Multiple Scattering and the Scattering of Light by Large or Small Molecules in Solution

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MULTIPLE SCATTERING AND THE SCATTERING OF LIGHT BY LARGE OR SMALL MOLECULES IN SOLUTION

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The scattering equations for two-component fluids are formulated so that individual scattering processes take place *in vacuo*. A gauge transformation is made which transforms these processes to ones taking place in a medium of refractive index m. Certain previously controversial factors apparently associated with the internal field are thereby isolated and shown to be multiple scattering terms. The formulae for the scattered intensity and turbidity of a two-component fluid of small molecules are calculated by an entirely molecular argument; they agree with the forms usually quoted as Einstein's formulae except that the additional term reported previously is confirmed. It is conjected that a very precise identity exists between the phenomenological and molecular treatments of scattering when multiple scattering is properly included. It is shown that the concept of an excess molecular polarizability in a two-component system of small molecules is valid only up to an approximation of single scattering: but the concept of excess scattering remains valid in the multiple scattering theory of such systems. It is also shown that without additional assumptions both these concepts cease to be valid even in the single scattering approximation when the solute molecules are large. These assumptions amount to a 'uniform distribution' (in a sense here specified) of the solvent round the solute in regions of radius of the order of $\frac{1}{8}\lambda$: they can be interpreted as hydration (or solvation) conditions. From a crude model of a macromolecular solution it is suggested that the Debye corrections which derive from a finite molecular size to estimates of molecular weights determined by light scattering, could be in error by as much as 100 % ($\sim$ 5 % of molecular weights) or perhaps even more: estimates of molecular size by dissymmetry can also be in similar error. For a given solute, both these and the molecular weight corrections should vary from solvent to solvent. As this has not been reported experimentally, solutions of large molecules may satisfy the hydration conditions which are indeed shown to be both necessary and sufficient for the formal reduction of the scattering equations to Debye's form. It may therefore, be possible to use light scattering to investigate the state of hydration of such molecules in a solvent and to investigate the three two-particle correlation functions of such systems.

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1. Introduction

The purpose of this paper is threefold: first, to offer an independent argument in support of the formula for the extinction coefficient of the transmitted light intensity (i.e. turbidity) in a two-component fluid suggested by the author in a previous paper (Bullough 1963 *a*) hereafter referred to as II (both the calculation here and that of II are based on the theory of complex refractive index given earlier (Bullough 1962) and this earlier paper is referred to as I). In particular it is purposed to confirm that the scattering of light from two component systems of small molecules is not additive as was reported in II.

Secondly the paper purposes to show that, whilst the source of non-additivity of the scattering from systems of small molecules becomes entirely unimportant when the molecular weight of the solute is large enough (and particularly so for the important case of macromolecules with molecular weights of 100000 or more) the scattering from solutions of large molecules can be non-additive for quite different reasons. We show in fact that if, *and only if*, the molecular distributions of the two components satisfy hydration (or solvation) conditions which may or may not obtain in any given system, is the scattering solely 'excess' scattering of the solute in the solvent: the interpretation of the scattering as nothing but excess scattering has previously been unquestioned (except by Grimley 1961) when the solute molecular weight M is high enough (see, for example, Flory & Bueche 1958).

The hydration conditions amount rather roughly to the condition that the region round a polarisable particle is uniformly occupied by particles although preferential occupation of the region by particles of one or other particular kind can remain. At an approximation of single scattering it is sufficient to put conditions on the three two-particle correlation functions of the system: if multiple scattering is also included these conditions must be extended to the three and more particle correlation functions. If the particles of the two different kinds display the same partial molar volumes the conditions on the two-particle correlation functions amounts in simplest form to a condition of no *total* correlation between pairs of particles of whatever kind: more generally the 'total occupation of volume' must be uniform and uncorrelated. The finite resolving power of a system illuminated by light of a finite wavelength λ relaxes this condition to one which must hold true on the average over regions of order $\frac{1}{8}\lambda$ in radius. These results are demonstrated in detail in § 6.

If these hydration conditions do not obtain it is not possible to abstract the 'excess' scattering. It will be shown, indeed, that for a postulated situation which does not satisfy these conditions but which may not be too remote from those occurring in real macromolecular solutions the scattering is not additive: further the non-additivity invalidates an assumption of the sole significance of 'excess' scattering to the extent that the corrections to molecular weights, which the finite size of the scattering units demand according to the simple theory of Debye (1947), cease to have significance. Since these corrections can certainly be 5% of M, neither these nor the corrections due to non-additivity can be ignored. *A fortiori* measurements of molecular size by light scattering measurements, e.g. from the dissymmetry, may have no meaning unless some conditions approximating sufficiently to the hydration condition always obtain. It follows conversely that precise *a priori* knowledge of M and molecular size may permit an investigation of the condition of hydration of macromolecules in a solution. That the simple scattering theory is theoretically valid for large molecules only when such hydration conditions are satisfied has been noted already in a preliminary report (Bullough 1960).

These two aims are carried through in § 4 and in §§ 6 and 7 respectively. The third purpose of the paper is to investigate the effect of multiple scattering on the estimated scattering cross-sections. This theme necessarily runs through the whole of the paper, except §§ 6 and 7 where the considerations are related only to single scattering because uncertainty of the form of the three two-particle correlation functions and *a fortiori* of the three- and more particle correlation functions, in systems containing large solute molecules, makes investigation of the nevertheless numerically important multiple scattering terms too much of a luxury. This is not the case for systems of small molecules, for which it is shown that up to first order in multiple scattering the molecular theory with multiple scattering *exactly* reproduces the result of the phenomenological theory (apparently a single scattering theory) except for the small non-additive term. Here detailed knowledge of the correlation functions is not required: the recurrence relations they satisfy are sufficient to prove identity between the very complicated molecular terms and the relatively remarkably simple terms which appear in Einstein's (1910) phenomenological theory.

It is shown in the paper that multiple scattering terms can be grouped either as though the individual scattering process takes place *in vacuo* or in a medium of refractive index m: the two formulations are essentially equivalent and in both cases the interference between the totality of scattered waves in a system of many particles builds up the refractive index m of the system. This is demonstrated for the formulation '*in vacuo*' in I: the corresponding formulation 'in the medium' must be given elsewhere. In II the complex refractive index from I was used to find the extinction: at an approximation of single scattering a factor $9m^{-1}(m^2+2)^{-2}$ different from that of Einstein (1910) appeared. By formulating the scattering process 'in the medium' here and calculating the scattered intensity rather than the extinction we show that, as hazarded in II, multiple scattering terms are just sufficient to eliminate the (significant $\sim\frac{1}{2}$ for $m = 1{\cdot}5$) factor $9(m^2+2)^{-2}$.

The calculation of the extinction in this formulation is a much more delicate matter: in the process it is necessary to transform the Lorentz radiation reaction field 'to the medium' and because this has not yet been completely achieved and because the calculation appears in any case to bear a close formal relationship to field theoretical calculations of the self energy of the electron we must consider it elsewhere. This transformation does, however, explain in part the factor m^{-1} in the extinction first reported by Rosenfeld (1951). The factor appears there quite 'naturally' as is shown in II but its 'obvious' interpretation as of scattered intensity *in vacuo* normalized against transmitted intensity in the medium is misleading. Instead, the factor is closely associated with the boundary conditions put into a very precise description of the scattering system. Because we cannot consider the problem in such detail here the omission of this factor in the result (4·29) for the extinction strictly speaking neither confirms or denies whether such a factor should be included in any estimate of the scattering. Within the terms implicit in the calculation below the factor should be omitted however, and I believe (4·29) to be correct to an order of scattering well beyond the first order in multiple scattering to which the calculation is carried out here—providing in the more general case a suitable depolarization factor is inserted. Probably the most significant conclusion from the multiple scattering theory as such is that firstly, scattering terms have no absolute significance and can be transformed from multiple scattering terms in the *in vacuo* formulation to single scattering terms in the 'in the medium' formulation. Secondly, a too precise physical interpretation of such terms can be very misleading: certainly the same terms can play quite complementary roles in different contexts.

In the following §2 we formulate an expression for the scattered electric field *in vacuo* and transform it and the scattered magnetic field 'to the medium'. In §3 we evaluate the scattered intensity at an initially unilluminated point within the medium arriving from an illuminated region V in the medium containing many small scattering centres: the scattered intensity is valid for both small and larger values of the correlation distances between the small scattering centres. In §4 the extended Einstein formula is calculated to first order in multiple scattering, that is one order more than in II. In §5 the remarkably simple result of §4 is discussed; in §6 the hydration conditions and sufficient conditions for the validity of the usual formulae for the scattering from system of molecules with correlation distances comparable with the wavelength of the incident radiation are discussed; in §7 a necessarily rough estimate of the possible error introduced into estimates of molecular weights because of failure of the formulae when no such conditions obtain is made.

2. THE SCATTERED MICROSCOPIC FIELD

The microscopic electric field vector $\mathbf{e}(\mathbf{x})$ at an arbitrary point $\mathbf{x}$ in or adjacent to a two-component system of N_a a-particles and N_b b-particles is† (I (8·8)‡):

$$\mathbf{e}(\mathbf{x}) = \mathbf{E}(\mathbf{x}) + \sum_{j_a=1}^{N_a} \mathbf{E}^s_{\mathbf{x}j_a} + \sum_{j_b=1}^{N_b} \mathbf{E}^s_{\mathbf{x}j_b}, \tag{2·1}$$

where

$$\mathbf{E}^s_{\mathbf{x}j_\beta} = (\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + k_0^2\mathbf{U})f(r_{j_\beta}) . \mathbf{P}_{j_\beta}, \quad \beta = a \quad \text{or} \quad b, \tag{2·2a}$$

$$f(r) = \mathrm{e}^{-\mathrm{i}k_0 r}/r, \qquad r_{j_\beta} = |\mathbf{x}_{j_\beta} - \mathbf{x}| \tag{2·2b}$$

$$\mathbf{E}(\mathbf{x}) = \mathbf{u}E_0\mathrm{e}^{-\mathrm{i}k_0 z}, \qquad \mathbf{x} = (x, y, z). \tag{2·2c}$$

In these relations $\mathbf{U}$ is the unit tensor and $\nabla_{\mathbf{x}}$ the usual gradient operator taken at the field point $\mathbf{x}$: $\mathbf{E}(\mathbf{x})$, with wave number $k_0 = 2\pi/\lambda$ and polarization vector $\mathbf{u}$ taken perpendicular to the z-axis, is the incident electric field and is the electric field at $\mathbf{x}$ *in vacuo*: this is augmented by the scattered fields $\mathbf{E}^s_{\mathbf{x}j_\beta}$ of each of the particles of kind β $(= a$ or $b)$ and labels $j_\beta = 1, \ldots, N_\beta$ assumed to have instantaneous positions $\mathbf{x}_{j_\beta}$. The word 'instantaneous' is used here and in the following only to distinguish a quantity from its corresponding 'average' quantity. In this sense the $\mathbf{P}_{j_\beta}$ are the instantaneous dipole moments of the particle j_β at $\mathbf{x}_{j_\beta}$: if $\mathbf{E}^s_{\mathbf{x}i_\beta}$ is omitted from (2·1), $\mathbf{e}(\mathbf{x}_{i_\beta})$ is the instantaneous field polarizing the particle i_β at $\mathbf{x}_{i_\beta}$; hence the induced dipole moments $\mathbf{P}_{j_\beta}$ depend on the positions $\mathbf{x}_{k_\gamma}$ $(\gamma = a$ or $b)$ of all particles.

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† We eventually particularize the situation by choosing the a-particles for the solvent and the b-particles for the solute. This introduces an element of asymmetry into the problem not merited by the mathematics, and as long as possible we treat a and b on equal footing. The eventual emergence of a solvent-solute asymmetry from the underlying symmetry between the particles is a striking feature of all aspects of the theory of two-component systems. This is no where better exemplified than in the theory of their optical scattering as I hope will become clear in the following—expecially §4.

‡ I (p.q) refers to equation (p.q) of I, that is of the author's (1962) paper.

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With $f(r)$ in the form of (2·2a) $\mathbf{E}^s_{\mathbf{x}j_\beta}$ is the scattered field at $\mathbf{x}$ from an induced dipole moment $\mathbf{P}_{j_\beta}$ at $\mathbf{x}_{j_\beta}$ *in vacuo*: thus (2·1) ignores contributions to $\mathbf{e}(\mathbf{x})$ from the scattered fields from induced multipoles. We shall suppose that the point $\mathbf{x}$ lies in the medium although we shall finally choose it to lie in an unilluminated portion of the medium, that is we choose $\mathbf{E}(\mathbf{x}) = \mathbf{0}$ at the field point $\mathbf{x}$: then (2·1) becomes the total scattered field at $\mathbf{x}$ in the unilluminated part of the medium. $\mathbf{E}$ induces the $\mathbf{P}_{i_\beta}$ both directly and by the scattered fields of the remaining $N_a + N_b - 1$ dipoles not at the point $\mathbf{x}_{i_\beta}$; thus the $\mathbf{P}_{i_\beta}$ are induced in part by $\mathbf{E}$, in part by single scattering from the neighbouring $\mathbf{P}_{j_\gamma}$ ($\gamma = a$ or b) induced by $\mathbf{E}$, in part by multiple scattering from $\mathbf{P}_{j_\gamma}$ induced by neighbouring $\mathbf{P}_{k_\delta}$ ($\delta = a$ or b), and so on. There is also multiple scattering between $\mathbf{P}_{i_\beta}$ and itself with other induced dipoles as intermediaries. The effect of multiple scattering is considerable and provides the key to an understanding of apparent discrepancies between the results of the several methods of calculating the scattering—as noted in §1 and in II earlier. One very interesting result is that the multiple scattering between $\mathbf{P}_{i_\beta}$ and itself appears to have just the property required of it of transforming the Lorentz radiation damping field, i.e. the equivalent field of the interaction between the scattering electrons of the system and their own radiation fields, from a form appropriate to single scattering *in vacuo* to a form appropriate to a scattering process in a medium. This result has important consequences to the direct calculation of the extinction and is one of the keys to an understanding of the factor m^{-1} which appeared in such a calculation in II as we note in §1. In the calculation of extinction via the scattered intensity the radiation damping can be neglected but equivalent multiple scattering terms necessarily appear in a different guise and make an important contribution to the scattered intensity: we must therefore, take multiple scattering into account implicitly in the following, but we only evaluate explicitly the first order corrections it introduces. As noted in §1 we also make a transformation of the scattering process 'to the medium': this is done by an appropriate gauge transformation of the potentials of the scattered fields which incidentally has the effect of re-grouping some of the multiple scattering terms: in this way the calculation takes into account certain very significant multiple scattering terms of order higher than the first. In so far as the 'unilluminated' medium is illuminated by the wave scattered from the 'illuminated' medium, the $\mathbf{P}_{j_\beta}$ are induced by other dipoles in both parts of the medium: we shall, however, restrict the $\mathbf{P}_{i_\beta}$ entirely to the illuminated region of assumed volume V and ignore secondary scattering from the scattered wave outside. A more precise treatment requires a specification of the system and its boundary conditions together with a development of multiple scattering theory inappropriate in the present context.

In order to transform the field (2·1) we note that, when the incident field $\mathbf{E}(\mathbf{x})$ has wave number k_0 *in vacuo* as in (2·2c), the statistical average of $\mathbf{e}(\mathbf{x})$ at a point $\mathbf{x}$ in the illuminated part of the medium is the Maxwell electric field vector $\mathscr{E}(\mathbf{x})$ propagated with wave number $k = mk_0$; m is therefore the refractive index of the medium. We transform 'to the medium' by a transformation which makes the individual scattering process in (2·1) depend on the wavenumber k of the medium rather than on the wavenumber k_0 of the vacuum. We emphasize that the possibility of such a transformation does not pose two irreconcileable physical interpretations of the individual scattering process. Individual scattering 'in the medium' is from a screened 'quasi-particle' whose existence is merely representative of a collective grouping of a selected set of multiple scattering terms. Because this grouping stems from a gauge transformation it is an arbitrary one and multiple scattering between screened particles continues to make a significant contribution. Thus neither scattering *in vacuo* or in the medium has that physical significance which simplifies the mathematical analysis. Too precise a physical interpretation of selected sets of multiple scattering terms leads indeed to apparent inconsistencies in the several calculations of scattered intensity as noted above. It remains an open question whether there is a gauge or other transformation which will lead to the simplification of the argument that the final formulae for the scattering from small molecules so strongly suggest.

In transforming 'to the medium' we recast $\mathbf{e}(\mathbf{x})$ of (2·1) to a form analogous to that first used by Fixman (1955) for the one component system. The method is essentially a trivial extension to the two-component system of that given by Mazur (1958) for the one-component system. The transformation is a gauge transformation and the scattered intensity should be invariant under it; but because of the changed boundary conditions this is not quite so. We shall be obliged to comment on this again, but the demonstration of the real invariance of the scattering must be given elsewhere as noted in §1.

