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Local field corrections for light absorption by fullerenes

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Abstract. With the aim of analysing measurements of absorption of electromagnetic radiation by fullerene molecules in the gas phase, in liquid solution, and in solid films, we consider the classical problem of correction for enhancement of the local field due to polarisation of the medium. We argue that for crystalline films the Clausius-Mossotti relation between the molecular polarisability and the dielectric function of the medium should be reasonably accurate, despite the fact that the polarised fullerene molecules are far from being point dipoles. For fullerene molecules in solution, the field derived by Onsager from a cavity model should be a good approximation, and we discuss and correct errors in earlier developments of this model. Owing to the large polarisability of fullerenes, the local field corrections are very important, leading to large changes in the relative strength of absorption lines and also to small shifts in the positions of these lines. Application of the corrections leads to improved consistency between measurements in the gas phase, in solution, and in the solid.

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1 Introduction

This study of the absorption of light by molecules or clusters embedded in a medium is closely connected to our development of dielectric models of fullerenes, published separately in a paper we shall refer to as I [1]. The parameters of the models were adjusted to give a fair account of published measurements of the complex polarisability of fullerene molecules. The absorption associated with electronic transitions has been determined by a variety of methods, [2] including measurement of absorption in the gas phase [3–6] and in liquid solution [7–10], photoionisation [11], ellipsometry [12], and electron energy loss in solid films [13–18]. We were primarily interested in the polarisability of isolated molecules but most measurements have been made for fullerenes in solution or in solid films. In the comparison with experiments we therefore encountered the problem of relating the polarisability of an individual molecule to the macroscopic dielectric properties of molecules embedded in a solid film or in a liquid. Surprisingly, there is no consensus on the magnitude of the local field corrections to be applied in this connection and the literature abounds in errors and misconceptions.

The general problem of the dielectric properties of inhomogeneous systems is a very complex one, with an interesting history and a vast literature [19–23]. However, here we focus on two simple types of system, relevant for experiments on absorption of light by fullerenes. The first one is a fullerite film which we may think of as an FCC lattice of polarisable spheres with vacuum in between. We shall argue that the standard Clausius-Mossotti (CM) relation between the molecular polarisability and the dielectric function and the associated Lorentz-Lorenz expression for the local field should be good approximations. In the standard derivation of these relations, usually ascribed to Lorentz, it is assumed that the molecules can be regarded as point dipoles, which is a questionable approximation for the very large fullerene molecules. However, corrections for a lattice of finite sized spheres were calculated already by Rayleigh in a beautiful paper from 1892 [24], and his results have later been amended and corrected for numerical errors [25,26]. We shall also consider the derivation of the CM relation presented in 1879 by Clausius, who used a somewhat different argument [27]. This derivation is less stringent but his qualitative explanation of the local field enhancement is valuable for understanding more complex inhomogeneous systems.

The absorption of light by an isolated molecule is determined by the imaginary part of the polarisability α alone. However, the CM formula relates α to the complex dielectric function ϵ of the material and hence one needs both the imaginary and the real part of ϵ for a determination of Imα. In I we compared the dielectric models mainly with data from inelastic electron scattering, since these data are sufficiently complete to allow application of Kramers-Kronig relations for evaluation of both Reϵ and Imϵ. For narrow absorption lines a simpler correction for polarisation of the medium is applicable, which in the literature is attributed to Smakula [28] or sometimes

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to Chako [29] but which was discussed by Voigt already in 1901 [20,30]. For fullerenes, the Smakula formula may be applied to measurements on infrared-active vibrations by attenuation of light in solid films [1].

The Smakula correction is often applied also to molecules in liquid solution but this is not justified. We shall base our discussion of the multi-component case on the concepts introduced by Onsager [31]. The solute molecule is placed in a cavity in the solvent and the field acting on the molecule is divided into a cavity field and a reaction field. The latter field results from the response of the medium to the perturbation by the dipole field from the molecule. Owing to this reaction, the local field correction is not determined by the dielectric properties of the medium alone, but depends also on the polarisability of the impurity molecule. The theory has broad applications to absorption by solute molecules and by defects in materials, and the large polarisability and the spherical shape of C_{60} make it an ideal molecule for application of the cavity concepts.

We compare measurements of absorption of light by C_{60} molecules in the gas phase with absorption measurements for C_{60} in solution and with absorption cross-sections in the solid phase derived from inelastic electron scattering. The measurements on solute molecules are restricted to wavelengths where the solvent does not absorb, and the frequency interval is too limited for a Kramers-Kronig analysis. However, as we shall show, it is possible to derive the complex polarisability $\alpha(\omega)$ for the limited interval through representation of $\alpha(\omega)$ as a sum of Lorentzians, with inclusion of a contribution from resonances outside the intervals estimated from the measurements on solid films. The Onsager correction for the local field enhancement leads to large changes in the relative strength of absorption lines and small shifts in the positions of these lines, thereby improving the consistency between measurements on molecules in different surroundings.

Our main aim has been to derive good estimates of the local field corrections to the absorption strength since these are crucial for our comparison in I of measured absorption of light in fullerenes with predictions from a dielectric model. In this connection, the line shifts are of minor importance. In the literature, on the other hand, the line shifts have received much more attention, probably because they are easier to determine accurately by experiments. Also for fullerenes there have been several studies of line shifts in different solvents [32–34]. A very interesting review of early work on both line shifts and line intensities is given in reference [20]. It appears that the small shifts caused by long range polarisation interactions can often be out-weighed by shifts due to other types of interactions with the nearby molecules, as for example hydrogen bonding or complex formation. Such interactions may also change the magnitude of the induced dipole moment of a solute molecule. However, for fullerenes in solution the large frequency dependent modification of the local field is expected to be the dominant correction to the absorption strength. In any case, large effects due to polarisation of the solvent are present and should be taken into account. As it turns out, polarisation effects account also in the main for the observed shifts of the strong *UV* absorption lines of buckminsterfullerene in solution and in solid films.

In the presentation we have aimed at providing a solid foundation for our conclusions and not just quote formulas from the literature. As illustrated by many examples, there are few articles on this subject that can be fully trusted. We therefore discuss the basic concepts in some detail and give derivations of the formulas applied, many of them collected in Appendix A. Since misconceptions and incorrect formulas are often accepted and passed on in the literature, we have discussed some influential papers and have made an effort to point out and correct the most important errors we have found. However, we have no ambitions of providing a comprehensive review of the field; we just hope to have avoided adding serious errors of our own.

2 Clausius-Mossotti relation

The standard discussion of the CM relation in textbooks [35] follows the formulation given by Lorentz [36]. We define the local field $\mathbf{E}_{\rm loc}(\mathbf{r})$, acting on a molecule at a crystal lattice site, as the field from external sources and from polarisation of the other molecules in the crystal. To find the magnitude of the local field, we introduce an auxiliary sphere centred on the molecule, with a radius which is large compared to the molecular separation but small compared to the length scale for variation of the macroscopic field. For electromagnetic radiation with frequency well up into the *UV* range the wavelength is sufficiently long for such a construction to be meaningful, and the following discussion applies equally well for static fields and for the amplitude of the complex fields representing radiation with a wavelength which is long in this sense.

