circularly polarized beams. The ratio of the slopes of these two straight lines was found to be about the same as the corresponding ratio of the vertical intercepts of these lines. The threshold ratios between circularly and linearly polarized beams were determined from the vertical intercept of these lines, and were found to be, respectively, 2.00, 1.66, 1.60, and 1.50 for CS_2, nitrobenzene, toluene, and benzene. For CCl_4, our maximum available laser power was insufficient to permit similar measurements with a circularly polarized beam.

It has been suggested[22] that the above threshold ratios should be identified with the corresponding ratios of the index changes in Eq. (11). It then follows that the observed threshold ratios of 2.0 to 1.5 would correspond to a range of values from 1.0 to 0.5 for the ratio $\chi_3^{1221}/(\chi_3^{1122}+\chi_3^{1221})$. These are the ratios which we determined in Table I to be close to 3. Thus it appears that discrepancy exists between the results deduced from the observed ratios of self-focusing threshold, and the results deduced jointly from measurements of intensity-induced rotation and measurements of self-focusing threshold for a linearly polarized beam. However, we feel that the results deduced from measurements of intensity-induced rotation and measurements of self-focusing threshold with a linearly polarized beam are probably correct. Since uncertainties exist both in theory and in experiment for the self-focusing effect of a circularly polarized beam, it is not clear if the ratio of self-focusing threshold is to be identified with the corresponding ratio of the index changes.

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Effect of Molecular Redistribution on the Nonlinear Refractive Index of Liquids*

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An expression for the static nonlinear dielectric constant of a nonpolar liquid is derived which takes into account the reorientation and local spatial redistribution of molecules in the presence of a strong electric field. This result is used to calculate the nonlinear index of refraction of various lossless liquids at "optical" frequencies which are much higher than molecular reorientation rates. From this nonlinear index, we obtain estimates of the optical power required to initiate self-focusing in a liquid over periods so short that macroscopic density changes do not have time to take place. This situation is commonly approached in experiment. The theory predicts that the effects of molecular redistribution, hitherto not considered, will be generally as important as the widely considered effects of molecular reorientation, and will in fact dominate the nonlinear index of many symmetric and nearly symmetric molecules. Furthermore, the results suggest that some purely symmetric molecules, such as $SiBr_4$, may exhibit self-focusing in liquid as readily as do some commonly studied asymmetric molecules, such as nitrobenzene. The calculation proceeeds from classical statistical mechanics with the aid of a variational principle that is valid for arbitrary density. In the low-density limit our results reflect only molecular reorientation and reduce to those of Debye and others. The accuracy of the results depends mainly on the accuracy of Kirkwood's "superposition approximation" in representing three- and four-particle correlation functions in liquids. Since the accuracy of this approximation is at present unknown, nonlinear index data may prove useful in checking it. As a by-product of our investigation, we have proven that the Clausius-Mossotti expression gives a lower bound for the dielectric constant of a fluid in which the two-particle correlation function is a function only of the interparticle spacing and approaches a constant at large spacing. Molecular redistribution must also play a role in induced birefringence (ac and dc Kerr effects), especially for symmetric molecules. However, the present treatment is limited to waves of a single linear polarization, and does not cover the Kerr effect.

I. INTRODUCTION

THE self-focusing of optical beams and the effects of this self-focusing on stimulated Raman scattering and other nonlinear effects have been studied in a variety of liquids.[1–6] The nonlinear index of refraction which causes self-focusing has been attributed to electrostrictive effects and to the reorientation of asymmetric molecules (ac Kerr effect) in the strong optical fields; the electronic nonlinearities are presumed

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[1] N. F. Pilipetskii and A. R. Rustamov, JETP Pis'ma Redaktsiyu 2, 88 (1965) [English transl.: JETP Letters 2, 55 (1965)].

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[3] Y. R. Shen and Y. J. Shaham, Phys. Rev. Letters 15, 1008 (1965).

[4] P. Lallemand and N. Bloembergen, Phys. Rev. Letters 15, 1010 (1965).

[5] C. C. Wang, Phys. Rev. Letters 16, 344 (1966).