The field (2·1) is generated by a Hertz potential

$$\boldsymbol{\pi}(\mathbf{x}) = \boldsymbol{\pi}_0(\mathbf{x}) + \boldsymbol{\pi}_1(\mathbf{x}),$$

where

$$(\nabla_{\mathbf{x}}^2 + k_0^2)\,\boldsymbol{\pi}(\mathbf{x}) = -4\pi\mathbf{q}(\mathbf{x})\,; \tag{2·3a}$$

the source function $\mathbf{q}(\mathbf{x})$ is

$$\mathbf{q}(\mathbf{x}) = \sum_{\beta}\sum_{j_\beta=1}^{N_\beta} \mathbf{P}_{j_\beta}\,\delta(\mathbf{x}-\mathbf{x}_{j_\beta}) \tag{2·3b}$$

and $\delta(\mathbf{x})$ is the three dimensional Dirac δ-function differentiable to any order; $\boldsymbol{\pi}_0(\mathbf{x})$ satisfies the homogeneous equation. We have

$$\mathbf{e}(\mathbf{x}) = (\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + k_0^2\mathsf{\mathbf{U}})\,.\,\boldsymbol{\pi}(\mathbf{x})$$

when

$$\mathbf{E}(\mathbf{x}) = (\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + k_0^2\mathsf{\mathbf{U}})\,.\,\boldsymbol{\pi}_0(\mathbf{x}),$$

while $\mathbf{e}(\mathbf{x})$ is the field corresponding to scalar and vector potentials

$$\phi = -\nabla_{\mathbf{x}}\,.\,\boldsymbol{\pi}(\mathbf{x}), \quad \mathbf{a} = \mathrm{i}k_0\boldsymbol{\pi}(\mathbf{x}).$$

With time dependence $\mathrm{e}^{\mathrm{i}\omega t}$, where $\omega/c = k_0$, the choice of gauge is

$$\frac{1}{c}\frac{\partial}{\partial t}(\phi\,\mathrm{e}^{\mathrm{i}\omega t}) + \nabla_{\mathbf{x}}\,.\,(\mathbf{a}\,\mathrm{e}^{\mathrm{i}\omega t}) = 0. \tag{2·4}$$

Introduce a Hertz potential $\tilde{\boldsymbol{\pi}}(\mathbf{x})$ such that

$$\tilde{\phi} = -\nabla_{\mathbf{x}}\,.\,\tilde{\boldsymbol{\pi}}(\mathbf{x}), \quad \tilde{\mathbf{a}} = \mathrm{i}m^2k_0\tilde{\boldsymbol{\pi}}(\mathbf{x}), \tag{2·5}$$

where m is initially an adjustable parameter to be fixed by the boundary conditions; the choice of gauge is now

$$\frac{1}{c}\frac{\partial}{\partial t}(\tilde{\phi}\,\mathrm{e}^{\mathrm{i}\omega t}) + \nabla_{\mathbf{x}}\,.\,(\tilde{\mathbf{a}}\,\mathrm{e}^{\mathrm{i}\omega t}) = -\mathrm{i}k_0(m^2-1)\,\tilde{\phi}\,\mathrm{e}^{\mathrm{i}\omega t} \tag{2·6}$$

and is the original choice (2·4) only if m is chosen equal to 1.

The field $\mathbf{e}(\mathbf{x})$ of (2·1) satisfies the partial differential equations

$$-\nabla_{\mathbf{x}}\wedge\nabla_{\mathbf{x}}\wedge\mathbf{e} + k_0^2\mathbf{e} = -4\pi k_0^2\mathbf{q}(\mathbf{x})\,; \quad \nabla_{\mathbf{x}}\,.\,(\mathbf{e}+4\pi\mathbf{q}) = 0. \tag{2·7}$$

According to (2·5) $$\mathbf{e} = (\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + m^2k_0^2\mathbf{U}).\tilde{\boldsymbol{\pi}} \tag{2·8}$$

so that $$\nabla_{\mathbf{x}}^2\tilde{\boldsymbol{\pi}}(\mathbf{x}) + m^2k_0^2\tilde{\boldsymbol{\pi}}(\mathbf{x}) = (1/m^2)\{-4\pi\mathbf{q}(\mathbf{x}) + (m^2-1)\,\mathbf{e}(\mathbf{x})\}. \tag{2·9}$$

According to (2·9) the field **e** itself is taken as part of the source function for **e** and this leads to a regrouping of multiple scattering terms. An implicit integral equation for **e** is from (2·9)

$$\tilde{\boldsymbol{\pi}}(\mathbf{x}) = \frac{1}{m^2}\int_V \tilde{f}(r)\left\{\sum_{\beta}\sum_{j_\beta}\mathbf{P}_{j_\beta}\delta(\mathbf{x}'-\mathbf{x}_{j_\beta}) - \frac{1}{4\pi}(m^2-1)\,\mathbf{e}(\mathbf{x}')\right\}\mathrm{d}\mathbf{x}' + \tilde{\boldsymbol{\pi}}_0(\mathbf{x}). \tag{2·10}$$

We define $$\tilde{f}(r) = \mathrm{e}^{-\mathrm{i}mk_0r}/r, \quad r = |\mathbf{x}-\mathbf{x}'|, \tag{2·11}$$

so that (2·10) is the solution of (2·3*a*) when $m = 1$. The source function of (2·9) given explicitly in (2·10) is the rather obvious extension to a two-component system of Fixman's (1955) source function for a one component one.

The new potential $\tilde{\boldsymbol{\pi}}_0(\mathbf{x})$ satisfies the homogeneous equation

$$\nabla_{\mathbf{x}}^2\tilde{\boldsymbol{\pi}}_0 + m^2k_0^2\tilde{\boldsymbol{\pi}}_0 = \mathbf{0} \tag{2·12}$$

and must be chosen to satisfy appropriate boundary conditions. In so far as the latter must themselves be appropriate to the particular physical situation envisaged, the field $\mathbf{e}(\mathbf{x})$ we derive by (2·8) on (2·10) is not necessarily identical with that of (2·1) as was claimed by Mazur (1958) in a similar context: the distinction between the two $\mathbf{e}(\mathbf{x})$ is one reason for apparent discrepancies in the formulae for the scattering cross sections as we have noted. Certainly if we choose $m = 1$ thereby restoring the gauge (2·4) we regain (2·1) precisely. However, we shall choose m to be the refractive index (> 1) of the medium with the condition on the Maxwell field vector $\bar{\mathscr{E}}(\mathbf{x})$ that

$$\bar{\mathscr{E}}(\mathbf{x}) = \frac{4\pi}{m^2-1}\{n_a\bar{\mathbf{P}}_a(\mathbf{x}) + n_b\bar{\mathbf{P}}_b(\mathbf{x})\}, \tag{2·13}$$

where $n_\beta = \langle N_\beta p(\boldsymbol{\varpi})\rangle/V$, $\beta = a$ or b, is the average number density of particles of kind β: $n_a\bar{\mathbf{P}}_a(\mathbf{x})$ and $n_b\bar{\mathbf{P}}_b(\mathbf{x})$ are the average total induced dipole moments per unit volume of the particles of kinds a and b respectively defined by

$$\left\langle\sum_{j_\beta=1}^{N_\beta}\mathbf{P}_{j_\beta}\delta(\mathbf{x}_{j_\beta}-\mathbf{x})\,p(\boldsymbol{\varpi})\right\rangle = n_\beta\bar{\mathbf{P}}_\beta(\mathbf{x}) \tag{2·14}$$

(cf. I for the comparable equation (4·5)). In the definitions of the average quantities n_β and $n_\beta\bar{\mathbf{P}}_\beta$, $p(\boldsymbol{\varpi})$ is the probability distribution of the grand canonical ensemble appropriate to chemical potentials $\mu_\beta(\beta = a$ or $b)$ of the two constituents, to a temperature T and to the chosen volume V: it describes the probability of N_a a-particles and N_b b-particles lying within the volume V in a configuration $\boldsymbol{\varpi} = (\mathbf{x}_{1_a}, \mathbf{x}_{2_a}, \ldots, \mathbf{x}_{N_a}; \mathbf{x}_{1_b}, \mathbf{x}_{2_b}, \ldots, \mathbf{x}_{N_b})$. (We shall not need the orientational co-ordinates of I here.)

An investigation of the propagation of the $\bar{\mathbf{P}}_\beta(\mathbf{x})$ through a material medium in response to the applied field (2·2*c*) shows as we expect (cf. I, (5·4)) that

$$\bar{\mathbf{P}}_\beta(\mathbf{x}) = \mathbf{u}\bar{P}_\beta\mathrm{e}^{-\mathrm{i}kz} \tag{2·15}$$

with $k = mk_0$, and, if we *define* $\bar{\mathscr{E}}(\mathbf{x})$ (cf. I, (8·7)) in terms of this m by (2·13), this defines this m in the usual way as the refractive index of the medium. Surprisingly the solution (2·15) must be scrutinized rather carefully when the system loses energy through scattering, but we assume it valid here for the direct calculation of scattered intensity.

We can also show that the average microscopic field $\langle \mathbf{e}(\mathbf{x})\, p(\varpi)\rangle$ is equal to the right hand side of (2·13), i.e.

$$\langle \mathbf{e}(\mathbf{x})\, p(\varpi)\rangle = \frac{4\pi}{m^2-1}\{n_a \bar{\mathbf{P}}_a(\mathbf{x}) + n_b \bar{\mathbf{P}}_b(\mathbf{x})\}; \tag{2·16}$$

so we now choose $\tilde{\boldsymbol{\pi}}_0(\mathbf{x})$ in (2·10) by making it consistent with (2·16). This puts boundary conditions on our system which however we need investigate no further in a direct calculation of scattering. Since $\tilde{\boldsymbol{\pi}}_0(\mathbf{x})$ is a solution of the homogeneous equation (2·12) it cannot depend on the sources at $\mathbf{x}_{j_\beta}$ and its average with $p(\varpi)$ is again $\tilde{\boldsymbol{\pi}}_0(\mathbf{x})$. We therefore identify m of (2·13), (2·15) and (2·16) with that in (2·10) and then find from this last equation that

$$\langle \tilde{\boldsymbol{\pi}}(\mathbf{x})\, p(\varpi)\rangle = \tilde{\boldsymbol{\pi}}_0(\mathbf{x}).$$

Thus $\tilde{\boldsymbol{\pi}}_0(\mathbf{x})$ is the Hertz vector of the average field $\langle \mathbf{e}(\mathbf{x})\, p(\varpi)\rangle$ and from (2·16) and (2·13) is then the Hertz vector of $\bar{\mathscr{E}}(\mathbf{x})$. From (2·8) and (2·10) it follows that

$$\mathbf{e}(\mathbf{x}) = \frac{1}{m^2}\int_V \{(\nabla_\mathbf{x}\nabla_\mathbf{x} + k^2\mathbf{U})\tilde{f}(r)\}\left\{\sum_\beta \sum_{j_\beta} \mathbf{P}_{j_\beta}\delta(\mathbf{x}_j - \mathbf{x}') - \left(\frac{m^2-1}{4\pi}\right)\mathbf{e}(\mathbf{x}')\right\}\mathrm{d}\mathbf{x}' + \bar{\mathscr{E}}(\mathbf{x}). \tag{2·17}$$

Moreover, at a point $\mathbf{x}$ in the unilluminated medium $\bar{\mathscr{E}}(\mathbf{x}) = \mathbf{0}$ and using this and (2·16) with (2·13) after defining

$$\tilde{\mathbf{T}}(\mathbf{x}, \mathbf{x}') \equiv (\nabla_\mathbf{x}\nabla_\mathbf{x} + k^2\mathbf{U})\,(\mathrm{e}^{-\mathrm{i}mk_0 r}/m^2 r) \tag{2·18a}$$

we have at such a point $\mathbf{x}$

$$\mathbf{e}(\mathbf{x}) = \int_V \tilde{\mathbf{T}}(\mathbf{x}, \mathbf{x}')\,.\left\{\sum_\beta \Big[\sum_{j_\beta} \mathbf{P}_{j_\beta}\delta(\mathbf{x}' - \mathbf{x}_{j_\beta}) - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}')\Big] - \left(\frac{m^2-1}{4\pi}\right)[\mathbf{e}(\mathbf{x}') - \bar{\mathscr{E}}(\mathbf{x}')]\right\}\mathrm{d}\mathbf{x}'. \tag{2·18b}$$

Define

$$\mathbf{T}(\mathbf{x}, \mathbf{x}') \equiv (\nabla_\mathbf{x}\nabla_\mathbf{x} + k_0^2\mathbf{U})\,(\mathrm{e}^{-\mathrm{i}k_0 r}/r). \tag{2·19a}$$

Of the several ways of iterating (2·18*b*) we choose the following: we use with $r' = |\mathbf{x}'' - \mathbf{x}'|$ and both $\mathbf{x}'$ and $\mathbf{x}''$ *inside* the illuminated region V

$$\mathbf{e}(\mathbf{x}') - \bar{\mathscr{E}}(\mathbf{x}') = \sum_\beta \int_V \mathbf{T}(\mathbf{x}', \mathbf{x}'')\,.\{\sum_{j_\beta} \mathbf{P}_{j_\beta}\delta(\mathbf{x}_{j_\beta} - \mathbf{x}'') - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}'')\}\,\mathrm{d}\mathbf{x}'' \tag{2·19b}$$

which relation we might obtain superficially by putting $m = 1$ in (2·18*b*) remembering that $\mathbf{x}'$ is illuminated. But bearing in mind that the parameter m of (2·18) from (2·10) has been fixed as the refractive index (> 1) of the medium we obtain (2·19*b*) in fact from (2·1) using (2·16); since

$$\mathbf{e}(\mathbf{x}') = \mathbf{E}(\mathbf{x}') + \sum_\beta \int_V \mathbf{T}(\mathbf{x}', \mathbf{x}'')\,.\sum_{j_\beta} \mathbf{P}_{j_\beta}\delta(\mathbf{x}'' - \mathbf{x}_{j_\beta})\,\mathrm{d}\mathbf{x}'' \tag{2·20}$$

it follows from (2·14) that

$$\langle \mathbf{e}(\mathbf{x}')\, p(\varpi)\rangle = \mathbf{E}(\mathbf{x}') + \sum_\beta \int_V \mathbf{T}(\mathbf{x}', \mathbf{x}'')\,.\,(n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}''))\,\mathrm{d}\mathbf{x}''; \tag{2·21}$$

identify the left-hand sides of (2·13) and (2·16) and eliminate $\mathbf{E}(\mathbf{x}')$ from (2·20) by (2·21) to obtain (2·19*b*).

We now split the illuminated region V of integration in (2·19*b*) into two parts—v, a small sphere of vanishingly small radius centred on $\mathbf{x}'$, and $U = V - v$, the region V with v omitted.

Since

$$\int_v \mathbf{T}(\mathbf{x}', \mathbf{x}'') \cdot \{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}'' - \mathbf{x}_{j_\beta}) - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}'')\} \, \mathrm{d}\mathbf{x}''$$
$$= \int_v \mathbf{T}(\mathbf{x}', \mathbf{x}'') \, \mathrm{d}\mathbf{x}'' \cdot \{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}' - \mathbf{x}_{j_\beta}) - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}')\} + O(v^{\frac{1}{3}}) \qquad (2{\cdot}22)$$

and the tensor is isotropic, we use

$$\lim_{v \to 0} \int_v \mathbf{T}(\mathbf{x}', \mathbf{x}'') \, \mathrm{d}\mathbf{x}'' \equiv \lim_{v \to 0} \int_v (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}) f(r') \, \mathrm{d}\mathbf{x}''$$
$$= \lim_{v \to 0} \tfrac{1}{3} \mathbf{U} \int_v \nabla_{\mathbf{x}}^2 f(r') \, \mathrm{d}\mathbf{x}'' = -\tfrac{4}{3}\pi \mathbf{U} \int_v \delta(\mathbf{x}' - \mathbf{x}'') \, \mathrm{d}\mathbf{x}'' = -\tfrac{4}{3}\pi \mathbf{U},$$

and obtain from (2·19*b*) that

$$\mathbf{e}(\mathbf{x}') - \bar{\mathscr{E}}(\mathbf{x}') = -\tfrac{4}{3}\pi \mathbf{U} \sum_\beta \{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}_{j_\beta} - \mathbf{x}') - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x})'\}$$
$$+ \sum_\beta \int_U \mathbf{T}(\mathbf{x}', \mathbf{x}'') \cdot \{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}_{j_\beta} - \mathbf{x}'') - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}'')\} \, \mathrm{d}\mathbf{x}''. \qquad (2{\cdot}23)$$

We substitute this form for $\mathbf{e}(\mathbf{x}') - \bar{\mathscr{E}}(\mathbf{x}')$ into the right-hand side of (2·18*b*).

Since m is the refractive index of the medium (and more precisely is the parameter m in the solution (2·15)) it satisfies the Lorentz–Lorentz relation (I (6·9))

$$\frac{m^2 - 1}{m^2 + 2} = \tfrac{4}{3}\pi \, (n_a \eta_a + n_b \eta_b) \, (1 + O(n_\alpha \eta_\alpha)), \qquad (2{\cdot}24)$$

where η_a and η_b are the (isotropic) scalar polarizabilities of the a and b particles: by $O(n_\alpha^\nu \eta_\alpha^\nu)$ we mean monomials in $n_a \eta_a$ and $n_b \eta_b$ of degree ν. From (2·24) it follows that

$$\frac{m^2 - 1}{4\pi} = \left(\frac{m^2 + 2}{3}\right) (n_a \eta_a + n_b \eta_b) \, (1 + O(n_\alpha \eta_\alpha)),$$

so that with (2·23) in (2·18) the latter relation is

$$\mathbf{e}(\mathbf{x}) = \tfrac{1}{3}(m^2 + 2) \sum_\beta \int_V \tilde{\mathbf{T}}(\mathbf{x}, \mathbf{x}') \cdot \Big[\{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}_{j_\beta} - \mathbf{x}') - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}')\}$$
$$- (n_a \eta_a + n_b \eta_b) \, (1 + O(n_\alpha \eta_\alpha)) \int_U \mathbf{T}(\mathbf{x}', \mathbf{x}'') \cdot \{\sum_{j_\beta} \mathbf{P}_{j_\beta} \delta(\mathbf{x}_{j_\beta} - \mathbf{x}'') - n_\beta \bar{\mathbf{P}}_\beta(\mathbf{x}'') \, \mathrm{d}\mathbf{x}''\}\Big] \, \mathrm{d}\mathbf{x}'. \qquad (2{\cdot}25)$$

The scattered field $\mathbf{e}(\mathbf{x})$ of (2·25) forms the basis of the calculations of the scattered intensity from an illuminated two-component fluid which we make in §3 below; this in its turn is used to derive the Einstein scattering relations for systems of small molecules in §4. It therefore seems appropriate to interpolate here some interpretation of both (2·18) and (2·25). The expression (2·18*b*) is an exact consequence of our initial assumptions: it shows that as a result of the gauge transformation from (2·4) to (2·6) the fluctuation of the instantaneous microscopic field about its average value ($\bar{\mathscr{E}}(\mathbf{x})$ or zero according as $\mathbf{x}$ is illuminated or not) is interpretable as that due to a source 'in the medium' composed of the excess fluctuation in the total induced dipole moment over a Maxwell polarization derived from the fluctuation of the Maxwell field $\mathbf{e}(\mathbf{x}') - \bar{\mathscr{E}}(\mathbf{x}')$. This source is screened and radiates through the medium with the scattering tensor $\tilde{\mathbf{T}}$ of ($2\cdot18a$), not that of ($2\cdot19a$) *in vacuo*.