We now consider the contributions to the local field from sources outside and inside the sphere. The polarisation charges outside may be replaced by a smeared out density of dipoles, *i.e.*, by the macroscopic polarisation $\mathbf{P}$. The macroscopic field $\mathbf{E}$ includes a contribution from the smeared out density of all polarisation charges and we therefore obtain the field from outside charges alone by subtraction of the constant field inside a sphere with polarisation $\mathbf{P}$, which is $-(4\pi/3)\mathbf{P}$ in Gaussian units (Eq. (A.7)). This leads to the relation

$$\mathbf{E}_{\rm loc}(\mathbf{r}) = \mathbf{E} + \frac{4\pi}{3}\mathbf{P} + \mathbf{E}_{\rm loc}^{\rm near}(\mathbf{r}), \tag{1}$$

where the last term derives from the correct charge distribution inside the sphere with omission of the molecule. In the standard argument, the following two assumptions are now introduced [35]: first, the spatial dimensions of the molecule are assumed to be small enough that the local field can be taken to be uniform over the whole molecule. We can then use the molecular polarisability α, defined for an isolated molecule in a uniform external field, to calculate the dipole moment,

$$\mathbf{p} = \alpha \mathbf{E}_{\rm loc}(\mathbf{r}), \tag{2}$$

where $\mathbf{r}$ now refers to the lattice site. Secondly we assume that the near field, $\mathbf{E}^{\rm near}_{\rm loc}(\mathbf{r})$, can be approximated by the sum of contributions from point dipoles at lattice points inside the auxiliary sphere. If the crystal has cubic symmetry, it follows from this second assumption that the near-field contribution in equation (1) is zero since the contributions from lattice points with coordinates relative to $\mathbf{r}$ which are related by mirror operations changing the sign of a coordinate or interchanging two coordinates cancel. Introducing the dielectric function ϵ for the solid,

$$\epsilon \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}, \tag{3}$$

we may then write equation (1) as

$$\mathbf{E}_{\rm loc}(\mathbf{r}) = \frac{\epsilon + 2}{3}\mathbf{E}. \tag{4}$$

The field given by this formula is usually referred to as the Lorentz-Lorenz local field. The CM relation is obtained from equations (2–4), with $\mathbf{P} = \mathbb{N}\mathbf{p}$ where $\mathbb{N}$ is the density of molecules in the solid,

$$\mathbb{N}\alpha = \frac{3}{4\pi}\frac{\epsilon - 1}{\epsilon + 2}\cdot \tag{5}$$

Solving for ϵ we may rewrite this relation as

$$\epsilon = \frac{1 + 2(4\pi/3)\mathbb{N}\alpha}{1 - (4\pi/3)\mathbb{N}\alpha}\cdot \tag{6}$$

For a dilute material with ϵ close to unity this equation reduces to

$$\epsilon \simeq 1 + 4\pi \mathbb{N}\alpha, \tag{7}$$

but when the term $(4\pi/3)\mathbb{N}\alpha$ approaches unity, the values of the dielectric function are much larger than given by equation (7).

C_{60} molecules condense into a lattice with cubic symmetry (FCC), but it is not immediately clear that the relations above apply to C_{60} films since the molecules can hardly be considered to be point dipoles, as apparently required by the two assumptions above. Consider the first assumption. In the C_{60} molecule, the carbon atoms are displaced by 3.5 Å from the centre but the molecule has close to spherical symmetry. As shown in I, the frequency dependent polarisability of the molecule may be modelled rather well by that of a classical dielectric with spherical symmetry, and the dipole moment induced by an arbitrary external field in such a system is identical to that induced by a constant external field with the same value at the centre (Appendix A).

We may also argue for reasonable accuracy of the second assumption. The dominant contribution to the field at a lattice point $\mathbf{r}$ from the polarisation of nearby molecules comes from the induced dipole moment of these molecules and equals the sum of fields from point dipoles at lattice points. The first correction is a sum of quadrupole fields and for a point with cubic symmetry also this sum vanishes; in fact, the sum vanishes for all multipole fields of even order. A careful discussion of corrections to the CM relation for a simple cubic lattice of dielectric spheres of finite size was given by Rayleigh [24]. This work has been extended by Günther and Heinrich [25] and by Doyle [26], who also discussed numerical errors in reference [24]. From the calculations in references [25,26] for an FCC lattice we estimate the corrections to the CM relation for fullerites to be below 2–3%. Landauer raises a third question concerning the point dipole approximation: for molecules of a finite size, the auxiliary sphere cuts through a number of molecules and their contribution to the near field becomes uncertain [21]. However, since the number of such molecules scales with the second power of the radius of the sphere and the contribution by individual molecules on the surface scales as the inverse third power, this problem vanishes in the limit of a macroscopic radius.

The importance of the symmetry argument is illustrated by the calculations by Senet *et al.* on graphite [37]. Following presumably the procedure described by Rayleigh, they found a modified CM relation, which may alternatively be expressed as a relation for the local field,

$$E_{\rm loc} = (1 - B_u + B_u\epsilon)E, \tag{8}$$

where B_u is a constant and the index u refers to the direction of the external electric field. For $B_u = 1/3$ equation (8) reproduces the Lorentz-Lorenz expression in equation (4), valid for a cubic crystal, but for graphite the values of the constant are different for field directions parallel to and perpendicular to the *c*-axis. Senet *et al.* found $B_{\|} = -0.606$ and $B_{\perp} = 0.803$ for the two directions and we have repeated the calculation and confirmed their results. As discussed in I, the large negative value for $B_{\|}$ is consistent with a simple layer model.

Rayleigh's paper contains the earliest clear presentation of the symmetry argument for cubic crystals that we have been able to find, but the origin of the argument is usually ascribed [21] to very early work (∼1870) by Lorentz. Rayleigh quotes papers from 1880 by Lorentz and by Lorenz, with the comment that the derivations in these papers are difficult to follow, and we can only agree. The association of the names Clausius and Mossotti with the relation in equation (5) is discussed in references [21,23], and Scaife quotes a barbed remark by Maxwell that Mossotti just copied earlier work on magnetism by Poisson, substituting magnetic fields by electric fields and French by Italian! We have found the reference to Clausius [27] given by Landauer very readable. The derivation is less precise than that given by Rayleigh and Lorentz but it contains an important qualitative explanation of the origin of the enhancement of the local field over the average field in the medium.

Clausius divides the medium into polarisable small bodies, which we shall denote molecules, and a non-polarisable substance between the molecules.

Furthermore, the medium is divided into small cells, each containing one molecule, and for simplicity the cell is approximated by a sphere. Treating the surrounding medium as a continuum characterized by a dielectric constant ϵ, Clausius finds that the field inside a cell stemming from sources outside, $E_{\rm loc}$, is constant, and he makes the important observation that the field polarising the molecule is this constant field and not the total field including the contribution from the molecule itself. He then finds that, independent of the cell volume, the integral over the spherical cell of the field from the molecule equals $-(4\pi/3)p$, where p is the dipole moment, and obtains the following relation between the local field and the average field E in the medium,

$$E = E_{\rm loc} - \frac{4\pi}{3}\frac{p}{v} = E_{\rm loc} - \frac{\epsilon - 1}{3}E, \qquad (9)$$

where v is the cell volume. This relation leads to equation (4) and hence also to equation (5). Thus the local field applied to calculate the dipole moment of a molecule in the medium from the polarisability α for an isolated molecule in an external field is larger than the average field in the medium because it does not include the field from the molecule itself, which locally is in the opposite direction. The name "local field" easily leads to the misconception that it refers to a local value of the total microscopic field, and hence the term "effective field", introduced for example in the review by Landauer [21], might be more appropriate.

The relation in equation (9) is applied by Landauer in a related but conceptually different argument, the "excluded volume approach" to the calculation of the dielectric constant of a medium containing a random distribution of "molecules" [21,38]. He argues that if the distribution were truly random the effective field polarising a molecule would obviously be the average field in the medium, and that therefore the enhancement of the effective or local field stems from the exclusion of overlap of the molecules. If an additional molecule is placed at random between the other molecules, it will be exposed to the average field between these. Since the integral of the field from a molecule over a spherical volume containing the molecule equals $-(4\pi/3)p$, the second term in equation (9) stems from the integration over the molecular volume, and when this region is excluded the average field becomes $E_{\rm loc}$ in equation (4). However, there is a great danger in this argument. It appears not to contain the influence of the additional molecule on the polarisation of its surroundings and the resulting change in the local field, the so-called reaction field. Although Landauer is aware of this problem and emphasizes that the reaction field should be included, it is a problem contained already in the formulation of the approach. Thus, it is not correct that for a truly random, uncorrelated distribution of molecules, the effective field would be equal to the average field[1]. As we shall see in the following section, the concept of a reaction field becomes even more important for multi-component systems.

