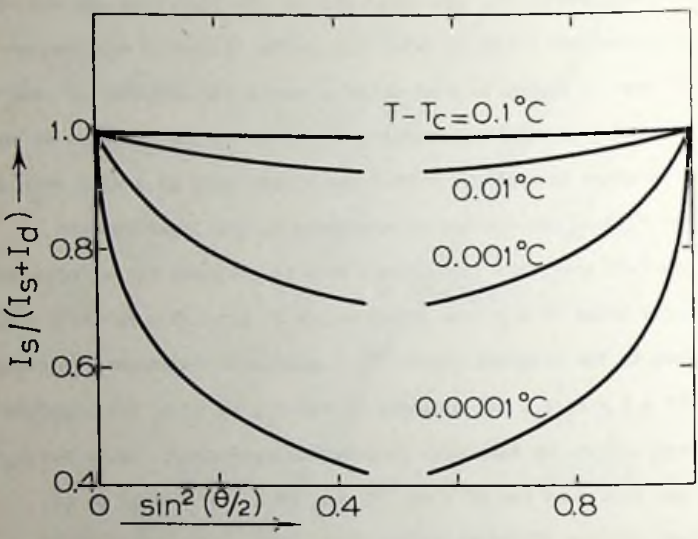


Fig. 10 The relative contribution of the single-scattering intensity to the single- plus double-scattering intensity as a function of $\sin^2 \frac{1}{2}\theta$.

small for $\Delta T = 0.01\ ^{o}C$. For $\Delta T = 0.001\ ^{o}C$ I_d contributes between zero and 30% to the total scattering intensity depending on the scattering angle. Closer to T_c the double scattering intensity becomes so large that it is in general no longer correct to neglect triple and higher order scattering contributions. An important and useful feature is that in both the forward and backward directions ($\theta=0$ and π) I_d becomes negligible compared to I_s. The reason for this phenomenon is that I_s is proportional to $V_S(\theta) \sim (\sin\theta)^{-1}$ *) whereas I_d may be shown to diverge as $\ln \theta$ respectively $\ln (\pi-\theta)$ in the forward and backward directions. Similarly it is to be expected that higher-order than double scattering will also vanish compared to I_s in the forward and backward directions. These results imply on the one hand that contributions due to multiple scattering can be minimized by measuring close to the forward and backward directions and on the other hand that even rather close to the critical point κ may be found by extrapolation to $\theta=0$ as long as this extrapolation is not done linearly. We want to emphasize that these conclusions depend strongly on the nature of the scattering geometry. This explains e.g. why Oxtoby and Gelbart [5] find a completely different behaviour.

Finally we note that linear extrapolation in the Ornstein-Zernike plot, using the temperature independent slope found further away from the critical point, will yield a value for κ which is somewhat too large closer to T_c. This may account for the sometimes observed apparent increase of the value of the critical exponent γ if one approaches T_c. [13]

*) See footnote on page 59.

Appendix A

In this appendix we will show that the use of the stationary-phase method in the body of the paper is justified by estimating the typical order of magnitude of the correction terms. We will use the following exact equality for a function $f(\vec{k})$:

$$\int d\vec{k}\, f(\vec{k}) e^{i\vec{k}\cdot\vec{r}} = 2\pi \int_{-\infty}^{\infty} dk \left[k^2 f(k\,\frac{\vec{r}}{r}) e^{ikr}/ikr \right] - \int d\vec{k} \left(\frac{\partial f(\vec{k})}{\partial \cos\theta}\right) e^{i\vec{k}\cdot\vec{r}}/ikr \qquad (A.1)$$

where θ is the angle between $\vec{r}$ and $\vec{k}$. The equality may be derived simply by partial integration with respect to cos θ. The first term on the right hand side of eq. (A.1) is the stationary-phase approximation [15] for the original integral; the second term represents therefore the correction to this approximation.

We will now first consider the derivation of eq. (3.13) from eq. (3.7). In this derivation we will disregard the frequency dependence of the scattered intensity in that we will integrate I_1^{22} over ω_s. Eq. (3.7) then becomes, taking for simplicity's sake $\alpha=0$, *)

$$I_1^{22}(\vec{\Omega}_s,\vec{u}_s) = C(2\pi)^{-3} \int d\vec{k} \left[\vec{u}_s\cdot\vec{K}(\vec{k},\omega_o)\cdot\vec{u}_o\right] S(\vec{k}_s-\vec{k}) S(\vec{k}-\vec{k}_o)$$

$$\int_{V_L} d\vec{r}_1 \int_{V_0} d\vec{r}_2 \exp\left[i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)\right] \left[\vec{u}_s\cdot\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (A.2)$$

where

$$C \equiv I_o \left[\omega_o^2 \alpha_o^2 \rho_o^2 (n^2+2)^2/36\pi\right]^2 \qquad (A.3)$$

We now split the integral in eq. (A.2) in two parts, one part with $|\vec{r}_2-\vec{r}_1|<\lambda_o = 2\pi/\omega_o n$ and the other part with $|\vec{r}_2-\vec{r}_1|>\lambda_o$. In the first integral one may restrict the integration over $\vec{r}_1$ to V_s and the integration over $\vec{r}_2$ may be replaced by an integration over $\vec{r} = \vec{r}_2-\vec{r}_1$ which is restricted to a sphere with radius λ_o. In the second integral we use equality (A.1) for the integration over $\vec{k}$. One then obtains

$$I_1^{22} = C(J_1+J_2+J_3) \qquad (A.4)$$

*) In view of the small value of α this will not affect the estimates of the correction terms in an essential way.

where

$$J_1 = V_S(2\pi)^{-3}\int d\vec{k}\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-\vec{k})S(\vec{k}-\vec{k}_o)\int_{r<\lambda_o} d\vec{r}\,\exp(i\vec{k}\cdot\vec{r})$$

$$\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r},\omega_o)\cdot\vec{u}_o\right]^* = 4\pi V_S(2\pi)^{-6}\int d\vec{k}d\vec{k}'\cdot\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right]$$

$$S(\vec{k}_s-\vec{k})S(\vec{k}-\vec{k}_o)\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k}'-\vec{k},\omega_o)\vec{u}_o\right]^*(k'\lambda_o\cos k'\lambda_o - \sin k'\lambda_o)k'^{-3} \qquad (A.5)$$

$$J_2 = (2\pi)^{-3}\int d\vec{k}\int_{V_L} d\vec{r}_1\int_{V_0,|\vec{r}_2-\vec{r}_1|>\lambda_o} d\vec{r}_2\,\left(\frac{\partial}{\partial\cos\theta}\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-\vec{k})S(\vec{k}-\vec{k}_o)\right)$$

$$(ik|\vec{r}_2-\vec{r}_1|)^{-1}\exp\left[i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)\right]\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (A.6)$$

$$J_3 = -i(2\pi)^{-2}\int_{-\infty}^{\infty} dk\,k\int_{V_L} d\vec{r}_1\int_{V_0,|\vec{r}_2-\vec{r}_1|>\lambda_o} d\vec{r}_2\,\left[\vec{u}_s\cdot\vec{\vec{K}}(k\vec{\Omega},\omega_o)\cdot\vec{u}_o\right]S(\vec{k}_s-k\vec{\Omega})S(k\vec{\Omega}-\vec{k}_o)$$

$$|\vec{r}_2-\vec{r}_1|^{-1}\exp(ik|\vec{r}_2-\vec{r}_1|)\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (A.7)$$

where θ is the angle between $\vec{k}$ and $\vec{r}_2-\vec{r}_1$ and $\vec{\Omega} = (\vec{r}_2-\vec{r}_1)/|\vec{r}_2-\vec{r}_1|$. We shall show that for critical scattering J_1 and J_2 may be neglected whereas J_3 is the approximation to I_1^{22} used in the body of the paper.

We may estimate J_1 in the limit of zero molecular diameter, $a=0$. In that limit the $\vec{\vec{K}}$ propagators are given by eq. (3.9) for all values of $\vec{k}$ and ω. For finite values of a the corrections to J_1 are of the order a/λ_o or a/ξ and may therefore be neglected. In the estimation of the order of magnitude of J_1 we will furthermore use that ε_L and ε_T are in good approximation equal and independent of k and ω [10], and put $\varepsilon_L=\varepsilon_T=\varepsilon$ constant. The integral over $\vec{x}'$ may then be performed explicitly by complex integration. The result is

$$J_1 = V_S(k_BT\kappa)^2\left(\frac{\varepsilon+2}{3}\right)^2(2\pi)^{-3}\int d\vec{k}\left[\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{u}_o\right](1+\xi^2|\vec{k}-\vec{k}_s|^2)^{-1}(1+\xi^2|\vec{k}-\vec{k}_o|^2)^{-1}$$

$$\left\{\vec{u}_s\cdot\left[(2k\lambda_o\varepsilon)^{-1}\left[(k\lambda_o+2\pi)^{-1}(e^{ik\lambda_o}-1)+(k\lambda_o-2\pi)^{-1}(e^{-ik\lambda_o}-1)\right]+\vec{k}\vec{k}/\varepsilon k^2-(\varepsilon+2)^{-1}\right]\cdot\vec{u}_o\right\}^* \qquad (A.8)$$

where we have also introduced the Ornstein-Zernike form of the correlation function, eq. (2.3) together with eq. (2.4).