In ($2\cdot25$) the fluctuation of the Maxwell field no longer appears explicitly; but its contribution to the total scattering is included in the extra factor $\frac{1}{3}(m^2+2)$ and by terms $O(n_\alpha \eta_\alpha)$. Discussion of the factor $\frac{1}{3}(m^2+2)$ has previously interpreted it as a Lorentz internal field factor and arguments for its rejection or retention have been internal field arguments (cf. e.g. Ramanathan 1927; Cabannes 1929; Yvon 1937; Zimm 1945; Fixman 1955). But it is a multiple scattering term and can be interpreted as an internal field factor only for the screened quasi-particles 'in the medium'† Although screened quasi-particles in the medium have an obvious if rather imprecise interpretation in the present context the concept contains an element of danger because the remaining multiple scattering terms are still important. To deal with these it is now possible to iterate ($2\cdot25$) by using, for example, the iterated expansions for $\sum_{j_\beta}\mathbf{P}_{j_\beta}\delta(\mathbf{x}'-\mathbf{x}_{j_\beta})-n_\beta\bar{\mathbf{P}}_\beta(\mathbf{x}')$ in equation (B 11) in Appendix 2 of I: it is clear, however, that internal field factors can be included or not depending solely on the initial method of iterating ($2\cdot18b$).

The iteration of ($2\cdot25$) brings in significant terms which describe scattering of amplitude $\mathbf{e}(\mathbf{x})$ at $\mathbf{x}$ from scatterers at $\mathbf{x}''$ and $\mathbf{x}'$, and so on, and these imply a scattering intensity involving three and more centres: indeed there is a one-to-one correspondence between these terms and the multiple scattering terms with gauge ($2\cdot4$). The advantage of the particular form ($2\cdot25$), however, is that iterated explicitly up to $O(n^3\eta^3)$ in the one-component case (where (say) $n_\alpha=\frac{1}{2}n$, $\eta_\alpha=\eta$ for $\alpha=a$ or b) it yields an expression for the scattered intensity which has been identified (Fixman 1955) up to a possible question of the interpretation of the intensity in the medium precisely with that given by Einstein (1910) namely

$$i(\mathbf{s})=\frac{E_0^2\pi V}{8\mathfrak{R}^2\lambda^4}\kappa k' T n^2\left(\frac{\partial m^2}{\partial n}\right)_T^2[1-(\mathbf{u}.\mathbf{s})^2]. \qquad (2\cdot26)$$

In ($2\cdot26$) the new symbols are $\lambda=2\pi/k_0$, k' is Boltzmann's constant, κ the isothermal compressibility of the one-component fluid; $\mathbf{s}$ is a unit vector in the scattering direction, $\mathbf{u}$ is the polarization direction of the incident field $\mathbf{E}$ of amplitude E_0 as in ($2\cdot2c$); $\mathfrak{R}$ is the distance between the scattering source and the collector. The identification uses the one component form of ($2\cdot24$) also iterated to $O(n^3\eta^3)$, and the iterated form ($2\cdot25$) in both the one and two component cases offers the advantage that the factor $[(m^2+2)/3]^2$ which appears explicitly‡ can be identified with the same factor appearing explicitly in $(\partial m^2/\partial n)_T$ in the case of one component or in the combination of derivatives in the two component case (cf. ($4\cdot13$), ($4\cdot14$) and ($4\cdot15$) below); otherwise this factor has to be identified term by term in its series expansion in the $n_\alpha\eta_\alpha$ as was the case in II. It is assumed in Fixman's one-component argument that all correlation distances between multiplets of four or fewer small isotropic molecules are small compared with λ. Equation ($2\cdot26$) is therefore strictly comparable with the equation ($4\cdot27$) we obtain below for the two component case.

† In the one-component system for which $n_a=0$ the quasi b-particles have 'polarizability' $\approx(m^2-1)/4\pi n_b\sim\frac{1}{3}(m^2+2)\,\eta_b$: thus the isolated b-particle of polarizability η_b has an apparent internal field factor $[\frac{1}{3}(m^2+2)]^2$. The Lorentz factor therefore comes in squared (cf. §3).

‡ See preceding footnote.

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3. THE SCATTERED INTENSITY FROM MOLECULES WITH LARGE OR SMALL CORRELATION DISTANCES

We continue to assume the molecules isotropically polarizable and of two sorts a and b. From I (B11) we have in the notation of (2·19a) that

$$\begin{aligned}\mathbf{P}_{j_\beta}\delta(\mathbf{x}'-\mathbf{x}_{j_\beta}) = {} & \bar{\mathbf{P}}_\beta(\mathbf{x}')\,\delta(\mathbf{x}'-\mathbf{x}_{j_\beta}) \\ & +\eta_\beta\delta(\mathbf{x}'-\mathbf{x}_{j_\beta})\left\{\sum_\gamma\int_{U'}\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\bar{\mathbf{P}}_\gamma(\mathbf{x}'')\left[\sum_{k_\gamma=1}^{N_\gamma}\delta(\mathbf{x}''-\mathbf{x}_{k\gamma})\right.\right. \\ & \left.\left.-\frac{1}{n_\beta}\left\langle\sum_{\substack{s_\beta=1\\ t_\beta\neq s_\beta}}^{N_\beta}\sum_{t_\gamma=1}^{N_\gamma}\delta(\mathbf{x}'-\mathbf{x}_{s_\beta})\,\delta(\mathbf{x}''-\mathbf{x}_{t_\gamma})\,p(\varpi)\right\rangle\right]\mathrm{d}\mathbf{x}''\right\},\end{aligned}$$

so that (2·25) becomes

$$\begin{aligned}\mathbf{e}(\mathbf{x}) = {} & \tfrac{1}{3}(m^2+2)\sum_\beta\int_V\tilde{\mathbf{T}}(\mathbf{x},\mathbf{x}')\,.\left[\bar{\mathbf{P}}_\beta(\mathbf{x}')\,\delta_\beta(\mathbf{x}')\right. \\ & \left.+\sum_\gamma\int_{U'}\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\{\eta_\beta\delta_{\beta\gamma}(\mathbf{x}',\mathbf{x}'')\,\bar{\mathbf{P}}_\gamma(\mathbf{x}'')-n_\gamma\eta_\gamma\delta_\beta(\mathbf{x}'')\bar{\mathbf{P}}_\beta(\mathbf{x}'')\}\,\mathrm{d}\mathbf{x}''\right]\mathrm{d}\mathbf{x}', \qquad (3\cdot1\,a)\end{aligned}$$

where

$$\delta_\beta(\mathbf{x}') = \sum_{j_\beta=1}^{N_\beta}\delta(\mathbf{x}'-\mathbf{x}_{j_\beta})-n_\beta, \qquad (3\cdot1\,b)$$

$$\delta_{\beta\gamma}(\mathbf{x}',\mathbf{x}'') = \sum_{j_\beta=1}^{N_\beta}\delta(\mathbf{x}'-\mathbf{x}_{j_\beta})\left\{\sum_{\substack{k\gamma=1\\ k_\beta\neq j_\beta}}^{N_\gamma}\delta(\mathbf{x}''-\mathbf{x}_{k_\gamma})-\frac{1}{n_\beta}\left\langle\sum_{\substack{s_\beta=1\\ t_\beta\neq s_\beta}}^{N_\beta}\sum_{t_\gamma=1}^{N_\gamma}\delta(\mathbf{x}'-\mathbf{x}_{s_\beta})\,\delta(\mathbf{x}''-\mathbf{x}_{t_\gamma})\,p(\varpi)\right\rangle\right\} \qquad (3\cdot1\,c)$$

and we omit $O(n_\alpha^2\eta_\alpha^2)$.

The scattered field $\mathbf{e}(\mathbf{x})$ is determined by a Hertz vector

$$\begin{aligned}\tilde{\boldsymbol{\pi}}(\mathbf{x}) = {} & \tfrac{1}{3}(m^2+2)\sum_\beta\int_V\frac{1}{m^2}\tilde{f}(r)\left[\bar{\mathbf{P}}_\beta(\mathbf{x}')\,\delta_\beta(\mathbf{x}')\right. \\ & \left.+\sum_\gamma\int_{U'}\mathbf{T}(\mathbf{x}',\,\mathbf{x}'')\,.\,\{\eta_\beta\delta_{\beta\gamma}(\mathbf{x}',\,\mathbf{x}'')\,\bar{\mathbf{P}}_\gamma(\mathbf{x}'')-n_\gamma\eta_\gamma\delta_\beta(\mathbf{x}'')\,\bar{\mathbf{P}}_\beta(\mathbf{x}'')\}\,\mathrm{d}\mathbf{x}''\right]\mathrm{d}\mathbf{x}' \qquad (3\cdot2)\end{aligned}$$

and so is accompanied by a magnetic field

$$\mathbf{h} = \nabla_\mathbf{x}\wedge\tilde{\mathbf{a}} = \mathrm{i}m^2k_0\nabla_\mathbf{x}\wedge\tilde{\boldsymbol{\pi}}. \qquad (3\cdot3\,a)$$

We require for $\mathbf{h}$ then

$$\mathrm{i}m^2k_0\nabla_\mathbf{x}\wedge[m^{-2}\tilde{f}(r)\,\bar{\mathbf{P}}_\beta(\mathbf{x}')] = \mathrm{i}k_0(\mathrm{d}\tilde{f}/\mathrm{d}r)\,(\mathbf{s}\wedge\bar{\mathbf{P}}_\beta(\mathbf{x}')), \qquad (3\cdot3\,b)$$

where $\mathbf{s}$ is a unit vector in the direction of $\mathbf{r}$, that is $\mathbf{s}=\mathbf{r}/r$.

Asymptotically, i.e. for large enough r,

$$\frac{\mathrm{d}\tilde{f}(r)}{\mathrm{d}r} = \left(-\frac{1}{r}-\mathrm{i}k\right)\frac{\mathrm{e}^{-\mathrm{i}kr}}{r}\sim-\mathrm{i}mk_0\frac{\mathrm{e}^{-\mathrm{i}kr}}{r}, \qquad (3\cdot4\,a)$$

whereas

$$\tilde{\mathbf{T}}(\mathbf{x},\mathbf{x}')\equiv m^{-2}(\nabla_\mathbf{x}\nabla_\mathbf{x}+k^2\mathbf{U})\,\mathrm{e}^{-\mathrm{i}kr}/r\sim k_0^2(\mathbf{U}-\mathbf{ss})\,\mathrm{e}^{-\mathrm{i}kr}/r. \qquad (3\cdot4\,b)$$

We use the results (3·3) and (3·4) to compute the asymptotic form of the complex Poynting vector

$$\mathbf{p} = [\mathbf{e}\wedge\mathbf{h}^*+\mathbf{e}^*\wedge\mathbf{h}]/16\pi$$

at an unilluminated point of the medium: * denotes complex conjugate. Because scattering leads to extinction m is complex and so is k. We shall need according to (3·4 a, b)

$$[k_0^2(\mathbf{U}-\mathbf{ss})\,\mathrm{e}^{-\mathrm{i}kr}r^{-1}]\wedge[m^*k_0^2\,\mathrm{e}^{+\mathrm{i}k^*r_1}r_1^{-1}\,\mathbf{s}\wedge\bar{\mathbf{P}}_\beta^*(\mathbf{x}_1')] \tag{3·4c}$$

and its complex conjugate: here $r_1=|\mathbf{x}_1'-\mathbf{x}|$ and as usual $r=|\mathbf{x}'-\mathbf{x}|$.

Define an origin in the illuminated region a large distance $\mathfrak{R}$ from the field point $\mathbf{x}$ in the unilluminated region: assume the linear dimensions of the illuminated region are small compared with $\mathfrak{R}$. Then

$$\mathrm{e}^{-\mathrm{i}(kr-k^*r_1)}(rr_1)^{-1}\sim\mathrm{e}^{-\mathrm{i}(kr-k^*r_1)}\,\mathfrak{R}^{-2}. \tag{3·4d}$$

We also need

$$\mathbf{u}\,.\,(\mathbf{U}-\mathbf{ss})\wedge(\mathbf{s}\wedge\mathbf{u})=(\mathbf{u}-(\mathbf{u}\,.\,\mathbf{s})\,\mathbf{s})\wedge(\mathbf{s}\wedge\mathbf{u})=[1-(\mathbf{u}\,.\,\mathbf{s})^2]\,\mathbf{s}. \tag{3·4e}$$

We now use the explicit solutions (2·15) for the waves of polarization $\bar{\mathbf{P}}_\beta$ propagated through the medium to evaluate the complex Poynting vector $\mathbf{p}$ in the form

$$\mathbf{p}(\mathbf{s})\sim(m+m^*)\,(k_0^4/16\pi\mathfrak{R}^2)\,|\tfrac{1}{3}(m^2+2)|^2\,[1-(\mathbf{u}\,.\,\mathbf{s})^2]\,\mathbf{s}\{I_1+I_2+I_3\}, \tag{3·5}$$

where

$$I_1=\int_V\int_{V_1}\mathrm{e}^{-\mathrm{i}k(r-r_1)}\,\mathrm{e}^{-\mathrm{i}k(z'-z_1')}\,[\sum_\beta\sum_\gamma\delta_\beta(\mathbf{x}')\,\delta_\gamma(\mathbf{x}_1')\,\bar{P}_\beta\bar{P}_\gamma^*]\,\mathrm{d}\mathbf{x}_1'\,\mathrm{d}\mathbf{x}', \tag{3·6a}$$

$$\begin{aligned}I_2=\int_{V_1}\int_V\mathrm{e}^{-\mathrm{i}k(r-r_1)}\,\mathrm{e}^{-\mathrm{i}k(z'-z_1')}\int&\mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k(z''-z')}\\&\times[\sum_\beta\sum_\gamma\sum_\delta(\eta_\beta\bar{P}_\gamma\delta_{\beta\gamma}(\mathbf{x}',\mathbf{x}'')-n_\gamma\eta_\gamma\delta_\beta(\mathbf{x}'')\,\bar{P}_\beta)\bar{P}_\delta^*\,\delta_\delta(\mathbf{x}_1')]\,\mathrm{d}\mathbf{x}''\,\mathrm{d}\mathbf{x}'\,\mathrm{d}\mathbf{x}_1',\end{aligned} \tag{3·6b}$$

$$\begin{aligned}I_3=\int_V\int_{V_1}\mathrm{e}^{+\mathrm{i}k(r_1-r)}\,\mathrm{e}^{+\mathrm{i}k(z_1'-z')}\int&\mathbf{u}\,.\,\mathbf{T}^*(\mathbf{x}_1',\mathbf{x}_1'')\,.\,\mathbf{u}\,\mathrm{e}^{+\mathrm{i}k(z_1''-z_1')}\\&\times[\sum_\beta\sum_\gamma\sum_\delta\bar{P}_\beta\delta_\beta(\mathbf{x}')\,(\bar{P}_\delta^*\,\eta_\gamma\,\delta_{\gamma\delta}(\mathbf{x}_1',\mathbf{x}_1'')-n_\delta\eta_\delta\,\delta_\gamma(\mathbf{x}_1'')\,\bar{P}_\gamma^*)]\,\mathrm{d}\mathbf{x}_1''\,\mathrm{d}\mathbf{x}_1'\,\mathrm{d}\mathbf{x}'.\end{aligned} \tag{3·6c}$$

In deriving (3·5) we make two assumptions: we note again and discuss later that m is complex so that the square of the *modulus* of $\frac{1}{3}(m^2+2)$ appears outside (3·5). To abstract the pure real factor $(m+m^*)$ out also we assume that k is real in the exponents of the exponentials under the integrals over V and V_1 in I_1, I_2 and I_3: these exponentials should really be of the form $\exp[-\mathrm{i}(kr-k^*r_1)-\mathrm{i}(kz'-k^*z_1')]$. We can of course abstract the factor $(m+m^*)$ from the terms leading to I_1 by using the symmetry of the remaining part of the integrand of I_1 in $\mathbf{x}_1'$ and $\mathbf{x}'$ and relabelling these quantities, but to avoid complication in the terms leading to I_2 and I_3 it is simplest to note that $\mathscr{I}\mathrm{m}\sim10^{-9}\mathscr{R}\mathrm{m}$ and adopt the forms (3·6b) and (3·6c) with the factor $(m+m^*)$ isolated: then, as we now require for $\mathbf{p}$ pure real, $I_3=I_2^*$. The second assumption is that $\bar{\boldsymbol{\pi}}(\mathbf{x})$ of (3·2) is parallel to $\mathbf{u}$ the polarization direction of the incident wave $\mathbf{E}$ of (2·2c) and hence that of $\bar{\mathbf{P}}_\beta(\mathbf{x})$ according to (2·15). This assumption will not be true for an arbitrary configuration of the molecules of the system but the step will be justified for the *average* Poynting vector if we show that the averages of both I_2 and I_3 are of the form $\mathbf{u}\,.\,\mathbf{J}\,.\,\mathbf{u}$, where $\mathbf{J}$ is an isotropic second rank tensor. This we demonstrate below. Both I_2 and I_3 depend on the three particle configurations $\mathbf{x}_1'$, $\mathbf{x}'$, $\mathbf{x}''$ and $\mathbf{x}'$, $\mathbf{x}_1'$, $\mathbf{x}_1''$. If we extend the calculation to include correlations of four particles it is no longer true that we can simply treat $\tilde{\boldsymbol{\pi}}$ as though it is parallel to $\mathbf{u}$: correlations between four and more particles can therefore yield some depolarization of the scattered light, but we shall not consider this here.