[6] E. Garmire, R. Y. Chiao, and C. H. Townes, Phys. Rev. Letters 16, 347 (1966).

to contribute much less.[2-6,7] In this paper we point out that another mechanism, the spatial redistribution of the molecules, can make a contribution to the nonlinear index of liquids which is generally comparable to, and may in some cases dominate, electrostrictive and reorientation effects.

We will consider only the index change experienced by a strong *linearly* polarized optical field in a liquid; the index changes for beams of other polarizations (and related phenomena such as induced birefringence) will involve added calculational complexities. The strong impressed field induces a dipole moment in each molecule so that extra anisotropic dipole-dipole forces, which are evidently proportional to the time average of the square of the field strength, occur between molecules in addition to the usual intermolecular forces already present. Therefore, after the molecules come into thermal equilibrium in the impressed field, the n-particle correlation functions for the liquid ($n>1$) are altered in an anisotropic way from their zero field forms. That is, the field causes the molecules to become "redistributed" in space, and this redistribution contributes to a change in index. For example, the induced dipole forces cause two nearby molecules of a fixed separation to be more probably found in line with the strong applied field (where their combined polarization is maximum) than on a line perpendicular to it (where their combined polarization is minimum). Of course, asymmetric molecules also tend to reorient themselves in the field, and thus increase their average polarizability, and the macroscopic mass motion caused by electrostrictive forces and thermal expansion also alters dielectric properties after macroscopic density variations have had time to form. It is the main object of this paper to assess the change in index of refraction brought about by the local redistribution and reorientation of molecules in a liquid, ignoring the effects of macroscopic density changes which take much more time to form.

Specifically, we calculate here the nonlinear index (to second order in the fields) which would exist in a fluid irradiated by an optical pulse of such short duration that macroscopic changes in density (such as might arise from electrostrictive effects and heating) do not have time to occur. We also assume that a molecule will undergo so many collisions during this optical pulse that a statistical mechanical equilibrium will exist which is appropriate to the modified intermolecular dipole-dipole forces and the torques resulting from the application of the strong optical fields. The refractive index for this altered equilibrium state of the fluid is then calculated in a standard way by differentiating the free energy $\mathfrak{F}$ of a uniform sample of fixed macroscopic density with respect to the applied electric field strength E_0 to obtain the induced dipole moment. From this one obtains, in the usual way, an expression for the total (linear plus nonlinear) index. This expression for the index contains only the effects of molecular redistribution and reorientation.

The densities of the liquids of interest are too large for a low density expansion of $\mathfrak{F}$ to be accurate. Therefore we employ a variational principle which gives an upper bound for $\mathfrak{F}$ regardless of density. A "local field approximation" is then made in which certain free parameters may be varied to obtain a lowest upper bound for $\mathfrak{F}$ within the local field approximation. From this, a lower bound results for the linear part of the index of refraction, which bound is the "Clausius-Mossotti" or "Lorentz-Lorenz" expression. This is a strong lower bound, true whenever two particle correlations depend only on the interparticle spacing. Unfortunately, a similar bound does not result for the nonlinear index which we calculate to second order in the field.

Because the Clausius-Mossotti expression for the linear dielectric constant (or the square of the index) is known to be accurate to within a few percent for liquids, one might expect our corresponding expression for the second-order part of the index to be accurate to within 10 to 50%. Unfortunately, many additional errors are introduced into the evaluation of the nonlinear index expressions by our having to use the Kirkwood "superposition approximation" for the three-and four-particle correlation functions. These errors are of uncertain magnitude within our present knowledge of statistical functions for liquids. Perhaps the nonlinear index experiments can be used to obtain an idea of the accuracy of the Kirkwood approximation, since the nonlinear index is more sensitive to the character of third- and fourth-order correlation functions than are other quantities which are as accurately measurable. It is reassuring that the term in our final expression for the nonlinear index which dominates at low densities and which is most sensitive to the asymmetry of the molecules is exactly the same as the expression of Debye[8] for the low-frequency nonlinear index of molecules having no permanent dipole moments (these don't interact with optical fields). However, optical, rather than low-frequency, polarizabilities appear. Although this "Debye" term in the nonlinear index is dominant (for asymmetric molecules) at densities somewhat lower than liquid densities, the other terms we find are important, if not dominant, at liquid densities. These other terms arise from the redistribution of molecules brought about by the field-induced changes in intermolecular forces.