3 Absorption of electromagnetic radiation

We are concerned with the absorption of electromagnetic radiation and first consider an isolated molecule which in the presence of a complex electric field $\mathbf{E}$ with frequency ω acquires a dipole moment $\mathbf{p} = \alpha\mathbf{E}$. The photon absorption cross-section $\sigma(\omega)$ corresponds in a classical description to the ratio between the time average of the rate of energy absorption by this dipole, $W = {\rm Re}(\mathbf{E}){\rm d}/{\rm d}t{\rm Re}(\alpha\mathbf{E})$, and the time average of the incident flux of energy determined by the Poynting vector. If we write the electric field as $\mathbf{E}_0 \exp\{{\rm i}\omega(z/c - t)\}$ the time averaged absorption rate becomes

$$\langle W\rangle = \frac{1}{2}{\rm Re}\big(E_0^*(-{\rm i}\omega\alpha E_0)\big) = \frac{1}{2}\omega|E_0|^2{\rm Im}\alpha, \qquad (10)$$

where the asterisk indicates complex conjugation. The average incident energy flux equals $(c/8\pi)|\mathbf{E}_0|^2$ and the cross-section is therefore given by

$$\sigma(\omega) = 4\pi(\omega/c){\rm Im}\alpha. \qquad (11)$$

For molecules in a medium with dielectric function ϵ, we may interpret the ratio of the average of the rate w of energy absorption per unit volume to the time averaged energy flux as the product of the density $\mathbb{N}$ of molecules and their effective absorption cross-section $\sigma_{\rm m}$. The absorption rate is obtained in close analogy to equation (10) and if we apply equation (3) to express the polarisation in terms of the field amplitude $\mathbf{E}_0$ we obtain

$$\langle w\rangle = \frac{1}{2}{\rm Re}\left(E_0^*(-{\rm i}\omega)\frac{\epsilon - 1}{4\pi}E_0\right) = \frac{\omega}{8\pi}|E_0|^2{\rm Im}\epsilon. \qquad (12)$$

According to the wave equation derived from Maxwell's equations, the space and time dependence of a plane wave is of the form $\exp({\rm i}\omega((n + {\rm i}k)z/c - t))$, with $(n + {\rm i}k)^2 = \epsilon$. From Faraday's law it follows that the ratio of magnetic to electric field equals the index of refraction n and the expression above for the energy flux is multiplied by this factor. For the product $\mathbb{N}\sigma_{\rm m}$ we then have

$$\mathbb{N}\sigma_{\rm m} = \frac{\omega}{c}\frac{1}{n}{\rm Im}\epsilon. \qquad (13)$$

This result agrees with the energy absorption coefficient $2\omega k/c$ obtained from the damping of the plane wave.

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[1] A simple model illustrating this situation is the superposition of a dielectric sphere on a homogeneous medium with dielectric constant ϵ. If we introduce the notation $\varepsilon = \epsilon + \Delta\epsilon$ for the dielectric constant inside the sphere, we obtain from equations (A.6, A.7) and the connection between polarisation and field that the effective field acting on the superposed sphere is given by $E_{\rm eff} = E(3+\Delta\epsilon)/(3+\Delta\epsilon/\epsilon)$, where E is the average field in the medium. The effective field includes a contribution from modified polarisation of the original medium, both outside and inside the sphere, but not the field due to polarisation of the superposed dielectric.

The formula may also be applied to obtain the absorption cross-section of impurity molecules in a non-absorbing medium, with $\mathbb{N}$ replaced by the density $\delta\mathbb{N}$ of impurities.

For a one-component medium with cubic symmetry, the dielectric function in equation (13) is connected to the polarisability α in equation (11) through the CM relation. Introducing equation (5) into equation (11) we find

$$\sigma = \frac{1}{\mathbb{N}}\frac{\omega}{c}\frac{9}{|\epsilon+2|^2}\mathrm{Im}\epsilon, \tag{14}$$

and combination with equation (13) yields

$$\sigma_{\mathrm{m}} = \frac{1}{n}\left|\frac{\epsilon+2}{3}\right|^2\sigma. \tag{15}$$

This formula has a simple interpretation: as expressed in equation (10), the absorption by a molecule is proportional to the absolute square of the field E_0 acting on the molecule, and in the medium E_0 should be replaced by the local field given by equation (4). The factor $1/n$ derives from the Poynting vector.

According to equation (14), it is in general necessary to measure both the real and the imaginary part of ϵ in order to determine the molecular absorption cross-section $\sigma(\omega)$. However, for a narrow line a simpler procedure may be applied, as discussed in Section 5. Within a frequency interval around the jth resonance, the dielectric function may be approximated by a real constant term, $\epsilon_{j\infty} = n_{j\infty}^2$, plus a Lorentzian resonance term, and as we shall show, the correct integrated cross-section for the line is then obtained if ϵ is replaced by $n_{j\infty}^2$ in the denominator in equation (14). As an approximation, the same replacement may be introduced into equation (15),

$$\sigma_{\mathrm{m}} \simeq \frac{1}{n_{j\infty}}\left(\frac{n_{j\infty}^2+2}{3}\right)^2\sigma. \tag{16}$$

This formula has been applied in the interpretation of measurements of vibrational absorption lines in solid C_{60}, although with some inconsistency, as discussed in I. In his derivation of the formula, Smakula [28] considered absorption by defects in a solid and he used the CM relation for this situation. Sometimes the formula is attributed to Chako [29] or to Polo and Wilson [39]. Chako considered the absorption by a solute molecule and apparently this was also the situation Polo and Wilson had in mind. As we shall see, these derivations were all incorrect because the CM relation – or equivalently, the Lorentz-Lorenz formula for the local field – only applies to a one-component medium (see also Ref. [20]).

4 Cavity model and Onsager relation

The local field enhancement is also important for light absorption by molecules in solution. When the molecule in question is one of the molecules forming the liquid, we may argue that the Lorentz-Lorenz formula in equation (4) should apply because the time averaged distribution of surrounding molecules should have approximate cubic symmetry [40]. However, when the solute and solvent molecules are different, the last term on the right hand side of equation (1) should be modified since the difference in the dipole field from the solute molecule causes a change in the polarisation of the surrounding liquid. To estimate this modification, Onsager replaced the solvent molecules by a dielectric with the dielectric function ϵ of the liquid and introduced a spherical cavity containing the solute molecule [31]. The large, spherical C_{60} molecule should be ideal for application of this model. (For a critical discussion of the cavity concept, see Ref. [41].)

For a molecule with polarisability α at the centre of a cavity with radius r_1 in a medium with dielectric function ϵ, the local field acting on the molecule is shown in Appendix A (Eq. (A.13)) to be given by

$$\mathbf{E}_{\mathrm{loc}} = G\frac{1}{1-R\alpha}\mathbf{E}, \tag{17}$$

where $\mathbf{E}$ is the average electric field in the medium far from the solute molecule, and the coefficients G and R are given by

$$G = \frac{3\epsilon}{2\epsilon+1} \quad \text{and} \quad R = \frac{2(\epsilon-1)}{(2\epsilon+1)r_1^3}\,\cdot \tag{18}$$

The factor G gives the enhancement of the field in an empty cavity while the second factor in equation (17) corrects (to infinite order) for the reaction field, *i.e.*, the field in the cavity due to the polarisation of the surrounding medium by the dipole field from the molecule in the cavity. If the molecule is identical to the molecules in the medium and the cavity volume is chosen to be the volume per molecule in the liquid, the Lorentz-Lorenz formula for the local field (Eq. (4)) is retrieved. However, if the cavity contains a molecule with greater polarisability, the dipole field is stronger and this causes an increased polarisation of surrounding molecules which, in turn, increases the local field acting on the molecule.