We shall now analyse the behaviour of J_1 for very small and very large values of $\omega_o\xi = 2\pi\xi/\lambda_o n$. In the limit that $\omega_o\xi$ goes to zero it is convenient to rescale the integration variable $\vec{x} = \vec{k}\xi$. If one then replaces $\omega_o\xi$ by zero in the resulting expression one obtains

$$J_1 = V_S(k_B T\kappa)^2 \left(\frac{\varepsilon+2}{3}\right)^4 \xi^{-3} (2\pi)^{-3} \int d\vec{x} \left|\vec{u}_s \cdot \left[\overleftrightarrow{xx}/\varepsilon x^2 - (\varepsilon+2)^{-1}\right] \cdot \vec{u}_o\right|^2 (1+x^2)^{-2} \qquad (A.9)$$

Using the fact that the integral, which may in fact be calculated exactly, is of order unity we find the following estimate of J_1

$$J_1 = \mathcal{O}(V_S(k_B T\kappa)^2 \xi^{-3}) \qquad \text{if} \quad \omega_o\xi << 1 \qquad (A.10)$$

In the limit that $\omega_o\xi$ goes to infinity it is more convenient to rescale the integration variable $\vec{x} = \vec{k}/k_o$. One then obtains

$$J_1 = V_S(k_B T\kappa)^2 \left(\frac{\varepsilon+2}{3}\right)^2 k_o^{-1} \xi^{-4} (2\pi)^{-3} \int d\vec{x} \left[\vec{u}_s \cdot \vec{K}(\vec{x}, n^{-1}) \cdot \vec{u}_o\right] \left((k_o\xi)^{-2} + \left|\vec{x} - \vec{\Omega}_s\right|^2\right)^{-1}$$

$$\left[(k_o\xi)^{-2} + \left|\vec{x} - \vec{\Omega}_o\right|^2\right]^{-1} \left\{\vec{u}_s \cdot \left[(8\pi^2 x\varepsilon)^{-1}\left[(x+1)^{-1}(e^{2\pi i x} - 1) + (x-1)^{-1}(e^{-2\pi i x} - 1)\right]\right.\right.$$

$$\left.\left. + \overleftrightarrow{xx}/\varepsilon x^2 - (\varepsilon+2)^{-1}\right] \cdot u_o\right\}^* \qquad (A.11)$$

In the limit $\omega_o\xi$ goes to infinity one may replace $(k_o\xi)^{-1}$ by zero in the integrand. The resulting integration is of order unity so that

$$J_1 = \mathcal{O}(V_S(k_B T\kappa\xi^{-2})^2 k_o^{-1}) \qquad \text{if} \quad \omega_o\xi >> 1 \qquad (A.12)$$

We see therefore that J_1 will, since κ is proportional to ξ^2, increase as ξ for $\xi k_o < 1$ and becomes constant for $\xi k_o > 1$.

Let us now consider J_2. In estimating the size of J_2 we may extend the integration over $\vec{r}_2 - \vec{r}_1$ to infinity. The integration over $\vec{r}_1$ may then be performed and gives a proportionality factor V_L. Substituting also the Ornstein-Zernike form of the correlation function one then obtains

$$J_2 = V_L(k_B T\kappa)^2 (2\pi)^{-3} \int d\vec{k} \int_{r>\lambda_o} d\vec{r} \left\{\frac{\partial}{\partial \cos\theta}\left[\vec{u}_s \cdot \vec{K}(\vec{k}, \omega_o) \cdot \vec{u}_o\right]\right\} (1+\xi^2\left|\vec{k} - \vec{k}_s\right|^2)^{-1}$$

$$(1+\xi^2\left|\vec{k} - \vec{k}_o\right|^2)^{-1} (ikr)^{-1} \exp(i\vec{k}\cdot\vec{r}) \left[\vec{u}_s \cdot \vec{K}(\vec{r}, \omega_o) \cdot \vec{u}_o\right]^* . \qquad (A.13)$$

For $\omega_o\xi >> 1$ it is convenient to rescale $\vec{x} = \vec{k}/k_o$ and $\vec{y} = \vec{r}k_o$

In the limit that $\omega_o\xi$ goes to infinity J_2 then becomes, using the same arguments as given in the corresponding discussion of J_1,

$$J_2 = \mathcal{O}(V_L(k_B T\kappa\xi^{-2})^2 k_c^{-1}) \qquad \text{if } \omega_o\xi >> 1 \tag{A.14}$$

For $\omega_o\xi << 1$ it is more convenient to rescale $\vec{x} = \vec{k}\xi$ and $\vec{y} = \vec{r}/\xi$. In the limit that $\omega_o\xi$ approaches zero J_2 then becomes

$$J_2 = V_L(k_B T\kappa)^2\xi^{-3}(2\pi)^{-3}\int d\vec{x} \int_{y>\lambda_o/\xi} d\vec{y}\left(\frac{\partial}{\partial\cos\theta}\left[\vec{u}_s\cdot\vec{K}(\vec{x},0)\cdot\vec{u}_o\right]\right)(1+x^2)^{-2}$$

$$(ixy)^{-1}\exp(i\vec{x}\cdot\vec{y})\left[\vec{u}_s\cdot\vec{K}(\vec{y},0)\cdot\vec{u}_o\right]^* \tag{A.15}$$

If the lower bound in the integration over y would be one, one would find $J_2 = \mathcal{O}(V_L(k_B T\kappa)^2\xi^{-3})$ similar to J_1 in that case. Because of the lower bound, however, an additional factor $k_o\xi$ is obtained so that

$$J_2 = \mathcal{O}(V_L(k_B T\kappa)^2\xi^{-2}k_o) \qquad \text{if } \omega_o\xi << 1 \tag{A.15}$$

In view of the fact that V_L and V_S are of the same order of magnitude this implies that

$$J_2 << J_1 \qquad \text{if } \omega_o\xi << 1 \tag{A.16}$$

whereas they are of the same order of magnitude for $\omega_o\xi >> 1$.

In the body of the paper the contribution due to J_3 is analyzed; there is shown that

$$J_3 = \mathcal{O}(V_S(k_B T\kappa)^2 k_o^4 d) \qquad \text{if } \omega_o\xi << 1 \tag{A.17}$$

$$J_3 = \mathcal{O}(V_S(k_B T\kappa)^2\xi^{-4}d) \qquad \text{if } \omega_o\xi >> 1 \tag{A.18}$$

where d is a typical diameter of the scattering sample. The relative order of magnitude is therefore

$$(J_1+J_2)/J_3 = \mathcal{O}((k_o\xi)^{-3}(k_o d)^{-1}) \qquad \text{if } \omega_o\xi << 1 \tag{A.19}$$

$$(J_1+J_2)/J_3 = \mathcal{O}((k_o d)^{-1}) \qquad \text{if } \omega_o\xi >> 1 \tag{A.20}$$

For a typical scattering experiment $k_o d \simeq 10^5$. This implies that J_3 will become dominant for $k_o\xi$ somewhere between 0.1 and 0.01.

Appendix B

In this appendix we shall show that the contributions of I_2^{22}, I^{13} and I^{31} are of the same order as the correction terms of the stationary phase approximation to I_1^{22} discussed in appendix A. Integrating the left- and right-hand sides of eqs. (3.5) and (3.8) over ω_s and substituting the Ornstein-Zernike structure factors we get, using again $\alpha=0$,

$$I^{31}(\vec{\Omega}_s,\vec{u}_s) = C(k_B T\kappa)^2(1+\xi^2|\vec{k}_s-\vec{k}_o|^2)^{-1}(\vec{u}_s\cdot\vec{u}_o)(2\pi)^{-3}\int d\vec{k}\ \vec{u}_s\cdot\vec{K}(\vec{k},\omega_o)$$

$$(1+\xi^2|\vec{k}_s-\vec{k}|^2)^{-1}\int_{V_S}d\vec{r}_1\int_{V_S}d\vec{r}_2\ \exp\left[i(\vec{k}_o+\vec{k}-\vec{k}_s)\cdot(\vec{r}_1-\vec{r}_2)\right]\cdot\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o \qquad (B.1)$$

$$I_2^{22}(\vec{\Omega}_s,\vec{u}_s) = C(k_B T\kappa)^2(2\pi)^{-3}\int d\vec{k}\ \left[\vec{u}_s\cdot\vec{K}(\vec{k},\omega_o)\cdot\vec{u}_o\right](1+\xi^2|\vec{k}_s-\vec{k}|^2)^{-1}$$

$$(1+\xi^2|\vec{k}-\vec{k}_o|^2)^{-1}\int_{V_S}d\vec{r}_1\int_{V_S}d\vec{r}_2\ \exp\left[i(\vec{k}_s+\vec{k}_o-\vec{k})\cdot(\vec{r}_2-\vec{r}_1)\right]$$

$$\left[\vec{u}_s\cdot\vec{K}(\vec{r}_2-\vec{r}_1,\omega_o)\cdot\vec{u}_o\right]^* \qquad (B.2)$$

with the constant C defined in eq. (A.3). Similar to the discussion of the correction term J_2 in appendix A we may now extend the integration over one of the space variables to infinity. One then obtains

$$I^{31}(\vec{\Omega}_s,\vec{u}_s) = CV_S(k_B T\kappa)^2(1+\xi^2|\vec{k}_s-\vec{k}_o|^2)^{-1}(\vec{u}_s\cdot\vec{u}_o)(2\pi)^{-3}\int d\vec{k}\ (1+\xi^2|\vec{k}_s-\vec{k}|^2)^{-1}$$

$$\vec{u}_s\cdot\vec{K}(\vec{k},\omega_o)\cdot\vec{K}(\vec{k}_o+\vec{k}-\vec{k}_s,\omega_o)\cdot\vec{u}_o \qquad (B.3)$$

$$I_2^{22}(\vec{\Omega}_s,\vec{u}_s) = CV_S(k_B T\kappa)^2\int d\vec{k}\ (1+\xi^2|\vec{k}_s-\vec{k}|^2)^{-1}(1+\xi^2|\vec{k}-\vec{k}_o|^2)^{-1}$$

$$\left[\vec{u}_s\cdot\vec{K}(\vec{k},\omega_o)\cdot\vec{u}_o\right]\left[\vec{u}_s\cdot\vec{K}(\vec{k}_s+\vec{k}_o-\vec{k},\omega_o)\cdot\vec{u}_o\right]^* \qquad (B.4)$$

Introducing rescaled integration variables similar to the ones we introduced in the discussion of J_1 and J_2 in appendix A the estimation of I_2^{22} is straight-forward. *) The result is

*) We exclude the special case that $\vec{k}_s = -\vec{k}_o$ in I_2^{22} and $\vec{k}_s = \vec{k}_o$ in I^{31}

$$I_2^{22} = CJ_1 = C\mathcal{O}(V_S(k_BT\kappa)^2\xi^{-3}) \qquad \text{for } \omega_o\xi << 1 \tag{B.5}$$

and

$$I_2^{22} = C\,\mathcal{O}(V_S(k_BT\kappa\xi^{-2})^2k_o^{-1}) \qquad \text{for } \omega_o\xi >> 1 \tag{B.6}$$