For the average Poynting vector, we observe that

$$\langle \delta_\beta(\mathbf{x}')\, p(\varpi)\rangle = 0, \quad \langle \delta_{\beta\gamma}(\mathbf{x}',\mathbf{x}'')\, p(\varpi)\rangle = 0$$

and define

$$\langle \sum_{\substack{j_\beta\\ k_\beta \neq j_\beta}} \sum_{k_\gamma} \delta(\mathbf{x}_{j_\beta}-\mathbf{x}')\, \delta(\mathbf{x}_{k_\gamma}-\mathbf{x}_1')\, p(\varpi)\rangle = n_\beta n_\gamma g_{\beta\gamma}(\mathbf{x}',\mathbf{x}_1'), \tag{3·7a}$$

$$\langle \sum_{\substack{j_\beta\\ k_\beta \neq j_\beta,\, l_\gamma \neq k_\gamma,\, j_\delta \neq l_\delta}} \sum_{k_\gamma} \sum_{l_\delta} \delta(\mathbf{x}_{j_\beta}-\mathbf{x}')\, \delta(\mathbf{x}_{k_\gamma}-\mathbf{x}'')\, \delta(\mathbf{x}_{l_\delta}-\mathbf{x}_1')\, p(\varpi)\rangle = n_\beta n_\gamma n_\delta g_{\beta\gamma\delta}(\mathbf{x}',\mathbf{x}'',\mathbf{x}_1'), \tag{3·7b}$$

to obtain in terms of the co-ordinates appearing in I_1

$$\langle \delta_\beta(\mathbf{x}')\, \delta_\gamma(\mathbf{x}_1')\, p(\varpi)\rangle = n_\beta n_\gamma (g_{\beta\gamma}(\mathbf{x}',\mathbf{x}_1') - 1) + n_\beta \delta(\mathbf{x}'-\mathbf{x}_1')\, \delta_{\beta\gamma}, \tag{3·8a}$$

and in terms of the co-ordinates appearing in I_2

$$\langle \delta_{\beta\gamma}(\mathbf{x}',\mathbf{x}'')\, \delta_\delta(\mathbf{x}_1')\, p(\varpi)\rangle = n_\beta n_\gamma n_\delta (g_{\beta\gamma\delta}(\mathbf{x}',\mathbf{x}'',\mathbf{x}_1') - g_{\delta\beta}(\mathbf{x}_1',\mathbf{x}')\, g_{\beta\gamma}(\mathbf{x}',\mathbf{x}''))$$
$$+ n_\beta n_\gamma \delta(\mathbf{x}''-\mathbf{x}_1')\, g_{\beta\gamma}(\mathbf{x}',\mathbf{x}'')\, \delta_{\gamma\delta}, \tag{3·8b}$$

in which the $\delta_{\beta\gamma}$ and $\delta_{\gamma\delta}$ are Kronecker δ's. A natural extension of the notation in (3·4*c*) is

$$\mathbf{r} = \mathbf{x}'-\mathbf{x}, \quad \mathbf{r}' = \mathbf{x}''-\mathbf{x}'; \quad \mathbf{r}_1 = \mathbf{x}_1'-\mathbf{x}, \quad \mathbf{r}_1' = \mathbf{x}_1''-\mathbf{x}_1'.$$

But it is easy to see that $I_3 = I_2^*$ in (3·6): relabel δ, γ, β as γ, β, δ in I_3 and assume the η_γ are purely real. (We note below that they are actually complex, but they are certainly real to the order we investigate in detail here, and their imaginary parts can in any case be neglected at this order in the polarizabilities.) Thus we can work with the explicit forms of I_1 and I_2 alone and need use only the triplet $\mathbf{x}', \mathbf{x}'', \mathbf{x}_1'$. To simplify these integrals we change these co-ordinates into ones relative to $\mathbf{x}'$ and adopt the new notation

$$\mathbf{r}' = \mathbf{x}''-\mathbf{x}', \quad \mathbf{r}_1 = \mathbf{x}_1'-\mathbf{x}'; \tag{3·9a}$$

this changes our definition of $r_1 = |\mathbf{r}_1|$ from that used in (3·4*c*), but we shall not need this symbol in that sense again. Then, with this new definition of $\mathbf{r}_1$, $g_{\beta\gamma}(\mathbf{x}',\mathbf{x}_1')$ in (3·8*a*), and implicitly contained in the average of I_1, depends on $r_1 = |\mathbf{r}_1|$ alone—because of the assumed isotropy and homogeneity of the system—whilst $g_{\beta\delta}(\mathbf{x}'',\mathbf{x}_1')$ implicitly contained in the average of I_2 depends only on $|\mathbf{x}_1'-\mathbf{x}''| = |\mathbf{r}_1-\mathbf{r}'|$. Further, for the same reason, $g_{\beta\gamma\delta}(\mathbf{x}',\mathbf{x}'',\mathbf{x}_1')$, which by (3·8*b*) is contained in the average of I_2, depends only on the two vectors relative to their common point $\mathbf{x}'$ and symbolically

$$g_{\beta\gamma\delta}(\mathbf{x}',\mathbf{x}'',\mathbf{x}_1') = g_{\beta\gamma\delta}(\mathbf{x}_1'-\mathbf{x}',\mathbf{x}''-\mathbf{x}') = g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}'). \tag{3·9b}$$

From (3·8*a*) we now obtain for the average of I_1

$$\langle I_1 p(\varpi)\rangle = V\left\{\sum_\beta n_\beta \bar{P}_\beta \bar{P}_\beta^* + \sum_{\beta,\gamma} n_\beta n_\gamma \bar{P}_\beta \bar{P}_\gamma^* \int_V [g_{\beta\gamma}(r_1) - 1]\, j_0(kSr_1)\, \mathrm{d}\mathbf{r}_1\right\}, \tag{3·10}$$

where $j_0(\xi) = \sin\xi/\xi$, $\mathbf{S} = \mathbf{s}-\mathbf{s}_0$† with $\mathbf{s}_0$ the direction of incident light—the z-axis from (2·2c)—and we use the fact that a three dimensional Fourier transform with kernel $\mathrm{e}^{-\mathrm{i}k\mathbf{S}\,.\,\mathbf{r}_1}$ is taken of a spherically symmetric function (we can eliminate the angular integrations and again restore them by taking a transform with kernel $j_0(kSr_1)$). V is the volume of the illuminated region.

From (3·8) and (3·9) we obtain for the average of (3·6b) ($= I_3^*$ of (3·6c))

$$\begin{aligned}\langle I_2 p(\varpi)\rangle = V\Big\{&\int_V \mathrm{e}^{-\mathrm{i}k\mathbf{S}\,.\,\mathbf{r}_1}\int_{U'} \mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'}\\ &\times\Big[\sum_\beta\sum_\gamma\sum_\delta \eta_\beta \bar{P}_\gamma \bar{P}_\delta^* n_\beta n_\gamma n_\delta\{g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}') - g_{\delta\beta}(r_1)\,g_{\beta\gamma}(r') - g_{\gamma\delta}(|\mathbf{r}_1-\mathbf{r}'|)+1\}\Big]\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}_1\\ &+\int_V \mathrm{e}^{-\mathrm{i}k\mathbf{S}\,.\,\mathbf{r}_1}\int_{U'} \mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'}\\ &\times\Big[\sum_\beta\sum_\gamma \eta_\beta \bar{P}_\gamma \bar{P}_\gamma^* n_\beta n_\gamma\,\delta(\mathbf{x}''-\mathbf{x}_1')\,(g_{\beta\gamma}(r')-1)\Big]\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}_1\Big\},\end{aligned}\tag{3·11}$$

where $\zeta' = z''-z'$ is the 'z component' of $\mathbf{r}' = (\mathbf{x}''-\mathbf{x}')$. We observe that (3·11) is a typical three-particle scattering term; the first integral describes the average scattered intensity from sets of three distinct correlated point scatterers; the second describes the scattering from sets of single particles by a process which involves a single correlated intermediary and is a part of the transformation of the Lorentz radiation damping field in a different guise noted in §2. We note also that the prime sources indicated by the presence of the $\bar{P}_\gamma$, $\bar{P}_\delta$ in (3·11) and whose magnitude satisfy (I (8·1) and I(8·6))

$$\bar{P}_\gamma = \tfrac{1}{3}(m^2+2)\,\eta_\gamma E_0[1+n_a\eta_a J_{\gamma a}+n_b\eta_b J_{\gamma b}+O(n_\alpha^2\eta_\alpha^2)]\tag{3·12}$$

are enhanced by a Lorentz 'internal field factor' $\frac{1}{3}(m^2+2)$ according to (3·12) but apparently also by a second one through the factor multiplying the whole of $\mathbf{p}$ (and hence its average) in (3·5). This emphasises again that simple considerations based on the ideas of the Lorentz field have no validity when the effect of multiple scattering is included: this factor is one of the two seats of discrepancy between the various forms of the scattering cross sections referred to in §§1 and 2.

In (3·12) the quantities $J_{\gamma\delta}$ are defined by

$$J_{\gamma\delta} = \int_{U'} \mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'}[g_{\gamma\delta}(r')-1]\,\mathrm{d}\mathbf{r}'.\tag{3·13}$$

They are complex with conjugates $J_{\gamma\delta}^*$; the polarizabilities η_β which refer to the isolated particles are also complex because they may be assumed to contain the effect of the Lorentz radiation damping field of the isolated particle (I §2). In systems of correlated particles

† If θ is the scattering angle $S = |\mathbf{S}| = 2\sin\frac{1}{2}\theta$ and the argument of the kernel is $kSr_1 = 2mk_0r_1\sin\frac{1}{2}\theta$. When the correlation lengths of the $g_{\beta\gamma}$ are $\approx 2\pi k_0^{-1}$ the integrals in (3·10) depend on θ and modulate the final scattering envelope of the system. Thus observed scattering envelopes can be (and are) used to determine correlation lengths. It is therefore important to point out that the argument kSr_1 of the kernel $j_0(kSr_1)$ takes this form as a direct consequence of the gauge transformation from *in vacuo* to the medium. The corresponding calculation of the scattering in the formulation *in vacuo* shows that $2mk_0r_1\sin\frac{1}{2}\theta$ becomes $k_0(1-2m\cos\theta+m^2)^{\frac{1}{2}}$ in agreement with this same form given by Rosenfeld (1951). From one point of view we can interpret this as a direct consequence of the influence of multiple scattering on the scattering envelope and infer that multiple scattering can introduce errors into the estimated correlation lengths in both one and two component systems: these errors are in addition to those peculiar to the two component system considered in §§6 and 7. They are clearly important but they obviously hinge on the relative status of the *in vacuo* and 'in the medium' formulations. It is hoped to treat this in detail elsewhere.

the refractive index m is also then necessarily complex through the $J_{\gamma\delta}$, and the similar terms from higher order correlations; but even in uncorrelated or very dilute systems m is complex through the radiation damping described by the complex η_β. The extinction of the transmitted waves $\bar{\mathbf{P}}_\beta(\mathbf{x}')$ of (2·15) which this implies is a second measure of the scattering and was used in II to derive the turbidity of multi-component systems of small molecules.

It follows from (3·12) that, with a real E_0 fixing the origin of phase, $\bar{P}_\gamma$ is also complex and from (2·13) that $\bar{\mathscr{E}}(\mathbf{x})$ and the $\bar{\mathbf{P}}_\gamma(\mathbf{x})$ are not in phase when there is scattering—(2·13) must however be modified when corrections of this order are considered. We note also that the complex factor m in (3·4a) means that the asymptotic forms of $\mathbf{e}$ and $\mathbf{h}$ are not in phase because of the scattering they represent and by the same token the transmitted Maxwell electric and magnetic fields $\bar{\mathscr{E}}(\mathbf{x})$ and $\bar{\mathscr{H}}(\mathbf{x})$ are not in phase when there is scattering: for, essentially by (2·13) and (2·15),

$$\bar{\mathscr{E}}(\mathbf{x}) = E_0\mathbf{u}\,\mathrm{e}^{-\mathrm{i}kz}, \tag{3·14a}$$

while it is shown (I (8·13)) that

$$\bar{\mathscr{H}}(\mathbf{x}) = mE_0(\mathbf{s}_0 \wedge \mathbf{u})\,\mathrm{e}^{-\mathrm{i}kz} \tag{3·14b}$$

essentially because

$$-\mathrm{i}k_0\bar{\mathscr{H}}(\mathbf{x}) = \operatorname{curl}\bar{\mathscr{E}}(\mathbf{x}).$$

We shall show elsewhere that even more remarkably scattering from a finite region induces a modification from the form assumed in (2·15) of the $\bar{\mathbf{P}}_\gamma(\mathbf{x})$ themselves, but this may be loosely thought of as a modification induced by the shape and size of the scattering region V and will not be considered here. It is, however, intimately connected with the factor $(m+m^*) = 2\mathscr{R}\mathrm{m}$ in the expression for $\mathbf{p}$ in (3·5): this factor appears also in the transmitted Poynting vector calculated from (3·14)

$$\mathbf{p}_0(\mathbf{s}_0) = \frac{1}{16\pi}[\bar{\mathscr{E}}(\mathbf{x}) \wedge \bar{\mathscr{H}}^*(\mathbf{x}) + \bar{\mathscr{E}}^*(\mathbf{x}) \wedge \bar{\mathscr{H}}(\mathbf{x})] = \frac{m+m^*}{16\pi}E_0^2\mathbf{s}_0. \tag{3·15}$$

That such a factor should appear has been noted already (I §8): it re-appears in a remarkably unsymmetrical way in the calculation of the turbidity from the extinction induced by $\mathscr{I}\mathrm{m}$ (cf. II) and leads to a discrepancy between the results of that calculation and the calculation of turbidity we make in §4 below from the scattered intensity. The paradox can be resolved only by modifying the solutions for the $\bar{\mathbf{P}}_\gamma(\mathbf{x})$ in (2·15) and must be treated elsewhere. The calculation of scattering we make in this paper will there be shown to be conceptually strictly comparable with that of Einstein (1910) and in the case of small molecules permits a direct comparison between this formula and that we obtain in §4 below.

From (3·10), (3·11) and (3·12) we find that

$$\langle (I_1+I_2+I_3)p\,(\varpi)\rangle = \{\bar{K}_1 + (\bar{K}_2+\bar{K}_2^*)\}\,E_0^2|\tfrac{1}{3}(m^2+2)|^2\,V,$$

where

$$\bar{K}_1 = \left\{\sum_\beta n_\beta|\eta_\beta|^2 + \sum_{\beta,\gamma} n_\beta n_\gamma \eta_\beta \eta_\gamma^* \int_V [g_{\beta\gamma}(r')-1]\,j_0(kSr')\,\mathrm{d}\mathbf{r}'\right\}, \tag{3·16a}$$

$$\begin{aligned}\bar{K}_2 = \Bigg\{\iint_V &\mathrm{e}^{-\mathrm{i}k\mathbf{s}\,.\,\mathbf{r}_1}\int_{U'} \mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'}\\ &\times[\sum_\beta\sum_\gamma\sum_\delta n_\beta n_\gamma n_\delta \eta_\beta \eta_\gamma \eta_\delta^*\{g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}') - g_{\delta\beta}(r_1)\,g_{\beta\gamma}(r') - g_{\gamma\delta}(|\mathbf{r}'-\mathbf{r}_1|)+1\}\\ &+\sum_\beta\sum_\gamma n_\beta n_\gamma \eta_\beta|\eta_\gamma|^2\,\delta(\mathbf{r}'-\mathbf{r}_1)\,(g_{\beta\gamma}(r')-1)]\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}_1\Bigg\}\\ &+\left\{\sum_\beta\sum_\gamma n_\beta n_\gamma|\eta_\beta|^2\eta_\gamma J_{\beta\gamma} + \sum_\beta\sum_\gamma\sum_\delta n_\beta n_\gamma n_\delta \eta_\beta \eta_\gamma^* \eta_\delta J_{\beta\delta}\int_V [g_{\beta\gamma}(r')-1]\,j_0(kSr')\,\mathrm{d}\mathbf{r}'\right\}.\end{aligned} \tag{3·16b}$$

We may simplify $\overline{K}_2$ to

$$\begin{aligned}\overline{K}_2 = \Big\{ & \iint_V \mathrm{e}^{-\mathrm{i}k\mathbf{s}\,.\,\mathbf{r}_1} \int_{U'} \mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'} \\ & \times [\sum_\beta \sum_\gamma \sum_\delta n_\beta n_\gamma n_\delta \eta_\beta \eta_\gamma \eta^*_\delta \{g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}') - g_{\delta\beta}(r_1) - g_{\beta\gamma}(r') - g_{\gamma\delta}(|\mathbf{r}'-\mathbf{r}_1|) + 2\}]\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}_1 \\ & + \int_{U'} \{\mathrm{e}^{-\mathrm{i}k\mathbf{s}\,.\,\mathbf{r}'} + 1\}\,\mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,.\,\mathbf{u}\,\mathrm{e}^{-\mathrm{i}k\zeta'}[\sum_\beta \sum_\gamma n_\beta n_\gamma \eta_\beta |\eta_\gamma|^2 \{g_{\beta\gamma}(r') - 1\}]\,\mathrm{d}\mathbf{r}'\Big\}. \qquad (3{\cdot}16c)\end{aligned}$$

We have also from (3·5) that

$$\bar{\mathbf{p}}(\mathbf{s}) \equiv \langle \mathbf{p}(\mathbf{s})\,p(\varpi)\rangle = \frac{E_0^2(m+m^*)\,Vk_0^4}{16\pi\mathfrak{R}^2}\left|\frac{m^2+2}{3}\right|^4 [1-(\mathbf{u}\,.\,\mathbf{s})^2]\,\mathbf{s}\{\overline{K}_1+\overline{K}_2+\overline{K}_2^*\}. \qquad (3{\cdot}17)$$

The magnitude of (3·17) is the scattered intensity from systems of molecules with correlation distances unrestricted except by neglect of correlations of four and more scattering centres. The molecules themselves must be assumed small compared with k_0^{-1} because only dipole scattering is considered: but this means that the magnitude of (3·17) is a valid scattered intensity for the two important cases of either small molecules with strong correlation over a few molecular diameters or of large (e.g. macro) molecules consisting of many strongly correlated units each small compared with k_0^{-1}. In §4 we use (3·17) to give a molecular argument for the scattered intensity from two component fluids with correlation distances much less than k_0^{-1} and thereby derive the phenomenological Einstein formula in the corrected form suggested previously (II) by a calculation of extinction. In §6 we consider (3·17) for coiling macromolecules consisting of *ca.* 10^5 polarizable units each of dimension ~ 10Å: the r.m.s. radius of such molecules is *ca.* 3000 Å $> k_0^{-1}$ with $k_0 = 2\pi/\lambda$ in the optical range.†