The application of the Onsager model to absorption by an impurity is discussed for example by Smith and Dexter in their review of the optical absorption by defects in solids [42][2]. Consider an impurity with concentration $\delta\mathbb{N}$ and polarisability α_{i}. The local field may be expressed by equations (17, 18) and the dipole moment of the impurity becomes

$$\boldsymbol{\mu}_{\mathrm{i}} = \alpha_{\mathrm{i}}\mathbf{E}_{\mathrm{loc}} = G\frac{\alpha_{\mathrm{i}}}{1-R\alpha_{\mathrm{i}}}\mathbf{E}. \tag{19}$$

In the evaluation of the change in polarisation of the medium due to the presence of the impurity, we should consider a thin slab with surfaces parallel to $\mathbf{E}$ to avoid contributions from polarisation charges at outer surfaces. As shown in Appendix A (Eq. (A.12)), the field in the medium then corresponds to the presence of point dipoles with magnitude $G\boldsymbol{\mu}_{\mathrm{i}}$. Denoting by α_{h} the polarisability

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[2] We show in Section 5 that due to a mathematical error, the final result in reference [42] is incorrect.

of the host medium removed from the cavity, we obtain for the change in polarisation

$$\delta\mathbf{P} = \delta\mathbb{N}\delta\mathbf{p} = \delta\mathbb{N}G^2\left(\frac{\alpha_\mathrm{i}}{1-R\alpha_\mathrm{i}} - \frac{\alpha_\mathrm{h}}{1-R\alpha_\mathrm{h}}\right)\mathbf{E}. \tag{20}$$

We assume that at the frequency ω under consideration there is no absorption by the host medium, *i.e.*, $\epsilon(\omega)$ is real, and we then obtain from equations (3, 20) for the change in the dielectric function,

$$\mathrm{Im}\delta\epsilon = 4\pi\delta\mathbb{N}G^2\frac{\mathrm{Im}\alpha_\mathrm{i}}{|1-R\alpha_\mathrm{i}|^2}\,\cdot \tag{21}$$

From a combination of equations (11, 13, 21) we find for the absorption cross-section

$$\sigma_\mathrm{m} = \sigma\frac{G^2}{|1-R\alpha_\mathrm{i}|^2}\frac{1}{n}\,\cdot \tag{22}$$

The interpretation of this formula is analogous to that of equation (15): the absorption by the impurity is proportional to the absolute square of the Onsager local field, given by equation (17). Since the impurity concentration is low, we may in equation (22) apply the index of refraction of the host material. To evaluate R we must estimate the volume of the cavity occupied by the molecule and, as noted by Onsager, the choice of a void radius will probably involve "some arbitrary exercise of judgment". An example is the discussion in Section 6 of the cavity radius for C_{60} in solution.

The expressions for G and R in equation (18) relate directly to the cavity model but the formulas in equations (17, 22) have a wider application. For example, for an impurity at a position $\mathbf{r}$ in a crystal we may interpret GE as the field at $\mathbf{r}$ in the absence of the impurity and $R\mu$ as the reaction field at $\mathbf{r}$ from the lattice, due to the presence at $\mathbf{r}$ of a dipole with moment μ. In the point dipole approximation, both G and R may be evaluated numerically in analogy to the determination of the coefficients in the modified CM relation for graphite [37].

For a system like a spherical metal cluster in liquid solution [43] or in a rare-gas matrix [44], we may apply the model discussed at the beginning of Appendix A directly and the absorption cross-section is obtained from equation (A.5). Thus, for a dilute solution with concentration $\delta\mathbb{N}$, we obtain an additive contribution $\delta\epsilon$ to the dielectric constant ϵ of the medium,

$$\delta\epsilon = 4\pi\delta\mathbb{N}r_1^3\frac{\epsilon(\varepsilon-\epsilon)}{\varepsilon+2\epsilon}, \tag{23}$$

where r_1 is the radius and $\varepsilon(\omega)$ the internal dielectric function of the cluster. If ϵ is real, the effective absorption cross-section in equation (13) is then given by

$$\sigma_\mathrm{m} = 9\frac{V}{c}\epsilon^{3/2}\frac{\omega\mathrm{Im}\varepsilon}{(\mathrm{Re}\varepsilon+2\epsilon)^2+(\mathrm{Im}\varepsilon)^2}, \tag{24}$$

where V is the cluster volume. This formula may appear simpler than equation (22) but it is equivalent to this formula and hence contains the correction for local field enhancement. This was not realized by the authors of reference [44] who applied equation (24) to describe absorption by silver clusters in a rare-gas matrix. The formula for the integrated oscillator strength given in their reference [25] contains a factor $(E_\mathrm{loc}/E)^2$ which they claim to be unknown and therefore set equal to unity. However, as shown in Appendix A, the local field is determined by the model used to derive equation (24) and the factor differs from unity (Eq. (A.8)). We discuss oscillator strengths and the sum rule in more detail in the following section (for the result, see Eq. (36)).

5 Narrow absorption lines

In Sections 3 and 4 we discussed the extraction of molecular absorption cross-sections from measurements on condensed media, and we derived formulas for the one-component case, equation (15), and for impurity molecules in a host medium, equation (22). In general, measurement of absorption in a condensed medium does not suffice for a determination of the molecular cross-section but, as we shall now show, this problem disappears for narrow absorption lines.

Close to a resonance frequency ω_j, the polarisability of a molecule may be expressed as a real constant plus a complex Lorentzian,

$$\alpha(\omega) = \alpha_{j\infty} - \frac{f_je^2/m}{\omega^2-\omega_j^2+\mathrm{i}\gamma_j\omega}, \tag{25}$$

where m and $-e$ are the mass and charge of the electron. The integrated oscillator strength of the resonance, f_j, is proportional to the integrated cross-section and from equations (11, 25) we obtain

$$f_j = \frac{mc}{2\pi^2e^2}\int\sigma(\omega)\mathrm{d}\omega. \tag{26}$$

We first consider a medium with only one kind of molecules. The dielectric function is connected to the molecular polarisability through the CM relation, and inserting equation (25) into equation (6) we find after some rearrangement that $\epsilon(\omega)$ takes the same mathematical form as $\alpha(\omega)$,

$$\epsilon(\omega) = n_{j\infty}^2 - \frac{S_j\omega_j'^2}{\omega^2-\omega_j'^2+\mathrm{i}\gamma_j\omega}, \quad \text{with}$$
$$n_{j\infty}^2 = \frac{1+2r_\mathrm{w}^{-3}\alpha_{j\infty}}{1-r_\mathrm{w}^{-3}\alpha_{j\infty}}, \quad (4\pi/3)r_\mathrm{w}^3 = \mathbb{N}^{-1}. \tag{27}$$

We have here introduced the Wigner-Seitz radius r_w. The shift of the resonance frequency may be expressed in terms of a plasma frequency ω_0,

$$\omega_j'^2 = \omega_j^2 - \omega_0^2f_j(n_{j\infty}^2+2)/9\,, \quad \omega_0^2 = 4\pi\mathbb{N}e^2/m, \tag{28}$$

and the strength of the resonance is given by

$$S_j\omega_j'^2 = \omega_0^2f_j(n_{j\infty}^2+2)^2/9. \tag{29}$$

With respect to the value for a dilute material with $\epsilon = 1 + 4\pi\mathbb{N}\alpha$, this strength is enhanced by the factor $(n_{j\infty}^2+2)^2/9$.

In a transmission experiment, the energy absorption coefficient $\mathbb{N}\sigma_{\mathrm{m}} = 2\omega k(\omega)/c$ is measured, where, as above, $\epsilon = (n + \mathrm{i}k)^2$. If the dielectric function is expressed in the form

$$\epsilon(\omega) = n_\infty^2 - \sum_j \frac{S_j \omega_j'^2}{\omega^2 - \omega_j'^2 + \mathrm{i}\gamma_j\omega}, \tag{30}$$

where n_∞ is the (known) index of refraction outside the absorption region, the parameters ω_j', γ_j, and S_j may be determined from a fit to the measured function $k(\omega)$. Close to the jth resonance, the expression may then be identified with equation (27), where the constant term $n_{j\infty}^2 = \mathrm{Re}\epsilon(\omega_j')$ is approximately equal to n_∞^2 but may include an additional contribution from the other resonances because the real part of $\epsilon(\omega)$ is less localized at resonances than the imaginary part. The integrated oscillator strength f_j of the resonance is now found from equation (29).

The Smakula formula in equation (16) is obtained as an approximation from equations (11, 13, 26–29) if we ignore the shift in the resonance frequency and replace the function $n(\omega)$ by the constant value $n_{j\infty}$. Using this formula we may determine the integral of the molecular cross-section σ directly from the integral of the measured absorption cross-section σ_{m}. We have checked by numerical calculation that the error is less than 10% when the ratio $S_j\omega_j'\gamma_j^{-1}/n_{j\infty}^2$ is smaller than unity but the error grows rapidly when this ratio increases beyond unity. The picture with narrow resonances is not appropriate for the electronic transitions of main interest in this paper but it is useful for the vibrational transitions as discussed in I.