In order to give an estimate of I^{31} we write this contribution as a sum of two terms

$$I^{31}(\vec{\Omega}_s,\vec{u}_s) = C(J_4+J_5) \tag{B.7}$$

with

$$J_4 = -V_S(k_BT\kappa)^2(1+\xi^2|\vec{k}_s-\vec{k}_o|^2)^{-1}(\vec{u}_s\cdot\vec{u}_o)(2\pi)^{-3}\int d\vec{k}\ (\xi|\vec{k}_s-\vec{k}|)^{-2}(1+\xi^2|\vec{k}_s-\vec{k}|^2)^{-1}$$

$$\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)\cdot\vec{\vec{K}}(\vec{k}_o+\vec{k}-\vec{k}_s,\omega_o)\cdot\vec{u}_o \tag{B.8}$$

$$J_5 = V_S(k_BT\kappa)^2\xi^{-2}(1+\xi^2|\vec{k}_s-\vec{k}_o|^2)^{-1}(\vec{u}_s\cdot\vec{u}_o)(2\pi)^{-3}\int d\vec{k}\ |\vec{k}_s-\vec{k}|^{-2}\vec{u}_s\cdot\vec{\vec{K}}(\vec{k},\omega_o)$$

$$\cdot\vec{\vec{K}}(\vec{k}_o+\vec{k}-\vec{k}_s,\omega_o)\cdot\vec{u}_o \tag{B.9}$$

Along the same lines as in appendix A one may estimate J_4 and one finds

$$J_4 = \mathcal{O}(V_S(k_BT\kappa)^2\xi^{-3}) \qquad \text{for } \omega_o\xi << 1 \tag{B.10}$$

$$J_4 = \mathcal{O}(V_S(k_BT\kappa\xi^{-2})^2k_o^{-1}) \qquad \text{for } \omega_o\xi >> 1 \tag{B.11}$$

The integrand in J_5 is of a different nature than e.g. the one in J_4 in that it tends to zero as k^{-2} instead of k^{-4} for large values of k if one uses eq. (3.9) for $\vec{\vec{K}}$. This would lead to a divergent integrand. In view of this, eq. (3.9) may not be used for all values of k; the fact that $\vec{\vec{K}}$ approaches zero for $k > k_M \equiv 2\pi/a$ is essential to make the integral convergent. Rather than using the more complicated general expression for $\vec{\vec{K}}$ valid for all values of k which was derived in ref. 10 we will simply use eq. (3.9) and introduce a cut-off at $k = k_M$. *) Neglecting furthermore terms of relative order a/λ_o we may take $\vec{k}_s$, $\vec{k}_o$ and ω_o equal to zero in the integrand.

*) In fact one finds $CJ_5 = \{(15\pi)^{-1}\alpha_o^2\rho_o^2k_BT\kappa\xi^{-2}a^{-1} + (\mathcal{O}(\alpha_o^3\rho_o^3))\}I_S(\vec{\Omega}_s,\vec{u}_s)$ if the proper expression for $\vec{\vec{K}}$ is used.

The result is, using as in appendix A the simplification $\varepsilon_T = \varepsilon_L = \varepsilon = n^2$,

$$J_5 = V_S(k_B T\kappa)^2\xi^{-2}(1+\xi^2|\vec{k}_s-\vec{k}_o|^2)^{-1}(\vec{u}_s\cdot\vec{u}_o)(2\pi)^{-3}\vec{u}_s\cdot\int_{k<k_M}d\vec{k}\; k^{-2}\vec{K}(\vec{k},0)\cdot\vec{K}(\vec{k},0)\cdot\vec{u}_o$$

$$= 3^{-5}\pi^{-2}\varepsilon^{-2}(\varepsilon+2)^2(\varepsilon^2+2)V_S\; k_B T\kappa\xi^{-2}\; k_M S(\vec{k}_s-\vec{k}_o)(\vec{u}_s\cdot\vec{u}_o)^2 \qquad (B.12)$$

This leads to the following contribution to the scattering intensity

$$CJ_5 = \left[3^{-5}\pi^{-2}\alpha_o^2\rho_o^2\varepsilon^{-2}(\varepsilon+2)^2(\varepsilon^2+2)k_B T\kappa\xi^{-2}k_M\right]\; I_s(\vec{\Omega}_s,\vec{u}_s) \qquad (B.13)$$

I^{13} obviously contains exactly the same contribution. The value of CJ_5 is in general a few per thousand of the single scattering intensity. This contribution will in a wide range of temperatures and densities around the critical point be submerged in, and therefore be indistinguishable from, the single-scattering intensity. The only effect of not correcting for it is a small error in the measured compressibility but not in the critical exponent γ. In view of this one may in general also neglect this contribution in the evaluation of the multiple-scattering intensity.

Appendix C

In this appendix we shall prove the existence of $\lim_{z\to 0}\Delta_z$, evaluate this limit and study the behaviour of Δ_z for small values of z.

We introduce the integration variables s and ϕ defined by $(x_1-x_2)|z|^{-1} \equiv s\sin\phi$ and $(y_1-y_2)|z|^{-1} \equiv -s\cos\phi$ into eq. (5.4). One then obtains

$$\Delta_z = \left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2\{S(k_o\sqrt{2})4\alpha^{-2}\sinh(\alpha x_0)\sinh(\alpha y_L)\}^{-1}$$

$$\int_{-x_0}^{x_0}dx_2\int_{-y_L}^{y_L}dy_1\exp[-\alpha(x_2+y_1)]\int_0^{2\pi}d\phi\,\sin^2\phi\int_0^{R/|z|}ds\; g(s,\phi)\exp[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}$$

$$+ s(\cos\phi+\sin\phi)\}] \qquad (C.1)$$

where

$$g(s,\phi) \equiv s^3(s^2+1)^{-3}S(k_o\{2[1+s\sin\phi/(s^2+1)^{\frac{1}{2}}]\})S(k_o\{2[1+s\cos\phi/(s^2+1)^{\frac{1}{2}}]\}) \tag{C.2}$$

and where $R = R(x_2,y_1,\phi) \equiv \sup\left[(x_1-x_2)^2+(y_1-y_2)^2\right]^{\frac{1}{2}}$ accounts for the position of the boundary.

We shall now prove that the following equality holds for any positive R

$$\lim_{z\to 0}\int_0^{R|z|^{-1}} ds\, g(s,\phi)\exp\left[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}+s(\cos\phi+\sin\phi)\}\right] = \int_0^{\infty} ds\, g(s,\phi) \tag{C.3}$$

Take s_ε such that for an arbitrarily chosen positive ε

$$\left|\int_{s_\varepsilon}^{\infty} ds\, g(s,\phi)\right| = \int_{s_\varepsilon}^{\infty} ds\, g(s,\phi) < \tfrac{1}{4}\varepsilon e^{-\alpha\ell} < \tfrac{1}{4}\varepsilon \tag{C.4}$$

where we have used the fact that $g(s,\phi) \geq 0$. The lenght ℓ is the maximum diameter of the sample which implies that $e^{-\alpha\ell}$ can be used as a lower bound for attenuation effects; in general $e^{-\alpha\ell}$ is of order one. Using furthermore that the exponential factor, cf. eq. (C.3), converges uniformly to one for $z\to 0$ in the interval $0<s<s_\varepsilon$, we may choose a δ such that for $|z|<\delta$

$$\left|\int_0^{s_\varepsilon} dsg(s,\phi)\exp\left[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}+s(\cos\phi+\sin\phi)\}\right] - \int_0^{s_\varepsilon} dsg(s,\phi)\right| < \tfrac{1}{4}\varepsilon \tag{C.5}$$

It then follows that *)

$$\begin{aligned}
&\left|\int_0^{R/|z|} dsg(s,\phi)\exp\left[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}+s(\cos\phi+\sin\phi)\}\right] - \int_0^{\infty} dsg(s,\phi)\right| \\
&\leq \left|\int_0^{s_\varepsilon} dsg(s,\phi)\exp\left[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}+s(\cos\phi+\sin\phi)\}\right] - \int_0^{s_\varepsilon} dsg(s,\phi)\right| \\
&+ \left|\int_{s_\varepsilon}^{R/|z|} dsg(s,\phi)\exp\left[-\alpha|z|\{(s^2+1)^{\frac{1}{2}}+s(\cos\phi+\sin\phi)\}\right]\right| + \left|\int_{s_\varepsilon}^{\infty} dsg(s,\phi)\right| < \varepsilon
\end{aligned} \tag{C.6}$$

It thus follows that the limit exists. Upon substitution of eq. (C.3) into eq. (C.1) the integrations over x_2 and y_1 may easily be performed

*) In fact it is assumed in the argument that $R \geq \delta$, which is not necessarily true for all values of x_2, y_1 and ϕ. This does not affect the conclusion, however.

and one obtains

$$\Delta_o = \lim_{z\to 0} \Delta_z = \left[(\omega_o/c)^2/(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2\left[S(k_o\sqrt{2})\right]^{-1}\int_0^{2\pi} d\phi\ \sin^2\phi \int_0^{\infty} ds\, g(s,\phi) \tag{C.7}$$

We shall now evaluate Δ_o for the case that the structure factor is given by the Ornstein-Zernike relation. Substituting the Ornstein-Zernike form for S, cf. eq. (2.3) with eq. (2.4), one obtains

$$\Delta_o = \left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2 k_B T\kappa (1+2\xi^2 k_o^2)\int_0^{\infty} ds \int_0^{2\pi} d\phi\ s^3 (s^2+1)^{-3}\sin^2\phi$$

$$\{1+2\xi^2 k_o^2\left[1+s\,\sin\phi\,/(s^2+1)^{\frac{1}{2}}\right]\}^{-1}\{1+2\xi^2 k_o^2\left[1+s\,\cos\phi\,/(s^2+1)^{\frac{1}{2}}\right]\}^{-1} \tag{C.8}$$