4. SCATTERING FROM SMALL MOLECULES: EINSTEIN'S SCATTERING FORMULAE

For small molecules correlating over distances small compared with a wavelength we may simplify $\overline{K}_2$ of (3·16*c*) further by introducing chemical potentials μ_a and μ_b of the two constituents: write $\chi = 1/k'T$, where k' is Boltzmann's constant, T the temperature. Particular cases of the recurrence relation of Buff & Brout (1955) are

$$\left[\frac{\partial n_\alpha}{\partial(\chi\mu_\delta)}\right]_{\chi,\,V,\,\chi\mu_{\delta'}} = \delta_{\delta\alpha} n_\alpha + n_\delta n_\alpha \int_V [g_{\delta\alpha}(r') - 1]\,\mathrm{d}\mathbf{r}', \qquad (4{\cdot}1a)$$

$$\left[\frac{\partial(n_\alpha n_\beta g_{\alpha\beta}(r'))}{\partial(\chi\mu_\delta)}\right]_{\chi,\,V,\,\chi\mu_{\delta'}} = (\delta_{\delta\alpha}+\delta_{\delta\beta})\,n_\alpha n_\beta g_{\alpha\beta}(r') + n_\alpha n_\beta n_\delta \int_V [g_{\alpha\beta\delta}(\mathbf{r}_1,\mathbf{r}') - g_{\alpha\beta}(r')]\,\mathrm{d}\mathbf{r}_1. \qquad (4{\cdot}1b)$$

From (4·1*a*) we derive

$$\left[\frac{\partial(n_\alpha n_\beta)}{\partial(\chi\mu_\delta)}\right]_{\chi,\,V,\,\chi\mu_{\delta'}} = (\delta_{\delta\alpha}+\delta_{\delta\beta})\,n_\alpha n_\beta + n_\alpha n_\beta n_\delta \int [g_{\alpha\delta}(r_1) + g_{\beta\delta}(r_1) - 2]\,\mathrm{d}\mathbf{r}_1 \qquad (4{\cdot}2)$$

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† A polystyrene molecule of molecular weight one million dissolved in benzene has an average end-to-end distance of 1100 Å; this may be a slightly more typical figure but it is still ≈ k_0^{-1}.

and from this and (4·1 *b*),

$$\sum_\beta\sum_\gamma\sum_\delta \eta_\beta\eta_\gamma\eta_\delta^*\left[\frac{\partial}{\partial(\chi\mu_\delta)}\{n_\beta n_\gamma(g_{\beta\gamma}(r')-1)\}\right]_{\chi,V,\chi\mu_{\delta'}} = \sum_\beta\sum_\gamma\sum_\delta \eta_\beta\eta_\gamma\eta_\delta^*\{(\delta_{\delta\beta}+\delta_{\delta\gamma})\,n_\beta n_\gamma[g_{\beta\gamma}(r')-1]$$

$$+n_\beta n_\gamma n_\delta\int_V[g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}')-g_{\beta\delta}(r_1)-g_{\gamma\delta}(r_1)-g_{\beta\gamma}(r')+2]\,\mathrm{d}\mathbf{r}_1\}. \quad (4·3)$$

We use $\delta' = b$ when $\delta = a$, $\delta' = a$ when $\delta = b$: the partial derivatives with respect to $\chi\mu_\delta$ are taken at constant temperature T, volume V and chemical potential of the second constituent and we shall henceforth frequently omit explicit reference to the constancy of these quantities in partial derivatives with respect to $\chi\mu_\delta$: we shall indicate what is being held constant in other partial derivatives however.

If, *but only if*, the correlation distances of $g_{\beta\gamma}(r')$ and $g_{\beta\gamma\delta}(\mathbf{r}_1,\mathbf{r}')$ are much less than k^{-1} we can replace $\mathrm{e}^{-ik\mathbf{s}.\mathbf{r}_1}$ by unity in $\overline{K}_2$ of (3·16*c*). Then $\overline{K}_2$ simplifies to

$$\overline{K}_2 \approx \sum_\beta\sum_\gamma\sum_\delta \eta_\beta\eta_\gamma\eta_\delta^*\left[\frac{\partial}{\partial(\chi\mu_\delta)}\left\{n_\beta n_\gamma\int_{U'}\mathbf{u}\,.\,\mathbf{T}(\mathbf{x}',\mathbf{x}'')\cdot\mathbf{u}\,\mathrm{e}^{-ik\zeta'}[g_{\beta\gamma}(r')-1]\,\mathrm{d}\mathbf{r}'\right\}\right]$$

$$= \sum_\beta\sum_\gamma\sum_\delta \eta_\beta\eta_\gamma\eta_\delta^*\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}. \quad (4·4)$$

$J_{\beta\gamma}$ is the integral defined in (3·13).

We may also simplify $\overline{K}_1$: we use (4·1 *a*) to deduce that

$$\sum_\beta\sum_\gamma \eta_\beta\eta_\gamma^*\frac{\partial(n_\beta)}{\partial(\chi\mu_\delta)} = \sum_\beta\sum_\gamma \eta_\beta\eta_\gamma^*\left[n_\beta\delta_{\beta\gamma}+n_\beta n_\gamma\int_V[g_{\beta\gamma}(r')-1]\,\mathrm{d}\mathbf{r}'\right] \quad (4·5)$$

and when *and only when* k^{-1} is much greater than the correlation distances of the $g_{\beta\gamma}(r')$

$$\overline{K}_1 \approx \sum_\beta\sum_\gamma \eta_\beta\eta_\gamma^*\frac{\partial n_\beta}{\partial(\chi\mu_\gamma)}. \quad (4·6)$$

It is worth noting that because of the symmetry of the $g_{\beta\gamma}$ in β and γ

$$\frac{\partial n_\beta}{\partial(\chi\mu_{\beta'})} = \frac{\partial n_{\beta'}}{\partial(\chi\mu_\beta)},$$

while because of the spherical symmetry of the $g_{\beta\gamma}(r')$ in $\mathbf{r}'$ the *tensor*

$$\mathbf{J}_{\beta\gamma} = \int_{U'}\mathbf{T}(\mathbf{x}',\mathbf{x}'')\,\mathrm{e}^{-ik\zeta'}[g_{\beta\gamma}(r')-1]\,\mathrm{d}\mathbf{r}',$$

(which has diagonal elements $J_{\beta\gamma} = \mathbf{u}\,.\,\mathbf{J}_{\beta\gamma}\,.\,\mathbf{u}$ for each of three orthogonal directions $\mathbf{u}$) is an isotropic tensor. It follows that $\partial(n_\beta n_\gamma\mathbf{J}_{\beta\gamma})/\partial(\chi\mu_\delta)$ is an isotropic tensor. This justifies the step noted in §3 (between equations (3·6*c*) and (3·7*a*)) in the case of small molecules and implies its justification for large (macro) molecules. We can in any case argue that because the $g_{\alpha\beta}$ and $g_{\alpha\beta\gamma}$ describe a spherically symmetric system, i.e. one isotropic at a molecular level on the average, the average of $I_2 = I_3^*$ (of (3·6*b*, *c*)) must be of the form $\mathbf{u}\,.\,\mathbf{J}\,.\,\mathbf{u}$, where $\mathbf{J}$ is an isotropic second rank tensor and $\bar{\boldsymbol{\pi}}$ of (3·2) is on the average parallel to $\mathbf{u}$: if we extend the calculation to include correlations of four and more particles the analogue of $\mathbf{J}$ is an isotropic fourth or higher rank tensor, $\bar{\boldsymbol{\pi}}$ is not necessarily parallel to $\mathbf{u}$ on the average and the isotropic system of *isotropically polarizable* particles can in principal show some depolarization (cf. Fixman (1955) also).

It follows from (4·4) and (4·6) that in the case of small molecules with short correlation distances

$$\overline{K}_1+\overline{K}_2+\overline{K}_2^* = \sum_\beta\sum_\gamma \eta_\beta\eta_\gamma^*\left[\frac{\partial n_\beta}{\partial(\chi\mu_\delta)}\right]+\sum_\beta\sum_\gamma\sum_\delta \frac{\partial}{\partial(\chi\mu_\delta)}\,[n_\beta n_\gamma(\eta_\beta\eta_\gamma\eta_\delta^*\,J_{\beta\gamma}+\eta_\beta^*\,\eta_\gamma^*\,\eta_\delta\,J_{\beta\gamma}^*)]. \tag{4·7}$$

An extension of the Lorentz–Lorentz relation is (I (7·2))

$$\frac{m^2-1}{m^2+2} = \tfrac{4}{3}\pi\,\{\sum_\beta n_\beta\eta_\beta+\sum_\beta\sum_\gamma n_\beta n_\gamma\eta_\beta\eta_\gamma\,J_{\beta\gamma}\}+O(n_\alpha^3\,\eta_\alpha^3) \tag{4·8}$$

(compare equation (2·24) above), so neglecting $O(n_\alpha^3\,\eta_\alpha^3)$

$$\frac{\partial m^2}{\partial(\chi\mu_\delta)} = 4\pi\left(\frac{m^2+2}{3}\right)^2\left\{\sum_\beta\eta_\beta\frac{\partial n_\beta}{\partial(\chi\mu_\delta)}+\sum_\beta\sum_\gamma\eta_\beta\eta_\gamma\,\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\right\}. \tag{4·9}$$

The partial derivatives keep $\chi = 1/k'T$, V and $\mu_{\delta'}$ constant. Taking instead of χ, V, μ_a and μ_b as independent variables successively χ, V, n_a, n_b and χ, V, p, n_b we have at constant χ, V

$$\left(\frac{\partial m^2}{\partial n_b}\right)_p = \sum_\gamma\left(\frac{\partial m^2}{\partial(\chi\mu_\gamma)}\right)_{\mu_{\gamma'}}\left(\frac{\partial(\chi\mu_\gamma)}{\partial n_b}\right)_p = \sum_\gamma\frac{\partial m^2}{\partial(\chi\mu_\gamma)_{\mu_{\gamma'}}}\left[\left(\frac{\partial(\chi\mu_\gamma)}{\partial n_b}\right)_{n_a}+\left(\frac{\partial n_a}{\partial n_b}\right)_p\left(\frac{\partial(\chi\mu_\gamma)}{\partial n_a}\right)_{n_b}\right]. \tag{4·10}$$

We introduce partial molar volumes v_a and v_b per molecule of a and b respectively: then

$$\left(\frac{\partial n_a}{\partial n_b}\right)_{p,\chi,V} = -\frac{v_b}{v_a}. \tag{4·11}$$

We also need the identity (at constant χ, V)

$$\sum_\gamma\left(\frac{\partial n_\beta}{\partial(\chi\mu_\gamma)}\right)_{\mu_{\gamma'}}\left(\frac{\partial(\chi\mu_\gamma)}{\partial n_\delta}\right)_{n_{\delta'}} = \delta_{\beta\gamma}. \tag{4·12}$$

We then find from (4·10) that

$$\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V} = 4\pi\left(\frac{m^2+2}{3}\right)^2\left\{(\eta_b-v_b v_a^{-1}\eta_a)+\sum_\beta\sum_\gamma\sum_\delta\eta_\beta\eta_\gamma\,\frac{\partial(n_\beta n_\gamma\,J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\left[\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\,\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]\right\} \tag{4·13a}$$

and that

$$\left|\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\right|^2\frac{\partial n_b}{\partial(\chi\mu_b)} = 16\pi^2\left|\frac{m^2+2}{3}\right|^4\left\{|\eta_b-v_b v_a^{-1}\eta_a|^2\,\frac{\partial n_b}{\partial(\chi\mu_b)}\right.$$

$$\left.+\sum_\beta\sum_\gamma\sum_\delta\left[(\eta_b^*-v_b v_a^{-1}\eta_a^*)\,\eta_\beta\eta_\gamma\,\frac{\partial(n_\beta n_\gamma\,J_{\beta\gamma})}{\partial(\chi\mu_\delta)}+\text{c.c.}\right]\left[\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\,\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]\frac{\partial n_b}{\partial(\chi\mu_b)}\right\}. \tag{4·13b}$$

Next (at constant χ, V)

$$\left(\frac{\partial m^2}{\partial N_a}\right)_{N_b} = \sum_\gamma\frac{\partial m^2}{\partial(\chi\mu_\gamma)_{\mu_{\gamma'}}}\left(\frac{\partial(\chi\mu_\gamma)}{\partial N_a}\right)_{N_b} = \frac{1}{V}\sum_\gamma\frac{\partial m^2}{\partial(\chi\mu_\gamma)}\left(\frac{\partial(\chi\mu_\gamma)}{\partial n_a}\right)_{n_b}$$

$$= \frac{4\pi}{V}\left(\frac{m^2+2}{3}\right)^2\left\{\eta_a+\sum_\beta\sum_\gamma\sum_\delta\eta_\beta\eta_\gamma\,\frac{\partial(\eta_\beta n_\gamma\,J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\,\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right\}, \tag{4·14a}$$

so that

$$\left|\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}\right|^2 = 16\pi^2\left|\frac{m^2+2}{3}\right|^4$$

$$\times\left\{|\eta_a|^2\,v_a^{-2}+\sum_\beta\sum_\gamma\sum_\delta v_a^{-2}\left[\eta_a^*\,\eta_\beta\eta_\gamma\,\frac{\partial(n_\beta n_\gamma\,J_{\beta\gamma})}{\partial(\chi\mu_\delta)}+\text{c.c.}\right]\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right\}. \tag{4·14b}$$

From (4·13*a*) and (4·14*a*) we have also that

$$\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)^*_{\chi,V,N_b}+\text{c.c.}\right]=16\pi^2\left|\frac{m^2+2}{3}\right|^4$$
$$\times\Big\{(\eta_b-v_bv_a^{-1}\eta_a)\,\eta_a^*v_a^{-1}n_b+\sum_\beta\sum_\gamma\sum_\delta n_bv_a^{-1}\eta_a^*\eta_b\eta_\gamma\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\left[\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_a}{v_b}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]$$
$$+\sum_\beta\sum_\gamma\sum_\delta n_bv_a^{-1}(\eta_b^*-v_bv_a^{-1}\eta_a^*)\eta_\beta\eta_\gamma\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\frac{\partial(\chi\mu_\delta)}{\partial n_a}+\text{c.c.}\Big\}. \tag{4·15}$$

We introduce the isothermal compressibility κ

$$\kappa=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\chi,N_a,N_b}, \tag{4·16}$$

so that $$\frac{n_\beta\kappa}{\chi}=\frac{1}{\chi}\left(\frac{\partial n_\beta}{\partial p}\right)_{\chi,N_a,N_b}=\left(\frac{\partial n_\beta}{\partial(\chi\mu_a)}\right)\left(\frac{\partial\mu_a}{\partial p}\right)_{\chi,N_a,N_b}+\left(\frac{\partial n_\beta}{\partial(\chi\mu_b)}\right)\left(\frac{\partial\mu_b}{\partial p}\right)_{\chi,N_a,N_b}.$$

Since $$\left(\frac{\partial\mu_\alpha}{\partial p}\right)_{\chi,N_a,N_b}=\left(\frac{\partial V}{\partial N_\alpha}\right)_{\chi,p\ N_\alpha}=v_\alpha.$$

we have $$\frac{n_\beta\kappa}{\chi}=v_a\frac{\partial n_\beta}{\partial(\chi\mu_a)}+v_b\frac{\partial n_\beta}{\partial(\chi\mu_b)}. \tag{4·17}$$

The terms $O(n_\alpha^2\eta_\alpha^2)$ in the sum of (4·13*b*) and κ/χ times the sum of (4·14*b*) and (4·15) are

$$16\pi^2\left|\frac{m^2+2}{3}\right|^4\Big\{|\eta_b-v_bv_a^{-1}\eta_a|^2\frac{\partial n_b}{\partial(\chi\mu_b)}+|\eta_a|^2v_a^{-2}\kappa/\chi+[(\eta_b-v_bv_a^{-1}\eta_a)\,\eta_a^*v_a^{-1}n_b\kappa/\chi+\text{c.c.}]\Big\}. \tag{4·18}$$

With the aid of (4·17), (4·18) easily reduces to precisely

$$16\pi^2\left|\frac{m^2+2}{3}\right|^4\Big\{\sum_\beta\sum_\gamma\eta_\beta\eta_\gamma^*\frac{\partial n_\beta}{\partial(\chi\mu_\gamma)}\Big\}=16\pi^2\left|\frac{m^2+2}{3}\right|^4\overline{K}_1. \tag{4·19}$$

We use here $$\frac{\partial n_b}{\partial(\chi\mu_a)}=\frac{\partial n_a}{\partial(\chi\mu_b)}.$$

The terms $O(n_\alpha^3\eta_\alpha^3)$ in the same sum are

$$16\pi^2\left|\frac{m^2+2}{3}\right|^4\Big[\sum_\beta\sum_\gamma\sum_\delta\Big\{(\eta_b^*-v_bv_a^{-1}\eta_a^*)\,\eta_\beta\eta_\gamma\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}$$
$$\times\left[\left(\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right)\frac{\partial n_b}{\partial(\chi\mu_b)}+\frac{\kappa}{\chi}\frac{n_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]$$
$$+\frac{\kappa}{\chi}\eta_a^*\eta_\beta\eta_\gamma\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\left[\left(\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right)\frac{n_b}{v_a}+\frac{\partial(\chi\mu_\delta)}{\partial n_a}\frac{1}{v_a^2}\right]+\text{c.c.}\Big\}\Big]. \tag{4·20}$$

We make use of the relations

$$\frac{\kappa}{\chi}\frac{n_\beta}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}+\left[\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]\frac{\partial n_\beta}{\partial(\chi\mu_b)}=\delta_{\beta\delta}, \tag{4·21 a}$$

$$\frac{\kappa}{\chi}\left[\left(\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right)\frac{1}{v_a^2}+\frac{n_b}{v_a}\left(\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right)-\frac{n_bv_b}{v_a^2}\left(\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right)\right]-\frac{v_b}{v_a}\frac{\partial n_b}{\partial(\chi\mu_b)}\left[\frac{\partial(\chi\mu_\delta)}{\partial n_b}-\frac{v_b}{v_a}\frac{\partial(\chi\mu_\delta)}{\partial n_a}\right]=\delta_{a\delta}, \tag{4·21 b}$$

to reduce (4·20) to precisely

$$16\pi^2\left|\frac{m^2+2}{3}\right|^4\left[\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta \eta^*_\alpha\eta_\beta\eta_\gamma\frac{\partial(n_\beta n_\gamma J_{\beta\gamma})}{\partial(\chi\mu_\delta)}\delta_{\alpha\delta}+\text{c.c.}\right]=16\pi^2\left|\frac{m^2+2}{3}\right|^4[K_2+K^*_2]. \quad (4·22)$$