The relative power thresholds for producing self-focusing or "self-trapping" in those liquids for which

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[7] R. Y. Chiao, E. Garmire, and C. H. Townes, Phys. Rev. Letters **13**, 479 (1964).

[8] P. Debye, *Marx's Handbuch der Radiologie VI* (Leipzig, 1925), Chap. V, p. 768. P. Langevin, J. J. Larmor, M. Born and others earlier derived similar relations to that of Debye, but none had evaluated correctly both the local fields producing the nonlinearities and the effect of the change in polarizability of a molecule on the local fields themselves. Furthermore, in *Optik* by M. Born (Springer-Verlag, Berlin, 1965), an extra error of 2 is introduced in passing from Eq. (33), p. 352 to Eq. (1), p. 366 which is copied in some of the later literature on nonlinear indices and the Kerr effect. See M. Born, *ibid.* for a general bibliography.

quantitative data is available are consistent with values calculated from our nonlinear indices and the formula for threshold power of Chiao *et al.*[7] In particular, the recent observation by Bret *et al.*[9] that the symmetric molecule CCl_4 exhibits a threshold anomaly characteristic of self-focusing in liquid when the asymmetric molecules choloform, acetone, and acetic acid do not is consistent with our predictions. Comparison of our results with the current data indicates that our predicted relative threshold powers may be accurate to around ±25%. If this is so, then we predict that several purely symmetric-molecule liquids, such as $SiBr_4$, will exhibit low self-trapping thresholds of the same order as, for example, that of the strongly self-focusing liquid nitrobenzene. Molecular redistribution must also affect the induced birefringence (Kerr effect), perhaps accounting for the general disagreement between the usual Debye theory[8] and experiment (especially pronounced for symmetric molecules). However, we do not consider such effects here.

The absolute magnitudes of our predicted thresholds tend to fall an order of magnitude lower than those estimated from experiments.[2–6] The errors inherent in the Kirkwood approximation might well be responsible for this. However, as we point out later in the discussion, there is some evidence that thresholds are actually lower than was at first supposed. The possible effects of relaxation processes which may prevent the achievement of the quasi-steady state we have assumed have not yet been examined, nor has the role of bubbles, impurities, normal thermal turbulence, etc.

II. FORMULATION

The induced orientation and intermolecular potentials are quadratic in the field strength. Therefore molecules, which can neither translate nor rotate at optical frequencies, will assume the same configuration in a uniform dc applied field as in a uniform optical field of equal mean square amplitude (if the optical and static polarizabilities are equal). We will take advantage of this fact to simplify the mechanics of the calculation and compute the nonlinear dielectric constant to second order in the fields as if the strong applied electric field were static. Of course, only induced polarizations need be considered; there is essentially no interaction between any permanent electric dipole moments and the optical fields and polarizations. The desired second order optical dielectric constant is then simply obtained from the static constant by replacing the square of the static field by the mean square optical field and using the optical values for molecular polarizabilities in all expressions.

To compute the static dielectric constant, we first compute the free energy $\mathfrak{F}$ of an ellipsoidal sample of uniform fluid in a uniform x-directed electric field E_0, with a principal axis of the ellipsoid parallel to the field. Then the total electric dipole moment of the sample M is obtained from the well known relation[10]

$$M=-d\mathfrak{F}/dE_0. \tag{1}$$

Because the sample is ellipsoidal and the external field uniform, the polarization per unit volume P inside the sample will be uniform and x-directed.[10] We assume the sample to have a fixed volume V, whence

$$P=M/V. \tag{2}$$

We desire the nonlinear index only to second order in the electric fields so we compute $\mathfrak{F}$ to fourth order in the fields and obtain a result of the form