Introduction of $t \equiv s^2/(s^2+1)$ yields

$$\Delta_o = \left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^2 k_B T\kappa (1+2\xi^2 k_o^2)^{-1}\int_0^1 dt\ t\ I(t) \tag{C.9}$$

with

$$I(t) = \int_0^{2\pi} d\phi\ \sin^2\phi\ (1+a\sqrt{t}\,\sin\phi)^{-1}(1+a\sqrt{t}\,\cos\phi)^{-1}$$

$$= b^2 \int_0^{2\pi} d\phi\ \sin^2\phi\ (\sin\phi+b)^{-1}(\cos\phi+b)^{-1} \tag{C.10}$$

where a and b are given by

$$a \equiv 2\xi^2 k_o^2/(1+2\xi^2 k_o^2) \quad \text{and} \quad b \equiv (a\sqrt{t})^{-1} \tag{C.11}$$

We now introduce the variable $\zeta \equiv \exp(i\phi)$. The integration is then over the unit circle in the complex ζ plane

$$I(t) = -b^2 \oint d\zeta\,(\zeta^4-2\zeta^2+1)\left[\zeta(\zeta^2+2ib\zeta-1)(\zeta^2+2b\zeta+1)\right]^{-1}$$

$$= -b^2 \oint d\zeta\,(\zeta^4-2\zeta^2+1)\left[\zeta(\zeta-\zeta_1)(\zeta-\zeta_2)(\zeta-i\zeta_1)(\zeta-i\zeta_2)\right]^{-1} \tag{C.12}$$

where

$$\zeta_1 \equiv -b-\sqrt{b^2-1} \quad \text{and} \quad \zeta_2 \equiv -b+\sqrt{b^2-1} \tag{C.13}$$

Taking the residues in the poles of the integrand inside the unit circle at $\zeta=0$, $\zeta=\zeta_1$ and $\zeta=i\zeta_1$ and using the identity $(\zeta_1^4+1) = \zeta_1^2(\zeta_1^2+\zeta_2^2)$ one obtains

$$I(t) = 2\pi\left[\sqrt{1-a^2t}\,(2-a^2t)\right]^{-1} \qquad (C.14)$$

The integral over t is easily calculated by the choice of $(1-a^2t)^{\frac{1}{2}}$ as the integration variable

$$\int_0^1 dt\; t\, I(t) = 4\pi a^{-4}\left(\frac{\pi}{2} - 1 - 2\,\mathrm{arctg}\,\sqrt{1-a^2} + \sqrt{1-a^2}\right) \qquad (C.15)$$

If one substitutes this result into eq. (C.9) one obtains eq. (5.6) with (5.7).

We now consider the behaviour of Δ_z for small values of z. If $\alpha R \ll 1$ for all values of x_2, y_1 and ϕ the exponential factor for the attenuation in eq. (C.1) may be replaced by unity. We subsequently write $\int_0^{R/|z|} ds\; g(s,\phi) = \int_0^{\infty} ds\, g(s,\phi) - \int_{R/|z|}^{\infty} ds\, g(s,\phi)$. The first integral yields Δ_0. In the second integral one may expand $g(s,\phi)$ in powers of $1/s$ ($g(s,\phi)$ is analytic in $s=\infty$). Integration of the resulting expression over s leads to a power series expansion in $(z/R)^2$. The lowest order correction goes as $(z/R)^2$. This leads immediately to eq. (5.10).

In the case that $\alpha R \gtrsim 1$ it is necessary to take the exponential factor, due to attenuation, in eq. (C.1) into account. This exponential factor, however, has an essential singularity in $s=\infty$. As a consequence of this it is no longer possible to construct an expansion in powers of $(|z|/R)$.

Appendix D

The double-scattering intensity given in eq. (6.4) may be written in the following form

$$I_d(\theta) = I_o\left[(\omega_o/c)^2(\varepsilon-1)(\varepsilon+2)/12\pi\right]^4 (k_B T\kappa)^2 (\tfrac{1}{4}\pi\ell_1^2)\ell_4 A(\theta)J \qquad (D.1)$$

where J is the integral appearing in eq. (6.4). Introducing two new variables t and ϕ by $(x_1-x_2) = r\cos(\theta-\phi)$, $x_2 = r\sin(\theta-\phi)\mathrm{cotg}\,\theta$

and $t = r^2(r^2+z^2)^{-1}$ the integral becomes

$$J = \pi(1+2\xi^2k_o^2)^{-2}\,(J_1+J_2+J_3) \tag{D.2}$$

with

$$J_1 = \frac{1}{2\pi}\int_{-\ell_3/2}^{\ell_3/2}dz\int_0^{2\pi}d\phi\int_0^{t_1}dt(1-t)^{-1}(1+a\sqrt{t}\,\cos\phi)^{-1}(1+a\sqrt{t}\,\cos(\theta-\phi))^{-1}A(z,\phi,t) \tag{D.3}$$

$$J_2 = -\frac{1}{2\pi}\int_{-\ell_3/2}^{\ell_3/2}dz\int_0^{2\pi}d\phi\int_0^{t_2}dt\,(1+t\cos^2\phi)(1+a\sqrt{t}\,\cos\phi)^{-1}(1+a\sqrt{t}\,\cos(\theta-\phi))^{-1}$$

$$A(z,\phi,t) \tag{D.4}$$

$$J_3 = \frac{1}{2\pi}\int_{-\ell_3/2}^{\ell_3/2}dz\int_0^{2\pi}d\phi\int_{t_1}^{t_2}dt(1-t)^{-1}(1+a\sqrt{t}\,\cos\phi)^{-1}(1+a\sqrt{t}\,\cos(\theta-\phi))^{-1}A(z,\phi,t) \tag{D.5}$$

where

$$t_1 \equiv \ell_2^2(\ell_2^2+4z^2)^{-1} \quad \text{and} \quad t_2 \equiv \ell_2^2(\ell_2^2+4z^2\phi^2)^{-1} \tag{D.6}$$

with

$$\Phi \equiv |\sin\theta|^{-1}\max\left[|\sin\phi|,\,|\cos\theta\,\sin(\theta-\phi)|\right] \tag{D.7}$$

The position of the plan-parallel plates which serve as boundaries of the sample is accounted for by Φ. The factor a has been defined in eq. (C.11). Effects due to attenuation are contained in

$$A(z,\phi,t) \equiv \exp\left[-\alpha z(t/(1-t))^{\frac{1}{2}}(\sin\theta)^{-1}(\sin\theta+\sin\phi+\sin(\theta-\phi))\right] \tag{D.8}$$

In the evaluation of these integrals we shall use the fact that ℓ_3/ℓ_2 and therefore z/ℓ_2 are small. In view of this, t_1 and t_2 are both close to one. In J_1 and J_3 the integrand is singular in t=1, the integrand in J_2, however, is not singular in t=1 and one may therefore replace in good approximation t_2 by 1 in this integral.

We shall now first evaluate J_1, J_2 and J_3 in the case that the attenuation may be neglected, $A(z,\phi,t) = 1$. Note that this does not necessarily imply that the factor $A(\theta)$ in I_d and I_s which accountsfor attenuation over larger distances, cf. eqs. (6.1) and (6.4), is also close to unity! Consider first J_1. The integration over ϕ may be replaced by an integration over the unit circle

in the complex plane by the substitution $\zeta = \exp\left[i(\phi-\theta/2)\right]$.

Similar to the discussion in appendix C this integral is then equal to the sum of the residues in the two poles inside the unit circle. The result is

$$J_1 = \int_{-\ell_3/2}^{\ell_3/2} dz \int_0^{t_1} dt\,(1-t)^{-1}(1-a^2t)^{-\frac{1}{2}}(1-a^2t\cos^2(\theta/2))^{-1} \qquad (D.9)$$

We now substitute $x = \sqrt{1-a^2}\,t$ and obtain

$$J_1 = (1-a^2\cos^2(\theta/2))^{-1} \int_{-\ell_3/2}^{\ell_3/2} dz \int_{x_1}^{1} dx\{(1-a^2)^{-\frac{1}{2}}\left[(x-\sqrt{1-a^2})^{-1}-(x+\sqrt{1-a^2})^{-1}\right]$$

$$-2\left[x^2+tg^2(\theta/2)\right]^{-1}\} \qquad (D.10)$$

where $x_1 = \sqrt{1-a^2}\,t_1$. The integration over x is elementary and yields

$$J_1 = \left[1-a^2\cos^2(\theta/2)\right]^{-1} \int_{-\ell_3/2}^{\ell_3/2} dz\{(1-a^2)^{-\frac{1}{2}} \ln\left|\frac{(1-\sqrt{1-a^2})(x_1+\sqrt{1-a^2})}{(1+\sqrt{1-a^2})(x_1-\sqrt{1-a^2})}\right|$$

$$+ \operatorname{cotg}(\theta/2)\left[\theta-2\operatorname{arcotg}(x_1\operatorname{cotg}(\theta/2))\right]\} \qquad (D.11)$$

In order to perform the integration over z we will use the fact that $z \leq \ell_3/2 << \ell_2/2$. Expanding x_1 one obtains

$$x_1 = \left[1-a^2\ell_2^2(\ell_2^2+4z^2)^{-1}\right]^{\frac{1}{2}} = \sqrt{1-a^2}\left[1+2\,\frac{z^2}{\ell_2^2}\,a^2(1-a^2)^{-1} + \mathcal{O}(z^4/\ell_2^4)\right] \qquad (D.12)$$

We note that very close to the critical point, where a approaches one, the expansion coefficients diverge. So close to the critical point, however, it is no longer justified to neglect attenuation effects and we will comment on that region later. Upon substitution of eq. (D.12) one obtains

$$J_1 = \ell_3(1-a^2\cos^2(\theta/2))^{-1}(1-a^2)^{-\frac{1}{2}}\{2\ln(\ell_2/\ell_3)+2+\ln\left[4a^{-2}(1-a^2)(1-\sqrt{1-a^2})(1+\sqrt{1-a^2})^{-1}\right]$$

$$+\sqrt{1-a^2}\operatorname{cotg}(\theta/2)\left[\theta-2\operatorname{arcotg}(\sqrt{1-a^2}\operatorname{cotg}(\theta/2))\right]\}\left[1+\mathcal{O}(\ell_3/\ell_2)\right] \qquad (D.13)$$

Note the occurrence of the term proportional to $\ell_3\ln(\ell_2/\ell_3)$. This term, which is due to the singularity of the integrand in t=1 (cf. eq. (D.9)), is the reason that the integration over z can not be evaluated in a more simple

manner, by making the integral essentially linear in ℓ_3, as was done for some other integrations.