So we have the result

$$\left|\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\right|^2\frac{\partial n_b}{\partial(\chi\mu_b)}+\frac{\kappa}{\chi}\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)^*_{\chi,V,N_b}+\text{c.c.}\right]$$

$$+\frac{\kappa}{\chi}\left|\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}\right|^2=16\pi^2\left|\frac{m^2+2}{3}\right|^4[\overline{K}_1+\overline{K}_2+\overline{K}^*_2]. \quad (4·23)$$

The left-hand side of (4·23) simplifies: we use

$$V\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}=\left(\frac{\partial m^2}{\partial p}\right)_{\chi,V,N_b}\kappa^{-1}v_a \quad (4·24\,a)$$

and introduce the osmotic pressure Π of solute b-molecules in solvent a-molecules; from the Gibbs–Duhem relation

$$dp+\sum_\beta n_\beta\,d\mu_\beta=0,$$

it follows that at constant μ_a

$$d\Pi=n_b\,d\mu_b \quad (4·24\,b)$$

and

$$\left(\frac{\partial\Pi}{\partial n_b}\right)_{\mu_a,V,T}=n_b\left(\frac{\partial\mu_b}{\partial n_b}\right)_{\mu_a,V,T}=\frac{n_b}{\chi}\Big/\left(\frac{\partial n_b}{\partial(\chi\mu_b)}\right)_{\mu_a,V,T}. \quad (4·25)$$

Then (4·23) becomes

$$\frac{1}{\chi}\left\{n_b^2\left|\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi}\right|^2\Big/n_b\left(\frac{\partial\Pi}{\partial n_b}\right)_{\mu_a,T}+\kappa\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi}\left(\frac{\partial m^2}{\partial p}\right)^*_{\chi,n_b}\kappa^{-1}+\text{c.c.}\right]+\kappa\left|\left(\frac{\partial m^2}{\partial p}\right)_{\chi,n_b}\kappa^{-1}\right|^2\right\}. \quad (4·26)$$

It follows from (3·17) that in the case when correlation distances are much less than k^{-1} and omitting $O(n_\alpha^4\eta_\alpha^4)$

$$\overline{\mathbf{p}}(\mathbf{s})=\frac{E_0^2k_0^4V(m+m^*)}{256\pi^3\mathfrak{R}^2\chi}[1-(\mathbf{u}.\mathbf{s})^2]\,\mathbf{s}G, \quad (4·27)$$

where G is the quantity in curly brackets in (4·26).

The flux of energy crossing a sphere Σ of large radius $\mathfrak{R}$ in unit time per unit volume of the scattering region V is

$$\frac{1}{V}\int_\Sigma\overline{\mathbf{p}}(\mathbf{s})\,.\,d\mathbf{S}=\frac{E_0^2k_0^4}{96\pi^2\chi}(m+m^*)\,G. \quad (4·28)$$

Normalized against the transmitted intensity *in the medium* given by $|\overline{\mathbf{p}}_0(\mathbf{s}_0)|$ of (3·15) this becomes the extinction (= turbidity) τ of the transmitted intensity:

$$\tau=\frac{k_0^4G}{6\pi\chi}=\frac{8\pi^3k'T}{3\lambda^4}\left\{n_b^2\left|\left(\frac{\partial m^2}{\partial n_b}\right)_{p,T}\right|^2\Big/n_b\left(\frac{\partial\Pi}{\partial n_b}\right)_{\mu_a,T}\right.$$

$$\left.+\kappa\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,T}\left(\frac{\partial m^2}{\partial p}\right)^*_{T,n_b}\kappa^{-1}+n_b\left(\frac{\partial m^2}{\partial n_b}\right)^*_{p,T}\left(\frac{\partial m^2}{\partial p}\right)_{T,n_b}\kappa^{-1}\right]+\kappa\left|\left(\frac{\partial m^2}{\partial p}\right)_{T,n_b}\kappa^{-1}\right|^2\right\}. \quad (4·29)$$

5. Discussion of the scattering cross-sections for small molecules

We first compare the form (4·29) with that obtained in the previous paper, II, from the imaginary part of the refractive index: neglecting differences between the squares of the real part of the refractive index and the square of its modulus—which quantities and their derivatives differ by $O(k_0^{-2}\tau^2)\approx 10^{-20}$ which is quite negligible—the expression (4·29) confirms the existence of the 'cross-term' $2n_b(\partial m^2/\partial n_b)_{p,T}(\partial m^2/\partial p)_{T,n_b}\kappa^{-1}$ reported in II in addition to the two other terms in curly brackets (that is in G of (4·27))†: usually only these two terms are quoted in the expression for the turbidity of a two-component isotropic fluid (see, for example, Doty, Zimm & Mark 1945). Experimental evidence in support of this additional term was adduced in the earlier paper: we note here that its existence, as indeed the whole form of G, has been demonstrated up to terms $O(n_\alpha^3\eta_\alpha^3)$, that is to one order higher in $n_\alpha\eta_\alpha$ than the previous calculation of II. By a calculation of the scattered intensity somewhat similar to that made here but for the one-component system Fixman (1955) demonstrates that the one-component analogue of G, namely $\kappa[(\partial m^2/\partial p)_T\kappa^{-1}]^2$ correctly describes the effect of multiple scattering up to correlations between sets of four particles and to terms $O(n^4\eta^4)$ after allowing for depolarization: the author (Bullough 1964) has demonstrated the same result up to $O(n^4\eta^4)$ in the extinction (i.e. a calculation of τ through $\mathscr{I}m$ and has shown that, up to a question of the factor m^{-1} noted in §§1 and 2 and in II and which appears to depend on the boundary conditions, the result is numerically correct up to $O(n^5\eta^5)$ after allowing for depolarization. Both at this order and at $O(n^4\eta^4)$ some numerically quite negligible terms are neglected from the formal reduction of the multiple scattering terms to the simple phenomenological result. It seems possible that the detailed molecular theory is attempting to reproduce the *exact* form of the Einstein (1910) equations —that is, it is even exactly generating the terms in the fourth order fluctuations whose coefficients depend on $(\partial^2(m^2)/\partial n^2)_T$ and $(\partial^3(m^2)/\partial n^3)_T$. Since, for example,

$$n^4[(\partial^2(m^2)/\partial n^2)_T]^2 \approx n^2[(\partial m^2/\partial n)_T]^2 \sim (4\pi n\eta)^2$$

we have to compare $\overline{\Delta n^4}/n^4$ against $\overline{\Delta n^2}/n^2$ or about $(k'T\kappa/V)^2$ with $(k'T\kappa/V)\sim 10^{-25}/V$. (We note that V^2 times $\overline{\Delta n^4}/n^4$ is independent of V.) We conclude with Einstein that except near to the critical point these terms would certainly be entirely negligible, but the formal identity of the omitted terms and these macroscopic expressions would be worthy of investigation. Indeed close to the critical point such an investigation becomes entirely necessary.

It seems indeed that (4·23) and its one-component analogue are examples of a 'trivial' identity between the macroscopic derivatives of macroscopic refractive index and the microscopic expression for these quantities: the final results are relatively so simple that a transformation from distribution functions to the thermodynamic parameters early on in the calculation might considerably reduce the complexity of the argument. A possible shot in the one-component case is to Fourier transform the density and work with its Fourier components as 'co-ordinates' instead of the particle components $\mathbf{x}_{i_\beta}$. This approach has been used by Nozieres & Pines (1958*a*, *b*) for a many body system in which the particles interact with the point charge potential $1/r$, but it is significant that even with this much simpler potential they were obliged to neglect the phenomena of greatest interest here, namely the real or apparent local field corrections. Indeed to prove up to all orders in $n_\alpha\eta_\alpha$ here what would surely be a very remarkable relation whatever level of 'triviality' its conceptional basis it would be necessary to cope with an additional complication in the depolarization terms which arise by correlations between sets of four and more particles: it seems fairly certain that these can always be absorbed into a variant of the Cabannes

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† With $n_a = \xi$, $n_b = n-\xi$ (so that $n_a+n_b = n$) and $\eta_a = \eta_b$, the cross-term is necessary for (4·27) to reduce to the one-component expression (2·26).

(1929) depolarization factor with some alteration of the numbers appearing in it (Bullough 1964), but this suggests that the identity can hardly really be a trivial one. It is not known whether a similar identity exists up to any order at all for multipole scattering of order greater than two, nor is it known how far other many-body problems hinge on identities of this kind. Certainly the *precise* identity we conjecture and have proved to first order here is remarkable enough to make the question of a best choice of variables an intriguing one: the transformation of the radiation damping term 'in the medium' which a like calculation of the extinction demands is surely remarkable by any standards. We must take these several points up elsewhere, however.

In support of the existence of the particular identity for dipole scattering we may here nevertheless remark that in an isotropic system with spherically symmetric $g_{\alpha\beta}(r')$ the integrals $J_{\alpha\beta}$ are $O(k^2 l^2_{\alpha\beta})$, where $l_{\alpha\beta}$ is a correlation distance: it follows that they could indeed be neglected (as was done by Fixman (1955) and Mazur (1958) in analogous one-component calculations). But it is clear they hold a natural place in the transition from microscopic quantities; in the one component case at least, terms in four particle correlations transform to macroscopic quantities in a similar way to these and can be neglected only because of the small magnitude of $n^4\eta^4$ relative to the zero order scattering which is $O(n^2\eta^2)$ ($n\eta \sim 1/16$ so $O(n^4\eta^4) \sim \frac{1}{4}\%$ of the zero order scattering, but relatively large coefficients partially destroy the apparent numerical insignificance of these terms†). We may remark also that terms in $J^2_{\alpha\beta}$ *must* be neglected in order to prove identity at the order $n^4_\alpha \eta^4_\alpha$ in the two-component case: these are presumably a contribution to the second derivatives of m^2 in Einstein's Taylor expansion or to the fourth order fluctuations. Whether the complete identity exists or not our calculation here certainly demonstrates up to $O(n^3_\alpha \eta^3_\alpha)$ the precise equivalence of Einstein's (1910) 'macroscopic' (phenomenological) fluctuation theory and the theory of distribution functions in the grand canonical ensemble embodied in the recurrence relations of Buff & Brout (1955).

As noted in § 1 the expression (4·29) differs from the earlier result in II in the omission of the factor $9m^{-1}(m^2+2)^{-2}$ there obtained: that the factor $9(m^2+2)^{-2}$ should be omitted was postulated in II by analogy with the argument for the one-component system embodying correlations between sets of up to four particles, that is by including multiple scattering (but with the gauge (2·4)) and investigating up to $O(n^4\eta^4)$. The gauge transformation in (2·6) demonstrates in a remarkable way how this factor is a multiple scattering term in the formulation from (2·1) in which the individual scattering process takes place *in vacuo*: the 'interpretation' of this factor simply as a Lorentz internal field factor is therefore very misleading.

More misleading still can be the 'interpretation' of the remaining factor m^{-1} which does not appear in (4·29): we note that such a factor must certainly appear if the factor $\frac{1}{2}(m+m^*) \approx m$ is omitted from (4·27) as it was by Mazur (1958) and Einstein (1910) in the one-component analogues of that expression‡. It is a remarkable fact that a calculation of the scattering from (2·1) directly, with gauge (2·4), restores the factor m^{-1} to τ and is in apparent agreement with τ calculated from $\mathscr{I}$m as in II: only when the individual scattering

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† See footnote on p. 411.

‡ Einstein was primarily concerned with the ratios of intensities but certainly computes these intensities as squared amplitudes simply. He calls them a measure (Maß) of the intensity however.

processes are transformed 'to the medium' of refractive index m (of which they are themselves the source) by a gauge transformation to the gauge of (2·6) is the m^{-1} eliminated from τ as in (4·29); then of course it must reappear as $\frac{1}{2}(m+m^*)$ in the scattered intensity of (4·27). The paradox can be resolved only by modifying the solution for the $\bar{\mathbf{P}}_\gamma(\mathbf{x})$ of (2·15) as noted in §§2 and 3: whether or not the factor m^{-1} should appear depends on a precise formulation of the boundary conditions which determine the choice of the solutions $\boldsymbol{\pi}_0$ or $\tilde{\boldsymbol{\pi}}_0$ of the homogeneous equations from (2·3a) and (2·12). Here we emphasize only that in the conceptual scheme implicit in Einstein's treatment of scattering the factor $\frac{1}{2}(m+m^*) \approx m$ must appear in (4·27) and not in (4·29).

Superficially this means that molecular weights measured from intensities and calculated with Einstein's expression for the scattered intensity would be in error by an omitted factor $\sim m(\approx 1{\cdot}5)$; in practice the Rayleigh ratio is taken but it is then necessary to normalize the scattered intensity against the transmitted intensity in the medium to eliminate the factor. The situation is however further complicated by the methods of scaling the apparatus measuring intensities, and the factor m is so closely related to the shape of the boundary of V that we must defer discussion of this point also.

Apart from the factor $\frac{1}{2}(m+m^*)$ in (4·27), both (4·27) and (4·29) agree precisely with the forms usually quoted as Einstein's formulae for the scattered intensity and turbidity of a two-component fluid except in the 'cross-term' in G of (4·27). Its presence shows that it is not quite correct to divide the scattering into either that from the pure solvent depending on[‡] $\kappa|(\partial m^2/\partial p)_{T,n_b}\kappa^{-1}|^2$ or 'excess' scattering depending on $n_b^2|(\partial m^2/\partial n_b)_{p,T}|^2$. We may also note that, at a molecular level, whilst a natural excess molecular excess polarizability $(\eta_b - v_b v_a^{-1}\eta_a)$ emerges at first order in η_α in (4·13a) this combination of the η_α seems to have no significance at higher orders in η_α: this has important consequences to the theory of scattering by large molecules where it has always been assumed that it is sufficient simply to add corrections due to interference terms arising from a finite molecular size or correlation distance in the excess scattering alone. We take this up in the following section.

6. Scattering from large molecules

By a 'large' molecule we mean a macromolecule for which the correlation distance of polarizable units small compared with k^{-1} is itself strictly comparable with k^{-1}. We introduce the concentration c (in grammes per cubic centimetre) of the solute 'b' in the solvent 'a'. Taking the reasonable value $\partial m^2/\partial c = 0{\cdot}1\,\mathrm{cm}^3/\mathrm{g}$, we have

$$n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,T} = c\left(\frac{\partial m^2}{\partial c}\right)_{p,T} = 10^{-1}c.$$

Taking the rough estimate $(\partial m^2/\partial p)_{\chi,n_b}\kappa^{-1} \approx \rho\,\partial m^2/\partial\rho \sim 1{\cdot}0$, where ρ is the density of the fluid (≈ 1) and we assume $\partial m^2/\partial\rho \sim 1{\cdot}0\,\mathrm{cm}^3/\mathrm{g}$, we find that the first and third terms in G of (4·26) or (4·29) have ratio

$$10^{-2}c^2[n_b(\partial\Pi/\partial n_b)_{\mu_a,T}]^{-1}\kappa^{-1}. \tag{6·1}$$

Since $$\Pi = n_b k' T + O(n_b) \quad \text{and} \quad c/n_b = M_b/N_0,$$

[‡] This quantity should of course be computed for the mixture but it is usually closely approximated by the analogous quantity for the pure solvent.

where M_b is the molecular weight of the solute, N_0 is Avogadro's number, it follows that the ratio (6·1) is

$$10^{-2}\,(cM_b/N_0)\,[k'T\kappa]^{-1} \sim cM_b\ \mathrm{g/cm^3}. \tag{6·2}$$

This becomes large for the large polymeric solute molecules ($M_b \sim 10^6$) whose molecular weights are determined by light scattering measurement. As long as the dimensions of such macromolecules remain $\ll k^{-1}$ it is therefore more than adequate to neglect the 'pure solvent' scattering in relation to the 'excess' scattering. Since the ratio of the first and second terms of G is

$$10^{-1}\{\tfrac{1}{2}(M_b/N_0)\,[k'T\kappa]^{-1}\} \sim 10M_b \tag{6·3}$$

the second term is negligible for $M_b \gtrsim 1000$: more precise estimates show that it may significantly affect molecular weights $M_b \lesssim 500$ (cf. II or Sicotte & Rinfret 1962).

A coiling macromolecule with $M_b \sim 10^6 - 10^7$ has r.m.s. dimensions $\sim 10^{\frac{5}{2}} \times 10$ Å ~ 3000 Å. This exceeds k^{-1} at optical frequencies by a factor of at least three, and even if this is extreme factors of more than unity are common enough. Following Debye (1947) it is usual to replace

$$\left[n_b\left(\frac{\partial \Pi}{\partial n_b}\right)_{\mu_a,\,T}\right]^{-1} = \chi n_b^{-2}\,\frac{\partial n_b}{\partial(\chi\mu_b)_{\mu_a,\,T}} = \chi n_b^{-1}\left\{1+n_b\int_V [g_{bb}(r')-1]\,\mathrm{d}\mathbf{r}'\right\}, \tag{6·4}$$

(where the first relation follows from (4·25) and the second from (4·1*a*)) by

$$\chi n_b^{-1}\left[1+n_b\int_V [g_{bb}(r')-1]\,j_0\,(kSr')\,\mathrm{d}\mathbf{r}'\right], \tag{6·5}$$

where $\mathbf{S} = \mathbf{s}-\mathbf{s}_0$ as in § 3. The 'excess' scattering is implicitly taken as the only significant scattering and is given in the ('well known' according to Flory & Bueche 1958) form in our notation

$$\bar{\mathbf{p}}(\mathbf{s}) = \frac{E_0^2k_0^4(m^*+m)V}{256\pi^3\,\mathfrak{R}^2}\,[1-(\mathbf{u}\,.\,\mathbf{s})^2]\,\mathbf{s}\left\{\left(\frac{\partial m^2}{\partial n_b}\right)^2_{p,\,T} n_b\left[1+n_b\int_V [g_{bb}(r')-1)]\,j_0\,(kSr')\,\mathrm{d}\mathbf{r}'\right]\right\}. \tag{6·6}$$

We include the factor $\frac{1}{2}(m^*+m)$ which does not usually appear: within the terms of the discussion in § 5 the factor is certainly required here.