For the impurity case, two rather separate traditions have developed, one for defects in solids and the other for solute molecules in liquids. For absorption of light by defects, it appears that Herring was the first to discuss the modification of the Smakula formula due to the change in polarisation of the molecules surrounding the defect, and from an energy argument he derived a formula equivalent to our equation (20) [45]. In a footnote, he commented on the many algebraic errors in the literature on this subject but in the subsequent evaluation of his own formula, also he committed a simple algebraic error, as first pointed out by Silsbee [46] and explained by Smith and Dexter in a footnote in reference [42], p. 191.

As it turns out, Smith and Dexter committed an analogous error in their evaluation on the following page! Following reference [42], we write equation (20) for a host medium with real ϵ at frequency ω as an expression for the energy absorption coefficient,

$$\begin{aligned}\delta\mathbb{N}\sigma_{\mathrm{m}} &= 2k\frac{\omega}{c} = \frac{\omega}{nc}\mathrm{Im}\delta\epsilon \\ &= \delta\mathbb{N}\frac{4\pi\omega}{c}\frac{G^2}{n}\mathrm{Im}\left(\frac{\alpha}{1-R\alpha}\right),\end{aligned} \tag{31}$$

where we have omitted the index i on α, and where we may insert the refraction index for the medium in the expressions for G and R. Close to a resonance, we may apply the expression in equation (25) for the polarisability of the impurity, and we obtain

$$\frac{\alpha(\omega)}{1-R\alpha(\omega)} = \frac{\alpha_{j\infty}}{1-R\alpha_{j\infty}} - \frac{1}{(1-R\alpha_{j\infty})^2}\frac{f_j e^2/m}{\omega^2 - \omega_j'^2 + \mathrm{i}\gamma_j\omega}, \tag{32}$$

where the resonance position is given by

$$\omega_j'^2 = \omega_j^2 - f_j(e^2/m)\frac{R}{1-R\alpha_{j\infty}}\cdot \tag{33}$$

For the absorption coefficient, or the absorption cross-section in the medium, we therefore find a Lorentzian with the same width as for the isolated molecule but with a shifted resonance frequency. The integral over the line is given by

$$\int \mathrm{d}\omega\sigma_{\mathrm{m}}(\omega) = \frac{1}{n}\frac{G^2}{(1-R\alpha_{j\infty})^2}\int \mathrm{d}\omega\sigma(\omega). \tag{34}$$

The enhancement factor is of the same type as in the more general formula in equation (22) but with the simplification that the frequency dependent polarisability of the impurity has been replaced by the real part of the value at the resonance frequency. In their review, Smith and Dexter introduced an expression equivalent to the one in equation (25) into the ratio $\alpha/(1-R\alpha)$. However, they apparently overlooked the contribution from $\alpha_{j\infty}$ to the numerator. With this omission, one immediately obtains the resonance term in equation (32), but with the factor $(1-R\alpha_{j\infty})^{-1}$ to the first power, only (Ref. [42], p. 192).

In analogy to the discussion at the end of the previous section, a simpler derivation of equation (34) may be given for metal clusters in solution. If the n_{e} active electrons in a spherical cluster with radius r_1 are represented by a dielectric function of Lorentz type,

$$\varepsilon(\omega) = 1 - \frac{\omega_{0,\mathrm{e}}^2}{\omega^2 - \omega_1^2 + \mathrm{i}\omega\gamma}, \tag{35}$$

where ω_1 is a binding frequency and $\omega_{0,\mathrm{e}} = (3n_{\mathrm{e}}e^2/mr_1^3)^{1/2}$ is the electronic plasma frequency, one finds that the polarisability α in vacuum, given by equation (A.14), takes the form in equation (25), with $\alpha_{1\infty} = 0$ and $f_1 = n_{\mathrm{e}}$. A more realistic description often requires that the constant term in equation (35) be changed from unity to a larger value, ε_∞, representing the polarisability of more strongly bound electrons. This introduces a constant term in $\alpha(\omega)$ and changes the oscillator strength to $f_1 = 9n_{\mathrm{e}}/(\varepsilon_\infty+2)^2$. For a cluster in a solvent with dielectric constant ϵ, the dipole moment is given in equation (A.5), and the corresponding effective polarisability may also be written in the form given by equation (25), with a modified oscillator strength. Including the factor $n^{-1} = \epsilon^{-1/2}$ as in equation (13), we then obtain

$$\int \mathrm{d}\omega\sigma_{\mathrm{m}}(\omega) = \epsilon^{3/2}\left(\frac{\varepsilon_\infty+2}{\varepsilon_\infty+2\epsilon}\right)^2\int \mathrm{d}\omega\sigma(\omega). \tag{36}$$

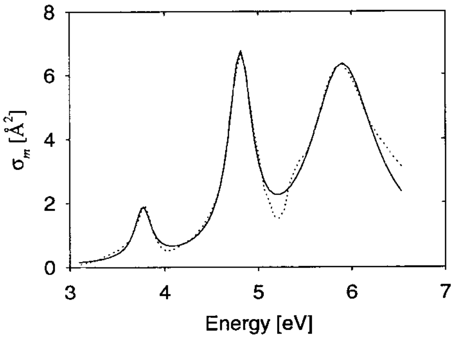

Fig. 1. Fit (solid line) to measured absorption cross-sections σ_{m} for C_{60} in hexane solution [8]. The procedure is discussed in the text and the parameters are given in Table 1.

Table 1. Parameters for a fit with the function in equation (B.1) to the molecular polarisability for C_{60} in hexane solution, derived from the data in reference [8] with the Onsager correction in equation (22). The parameters in equation (18) were $\epsilon = 1.89$ [49] and $r_1 = 5.26$ Å. The value of the constant was $\alpha_\infty = 48.08$ Å^3. The asterisks indicate numbers kept fixed in the least squares fit.

$\hbar\omega_j$ [eV]	f_j	$\hbar\gamma_j$ [eV]
3.78	0.26	0.21
4.87	1.41	0.3
6.04	5.32	0.84
9*	9.19*	1*

The concept of a local field enhancement is not invoked in this derivation but insertion into equation (34) of the values of G and R in equation (18) shows that the two equations are consistent. Inclusion of the enhancement would increase the estimated oscillator strength in Figure 4 of reference [44] by a factor $\sim 4/3$.

6 Absorption by electronic transitions in fullerenes

In this section we apply the local field correction discussed in Section 4 to derive the cross-section for an isolated molecule from absorption by C_{60} molecules in solution. The molecular absorption cross-section is obtained most directly from the attenuation of radiation in a gas cell and such measurements have been carried out for both C_{60} and C_{70} [3–6]. However, to derive absolute cross-sections one must know the density of the gas, and different determinations of the gas pressure differ by a factor ~ 2. The more accurate measurements for fullerenes in solution have therefore been used for normalisation, corrected for local field enhancement with the standard Smakula formula in equation (16) [5,6]. As we shall see, this leads to a fairly large error in the calibration.

The derivation of absorption cross-sections for free molecules from measurements of absorption by solute molecules presents a tricky problem since we have neither direct information about the real part of the molecular polarisability α nor the possibility of a Kramers-Kronig analysis. However, as demonstrated in Appendix B, the complex α derived from inelastic electron scattering in C_{60} films can be represented very well by a sum of Lorentzians (Eq. (B.1)), and with a similar representation of α we can fit the measured cross-section $\sigma_{\mathrm{m}}(\omega)$ in solution to the expression given by equations (11, 18, 22). This is illustrated in Figure 1 for the measurements of Leach *et al.* [8]. The function $\alpha(\omega)$ contains four resonance terms and the parameters are given in Table 1. The value of α at $\omega = 0$ was required to be 85 Å^3 as for molecules in the solid (Fig. 5), and the contribution from higher lying resonances was represented by the 9 eV resonance included in Table 2. The justification for this is the similarity between molecules in solution and in films regarding the oscillator strengths for the lines near 5 and 6 eV and the fact that only the real part of the 9 eV resonance is significant for energies below 7 eV. The width of this resonance is therefore not important for the fit. The estimate of the cavity radius for the Onsager correction, $r_1 = 5.26$ Å, has been derived from the spacing in C_{60} films. Half the distance between the centres of nearest neighbours is 5.0 Å and it seems reasonable to assume that solvent molecules cannot approach closer than that to a solute C_{60} molecule, *i.e.*, $r_1 > 5.0$ Å. At the same time, since the solvent molecules are smaller they can pack more closely around the sphere, and r_1 should therefore be smaller than the Wigner-Seitz radius, $r_{\mathrm{w}} = 5.52$ Å. The resulting real and imaginary parts of the molecular polarisability are in Figure 2 compared with the corresponding functions derived with the CM relation from the data on solid films in reference [15], as discussed also in I. The structures in the functions are rather similar but with a considerable broadening of the resonances for the film due to the broadening of the molecular levels into the bands of the solid [47].