In J_2 we may safely replace t_2 by 1 neglecting again terms of higher order in ℓ_3/ℓ ; the integrand is not singular in $t=1$. The integration over z is simply an integration over a constant. Furthermore the integral over ϕ may be performed in the same way as the ϕ integration in J_1. The result is

$$J_2 = -\ell_3 \int_0^1 dt\left[(1-a^2t)^{-\frac{1}{2}}(1+t\cos^2(\tfrac{1}{2}\theta))(1-a^2t\cos^2(\tfrac{1}{2}\theta))^{-1}\right.$$

$$\left. + a^{-2}\cos\theta(1-(1-a^2t)^{-\frac{1}{2}})\right] \qquad (D.14)$$

Using again the substitution $x = \sqrt{1-a^2}\,t$ one obtains for this integral

$$J_2 = \ell_3 a^{-4}\left[2(1+a^2)(\sin\theta)^{-1}(\theta-2\,\mathrm{arcotg}(\sqrt{1-a^2}\,\cot g(\theta/2))\right.$$

$$\left. + 2(1+\cos\theta)(1-\sqrt{1-a^2})-a^2\cos\theta\right] \qquad (D.15)$$

Finally in J_3 we use the fact that both t_1 and t_2 are close to one. In good approximation one may then replace the $\sqrt{t}$ factors in eq. (D.5) by unity, assuming again that a is not so close to unity that complications may arise for small values of ϕ or $\theta-\phi$. The integration over t may then be performed and gives

$$J_3 = -\frac{1}{2\pi}\int_{-\ell_3/2}^{\ell_3/2} dz \int_0^{2\pi} d\phi\ (\ell n\,\Phi)(1+a\cos\phi)^{-1}(1+a\cos(\theta-\phi))^{-1} \qquad (D.16)$$

where higher-order terms in z/ℓ_2 have been neglected. Performing the integration over z one then obtains

$$J_3 = -\frac{1}{2\pi}\ell_3\int_0^{2\pi} d\phi\ (\ell n\,\Phi)(1+a\cos\phi)^{-1}(1+a\cos(\theta-\phi))^{-1} \qquad (D.17)$$

Substituting J_1, J_2 and J_3 as given by eqs. (D.13), (D.15) and (D.17) into eq. (D.1), using also eq. (D.2), one obtains the result used in section 6.

Effects due to attenuation cannot be calculated analytically in such detail. In principle one could probably evaluate the lowest order terms in an expansion of $A(z,\phi,t)$ and therefore the integrals in powers of α.

The higher-order terms contain powers of $z(1-t)^{-\frac{1}{2}}$. Using this fact one may easily convince oneself by inspection of the various integrals that the higher-order terms in a do not contribute to the term proportional to $\ell_3 \ell n(\ell_2/\ell_3)$ but only to the linear term. In the calculation we also used that a is not too close to one; if one is very close to the critical point ($T-T_c \lesssim 3\times10^{-5}\ ^oC$) this is no longer true. One may in fact also evaluate J_1 for such values of a but the resulting expressions are even more complicated and we will therefore not give them explicitly but limit ourselves to the remark that for $k_o\xi >> \ell_2/\ell_3$ the logarithmic dependence vanishes.

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III. LIGHT SCATTERING FROM CRITICAL BINARY MIXTURES

Synopsis

The theory of chapters I and II is extended to apply to scattering from critical binary mixtures. This extension leaves the essential structure of the scattering formulae unaltered.

I. Introduction

In chapters I and II relatively simple formulae were derived for light scattering from a critical nonpolar simple fluid on the basis of a molecular theory. The consequences of these results have been considered in detail for two experimental geometries. In this chapter the theory is extended to light scattering from a critical nonpolar binary fluid mixture. Kim and Mazur [3] have given an analogous extension of the theory by Bedeaux and Mazur [4] for the dielectric tensor of a critical simple fluid.

In section 2 a short summary is given of that part of the scattering theory of chapter I, which applies also to multicomponent systems. The scattering intensity is again expressed in terms of fluctuations of the dielectric tensor around its macroscopic value.

In section 3 the intensity of the scattered light is expressed in fluctuations of the densities of the two components or equivalently in concentration fluctuations. For this purpose we use a relation between the fluctuating dielectric tensor and the fluctuating total polarizability density of the binary mixture. This relation, which was derived by Kim and Mazur [3], enables us to express the scattering intensity in terms of fluctuations of the polarizability density around its average value. The only difference with the formulae for simple fluids is the fact that the polarizability density is now the sum of the polarizability densities of the components of the mixture. The scattering intensity is therefore expressed in terms of cross- and autocorrelation functions of fluctuations of the densities of the components. For the evaluation of higher-order scattering intensities use is again made of the Gaussian approximation for the correlation functions. It is found, that, similar to the case of simple fluids, multiple scattering near the critical point is in essence a contraction of consecutive uncorrelated single-scattering events.

2. Summary of the formal scattering theory

In sections 2 and 3 of chapter I we presented a formalism for the scattering of light from a fluctuating dielectric. Since no explicit form of the fluctuating dielectric tensor was used in these sections, the theory applies not only to nonpolar simple fluids but also to nonpolar fluid mixtures, which will be considered below. We shall briefly review this formalism in this section.

For the intensity (per unit of solid angle) of the light which is scattered in the direction $\vec{\Omega}_s$ with polarization vector $\vec{u}_s$ and frequency ω_s, eq. (I.3.6) yields

$$I(\vec{\Omega}_s,\vec{u}_s,\omega_s)2\pi\delta(\omega-\omega_s) = (4\pi)^{-2}\omega_s^4 \int_{V_0} d\vec{r}\, d\vec{r}'\, \vec{u}_s\cdot\vec{\vec{M}}(\vec{r},\omega_s|\vec{r}',\omega)\cdot\vec{u}_s$$

$$\exp\left[-\alpha(\omega_s)d_s+i\vec{k}_s\cdot(\vec{r}'-\vec{r})\right] \qquad (2.1)$$

where units are chosen in such a way that the light velocity in vacuum is unity and where V_0 is the observed volume, d_s the average distance from $\vec{r}$ and $\vec{r}'$ to the surface in the direction of the observer and α the extinction coefficient, which is related to the complex refractive index n by

$$\alpha(\omega) \equiv 2\omega \operatorname{Im} n(\omega) \qquad (2.2)$$

The wavevector of the scattered light is

$$\vec{k}_s \equiv [\omega_s \operatorname{Re} n(\omega_s)]\vec{\Omega}_s \qquad (2.3)$$

The tensor $\vec{\vec{M}}$ which contains the effects due to correlations in the fluid sample and the incident field in the medium is given by

$$\vec{\vec{M}}(\vec{r},\omega|\vec{r}'\omega') \equiv \langle\Delta\vec{p}(\vec{r},\omega)\Delta\vec{p}^{*}(\vec{r}',\omega')\rangle \qquad (2.4)$$

where the brackets indicate an ensemble average. Due to stationarity

$\vec{\vec{M}}$ contains a δ-function in the frequencies, which was already used in writing eq. (2.1). The fluctuating variable $\Delta\vec{p}$, which is defined as

$$\Delta p \equiv (\vec{\vec{\varepsilon}}_b - \vec{\vec{\varepsilon}})\cdot\vec{e} \equiv \Delta\vec{\vec{\varepsilon}}_b\cdot\vec{e}, \tag{2.5}$$

is the source of the total scattered field. In eq. (2.5) $\vec{\vec{\varepsilon}}_b$ is the fluctuating dielectric tensor, relating the fluctuating polarization density $\vec{p}$ to the fluctuating field $\vec{e}$,

$$\vec{p} = (\vec{\vec{\varepsilon}}_b - 1)\cdot\vec{e} \tag{2.6}$$

while $\vec{\vec{\varepsilon}}$ is the macroscopic dielectric tensor, relating the macroscopic polarization $\vec{P} \equiv \langle\vec{p}\rangle$ to the macroscopic field $\vec{E} \equiv \langle\vec{e}\rangle$,

$$\vec{P} = (\vec{\vec{\varepsilon}} - 1)\cdot\vec{E} \tag{2.7}$$

Thus $\Delta\vec{\vec{\varepsilon}}_b$ is the fluctuation of the dielectric tensor around its macroscopic value.

Using the wave equation in the medium one may express the fluctuating field (and hence $\Delta\vec{p}$) in terms of $\Delta\vec{\vec{\varepsilon}}_b$, $\vec{E}$ and the wave propagator $\vec{\vec{F}}_\varepsilon$ which propagates light through a non-fluctuating medium with dielectric tensor $\vec{\vec{\varepsilon}}$. This yields for $\Delta\vec{p}$ (cf. eq. (I.2.15))

$$\Delta\vec{p} = \Delta\vec{\vec{\varepsilon}}_b\cdot(1+\vec{\vec{F}}_\varepsilon\cdot\Delta\vec{\vec{\varepsilon}}_b)^{-1}\cdot\vec{E} \tag{2.8}$$

so that $\vec{\vec{M}}$ is given in terms of $\Delta\vec{\vec{\varepsilon}}_b$ and $\vec{E}$ by

$$\vec{\vec{M}}(\vec{r},\omega|\vec{r}',\omega') = \langle\left[\Delta\vec{\vec{\varepsilon}}_b\cdot(1+\vec{\vec{F}}_\varepsilon\cdot\Delta\vec{\vec{\varepsilon}}_b)^{-1}\cdot\vec{E}\right](\vec{r},\omega)\left[\Delta\vec{\vec{\varepsilon}}_b\cdot(1+\vec{\vec{F}}_\varepsilon\cdot\Delta\vec{\vec{\varepsilon}}_b)^{-1}\cdot\vec{E}\right]^*(r',\omega')\rangle \tag{2.9}$$

From eqs. (2.5), (2.6) and (2.7) it follows that $\langle\Delta\vec{p}\rangle = 0$ and hence, that (cf. eq. (I.2.16))

$$\langle\Delta\vec{\vec{\varepsilon}}_b\cdot(1+\vec{\vec{F}}_\varepsilon\cdot\Delta\vec{\vec{\varepsilon}}_b)^{-1}\rangle = 0 \tag{2.10}$$

The fact that the average of $\Delta\vec{p}$, which is the "source" not only of the singly but also of the multiply scattered fields, is equal to zero, is

an important and useful feature, which is absent in other theories of multiple scattering. In the next section we shall relate the fluctuations of the dielectric tensor $\Delta\vec{\vec{\varepsilon}}_b$ to fluctuations of the densities of the two components of the fluid.