$$\mathfrak{F}=(bE_0^2/2+cE_0^4/4)V, \tag{3}$$

from which we have

$$P=bE_0+cE_0^3. \tag{4}$$

In an ellipsoidal sample uniformly polarized along a principal axis, the relation of the polarization density to the macroscopic electric field E is generally written[10]

$$E=E_0-LP, \tag{5}$$

where L is called the depolarization factor for that axis of the ellipsoid. The factor L can have values between 0 and 4π depending only on the shape of the ellipsoid.[10] If we define a linear susceptibility χ and a nonlinear susceptibility η by the relation

$$P\equiv\chi E+\eta E^3, \tag{6}$$

then a comparison of (4) and (6) with the aid of (5) shows that

$$\chi=b/(1-Lb) \tag{7}$$

and

$$\eta=c(1-Lb)^{-4}=c(1+L\chi)^4. \tag{8}$$

The nonlinear dielectric constant ϵ_{NL} is

$$\begin{aligned}\epsilon_{NL}&=1+4\pi P/E\\&=1+4\pi(\chi+\eta E^2)\end{aligned} \tag{9}$$

and, in extrapolating our results to the optical case, we would therefore have an index of refraction $\epsilon_{NL}^{1/2}$ given, to second order in E, by

$$\epsilon_{NL}^{1/2}=n+(2\pi/n)\eta\bar{E}^2, \tag{10}$$

where $\bar{E}$ is the root mean square electric field averaged over many optical cycles and n is the ordinary linear index of refraction. Following the standard practice, we define a "nonlinear index" n_2 by

$$n_2\equiv2\pi\eta/n. \tag{11}$$

Then the threshold power P_c required to begin trapping a uniform cylindrical beam much broader than a wave-

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[9] G. Bret, F. Gires, and G. Mayer, in IEEE J. Quant. Electron. **QE-2,** No. 4, 18 (1966).

[10] W. F. Brown, Jr., *Handbuch der Physik XVII, Dielectrics,* edited by S. Flügge (Springer-Verlag, Berlin, 1956), pp. 1–153.

length is given approximately by[7]

$$P_c \approx (1.22\lambda_0)^2 c_0/(128 n_2)\,, \tag{12}$$

where λ_0 and c_0 are the vacuum wavelength and velocity of light, respectively. We now have all the relations necessary to connect the nonlinear index effects with the electric free energy $\mathfrak{F}$.

In computing the free energy $\mathfrak{F}$, we will assume that we are dealing with a classical fluid and use classical statistical mechanics. We must therefore formulate the total potential energy v of the N molecules in the sample when they are placed at positions $\mathbf{r}^1, \cdots \mathbf{r}^N$, have electric dipole moments $\mathbf{m}^1, \cdots \mathbf{m}^N$, and are oriented at the Euler angles $\theta_1, \phi_1, \psi_1, \cdots, \theta_N, \phi_N, \psi_N$, which we symbolize by $\Omega_1, \cdots, \Omega_N$.

We may anticipate that the electronic nonlinearities will be small compared to those with which we are concerned here and assume that the internal energy v_γ of the γth molecule is quadratic in the components of its electric dipole moment $\mathbf{m}^\gamma$. If $m_a{}^\gamma$ are the components of this moment along the principal axes $a = 1, 2, 3$, of its polarizability ellipsoid, then[10]

$$v_\gamma = \tfrac{1}{2} \sum_{a=1}^{3} (m_a{}^\gamma)^2/\alpha_a\,, \tag{13}$$

where $\alpha_1, \alpha_2, \alpha_3$ are the polarizabilities of the molecule along its principal axes. The components $m_a{}^\gamma$ are related to the components $m_i{}^\gamma$ measured in a laboratory-fixed coordinate system by[11]

$$m_i{}^\gamma = R_{ia}(\Omega_\gamma) m_a{}^\gamma\,. \tag{14}$$

The repeated space indices here and elsewhere are assumed to be summed. The matrix $R_{ia}(\Omega_\gamma) = R^{-1}{}_{ai}(\Omega_\gamma)$ represents the rotation operator for the Euler angles Ω_γ of the γth molecule, and will be abbreviated $R_{ia}{}^\gamma$.