The molecular absorption cross-section corresponding to the polarisability in solution (Eq. (11)) is in Figure 3 compared with gas-phase cross-sections at 684 °C [3]. The gas-phase data have been normalised to give about the same integrated oscillator strength as the solution measurements for this energy region (see Fig. 8 in I), and this normalisation is lower by a factor $\sim 2/3$ than that recommended by Coheur *et al.* [5]. The reason is the difference, illustrated in Figure 3, between the Smakula and the Onsager corrections in equations (16, 22). At the lower energies, the large polarisability of the solute molecule leads to a stronger local field at the molecule than given by the Lorentz-Lorenz formula, and hence the measured absorption cross-section should be reduced by a larger factor to obtain the cross-section for an isolated molecule.

According to reference [5], the change in normalisation of the gas-phase data implies that the vapour pressure reported by Piacente *et al.* [48] would appear to be too low by about 30%. With this correction, the gas-phase cross-sections presented by Smith in Figure 1 of reference [6] become consistent with the values given in our Figure 3. Smith also compared with absorption in solution and applied the Smakula formula (named the Chako-Linder

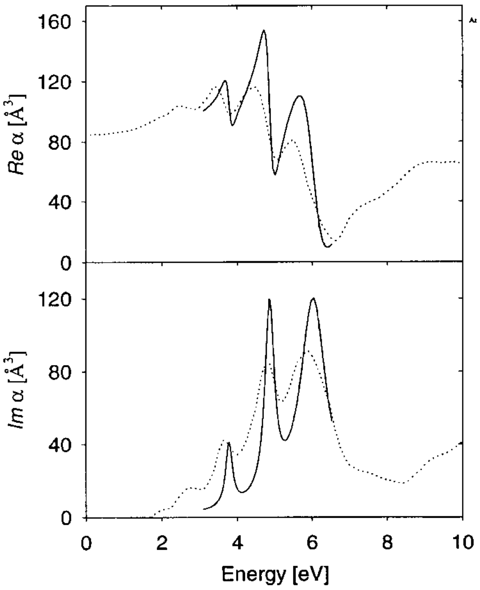

Fig. 2. The molecular polarisability for C_{60} in hexane solution, corresponding to the fit illustrated in Figure 1, compared with the molecular polarisability in solid films (dotted line). The polarisability in the solid has been derived from the dielectric function determined by electron scattering experiments [15] through the CM relation in equation (5).

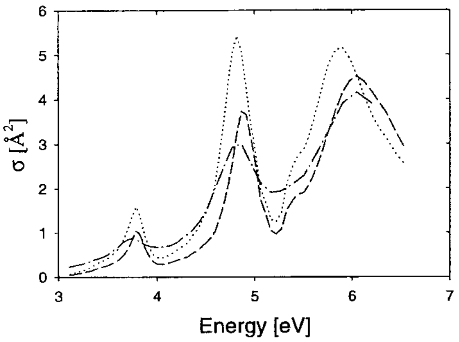

Fig. 3. Comparison of molecular absorption cross-sections for C_{60}, measured in the gas phase at 684 °C (dot-dashed) [3] and in hexane solution [8]. The latter data have been corrected for polarisation of the solvent, alternatively with the Smakula formula in equation (16) (dotted) and with the Onsager relation in equation (22) (dashed).

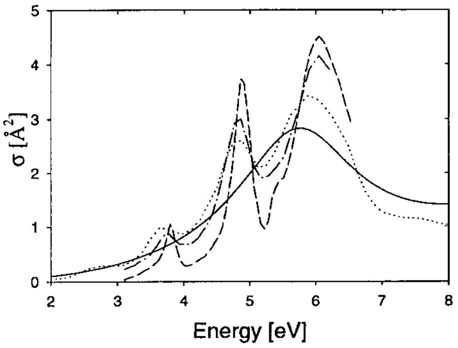

Fig. 4. Comparison of molecular absorption cross-sections for C_{60}, for solid films (dotted), for molecules in hexane solution (dashed), and in the gas phase (dot-dashed) [3]. The cross-section in the solid is derived according to equation (11) from the imaginary part of the polarisability, shown as the dotted curve in Figure 2, while the cross-section in solution is represented by the dashed curve in Figure 3. The full drawn curve gives the prediction from the model discussed in I.

correction) to account for the local field enhancement. As we have argued, this is incorrect and, as illustrated in Figure 3, the error is quite large. Furthermore, as is evident from Table 3 of reference [6], Smith overlooked a zero off-set by 2 eV on the energy axis in Figure 3 of reference [49] and therefore used incorrect values of the index of refraction for the solvent. As a result, the peak near 6 eV appeared to be significantly lower than that near 5 eV for absorption in solution, whereas the relative magnitude is inverted for the gas-phase measurements. The relative strength of the two peaks is seen in Figure 3 to be in good agreement with the gas-phase measurement when the solution measurements are analysed with the Onsager formula.

Because of the large wiggle in Reα around 6 eV, seen in Figure 2, the Onsager correction causes a large shift of the 6 eV line, from the observed position to the resonance frequency for an isolated molecule. According to the formula in equation (28), the shift should be 2.4% for $f = 5.3$ (Tab. 1) and this agrees roughly with the shift observed in Figure 3 relative to the curve based on the Smakula correction, which is energy independent and therefore does not introduce a shift. Shifts much larger than predicted from equation (28) have been observed for the 6 eV peak in solvents with varying index of refraction [32,34] but the interpretation is unclear since extrapolation of these data to $\epsilon = 1$ leads to a position near 6.5 eV for gas-phase absorption, in disagreement with measurements. A conspicuous difference between the two sets of data in Figure 3 is a considerable broadening of the peaks in the gas measurement. This may be interpreted as a consequence of the elevated temperature which leads to population of excited vibrational states [50].

In Figure 4 we compare the molecular absorption cross-sections derived from measurements in the gas phase, in solution, and in solid films. The three sets of measurements are in fair agreement apart from the broadening discussed above. In addition, a band between 2 and 3 eV, which is strongly suppressed in solution, is activated in the solid [8]. Also for the high-temperature measurements for molecules in the gas phase, the cross-section is higher at low photon energies than observed for molecules in solution. As discussed in I, the strength of absorption at low energies is decisive for the emission of heat radiation from hot molecules.

7 Concluding remarks

In connection with our study of the electromagnetic response of fullerenes, we have considered the classical problem of determining the local field corrections which one must apply to extract information on the response of an isolated molecule from measurements on molecules embedded in a medium. We have argued that for C_{60} in solid form, the Lorentz-Lorenz expression for the local field and hence the Clausius-Mossotti relation between the molecular polarisability and the dielectric function of the solid should be applicable, despite the fact that the polarised molecules are far from being point dipoles, as is usually assumed in derivations of this relation.

In solution, the local field at a molecule deviates from the Lorentz-Lorenz value because the polarisation of surrounding solvent molecules depends on the dipole moment of the solute molecule, *i.e.*, on its polarisability. We have argued that the large, nearly spherical C_{60} molecule is ideal for application of the Onsager cavity concepts and have derived the formula which replaces the Lorentz-Lorenz result and also the corresponding correction to measured absorption cross-sections. Application of the Onsager correction improves the consistency of absorption by C_{60} in solution, in the gas phase, and in solid films, regarding both the line positions and the relative intensities of the lines. For narrow lines the local field correction simplifies, and for a one-component medium one obtains the standard Smakula or Chako-Linder formula. However, this formula does not apply for a multi-component system, like a solute molecule or an impurity in a solid. We have discussed this case following the treatment in the review by Smith and Dexter [42] and have corrected a serious mistake.