3. The scattering intensity in terms of concentration fluctuations

In this section we shall first express the scattering intensity in terms of autocorrelation functions of the polarizability-density fluctuations in the fluid mixture. For that purpose we introduce the polarizability density γ_b as the sum of the polarizability densities of the components

$$\gamma_b(\vec{r},t) \equiv \sum_\nu \alpha_\nu \rho_\nu(\vec{r},t) \tag{3.1}$$

with α_ν and ρ_ν the molecular polarizability and molecular density of component ν. For the average polarizability density γ_o we then find

$$\gamma_o \equiv \langle\gamma_b\rangle = \sum_\nu \alpha_\nu \langle\rho_\nu\rangle = \sum_\nu \alpha_\nu \rho_\nu^o \tag{3.2}$$

The fluctuation of the polarizability density around its average value is then

$$\Delta\gamma_b^o \equiv \gamma_b - \gamma_o = \sum_\nu \alpha_\nu(\rho_\nu - \rho_\nu^o) = \sum_\nu \alpha_\nu \Delta\rho_\nu \tag{3.3}$$

with ρ_ν^o the average density and $\Delta\rho_\nu$ the density fluctuation of component ν.

In ref. 3 the relation between the polarizability density γ_b and the fluctuating dielectric tensor was shown to be

$$\vec{\vec{\varepsilon}}_b - 1 = \gamma_b(1 - \vec{\vec{G}}\gamma_b)^{-1} \tag{3.4}$$

where the operator $\vec{\vec{G}}$ is given by

$$G(\vec{r}-\vec{r}';t-t') \equiv \begin{cases} 0 & \text{if } |\vec{r}-\vec{r}'|>a \\ \frac{1}{2}(\vec{F}+\vec{F}^{+})(\vec{r}-\vec{r}',t-t') & \text{if } |\vec{r}-\vec{r}'|<a \end{cases} \tag{3.5}$$

with a the smallest molecular diameter in the mixture and $\vec{F}$ the retarded vacuum wave-propagator, cf. eq. (I.2.7). For density fields $\rho_\nu(\vec{r},t)$ which vary slowly in space and time compared to the molecular diameter, i.e. for the long-wavelength, small-frequency components of the molecular densities, eq. (3.4) reduces to (see ref. 4)

$$\varepsilon_b(\vec{r},t)-1 = \gamma_b(\vec{r},t)\left[1-\frac{1}{3}\gamma_b(\vec{r},t)\right]^{-1} \tag{3.6}$$

which is the Clausius-Mossotti (or Lorentz-Lorenz) relation on the level of the fluctuations. For the considerations in this chapter it is sufficient to use the simpler eq. (3.6) rather than eq. (3.4). Confer also appendices B of chapters I and II for a discussion of this point.

As in section (I.4) the macroscopic Clausius-Mossotti function $\vec{\vec{\gamma}}$ is defined by the relation

$$\vec{\vec{\varepsilon}}-1 \equiv \vec{\vec{\gamma}}\cdot(1-\frac{1}{3}\vec{\vec{\gamma}})^{-1} \tag{3.7}$$

and the fluctuation of the polarizability density around the macroscopic Clausius-Mossotti function

$$\Delta\vec{\vec{\gamma}}_b \equiv \gamma_b-\vec{\vec{\gamma}} = \Delta\gamma_b^{o}+\gamma_o-\vec{\vec{\gamma}} \tag{3.8}$$

In appendix (I.B) it has been shown that $\Delta\vec{\vec{\gamma}}_b$ and $\Delta\vec{\vec{\varepsilon}}_b$ satisfy the following very useful relation

$$\Delta\vec{\vec{\varepsilon}}_b\cdot(1+\vec{\vec{F}}_\varepsilon\cdot\Delta\vec{\vec{\varepsilon}}_b)^{-1} = \frac{1}{9}(\vec{\vec{\varepsilon}}+2)\cdot\Delta\vec{\vec{\gamma}}_b\cdot(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}\cdot(\vec{\vec{\varepsilon}}+2) \tag{3.9}$$

with a propagator $\vec{\vec{K}}$ defined by

$$\vec{\vec{K}} \equiv \frac{1}{9}(\vec{\vec{\varepsilon}}+2)\cdot\left[\vec{\vec{F}}_\varepsilon-(\vec{\vec{\varepsilon}}+2)^{-1}\right]\cdot(\vec{\vec{\varepsilon}}+2) \tag{3.10}$$

Using eqs. (3.9), (2.8) and (2.9) we may express $\Delta\vec{p}$ and $\vec{\vec{M}}$ in terms of $\Delta\vec{\vec{\gamma}}_b$.

The result for $\vec{\vec{M}}$ is

$$\vec{\vec{M}}(\vec{r},\omega|\vec{r}'\omega') = 3^{-4}<\left[(\vec{\vec{\varepsilon}}+2)\cdot\Delta\vec{\vec{\gamma}}_b\cdot(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}\cdot(\vec{\vec{\varepsilon}}+2)\cdot\vec{\vec{E}}\right](\vec{r},\omega)$$

$$\left[(\vec{\vec{\varepsilon}}+2)\cdot\Delta\vec{\vec{\gamma}}_b\cdot(1+\vec{\vec{K}}\cdot\Delta\gamma_b)^{-1}\cdot(\vec{\vec{\varepsilon}}+2)\cdot\vec{\vec{E}}\right]^*(\vec{r}',\omega')> \tag{3.11}$$

In order to express $\vec{\vec{M}}$ in correlation functions of $\Delta\gamma_b^o$, i.e. in the various cross- and autocorrelation functions of the density fluctuations of the components we need a relation between $\Delta\vec{\vec{\gamma}}_b \equiv \gamma_b - \vec{\vec{\gamma}}$ and $\Delta\gamma_b^o \equiv \gamma_b - \gamma_o$. This relation may be otained in the following way (cf. eqs. (I.4.11) - (I.4.14)). From eqs. (2.10) and (3.9) one gets

$$<\Delta\vec{\vec{\gamma}}_b\cdot(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}> = 0 \tag{3.12}$$

As is clear from eq. (3.8), $\Delta\vec{\vec{\gamma}}_b - \Delta\gamma_b^o$ does not fluctuate (γ_b, the only fluctuating quantity involved, cancels), so that

$$(\Delta\vec{\vec{\gamma}}_b - \Delta\gamma_b^o)\cdot<(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}> + <\Delta\gamma_b^o(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}> = 0 \tag{3.13}$$

It follows that

$$\Delta\vec{\vec{\gamma}}_b = \Delta\gamma_b^o - <\Delta\gamma_b^o(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}>\cdot<(1+\vec{\vec{K}}\cdot\Delta\vec{\vec{\gamma}}_b)^{-1}>^{-1} \tag{3.14}$$

Solving this equation by iteration one obtains an expansion for $\Delta\vec{\vec{\gamma}}_b$ in terms of $\Delta\gamma_b^o$

$$\Delta\vec{\vec{\gamma}}_b = \Delta\gamma_b^o + <\Delta\gamma_b^o\vec{\vec{K}}\Delta\gamma_b^o> - <\Delta\gamma_b^o\vec{\vec{K}}\cdot\Delta\gamma_b^o\vec{\vec{K}}\,\Delta\gamma_b^o> + \mathcal{O}((\Delta\gamma_b^o)^4) \tag{3.15}$$

If we expand $\vec{\vec{M}}$ in terms of $\Delta\vec{\vec{\gamma}}_b$ and insert this expansion for $\Delta\vec{\vec{\gamma}}_b$, an expression is obtained for the tensor $\vec{\vec{M}}$ in terms of autocorrelation functions of the polarizability-density fluctuations $\Delta\gamma_b^o$. Using translational invariance and stationarity we may define the correlation function S as

$$S(\vec{r}-\vec{r}',t-t') \equiv \gamma_o^{-2}<\Delta\gamma_b^o(\vec{r},t)\Delta\gamma_b^o(\vec{r}',t')> \tag{3.16}$$

For the higher-order correlation functions we use the Gaussian

approximation as was done in chapters I and II. Up to fourth order one then has

$$\langle \Delta\gamma_b^o(1)\Delta\gamma_b^o(2)\Delta\gamma_b^o(3)\rangle = 0 \tag{3.17}$$

$$\gamma_o^{-4}\langle \Delta\gamma_b^o(1)\Delta\gamma_b^o(2)\Delta\gamma_b^o(3)\Delta\gamma_b^o(4)\rangle = S(1-2)S(3-4) + S(1-3)S(2-4)+S(1-4)S(2-3) \tag{3.18}$$

where the arguments $i(i=1,2,3,4)$ stand for $(\vec{r}_i,t_i)$. The program sketched above has been worked out for a one-component system in chapter I. The more general results, which are obtained in a similar way, are the following

$$\vec{\vec{M}} = \sum_{i,j} \vec{\vec{M}}_{ij} \tag{3.19}$$

$$\vec{\vec{M}}_{11} = 3^{-4}\langle \left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]^*\rangle \tag{3.20}$$

$$\vec{\vec{M}}_{12} = \vec{\vec{M}}_{21}^{\dagger} = 0 \tag{3.21}$$

$$\vec{\vec{M}}_{13} = \vec{\vec{M}}_{31}^{\dagger} = 3^{-4}\langle \overbrace{\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]^*}\rangle \tag{3.22}$$

$$\vec{\vec{M}}_{22} = 3^{-4}\langle \overbrace{\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]^*}\rangle$$

$$+ 3^{-4}\langle \overbrace{\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]\left[(\vec{\varepsilon}+2)\cdot\Delta\gamma_b^{o\vec{K}}\cdot\Delta\gamma_b^o(\vec{\varepsilon}+2)\cdot\vec{E}\right]^*}\rangle \tag{3.23}$$

where the dagger denotes hermitian conjugation and the horizontal lines indicate which pairs of $\Delta\gamma_b^o$ are correlated.