Yet it is plain from the arguments of § 4 which replace the microscopic polarizabilities of (3·17) by easily measurable derivatives of macroscopic refractive index that the formal equivalence of (3·17) and (6·6) is simply false when correlation distance and molecular size approach or exceed k^{-1}. In the first place we can simplify $\bar{K}_2$ of (3·16*c*) to the form of (4·4) only when we can replace $\mathrm{e}^{-ik\mathbf{S}.\mathbf{r}_1}$ by unity in that expression: in the second place an 'excess' scattering term emerges from (4·6) only when we can reverse the argument of (6·4) to (6·5) for *each* of the four terms—or three since two are equal—

$$G_{\alpha\beta}(\mathbf{s}) \equiv \int_V [g_{\alpha\beta}(r')-1]\,j_0(kSr')\,\mathrm{d}\mathbf{r}'. \tag{6·7}$$

The fundamental scattering equation (3·17) is correct up to first order in multiple scattering within the terms of our initial assumptions of polarizable particles and no multipole scattering, but the lack of experimental or theoretical knowledge of the correlation functions $g_{\alpha\beta}(r')$ when one or both of α and β is an 'a' appropriate to the solvent and an even greater lack of knowledge of all the $g_{\alpha\beta\gamma}(\mathbf{r}_1, \mathbf{r}')$ means that we can at the moment hope to deal only with the excess scattering: the Gaussian model of a coiling macromolecule with intermolecular solute interactions (Zimm 1948; Flory & Bueche 1958) seems the source of a reasonable approximation to $g_{bb}(r')$ at extreme dilution and indeed this model can be used to derive the intra-molecular three particle distribution $g_{bbb}(\mathbf{r}_1, \mathbf{r}')$ (Bullough 1963*b*; Bullough & Davison 1963). It remains to investigate here conditions, if any, sufficient to make (6·6) a numerically valid approximation to (3·17); this we do below.

In so complex an analytic situation at the molecular level and in the absence of detailed knowledge of all the $g_{\alpha\beta\gamma}(\mathbf{r}_1, \mathbf{r}')$, except possibly $g_{bbb}(\mathbf{r}'_1, \mathbf{r})$, we investigate here only the second of the approximations which render (3·17) and (6·6) equivalent. Since we shall conclude that this second approximation can lead to serious error in estimations of molecular size and shape by Debye's method and can even make significant error in estimates of molecular weight M_b, and since the replacement of $e^{-ik\mathbf{s}.\mathbf{r}_1}$ in $\bar{K}_2$ of (3·16*c*) is the same type of approximation as that involved in reaching (6·6) from the excess scattering term in (4·17) via the reinterpretation of (6·4), we do no more than emphasize here that the appearance of the simple macroscopic term $[n_b(\partial m^2/\partial n_b)_{p,T}]^2$ in (6·6) rather than a complicated expression depending explicitly on microscopic correlation functions and polarizabilities, does appear to introduce serious error comparable with that from the second approximation which we here examine in detail. Essentially the first approximation is a neglect of multiple scattering terms: the argument of this paper indicates that this is far from justifiable in condensed media.†

If we ignore the multiple scattering terms $\bar{K}_2$ and $\bar{K}_2^*$ in (3·17) we have for single scattering by quasi-particles in the medium that

$$\bar{\mathbf{p}}(\mathbf{s}) = \frac{E_0^2(m+m^*)\,Vk_0^4}{16\pi\mathfrak{R}^2}\left|\frac{m^2+2}{3}\right|^4 [1-(\mathbf{u}.\mathbf{s})^2]\,\mathbf{s}\{\sum_{\beta,\gamma} n_\beta n_\gamma \eta_\beta \eta_\gamma^* G_{\beta\gamma}(\mathbf{s}) + \sum_\beta n_\beta|\eta_\beta|^2\} \tag{6·8}$$

with the $G_{\beta\gamma}(\mathbf{s})$ defined in (6·7). Since m is complex the $G_{\beta\gamma}$ are complex but it is consistent with the argument of § 3 to treat k in the $G_{\beta\gamma}$ as its real part $\frac{1}{2}(m+m^*)k_0$. For the quantity in curly brackets in (6·8) we have

$$\begin{aligned}\sum_\beta n_\beta|\eta_\beta|^2 + \sum_{\beta,\gamma} n_\beta n_\gamma \eta_\beta \eta_\gamma^* G_{\beta\gamma}(\mathbf{s}) = {} & n_b|\eta_b - v_b v_a^{-1}\eta_a|^2\,(1+n_b G_{bb}(\mathbf{s})) \\ & + n_b[(\eta_b - v_b v_a^{-1}\eta_a)\,\eta_a^* v_a^{-1} + \text{c.c.}]\,[v_b + n_b v_b G_{bb}(\mathbf{s}) \\ & + n_a v_a G_{ab}(\mathbf{s})] + |\eta_a|^2 v_a^{-2}[n_a v_a(v_a + n_b v_b G_{ab}(\mathbf{s}) + n_a v_a G_{aa}(\mathbf{s})) \\ & + n_b v_b(v_b + n_b v_b G_{bb}(\mathbf{s}) + n_a v_a G_{ab}(\mathbf{s}))].\end{aligned} \tag{6·9}$$

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† While these multiple scattering terms should differ one to the other for small and large correlation lengths it may be argued that these terms are nonetheless small in both cases compared with the single scattering terms. This does indeed seem to be the assertion of Fixman (1960) in discussing scattering from a one component system close to the critical point. But these terms cannot be small in the case of small correlation lengths at least: for in this case we could take for $[n(\partial m^2/\partial n)]^2$ in the one component case just

$$[\tfrac{1}{3}(m^2-1)\;(m^2+2)]^2.$$

Carr and Zimm (1950) show that these two quantities differ by as much as 35 % for pure liquids like carbon disulphide ($m = 1·632$). For long correlation distances the relative importance of these terms could well be enhanced: it is therefore remarkable that, for example, the Ornstein–Zernike theory of critical scattering shows the good agreement with experiment that has sometimes been reported. There are many examples of its failure however (see references quoted by Fixman (1963)). In connexion with critical scattering the footnote on p. 400 seems important.

From (4·13), (4·14) and (4·15) on the assumption that the terms from $\overline{K}_2$ (of $O(n_\alpha^2\eta_\alpha^2)$) in these expressions can be neglected—and we repeat that this approximation is probably not valid—(6·9) into (6·8) yields

$$\begin{aligned}\bar{\mathbf{p}}(\mathbf{s}) = \frac{E_0^2(m+m^*)Vk_0^4}{256\pi^3\mathfrak{R}^2}[1-(\mathbf{u}.\mathbf{s})^2]\,\mathbf{s}\Bigg\{&\left|\frac{\partial m^2}{\partial n_b}\right|^2_{p,\chi,V} n_b(1+n_bG_{bb}(\mathbf{s}))\\ &+\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)^*_{\chi,V,N_b}+\text{c.c.}\right][v_b+n_bv_bG_{bb}(\mathbf{s})+n_av_aG_{ab}(\mathbf{s})]\\ &+\left|\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}\right|^2[n_av_a(v_a+n_bv_bG_{ab}(\mathbf{s})+n_av_aG_{aa}(\mathbf{s}))\\ &+n_bv_b(v_b+n_bv_bG_{bb}(\mathbf{s})+n_av_aG_{ab}(\mathbf{s}))]\Bigg\}. \qquad (6{\cdot}10)\end{aligned}$$

Equation (6·10) reduces to (6·6) if *and only if* (since m^2 does depend on n_b and N_a)

$$\begin{aligned}&\left[n_b\left(\frac{\partial m^2}{\partial n_b}\right)_{p,\chi,V}\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}+\text{c.c.}\right][v_b+n_bv_bG_{bb}(\mathbf{s})+n_av_aG_{ab}(\mathbf{s})]\\ &\quad+\left|\frac{V}{v_a}\left(\frac{\partial m^2}{\partial N_a}\right)_{\chi,V,N_b}\right|^2[n_av_a(v_a+n_bv_bG_{ab}(\mathbf{s})+n_av_aG_{aa}(\mathbf{s}))\\ &\qquad+n_bv_b(v_b+n_bv_bG_{bb}(\mathbf{s})+n_av_aG_{ab}(\mathbf{s}))]=0. \qquad (6{\cdot}11)\end{aligned}$$

Define U_α by V with a small region of volume v_α about the origin omitted: we shall identify these v_α with the partial molar volumes of kind α as before and we assume that $v_\alpha \ll k^{-3}$ whilst the correlation distances are assumed $\approx k^{-1}$. Implicitly we therefore identify the small polarizable 'molecules' of volume v_α with equivalent polarizable sub-units of a macromolecule. The equivalent random links of Kuhn & Grün (1942) have linear dimensions 10 to 20 Å or more and the macromolecule may contain 10^4 to 10^5 of these units. The intramolecular correlation distance is *ca.* 3000 Å and the intermolecular correlation distances between solute molecules must exceed this. At concentrations of 1 or 2 % these intermolecular correlation distances could considerably exceed this figure (compare, for example, the rubber-like model of such a solution adopted by Lodge (1956)).

Since $g_{\alpha\beta} = 0$ within a region $\approx v_\alpha$ about the origin and $j_0(kSr) \approx 1$ there,

$$n_bv_bG_{ab}(\mathbf{s})+n_av_aG_{aa}(\mathbf{s}) = n_bv_bK_{ab}(\mathbf{s})+n_av_aK_{aa}(\mathbf{s})-v_a, \qquad (6{\cdot}12a)$$

where

$$K_{\alpha\beta}(\mathbf{s}) = \int_{U_\alpha}(g_{\alpha\beta}(r')-1)\,j_0(kSr')\,\mathrm{d}\mathbf{r}' \qquad (6{\cdot}12b)$$

and we have used

$$n_av_a+n_bv_b = 1.$$

Since $g_{\alpha\beta} = g_{\beta\alpha}$, $G_{ab} = G_{ba}$ (but it is of course not true that $K_{ab} = K_{ba}$ unless $v_a \approx v_b$) and (6·12) together with the analogous relation to (6·12a) with a and b interchanged when substituted into (6·11) imply

$$[C_1+C_2n_bv_b]\,[n_bv_bK_{bb}(\mathbf{s})+n_av_aK_{ba}(\mathbf{s})]+C_2n_av_a[n_bv_bK_{ab}(\mathbf{s})+n_av_aK_{aa}(\mathbf{s})] = 0: \qquad (6{\cdot}13)$$

C_1 and C_2 in (6·13) are the two coefficients of the terms in the $G_{\alpha\beta}$ in (6·11). If (6·13) is to have general validity it is to be true for a range of concentrations and derivatives of refractive index. Then we must have that

$$n_bv_bK_{bb}(\mathbf{s})+n_av_aK_{ba}(\mathbf{s}) = n_bv_bK_{ab}(\mathbf{s})+n_av_aK_{aa}(\mathbf{s}) = 0. \qquad (6{\cdot}14)$$

Were (6·14) true for all wavelengths 0 to ∞ we have immediately from the Fourier inversion theorem that within U_a, a region in the two-body space of one a-molecule and a second molecule

$$\left.\begin{aligned} n_a v_a g_{aa} + n_b v_b g_{ab} &= 1; \\ \text{likewise in } U_b \qquad n_a v_a g_{ba} + n_b v_b g_{bb} &= 1. \end{aligned}\right\} \tag{6·15}$$

According to superficial arguments leading to (6·6) we have neglected 'pure solvent' scattering proportional to $\kappa k' T = \kappa/\chi$. If we add the two terms in κ/χ in (4·27) to the right-hand side of (6·6) $\bar{\mathbf{p}}(\mathbf{s})$ reduces to the form of (6·10) now, if and only if,

$$\left.\begin{aligned} n_a v_a g_{aa} + n_b v_b g_{ab} &= U_a(r) + \kappa k' T \delta(r), \\ n_a v_a g_{ba} + n_b v_b g_{bb} &= U_b(r) + \kappa k' T \delta(r), \end{aligned}\right\} \tag{6·16}$$

where $\delta(r)$ is a δ-function satisfying $4\pi \int_0^\infty \delta(r)\, r^2 \,\mathrm{d}r = 1$ and

$$\begin{aligned} U_\alpha(r) &= 1 \quad (r > \text{radius of } v_\alpha), \\ &= 0 \quad (r < \text{radius of } v_\alpha). \end{aligned}$$

Equation (6·16) is to hold over the whole of two-body space; it implies

$$\left.\begin{aligned} v_a + n_a v_a \int (g_{aa} - 1)\, \mathrm{d}\mathbf{r}' + n_b v_b \int (g_{ab} - 1)\, \mathrm{d}\mathbf{r}' &= \kappa k' T, \\ v_b + n_a v_a \int (g_{ba} - 1)\, \mathrm{d}\mathbf{r}' + n_b v_b \int (g_{bb} - 1)\, \mathrm{d}\mathbf{r}' &= \kappa k' T, \end{aligned}\right\} \tag{6·17}$$

which are indeed relations implicit in (4·17). But equations (6·16) are microscopic conditions between the correlation functions themselves and are not macroscopic relations between the space averages of the correlation functions and measurable thermodynamic parameters as are (6·17). In particular (6·15) *implies* an incompressibility condition (or neglect of terms in $\kappa k' T$); but neglect of terms in $\kappa k' T$ does not imply (6·15)—the microscopic conditions (6·15) are far more stringent.

The conditions are indeed over stringent in that, in practice, for fixed wave length λ, there is a cut-off at a maximum scattering angle of π, $k|\mathbf{S}| \leqslant 4\pi m \lambda^{-1}$, and we obtain instead of (6·15) the pair of equations that in U_α for $\alpha = a$ or b

$$\int [n_\alpha v_\alpha g_{\alpha\beta}(r') + n_\beta v_\beta g_{\beta\beta}(r') - 1]\, J(|\mathbf{r} - \mathbf{r}'|)\, \mathrm{d}\mathbf{r}' = 0 \quad (\alpha \neq \beta), \tag{6·18}$$

in which
$$J(r) = (k^3/8\pi^3) \int_{|\sigma| \leqslant 2} \mathrm{e}^{\mathrm{i}k\boldsymbol{\sigma}\cdot\mathbf{r}}\, \mathrm{d}\boldsymbol{\sigma}:$$

when $k \to \infty$, $J(r) \to \delta(r)$. The function $J(r)$ has a first zero at the smallest non-zero root of $\tan 2kr = 2kr$, i.e. at $2mk_0 r = l\pi$, where $1 < l < 2$. The condition (6·18) is much coarser than (6·15) and leads to the conclusion that (6·15) is necessarily true only 'on the average' over regions of dimension† $\sim l\lambda/4m$: thus we require only that

$$\int_{U_{\alpha,\lambda}} (n_\alpha v_\alpha g_{\alpha\alpha} + n_\beta v_\beta g_{\alpha\beta})\, \mathrm{d}\mathbf{r}' = U_{\alpha,\lambda} \quad (\alpha \neq \beta),$$

---

† If the cutoff is taken at scattering angle $\theta_0 < \pi$ the dimension $\sim l\lambda/4m \sin \frac{1}{2}\theta_0$ and $\to \infty$ for pure forward scattering $\theta_0 = 0$.

where $U_{\alpha,\lambda}$ is any roughly spherical region of that volume and radius $\approx l\lambda/8m$ within the region U_α defined above. If we replace the small sphere of volume v_α at the origin of $U_{\alpha,\lambda}$ and U_α, then calling $U_{\alpha,\lambda}+v_\alpha = V_\lambda$, we have

$$v_\alpha + \int_{V_\lambda} (n_\alpha v_\alpha g_{\alpha\alpha} + n_\beta v_\beta g_{\alpha\beta})\,\mathrm{d}\mathbf{r}' = V_\lambda + \kappa k' T \quad (\alpha \neq \beta), \tag{6·19}$$

where we introduce $\kappa k' T = \kappa k' T \int_{V_\lambda} \delta(r)\,\mathrm{d}\mathbf{r}$ analogously to the step from (6·15) to (6·16).

When the dimensions of V_λ greatly exceed the correlation lengths of the $g_{\alpha\beta}$, (6·19) is the same as (6·17). However, for large macromolecules the intramolecular correlation distances are ~ 3000 Å and it is this fact alone which makes the shapes of these molecules accessible to investigation by scattering. It is clear that these measurements can be interpreted by the ideas of Debye (1947) and in particular by (6·6) if and only if (6·19) holds. We emphasize that the radius of $V_\lambda \approx l\lambda/8m \sim \lambda/8$ and so is significantly less than a correlation distance $\gtrsim \frac{1}{2}\lambda$. It follows that if the usual estimates of molecular size and shape are to have any validity special packing conditions, namely (6·19), must exist for the two sets of molecule in the system.

The conditions (6·19) and (6·15) are hydration conditions in the sense that in (6·15)

$$(n_\alpha v_\alpha g_{\alpha\alpha} + n_\beta v_\beta g_{\alpha\beta})\,\delta\mathbf{r} \quad (\alpha \neq \beta)$$

is the probability of 'occupation of volume' in a volume element $\delta\mathbf{r}$ at a distance $\mathbf{r}$ from a point known to be at the centre of a molecule of kind α; the condition (6·15) then asserts that this occupation of volume is uniform on a molecular scale—or on the scale of the partial molar volumes v_α of dimension *ca.* 10 Å. The condition (6·19) then asserts that, for $\kappa k' T \sim 0$, the occupation shall be uniform over regions of radius *ca.* $\frac{1}{8}\lambda$. The term $\kappa k' T$ simply introduces a systematic excess occupation of volume. Equation (6·6) is therefore valid if, and only if, molecules of solute are hydrated by the solvent according to (6·19). In fact the phrase 'if and only if' ignores the inadequate treatment of the terms $\bar{K}_2$ and $\bar{K}_2^*$ at the beginning of this section: presumably hydration conditions like (6·19) must apply to the correlation functions of multiplets of particles of any number or to combinations of these.

In the following section we attempt a numerical estimate of the possible error inherent in using (6·6) to estimate the sizes and molecular weights of large molecules; the calculations are necessarily rough because of our ignorance of the $g_{\beta\gamma}$.