In the literature there is considerable confusion on the issue of local field corrections to absorption measurements. The different points of view can perhaps best be understood from the expression in equation (17) for the local field in terms of the field in an empty cavity and a renormalisation accounting for the response of the medium to the molecular dipole in the cavity. The interaction of the reaction field with the molecular dipole can be considered a self energy and, as discussed in reference [39], some authors have argued that this self energy should not be included in the evaluation of absorption and, as a consequence, that the formula for the cavity field without the renormalisation should be used. Other authors have argued that the renormalisation factor only shifts absorption lines without changing the intensity [46], or that it should enter to the first power, only, in the enhancement factor [42]. The erroneous result of Smith and Dexter has been adopted in Stoneham's standard textbook on defects in solids [51], but Stoneham also notes that there is no consensus at all in the literature on application of corrections for local field enhancement, and he gives a number of references to authors with different opinions. A paper by Leigh and Szegeti has often been quoted as proof that local field effects are not large [52]. However, these authors from the outset make the erroneous assumption that there can be no microscopic variations of a radiation field.

We have found similar statements, that the local field corrections are small, in the chemical literature on absorption by solute molecules, with reference to a paper by Buckingham from 1958 [53]. He chose a spherical specimen with radius large compared to molecular dimensions but small compared to the wavelength of the radiation to be able to apply a result derived by Kirkwood [54]. We quote from page 176 in reference [53]: "It could be said that small spheres are not experimentally realistic, but unless the shape of the absorption cell affects the intensities of the solute's bands the model system considered is arbitrary. The spherical one is mathematically tractable". The problem is that the shape of the specimen does affect the intensities. According to the discussion at the end of Appendix A, the external dipole moment μ_s of a spherical sample is reduced by the factor $3/(\epsilon + 2)$ relative to the value μ_e to be used for calculation of absorption in a flat specimen with perpendicular incidence of the photons. The error (or misinterpretation [20]) was corrected by Buckingham in a later paper [55], where a result consistent with our Onsager formula in equation (34) was derived.

Although our treatment of the local field enhancement has been aimed at the analysis of measurements on fullerenes, we hope through our discussion of the literature on the subject also to have made a small contribution towards a general conceptual clarification of this old problem. The theory of dielectrics is not technically very difficult but the concepts and arguments are subtle. As our discussion has shown, it is easy to make mistakes, even for experts in the field!

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Appendix A

In this appendix we derive a number of formulas needed for the discussion of the Onsager model of a solute molecule as a polarisable entity inside a spherical cavity in a homogeneous dielectric. The molecule is exposed to monochromatic radiation and for wavelengths long compared to the extension of the cavity, the complex amplitude of the electric field in and around the cavity may be derived from the same equations as in electrostatics [1,56]. Owing to the spherical symmetry we may expand the potential in spherical harmonics $Y_{lm}(\theta, \phi)$, and since it satisfies the Laplace equation the expansion coefficients contain just two terms, proportional to r^l and $r^{-(l+1)}$ [40],

$$\Phi(\mathbf{r}) = \sum_{l,m} Y_{lm}(\theta, \phi)(A_{lm} r^l + B_{lm} r^{-(l+1)}). \tag{A.1}$$

Continuity of the normal component of the displacement $\mathbf{D}$ and the tangential component of the electric field $\mathbf{E}$ at the spherical boundary gives two linear equations which couple the values of the coefficients A and B inside and outside the boundary but do not mix coefficients with different labels (l, m). When no sources are present inside the sphere, all B coefficients vanish here, and for each pair (l,m) there is then only one free parameter. The induced dipole moment is represented by the B coefficients with $l=1$ in the external region and they may then be determined from the corresponding A coefficients in the same region. These represent a constant external field which for a spherical dielectric in vacuum equals the total external field at the centre. An example of this situation is a spherical molecule surrounded by a lattice of other molecules, as discussed in Section 2.

In the Onsager model, the local field is divided into a cavity field for an empty cavity and a reaction field caused indirectly by the presence of a dipole in the cavity. We consider first the case of a sphere with radius r_1 and dielectric function ε, exposed to an external field in a medium with dielectric function ϵ. For $\varepsilon=1$ we obtain the cavity field from this calculation and the result for $\varepsilon \neq 1$ is needed both for the discussion of the CM relation and for the representation of molecules or clusters by a simple model. To determine the reaction field, we then discuss the case of a dipole with fixed magnitude at the centre of an empty cavity in a medium without an external field.

In the calculation of the dipole moment induced in a sphere in a medium, we may neglect all components of the potential with $l \neq 1$ and choose the asymptotic form of the potential,

$$\Phi(\mathbf{r}) = -Er\cos\theta, \quad r \to \infty, \tag{A.2}$$

corresponding to a constant external field E in the z-direction. If we introduce the internal field E_i, the potential may be written as

$$\Phi(\mathbf{r}) = \begin{cases} -E_\mathrm{i} r\cos\theta, & r < r_1 \\ (-Er + \delta p \epsilon^{-1} r^{-2})\cos\theta, & r > r_1 \end{cases}, \tag{A.3}$$

where the notation δp for the induced dipole moment refers to the fact that the dipole field is proportional to the difference between the dipole moment of the sphere and that of a sphere with dielectric function ϵ. The continuity equations for $\mathbf{E}$ and $\mathbf{D}$ at the boundary become

$$\begin{aligned} -E + \delta p \epsilon^{-1} r_1^{-3} &= -E_\mathrm{i} \\ -\epsilon E - 2\delta p r_1^{-3} &= -\varepsilon E_\mathrm{i}, \end{aligned} \tag{A.4}$$

and for the dipole moment and the internal field we obtain

$$\delta\mathbf{p} = \epsilon r_1^3 \frac{\varepsilon - \epsilon}{\varepsilon + 2\epsilon}\mathbf{E}, \tag{A.5}$$

and

$$\mathbf{E}_\mathrm{i} = \frac{3\epsilon}{\varepsilon + 2\epsilon}\mathbf{E}. \tag{A.6}$$

Within the sphere, the induced polarisation, $\mathbf{P} = (\varepsilon - 1)\mathbf{E}_\mathrm{i}/4\pi$, gives rise to a field which we denote by $\mathbf{E}_\mathrm{i} - \mathbf{E}_\mathrm{loc}$. The magnitude of this field is calculated most easily for a sphere in vacuum where $\mathbf{E}_\mathrm{loc} = \mathbf{E}$, and using equation (A.6) with $\epsilon = 1$ we obtain the general result for uniform polarisation of a sphere,

$$\mathbf{E}_\mathrm{i} - \mathbf{E}_\mathrm{loc} = -\frac{4\pi}{3}\mathbf{P}. \tag{A.7}$$

Expressing again $\mathbf{P}$ in terms of $\mathbf{E}_\mathrm{i}$, we obtain from equations (A.6, A.7) for the local field acting on the sphere in a medium,

$$\mathbf{E}_\mathrm{loc} = \frac{\epsilon(\varepsilon + 2)}{2\epsilon + \varepsilon}\mathbf{E}, \tag{A.8}$$

and for $\varepsilon = 1$ this formula gives the cavity field $G\mathbf{E}$ with the expression for G in equation (18).

We now consider a spherical cavity in a dielectric, with a dipole moment μ at the centre. The potential in equation (A.3) is replaced by

$$\Phi(\mathbf{r}) = \begin{cases} (-E_\mathrm{i} r + \mu r^{-2})\cos\theta, & r < r_1 \\ \mu_\mathrm{e} \epsilon^{-1} r^{-2}\cos\theta, & r > r_1 \end{cases}, \tag{A.9}$$

and the boundary conditions become

$$\begin{aligned} \mu_\mathrm{e}\epsilon^{-1} r_1^{-3} &= -E_\mathrm{i} + \mu r_1^{-3}, \\ -2\mu_\mathrm{e} r_1^{-3} &= -E_\mathrm{i} - 2\mu r_1^{-3}. \end{aligned} \tag{A.10}$$

From these equations we obtain the value of the reaction field,

$$E_\mathrm{i} = \frac{2(\epsilon - 1)}{2\epsilon + 1} r_1^{-3}\mu = R\mu, \tag{A.11}$$

and of the external dipole moment,

$$\mu_\mathrm{e} = \frac{3\epsilon}{2\epsilon + 1}\mu = G\mu. \tag{A.12}$$

If the dielectric medium were penetrating into the dipole and the two opposite charges were screened independently, being placed for example at the centres of two non-overlapping cavities, the effect of the screening would be represented fully by the factor ϵ^{-1} in equation (A.9), *i.e.*, μ_e would be equal to μ, but as expressed in equation (A.12), the polarisation of the medium is somewhat different when the two charges are placed in one cavity, both slightly off centre.