In order to study these formulae for scattering from a critical binary mixture we need the properties of the correlation function S. In the critical point the equal-time (equilibrium) correlation function

$$S(\vec{k}) \equiv S(\vec{k},t=0) = (2\pi)^{-1}\int d\omega\, S(\vec{k},\omega) \tag{3.24}$$

is singular in the zero k limit due to composition fluctuations. Neglecting molecular contributions and contributions to $S(\vec{k})$ arising from "reduced total density" fluctuations of the fluid, we write for the dominant part of $S(\vec{k})$ near the critical point of the mixture (cf. ref. 3)

$$S(\vec{k}) = S(\vec{k},t=0) = (2\pi)^{-1}\int d\omega\, S(\vec{k},\omega)$$

$$= f(\xi k) k_B T \left(\frac{\partial \gamma_o}{\partial x_1}\right)^2_{T,P} \left[\left(\frac{\partial \mu_1'}{\partial x_1}\right)_{T,P} \rho_o \gamma_o^2\right]^{-1} \qquad (3.25)$$

with k_B Boltzmann's constant, T the temperature, P the pressure, $x_1 \equiv \rho_1^o(\rho_1^o+\rho_2^o)^{-1}$ the molar fraction of component 1 and μ_1' the difference in the chemical potentials of components 1 and 2. The correlation function depends on $\vec{k}$ via the scaling function $f(\xi k)$ where ξ is the correlation length. If $\xi k \lesssim 1$ we may use the Ornstein-Zernike form for $f(\xi k)$

$$f(\xi k) = (1+\xi^2 k^2)^{-1} \qquad (3.26)$$

The correlation function $S(\vec{k},\omega)$ depends on the frequency in a complicated way. One not only has to take into account the frequency dependence of the composition-fluctuation correlation function, but also the effect of the cross-correlation for different times between the composition fluctuations and the "reduced-density fluctuations" (which are defined in ref. 3). We shall not analyze here the frequency behaviour of $S(\vec{k},\omega)$ in more detail (cf. ref. 5). For the binary-mixture analogues of the estimates in appendices (II.A) and (II.B) it is again sufficient to analyze the contributions to the frequency-integrated intensity, which does not contain frequency-dependent correlation functions.

The remaining analysis of multiple-scattering intensities is the same as in chapters I and II and one arrives at results which are identical to the ones summarized in section (II.2) if one replaces

$\alpha_o^2 \rho_o^2$ by γ_o^2

κ by $\left(\frac{\partial \gamma_o}{\partial x_1}\right)^2_{T,P} \left[-\left(\frac{\partial \mu_1'}{\partial x_1}\right)_{T,P} \rho_o \gamma_o^2\right]^{-1}$

in the corresponding formulae of chapter I and II.

One thus sees, as was to be expected, that the results for critical binary mixtures are not really different from the results obtained for a simple fluid. One may again conclude that critical multiple scattering from fluctuations is essentially repeated single scattering.

References

1. Boots, H.M.J., Bedeaux, D., and Mazur, P., Physica 79A (1975) 397.
2. Boots, H.M.J., Bedeaux, D., and Mazur, P., Physica, to be published.
3. Kim, S.K., and Mazur, P., Physica 71 (1974) 579.
4. Bedeaux, D., and Mazur, P., Physica 67 (1973) 23.
5. Cohen, C., Sutherland, J.W.H., and Deutch, J.M., Phys. Chem. Liquids 2 (1971) 213.

Samenvatting

De moderne theorie van de verstrooiing van licht aan niet-polaire vloeistoffen en gassen gaat terug op het werk van Smoluchowski en Einstein in het begin van deze eeuw. Zij verklaren de verstrooiing uit de fluctuaties van de diëlectrische constante rond de waarde bij de gemiddelde dichtheid. Met behulp van de dichtheidsafhankelijkheid van de diëlectrische constante kan men dan de verstrooiingsintensiteit in laagste orde uitdrukken in de correlatiefunctie van dichtheids-fluctuaties. Vanwege juist deze relatie (en uitbreidingen hiervan) is lichtverstrooiing een belangrijke techniek geworden voor het onderzoeken van de eigenschappen van een grote klasse van systemen. Uit de over de frequentie geïntegreerde verstrooiingsintensiteit kan men eigenschappen bepalen van fluïda in evenwicht, zoals de compressibiliteit; uit de van de frequentie afhankelijke verstrooiingsintensiteit zijn transport-eigenschappen te bepalen, zoals de viscositeit en de warmtegeleiding. In het bijzonder bij het kritische punt, waar veel van deze grootheden divergeren, heeft de lichtverstrooiing een wezenlijke rol gespeeld in het onderzoek naar, en dus het begrijpen van, de verschillende singulariteiten.

In 1937 ontwikkelde Yvon een moleculaire theorie voor lichtverstrooiing aan een gas of vloeistof bestaande uit klassieke puntdipolen. Het inkomende veld, dat aan de vergelijkingen van Maxwell in vacuum voldoet, induceert dipoolmomenten in de moleculen; deze dipoolmomenten wekken secundaire velden op, die andere dipoolmomenten induceren, enz.. Op deze wijze ontstaan de enkel- en meervoudig verstrooide velden. De formule voor enkelvoudige verstrooiing verschilt van het resultaat van Einsteins fenomenologische theorie in die zin, dat zij niet de "lokale-veldcorrectie" bevat. Pas in 1955 is deze tegenspraak tussen de twee theorieën opgeheven door Fixman, die

aantoonde dat de moleculaire theorie tot dezelfde uitdrukking als de fenomenologische leidt als ook bijdragen van hogere orde in rekening worden gebracht in de moleculaire theorie.

Er zijn verscheidene redenen waarom meervoudige verstrooiing van belang is. Ten eerste bevat de intensiteit van meervoudig verstrooid licht informatie over correlatiefuncties van hogere orde. Ten tweede wordt de interpretatie van gegevens van verstrooiingsexperimenten bemoeilijkt door de bijdragen van meervoudig verstrooid licht aan de totale verstrooiings-intensiteit, vooral als die groot zijn, zoals bijvoorbeeld dicht bij het kritische punt.

Een theorie voor meervoudige verstrooiing kan ofwel fenomenologisch, ofwel moleculair zijn. In de fenomenologische theorie zijn de meervoudig verstrooide velden het gevolg van meervoudige verstrooiing aan fluctuaties in de diëlectrische constante en dus in de dichtheid. De resulterende formules bevatten wel de bekende lokale-veldcorrecties, maar ze hebben het nadeel, dat ze divergeren, tenzij men ad hoc de electromagnetische propagator afkapt voor golfvectoren die groot zijn in vergelijking met de inverse moleculaire diameter. In de moleculaire theorie zijn de meervoudig verstrooide velden het gevolg van meervoudige verstrooiing aan moleculen. In dat geval kunnen lokale-veldcorrecties alleen door uitgebreide resommaties worden verkregen; er treden echter geen divergenties op. Beide theorieën bevatten seculiere (of schaduw-) termen. Deze termen corresponderen niet echt met verstrooiing, maar ze beschrijven de verandering in de doorgaande bundel en de verstrooide velden ten gevolge van intensiteitsverliezen door verstrooiing.

Het doel van dit proefschrift is, een moleculaire theorie te geven waarin de verstrooiingsintensiteit wordt ontwikkeld naar correlatiefuncties van fluctuaties in de dichtheid en niet, zoals in gebruikelijke moleculaire

theorieën, naar correlatiefuncties van de dichtheid zelf. Op deze wijze heeft men enerzijds het voordeel, dat de theorie vanwege haar moleculaire karakter geen divergenties bevat, terwijl ze anderzijds nauw aansluit bij de fenomenologische theorie zodat bijvoorbeeld de correcties voor het lokale veld zonder resommatie worden verkregen. De mogelijkheid van een dergelijke theorie werd gesuggereerd door het werk van Bedeaux en Mazur, die de diëlectrische constante voor hetzelfde systeem op soortgelijke wijze hebben bestudeerd. Als een verdere verfijning van de theorie wordt de fluctuerende diëlectrische constante ontwikkeld rond de macroscopische waarde en niet rond de waarde bij de gemiddelde dichtheid. Hierdoor blijken de seculiere termen niet op te treden; in plaats daarvan worden attenuatie-effecten in de bundel en in de verstrooide velden in rekening gebracht.

In hoofdstuk I wordt een eenvoudig model van een eencomponentig isotroop niet-polair fluïdum beschouwd. Hierin bestaat het fluïdum uit puntdipolen met constante polariseerbaarheid. Dit "model van klassieke puntdipolen", dat ook gebruikt is door Yvon, Fixman en Bedeaux en Mazur, is slechts geldig zolang de electrische velden weinig variëren over afstanden van de orde van de moleculaire diameter. Met behulp van de technieken van Bedeaux en Mazur kan men een expliciete formule afleiden voor de fluctuerende diëlectrische constante in termen van de moleculaire polariseerbaarheid en de fluctuerende moleculaire dichtheid. Verder worden formele uitdrukkingen gevonden voor het totale verstrooide veld en de totale verstrooiingsintensiteit. Door het toepassen van alleen algebraïsche transformaties wordt het verstrooide veld eerst uitgedrukt in fluctuaties van de diëlectrische constante rond de macroscopische waarde en vervolgens in fluctuaties van de dichtheid. Tenslotte worden het verstrooide veld (en de verstrooiingsintensiteit) ontwikkeld naar deze fluctuaties. De term in deze ontwikkeling die evenredig is met de n^{de}

macht van de dichtheidsfluctuaties is dan gedefinieerd als het n maal verstrooide veld. Er moet op worden gewezen, dat de precieze betekenis van "het n maal verstrooide veld" afhangt van de wijze van ontwikkelen en dus verschilt van de ene theorie tot de andere. Het algemene gedeelte van dit hoofdstuk is hiermee afgesloten. Bij de expliciete bepaling van de intensiteit van meervoudig verstrooid licht moet men integreren over correlatiefuncties van hogere orde, die niet goed bekend zijn. Met het oog op de behandeling van kritische verstrooiing zijn formules gegeven voor het geval de Gaussische benadering mag worden gebruikt voor de correlatiefuncties van hogere orde. Voor dit geval wordt een diagrammatische ontwikkeling in het kort besproken.