7. Errors in molecular weights because of non-additive scattering

For solutions of large molecules it has been observed (Zimm 1948) that

$$n_b^2 g_{bb} = N_b Z(Z-1)\,\gamma_{bb} + N_b^2 Z^2 \Gamma_{bb}, \tag{7·1}$$

where N_b is now the number of macromolecules per cubic centimetre (*not* the total number of b-particles in the region V), Z is the number of sub-molecules per macromolecule, $n_b = N_b Z$ and γ_{bb} and Γ_{bb} refer respectively to intra- and intermolecular correlations between submolecules. From (6·6) we then obtain, following Zimm (1948), that

$$\bar{\mathbf{p}}(\mathbf{s}) = \mathbf{s}C(\mathbf{s})\left[\left(\frac{\partial m^2}{\partial N_b}\right)_{p,T}\right]^2 N_b\{P(\mathbf{s}) + N_b Q(\mathbf{s})\}, \tag{7·2}$$

where
$$P(\mathbf{s}) = \int_V \gamma_{bb}(r')\, j_0(kSr')\, \mathrm{d}\mathbf{r}'$$

and
$$Q(\mathbf{s}) = \int_V (\Gamma_{bb}(r')-1)\, j_0(kSr')\, \mathrm{d}\mathbf{r}'.$$

We assume $Z^{-1}+(1-Z^{-1})\,P(\mathbf{s}) \approx P(\mathbf{s})$ (for $Z \sim 10^4$) and $C(\mathbf{s})$ contains the factors making (7·2) equivalent to (6·6).

Both γ_{bb} and Γ_{bb} can be expanded about their values $\gamma_{bb}^{(0)}$ and $\Gamma_{bb}^{(0)}$ at infinite dilution in powers of the concentration c of the solute b: if M_b is the molecular weight of the solute and N_0 is Avogadro's number, $c = N_b M_b / N_0$. It follows that

$$M_b = \lim_{c\to 0} \frac{|\bar{\mathbf{p}}(\mathbf{s}_1)|}{Hc}\,[P(\mathbf{s}_1)]^{-1}, \tag{7·3}$$

where
$$H = \frac{C(\mathbf{s}_1)}{N_0}\left[\left(\frac{\partial m^2}{\partial c}\right)_{p,\,T}\right]^2$$
$$= \frac{E_0^2 k_0^4 (m+m^*)\, V}{256\pi^3 \mathfrak{R}^2}\,[1-(\mathbf{u}\,.\,\mathbf{s}_1)^2]\,\frac{1}{N_0}\left[\left(\frac{\partial m^2}{\partial c}\right)_{p,\,T}\right]^2$$

and following usual practice $\mathbf{s}_1$ is one of the particular scattering directions appropriate to a scattering angle of $\frac{1}{2}\pi$,
$$\mathbf{s}_1 = \pm \mathbf{u} \wedge \mathbf{s}_0,$$

(so that $\mathbf{u}\,.\,\mathbf{s}_1$ is actually zero). Since (7·2) follows from (6·6) with (7·1), the expression (7·3) which is that usually taken is valid if and only if the hydration condition (6·19) holds. We now show that the possible error in $P(\mathbf{s}_1)$ when (6·19) does *not* hold is comparable with the correction which $P(\mathbf{s}_1)$ itself introduces into the estimates of M_b from (7·3). We note that for small molecules $P(\mathbf{s})$ reduces to

$$\int_V \gamma_{bb}(r')\, \mathrm{d}\mathbf{r}' = 1 \tag{7·4}$$

because $\gamma_{bb}(r)$ is normalized to unity in (7·1): $P(\mathbf{s})$ differs from one for large molecules.

The corrections to M_b from concentration dependent terms in (4·27) in the case of small molecules were given in II. For the additional corrections which are now the important ones when M_b is large we split off from the contents of the curly brackets in (6·8)

$$\sum_{\beta,\,\gamma} n_\beta n_\gamma \eta_\beta \eta_\gamma^* \, G'_{\beta\gamma}(\mathbf{s}), \tag{7·5}$$

where
$$G'_{\beta\gamma}(\mathbf{s}) = \int (g_{\beta\gamma}-1)\,(j_0(kSr')-1)\, \mathrm{d}\mathbf{r}'.$$

Then the remainder of (6·8) reduces to (4·27), while if the hydration conditions (6·15) or (6·19) hold (7·5) reduces to essentially

$$n_b^2 \left(\frac{\partial m^2}{\partial n_b}\right)^2 G'_{bb}(\mathbf{s})$$

neglecting terms in $\overline{K}_2$ and $\overline{K}_2^*$ as in § 6.

Now consider the case of extreme dilution of b. The chance of finding a second submolecule at distance r from a first one in the same macromolecule is independent of N_b and is proportional to $Z-1$. Then

$$n_b^2(g_{bb}-1) = N_b Z(Z-1)\,\gamma_{bb}+O(N_b^2) \tag{7·6a}$$

with γ_{bb} normalized to unity as in (7·1). The chance of finding a pair of a-molecules r apart will differ from that when $n_b = 0$ by $O(n_b)$, that is

$$n_a^2(g_{aa}-1) = \rho_a^2(\delta_{aa}-1)+n_b\gamma_{aa} \quad \text{(say)}, \tag{7·6b}$$

where ρ_a is the number density of a-molecules and δ_{aa} is the pair correlation function (normalized to a single pair) when $n_b = 0$: γ_{aa} is also normalized to a single pair†. The key point here is that the correction $n_b\gamma_{aa}$ in (7·6b) is of order Z^{-1} to the first term on the right hand side of (7·6a) when the functions $\gamma_{bb}(r)$ and $\gamma_{aa}(r)$ range through similar magnitudes. The idea here is that near a b-particle there is a very high density of b-particles proportional to $Z-1$: at comparable distances from an a-particle there is no such extra expectation of a-particles unless of course the system attempts in more or less degree to satisfy a hydration condition.

For g_{ab} we assume the following: suppose that the molecule is not hydrated in the sense that the probability of finding an a-molecule within a sphere of radius r_0 about a b-submolecule is zero, but that a and b are uncorrelated for $r > r_0$ so that $g_{ab} = 1$. We have

$$\begin{aligned} n_a n_b(g_{ab}-1) &= -n_a n_b \quad && (r < r_0) \\ &= 0 && (r > r_0). \end{aligned}$$

Choose r_0 such that $\frac{4}{3}\pi r_0^3 = \mu Z v_b$, where Zv_b is a volume of the submolecules in the b-macromolecule: μ is an as yet undetermined parameter. Introduce the function

$$\begin{aligned} \gamma_{ab} &= \mu^{-1}Z^{-1}v_b^{-1} \quad && (r < r_0), \\ &= 0 && (r > r_0), \end{aligned} \tag{7·6c}$$

so that $\int \gamma_{ab}(r')\,\mathrm{d}\mathbf{r}' = 1$. Then

$$n_a n_b(g_{ab}-1) = -\mu n_b Z n_a v_b \gamma_{ab}. \tag{7·6d}$$

Grimley (1961) has given order of magnitude estimates of the fluctuations determined by the $n_\beta n_\gamma(g_{\beta\gamma}-1)$ based on an unspecified analysis from the grand partition function: as far as the important dependencies on Z are concerned the choices (7·6) are in complete accord with Grimley's estimates. In addition they must satisfy (6·17). We can easily achieve this for the first relation in (6·17) because the compressibility in the pure solvent a is given by

$$\kappa_0 k'T = \rho_a^{-1}+\int(\delta_{aa}(r')-1)\,\mathrm{d}\mathbf{r}';$$

then we can still choose the parameter μ to satisfy the second relation of (6·17) which becomes

$$\begin{aligned} \kappa k'T &= v_b - v_a\mu Z n_a v_b + v_b Z \\ &= v_b + Z v_b[1-\mu n_a v_a]. \end{aligned}$$

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† We can expect that γ_{aa} is a complex of terms including, for example, one of the form $\rho_a(\delta_{aa}-1)$ which is $O(\rho_a)$ *not* $O(1)$ at the very short a-a correlation distances. Nevertheless such a term is $O(1)$ at the longer correlation distances important here and its integral is $O(1)$. The same remarks will apply to any multiplet correlation functions (at infinite dilution) concealed in γ_{aa}.

With (in c.g.s. units) $\kappa k' T \sim 10^{-25}$, $Z \sim 10^4$, $v_b \approx 10^{-21}$ and $n_a v_a \approx 1$ this makes $\mu \approx 1$. As a final check of consistency we have for the first relation of (6·17) and $\mu \approx 1$

$$\kappa k' T = v_a + v_a n_a^{-1} \rho_a^2 \int (\delta_{aa} - 1)\, \mathrm{d}\mathbf{r}' + n_a^{-1} v_a n_b \int \gamma_{aa}(r')\, \mathrm{d}\mathbf{r}' - \mu n_b v_b^2 Z \int \gamma_{ab}(r')\, \mathrm{d}\mathbf{r}'$$

$$\approx \rho_a^2 v_a n_a^{-1} \kappa_0 k' T + v_a [1 - \rho_a n_a^{-1}] - \mu Z n_b v_b^2. \qquad (7·7)$$

Because of assumptions above of extreme dilution of b in a, i.e. $n_b \ll n_a$, we can see that despite the large size of Z it is certainly not inconsistent to have γ_{aa} and $\int \gamma_{aa}(r')\, \mathrm{d}\mathbf{r}'$ of order Z^{-1} to $(Z-1)\,\gamma_{bb}$ and $Z-1$. (In contrast, if (7·7) were to be true at $n_b v_b / n_a v_a \sim 1/10$, say, it could only be satisfied by taking $n_a v_a n_b \int \gamma_{aa}(r')\, \mathrm{d}\mathbf{r}' \approx \mu Z n_b v_b^2$).

It is worth noting that if the hydration condition (6·15) holds, then in U_b (when $v_b > v_a$)

$$n_a v_a (g_{aa} - 1) = -n_b v_b (g_{ab} - 1) = -\frac{n_b v_b}{n_a v_a} [n_a v_a (g_{ba} - 1)],$$

so that

$$n_a^2 v_a^2 (g_{aa} - 1) = n_b^2 v_b^2 (g_{bb} - 1);$$

and if $(\delta_{aa} - 1) \approx 0$ in most of this region

$$n_b v_a^2 \gamma_{aa} = n_b^2 v_b^2 (g_{bb} - 1) = n_b v_b^2 (Z-1)\, \gamma_{bb} + O(n_b^2),$$

so that $\gamma_{aa} \approx \gamma_{bb} v_b^2 v_a^{-2} (Z-1)$. Thus γ_{aa} is necessarily of the same order in Z as $(Z-1)\,\gamma_{bb}$: the hydration condition forces a preferential expectation of finding a second a-particle close to a first as a direct consequence of the assumption of a preferential expectation of finding a second b-particle close to a first. In contrast, when the hydration condition does not hold it is even unnecessary to assume that both γ_{aa} and γ_{bb} be essentially unity in Z as we did above except that then we require the function γ_{aa} explicitly: if γ_{aa} is such that the hydration conditions are not satisfied we can still be left with additional terms to (6·6) of the same order as those we compute below. We shall assume in the following, however, that the choices (7·6) are sound in their Z dependence at least: these dependences then agree with Grimley's as we note.

Because of the small correlation distances which we assume for the pure solvent

$$n_a^2 G'_{aa} = n_b \int \gamma_{aa}(r')\, [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}'$$

and is of order Z^{-1} relative to

$$n_a n_b G'_{ab} = -\mu n_b Z n_a v_b \int \gamma_{ab}(r')\, [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}'$$

and

$$n_b^2 G'_{bb} = n_b Z \int \gamma_{bb}(r')\, [j_0\,(kSr') - 1]\, \mathrm{d}\mathbf{r}'.$$

Then (7·5) becomes to $O\,(Z)$ (with η_γ replaced by its real part but still written η_γ)

$$n_b \eta_b Z \left\{ \eta_b \int \gamma_{bb}(r')\, [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}' - 2\mu n_a v_b \eta_a \int \gamma_{ab}(r')\, [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}' \right\}. \qquad (7·8)$$

We could now choose for γ_{bb} the Gaussian chain model taken by Debye (1947) and later workers, but because the essential point we make in this section is that it is not in general sufficient to know only γ_{bb} explicitly and because we do not in any case know anything about the real form of γ_{ab} in any practical case we simplify the argument here and take $\gamma_{bb} \equiv \gamma_{ab}$

with γ_{ab} defined in (7·6*c*): this means that the macromolecule approximates to a sphere of volume $\mu Z v_b$ (or more precisely the two particle correlation function which is essentially the convolution of the one body molecular distribution approximates to a sphere). Then (7·8) becomes

$$\mu^{-1} v_b^{-1} n_b \left\{\eta_b(\eta_b - 2\mu n_a v_b \eta_a) \int_{|\mathbf{r}'|<r_0} [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}'\right\}$$

and for this model of the macromolecule

$$[P(\mathbf{s}) - 1] = \mu^{-1} v_b^{-1} Z^{-1} \int_{|\mathbf{r}'|<r_0} [j_0(kSr') - 1]\, \mathrm{d}\mathbf{r}'.$$

This means that instead of (7·3)

$$M_b = \lim_{c\to 0} \frac{|\overline{\mathbf{p}}(\mathbf{s}_1)|}{Hc} \left[1 + \frac{\eta_b(\eta_b - 2\mu n_a v_b \eta_a)\,[P(\mathbf{s}_1) - 1]}{(\eta_b - v_b v_a^{-1} \eta_a)^2}\right]^{-1}. \qquad (7{\cdot}9)$$

Since the magnitude of the ratio in the polarizabilities can differ considerably from unity it is plain that corrections very much of order $[P(\mathbf{s}) - 1]$ itself must be added to the simple Debye correction $[P(\mathbf{s}) - 1]$. When the hydration conditions (6·15) or (6·19) are satisfied and the terms in $\kappa k' T$ are negligible the ratio in the polarizabilities becomes

$$\frac{(\eta_b - v_b v_a^{-1} \eta_a)^2}{(\eta_b - v_b v_a^{-1} \eta_a)^2} = 1$$

and we regain (7·3). When the refractive index increment is very large,

$$(\eta_b - v_b v_a^{-1} \eta_a) \approx \frac{9}{(m^2+2)^2} \frac{1}{4\pi} \left(\frac{\partial m^2}{\partial n_b}\right)_{p,T}$$

is very large and is approximately η_b: then (7·9) again reverts to (7·3). But for a typical figure of $(\partial m^2/\partial c)_{p,T} \approx 0{\cdot}1\ \mathrm{cm^3/g}$ and the assumption $\mu = \frac{1}{2}$ (which is not really consistent with the $\mu \approx 1$ required for consistency with (6·17) but the point of the example seems valid) the ratio in the polarizabilities is approximately

$$\frac{3}{4\pi\rho_b} \frac{m_b^2 - 1}{m_b^2 + 2} \frac{4\pi(m^2+2)^2}{9(\partial m^2/\partial n_b)_{p,T}} \sim \frac{10 n_b}{\rho_b c} \sim 10, \qquad (7{\cdot}10)$$

where ρ_b and m_b are the number density and refractive index of pure b; we use $n_b/\rho_b c \approx 1$ when pure b has mass density ≈ 1.

Possibly within the terms of this model, this ratio is extreme: certainly the model is too imprecise to confidently assert from it that the correction this ratio implies can actually occur. But the correction corresponding to a ratio of two (say) seems not impossible and even this makes the Debye correction in error by 100 %. Thus if the assumptions of this section are not too remote from actual situations we must conclude that the estimates $[P(\mathbf{s}) - 1]$ of the corrections to molecular weight M_b which are contained in (7·3) can be meaningless: then for the same reasons the estimates of molecular size from the dissymmetry are meaningless. The crux of the calculation here is that G'_{aa} is negligible, by one order Z^{-1}, compared with G'_{ab} and G'_{bb}. This assumption may be an extreme one, but if this is so it shows that the hydration conditions are to this extent often satisfied—for we showed above that the hydration conditions *demanded* that G'_{aa} and G'_{bb} should be the same order in Z: yet if they are still not precisely satisfied, corrections of significant magnitude may still be needed to convert (6·6) to the 'correct' equation (3·17).

Since the ratio of polarizabilities in (7·9) depends on the solvent for a given solute so should the apparent molecular weight M_b: in practice this does not seem to have been observed. This may be because the hydration conditions hold well enough or because if the example leading to (7·10) is true the variation would be small unless the refractive index increments show a sufficient change. The measured molecular sizes also seem to be consistent with dimensions found by other methods though it is difficult to obtain estimates of experimental error from the literature. It would therefore be of interest to use molecules of known M_b and dimensions to investigate the validity of (6·6): it may then be possible to infer the state of hydration of a solute molecule in the solvent and thus to obtain information about the correlation functions g_{ab} and g_{aa}. The theoretical treatment of scattering from large molecules does not simplify as does the theory for small molecules given in §4: we must also remember therefore that the arguments of §§6 and 7 are based on single scattering so that the validity of (6·6) would also give some information, rather unspecific from the present treatment, about hydration conditions on the $g_{\alpha\beta\gamma}$.

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[*Note added in proof*, 8 *June* 1965.] Since going to press I have found the interesting paper of Dr F. J. Pearson, *Proc. Phys. Soc.* **75**, 633 (1960) on 'The theory of critical opalescence in binary mixtures' which considers to the single scattering approximation a problem closely related to that we have discussed here in §§6 and 7. This is not the place to discuss the relationship of our two rather different approaches to this problem of long correlation distances: it seems worth noting here, however, that Pearson's 'condition for phase separation' (his equation (12)) will, in our different context actually follow directly from the 'hydration condition' (6·15). However, §§6 and 7 here show that, whilst these conditions are, for example, necessary and sufficient for the isolation of the 'excess' scattering, their applicability to the quite general physical situation of large correlation distances requires further investigation, both theoretically and, in the light of the conclusion of §7, experimentally. It is hoped to discuss the precise case of critical opalescence elsewhere (cf. e.g. R. K. Bullough, *Proceedings of the Interdisciplinary Conference on Electromagnetic Scattering, Amherst, Mass.* June 1965. To be published by Gordon and Breach.)

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