In Section 4 of the main text, the dipole $\boldsymbol{\mu}$ in the cavity derives from a molecule with polarisability α, placed in a dielectric with constant electric field $\mathbf{E}$ far from the molecule. In the absence of the molecule, the field in the cavity is $G\mathbf{E}$, and to lowest order the induced dipole moment then becomes $\alpha G\mathbf{E}$ and the reaction field $R(\alpha G\mathbf{E})$. This in turn modifies the induced dipole and including this modification to infinite order we obtain for the local field acting on the molecule,

$$\mathbf{E}_\mathrm{loc} = G\mathbf{E} + \sum_{n=1}^{\infty}(R\alpha)^n G\mathbf{E} = G\frac{1}{1 - R\alpha}\mathbf{E}. \tag{A.13}$$

For the special case that the molecule is represented by a sphere with dielectric constant ε, the polarisability α is obtained from equation (A.5) with $\epsilon = 1$,

$$\alpha = r_1^3 \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \tag{A.14}$$

Inserting this expression and the formulas for G and R into equation (A.13), we retrieve equation (A.8). Combining equations (A.12, A.13), we obtain for the magnitude of the induced external dipole moment,

$$\mu_{\mathrm{e}} = G^2 \frac{\alpha E}{1 - R\alpha}, \tag{A.15}$$

which is the relation used in the discussion of the Onsager correction in Section 4. If the molecule is represented by a dielectric medium in the cavity, with a dielectric function ε related to α through equation (A.14), and the dipole moment of a sphere with dielectric function ϵ is subtracted, the expression in equation (A.15) reduces to the formula in equation (A.5).

The geometry is important in polarisation problems. The dipole moment μ_{e}, minus the dipole moment of the displaced material, may be interpreted as the additional dipole moment of a macroscopic specimen due to the presence of the impurity molecule. The specimen should be shaped like a needle or a thin slab, with the surfaces parallel to the **E** field, to avoid contributions from polarisation charges on the surfaces. If instead we consider a spherical sample with radius $r_2 \gg r_1$, the external dipole moment μ_{s} stemming from the molecular dipole moment μ is reduced by the induced surface charges. For this geometry, the potential in equation (A.9) is replaced by

$$\Phi(\mathbf{r}) = \begin{cases} (-E_1 r + \mu r^{-2}) \cos\theta, & r < r_1 \\ (-E_2 r + \mu_{\mathrm{e}} \epsilon^{-1} r^{-2}) \cos\theta, & r_1 < r < r_2, \\ \mu_{\mathrm{s}} r^{-2} \cos\theta, & r_2 < r \end{cases} \tag{A.16}$$

and from the boundary conditions at the outer surface we obtain the relation

$$\mu_{\mathrm{s}} = \frac{3}{\epsilon + 2} \mu_{\mathrm{e}}. \tag{A.17}$$

Owing to the presence of the field E_2 in the dielectric, the value of μ_{e} is modified relative to that given in equation (A.12) by an additive term proportional to $(r_1/r_2)^3$, but for a macroscopic sample this term is negligible. We have used the notation of Fröhlich [19] and note that there is a misprint in the corresponding equation (A2.32), where μ_{e} has been replaced by μ_{i}.

It is easy to get confused by the many different definitions of dipole moments associated with an impurity [19]. Let us therefore show by a simple argument that the dipole moment δp, defined in equation (A.3) from the dipole field, is indeed the proper value to use in a calculation of the change in dielectric function of the medium due to the presence of the impurity dipoles. Consider a charged parallel plate capacitor containing the medium. Now introduce a density $\delta\mathbb{N}$ of dipoles, directed from the positive towards the negative plate and with fields corresponding to the potential in equation (A.3). The extra field between the plates equals the one from a dipole density $\delta\mathbb{N}(\delta p/\epsilon)$ in vacuum or, equivalently, from surface charge densities $\mp\delta\mathbb{N}(\delta p/\epsilon)$ in vacuum. To retain the original field in the dielectric, we must augment the charge densities on the plates by $\pm\epsilon\delta\mathbb{N}(\delta p/\epsilon)$. Thus the introduction of the dipoles changes the polarisation by $\delta\mathbb{N}\delta p$, as surmised.

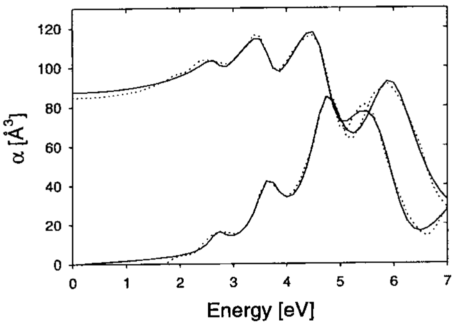

Fig. 5. Illustration of the fit with the expression in equation (B.1) (solid lines) to the molecular polarisability of C_{60} derived from the electron energy loss measurements in reference [15]. The curves which are highest at low energies correspond to Reα and the lower curves to Imα. The parameters for the fit are given in Table 2.

Appendix B

From electron energy loss measurements on C_{60} films, the function $\mathrm{Im}(-1/\epsilon(\omega))$ has been derived within a broad frequency range and both the real and the imaginary part of $\epsilon(\omega)$ have been determined by a Kramers-Kronig analysis. We show in this appendix that the corresponding molecular polarisability $\alpha(\omega)$ can be parameterised through a fit with a sum of Lorentzians. In Section 6 we apply this result and introduce a similar fit to obtain an estimate of the complex polarisability of C_{60} molecules in solution, based on measurements of photoabsorption.

In their Figure 1 Sohmen *et al.* present the real and imaginary parts of the dielectric function $\epsilon(\omega)$ of the solid in the range 0–40 eV [15]. Assuming the Clausius-Mossotti relation to hold, we obtain the molecular polarisability from equation (5) and represent the data by the sum

$$\alpha(\omega) = \alpha_\infty - \sum_{j=1}^{5} \frac{f_j e^2/m}{\omega^2 - \omega_j^2 + \mathrm{i}\gamma_j\omega} \cdot \tag{B.1}$$

The parameters obtained are given in Table 2 and the quality of the fit is illustrated in Figure 5. A similar representation was introduced by Ren *et al.* for their measurements on C_{60} films by ellipsometry [12]. With this experimental method, both of the optical functions $n(\omega)$ and $k(\omega)$ are obtained and one does not have to rely

Table 2. Parameters for a fit with the function in equation (B.1) to the molecular polarisability for C_{60} in solid films, derived from the data in Figure 1 of reference [15] with the Clausius-Mossotti relation and with a density $\mathbb{N} = 1.42 \times 10^{-3}$ Å^{-3}. The value of the constant is $\alpha_\infty = 40.83$ Å^3. The asterisks indicate numbers kept fixed in the least squares fit.

$\hbar\omega_j$ [eV]	f_j	$\hbar\gamma_j$ [eV]
2.72	0.082	0.38
3.66	0.549	0.57
4.76	2.01	0.75
5.97	6.13	1.35
9*	9.19	1*

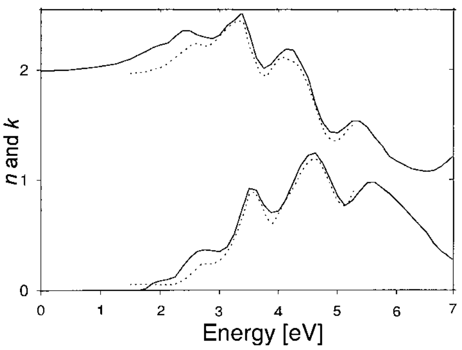

Fig. 6. Comparison of the optical functions n (upper curves) and k derived from electron energy loss measurements [15] and from ellipsometry (dotted lines) [12].

on a Kramers-Kronig analysis to extract the dielectric function. However, the experiment in reference [12] was limited to a rather narrow energy interval, ~ 1.5–5.3 eV. A comparison between energy-loss and ellipsometry data is shown in Figure 6 and the agreement is seen to be quite good.

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