In hoofdstuk II wordt de theorie toegepast op meervoudige verstrooiing bij het gas-vloeistof kritische punt. In dit hoofdstuk is overal de Gaussische benadering gebruikt; afwijkingen hiervan kunnen in principe zeer dicht bij het kritische punt tot belangrijke bijdragen leiden, die hier niet in rekening zijn gebracht. Met behulp van de benadering van stationaire fase worden de verstrooiingsformules verder vereenvoudigd. We vinden als resultaat, dat, ten gevolge van de lange dracht van de correlatiefuncties van dichtheidsfluctuaties, nabij het kritische punt die situaties het meeste bijdragen waarin de afstand tussen twee opeenvolgende verstrooiingen groot is in verhouding tot de golflengte van het licht. Bijgevolg reduceert de intensiteit van meervoudig verstrooid licht tot een contractie van opeenvolgende onderling onafhankelijke enkelvoudige verstrooiingen. Dat dit het geval is, is door Reith en Swinney onlangs (op grond van de theorie van Oxtoby en Gelbart voor kritische meervoudige verstrooiing) als verwachting uitgesproken en experimenteel geverifieerd.

In paragraaf (II.5) wordt dit resultaat gebruikt om de depolarisatiefactor te berekenen voor het experiment van Trappeniers, Michels en Huijse

die deze factor hebben gemeten voor CO_2 dicht bij het kritische punt. In dit geval is de depolarisatiefactor in laagste orde gelijk aan de verhouding van de intensiteit van twee maal en van één maal verstrooid licht. De theoretische voorspelling kan analytisch worden berekend en stemt erg goed overeen met het experimentele resultaat. Hierdoor wordt de conclusie bevestigd, dat nabij het kritische punt meervoudige verstrooiing een contractie is van opeenvolgende onderling onafhankelijke enkelvoudige verstrooiingen.

In paragraaf (II.6) berekenen we de invloed van dubbele verstrooiing op de "Ornstein-Zernike grafiek". Deze grafiek waarin het omgekeerde van de verstrooiingsintensiteit gegeven wordt als functie van $\sin^2\frac{1}{2}\theta$ met θ de strooihoek, zou een rechte lijn zijn als er alleen enkelvoudige verstrooiing was. Uit het snijpunt van deze rechte met de verticale as (θ=0) berekent men de compressibiliteit, die naar oneindig gaat in het kritische punt. Op deze wijze wordt de kritische exponent γ door middel van lichtverstrooiing bepaald. Teneinde de rechte lijn te vinden die door de theorie voor enkelvoudige verstrooiing wordt voorspeld, moet men de intensiteit van meervoudig verstrooid licht aftrekken van de totale verstrooiingsintensiteit. De correcties voor meervoudige verstrooiing blijken voor voor- en achterwaartse verstrooiing naar nul te gaan in verhouding tot de intensiteit van de enkelvoudige verstrooiing. De intensiteit van dubbele verstrooiing is expliciet berekend voor een preparaat van CO_2 en de geometrie van het verstrooiingsexperiment van White en Maccabee. Het blijkt, dat dubbele verstrooiing belangrijk wordt, als, bij de kritische dichtheid, de temperatuur minder dan 0,01 ^{o}C van de kritische temperatuur afwijkt.

Aangezien veel experimenten worden gedaan bij het kritische punt van binaire mengsels, is het van belang een soortgelijke theorie te ontwikkelen

voor meervoudige verstrooiing aan kritische binaire mengsels. Dit gebeurt in hoofdstuk III gebruikmakend van de uitbreiding die Kim en Mazur gegeven hebben voor de theorie van Bedeaux en Mazur. Weer is het resultaat, dat kritische meervoudige verstrooiing een contractie is van opeenvolgende onderling onafhankelijke enkelvoudige verstrooiingen.

Studieoverzicht

23 mei 1969:	eindexamen gymnasium β; Xaveriuscollege, Vught.
september 1969:	aanvang natuurkundestudie, Rijksuniversiteit Leiden.
25 januari 1972:	kandidaatsexamen natuurkunde en wiskunde met scheikunde.
herfst 1972:	experimentele stage in de Metalengroep van Dr. Van den Berg; onderzoek naar o.a. massadefecten in kristalroosters.
23 oktober 1973:	doctoraalexamen natuurkunde met bijvak wiskunde.
1 november 1973:	indiensttreding bij de Stichting F.O.M.; aanvang van het onderzoek voor dit proefschrift onder leiding van Prof. Mazur en Dr. Bedeaux.

De Stichting F.O.M. stelde mij in staat in 1974 aan de NUFFIC zomerschool te Wageningen en in 1975 aan de IUPAP conferentie in Boedapest deel te nemen. Door een beurs in het kader van het Nato Scientific Research Program was het mij mogelijk in 1976 vier weken te werken aan de University of Maryland bij Prof. J.V. Sengers en Prof. R.F. Chang.

Mevrouw H.E. Kruyt-Mesman heeft dit proefschrift getypt; de figuren in hoofdstuk II zijn getekend door de heer W.F. Tegelaar. Tot degenen buiten de Leidse universiteit die ik dankbaar ben voor de met hen gevoerde discussies en/of de van hen verkregen experimentele gegevens behoren in ieder geval Prof. J.V. Sengers, Dr. J.M.H. Levelt-Sengers, Prof. R.F. Chang, Prof. N.J. Trappeniers, Drs. A.C. Michels, Drs. R.H. Huijser, Prof. J.A. White en Dr. B.S. Maccabee.

STELLINGEN

en

ERRATA

behorende bij het proefschrift van

H.M.J. Boots

Leiden

1 september 1976

STELLINGEN

1. Met behulp van de in dit proefschrift ontwikkelde theorie is ook de intensiteit van meer dan twee maal verstrooid licht te berekenen voor experimentele geometrieën. Hierbij kunnen in de sterrenkunde ontwikkelde technieken van dienst zijn.

   Dit proefschrift.

   H.C. van de Hulst, I.C.E.S. 118 (1963) 583.

2. De in hoofdstuk I van dit proefschrift gegeven theorie leidt ook tot redelijke resultaten voor de depolarisatiefactor van argon bij zeer lage dichtheid.

   Dit proefschrift.

   W.M. Gelbart, J.Chem.Phys. 57 (1972) 699.

3. Het is niet verwonderlijk, dat de experimentele resultaten van Beysens e.a. betreffende kritische dubbele verstrooiïng overeenstemmen met de theorie van Oxtoby en Gelbart.

   D. Beysens, A. Bourgou en H. Charlin, Phys.Lett. 53A (1975) 236.

   D.W. Oxtoby en W.M. Gelbart, J.Chem.Phys. 60 (1974) 3359.

4. De kleine systematische afwijkingen tussen de experimentele resultaten van Chang en Sengers betreffende lichtverstrooiïng bij het kritische punt van een binair mengsel en de door hen theoretisch voorspelde resultaten, zijn niet te wijten aan dichtheidsfluctuaties.

   H. Burstyn, R.F. Chang en J.V. Sengers, niet gepubliceerde resultaten.

5. In een groot gebied nabij het kritische punt van een binair mengsel is de centrale piek in het spectrum van de verstrooiingsintensiteit de superpositie van de centrale pieken ten gevolge van concentratie- en temperatuurfluctuaties.

   C. Cohen, J.W.H. Sutherland en J.M. Deutch, Phys.Chem.Liq. 2 (1971) 213.

6. De door Kim e.a. berekende correlatielengte vertoont niet de te verwachten symmetrie in de afstand tot de kritische hoogte.

D.M. Kim, D.L. Henry en R. Kobayashi, Phys.Rev. A10 (1974) 1808.

7. De conclusie van Marchand, dat de irreversibiliteit in het verkrijgen van informatie uit negentropie te maken heeft met het feit dat deze informatie "vrij" zou zijn (in de zin van Brillouin) is aanvechtbaar.

A. Marchand, J. Physique 37 (1976) 297.

L. Brillouin, Science and Information Theory, Academic Press, New York, 1962.

8. De analyse die door G.O. Zimmerman e.a. wordt gegeven van het kritische gedrag van de magnetische susceptibiliteit van CMN, leidt tot tegenstrijdige resultaten.

G.O. Zimmerman, D.J. Abeshouse, E. Maxwell en D.R. Kelland, Proc. 14th Int. Conf. on Low Temperature Physics, Otaniemi, 3 (1975) 180.

9. Op eenvoudige wijze is in te zien dat ideaal vierde geluid in helium II een chemische-potentiaalgolf is bij constante entropie per volume-eenheid.

S.J. Putterman, Superfluid Hydrodynamics, North Holland, Amsterdam, 1974.

10. Het is mogelijk voor het door Dekeyser en Rogiers besproken gegeneraliseerde XY model in één dimensie een impliciete oplossing te geven voor de vrije energie per spin.

R. Dekeyser en J. Rogiers, Physica 81A (1975) 72.

ERRATA

p. 51	$\kappa = p_c^{-1}\,\Gamma(\Delta T)^{-\gamma}$	→	$\kappa = p_c^{-1}\,\Gamma(\Delta T)^{-\gamma}T_c^{\gamma}$
p. 57	$\lvert\vec{k}_s-\vec{k}_o\rvert^2/k_o^2$	→	$\lvert\vec{k}_s-\vec{k}_o\rvert^2/4k_o^2$
p. 58, eq.(6.1)	$1+2\xi^2k_o^2\sin^2\frac{1}{2}\theta$	→	$1+4\xi^2k_o^2\sin^2\frac{1}{2}\theta$
p. 65	integral over $\vec{x}'$	→	integral over $\vec{k}'$
p. 66, eq.(A.13)	$(1+\xi^2\lvert\vec{k}-\vec{k}_o\rvert^2)^{-1}$	→	$(1+\xi^2\lvert\vec{k}-\vec{k}_o\rvert^2)^{-1}\}$