The interaction energy $v_{\gamma\mu}$ between two molecules at positions $\mathbf{r}^\gamma$ and $\mathbf{r}^\mu$ will be assumed to be[10]

$$v_{\gamma\mu} = v_{0\gamma\mu} + m_i{}^\gamma m_j{}^\mu D_{ij}{}^{\gamma\mu} \tag{15a}$$

where $v_{0\gamma\mu}$ is a hard core repulsive potential and the remaining term is the dipole-dipole interaction energy.

$$D_{ij}{}^{\gamma\mu} \equiv \frac{(\delta_{ij}\delta_{kl} - 3\delta_{ik}\delta_{jl})(r_k{}^\gamma - r_k{}^\mu)(r_l{}^\gamma - r_l{}^\mu)}{|\mathbf{r}^\gamma - \mathbf{r}^\mu|^5}\,. \tag{15b}$$

The $m_a{}^\gamma$ which measure the displacement of electronic charge may be taken to be the independent harmonic "internal" coordinates of the molecules which describe the electronic polarization. That is, it is appropriate to integrate over all values of these coordinates in evaluating the free energy from the potential energy function.[10] The free energy $\mathfrak{F}$ of the liquid in the x-directed external field may therefore be written

$$e^{-\beta\mathfrak{F}} = \int\int\int d\{\mathbf{r}\} d\{\Omega\} d\{m_a\} e^{-\beta v} \tag{16a}$$

where

$$v = \sum_\gamma (-m_x{}^\gamma E_0 + v_\gamma) + \tfrac{1}{2} \sum_{\gamma,\mu} v_{\gamma\mu} \tag{16b}$$

is the total energy of a configuration of the positions, moments, and orientations of the molecules. $\int d\{\mathbf{r}\}$ symbolizes the integration $\int d\mathbf{r}^1 \cdots \int d\mathbf{r}^N$ over the entire volume V of the ellipsoid of every molecular position. Similarly, $\int d\{\Omega\}$ symbolizes the integral $\int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\psi_1, \cdots \int_0^\pi \sin\theta_N d\theta_N \int_0^{2\pi} d\phi_N \times \int_0^{2\pi} d\psi_N (8\pi^2)^{-N}$ over all molecular orientations $\{\Omega\}$, and $\int d\{m_a\}$ symbolizes the integral $\int dm_1{}^i dm_2{}^i dm_3{}^i \cdots \int dm_1{}^N dm_2{}^N dm_3{}^N$ over all internal molecular coordinates $\{m_a\}$. β is defined as the inverse of (the temperature times Boltzmann's constant).

This completes the formulation of the static dipolar free energy suitable for classical liquids. The relations (1) to (12) connect the dependence of $\mathfrak{F}$ on an externally applied electric field E_0 with the threshold power for self-focusing or self-trapping which we wish to predict. It remains to carry through the evaluation of the free energy starting from the basic definition (16).

III. A VARIATIONAL PRINCIPLE FOR CALCULATION

In order to obtain from (16) an accurate estimation of $\mathfrak{F}$ for liquids, it does not suffice to expand $\mathfrak{F}$ in powers of the number density $\rho = N/V$. We therefore employ a variational approach which obtains an upper bound for $\mathfrak{F}$. Parameters will exist in the upper bound which can be varied to obtain a lowest upper bound within any approximation scheme.

To obtain a variational principle, we note that the total potential energy v is a quadratic function of the dipole moment coordinates $m_a{}^\gamma$. This means that if we define new coordinate variables of integration $\nu_a{}^\gamma$ by

$$\nu_a{}^\gamma = m_a{}^\gamma - \mu_a{}^\gamma\,, \tag{17}$$

where the $\mu_a{}^\gamma$ are those values which minimize v for a given positional and orientational configuration, then we can rewrite (16) as

$$e^{-\beta\mathfrak{F}} = \int\int d\{\mathbf{r}\} d\{\Omega\} \exp(-\beta \textstyle\sum_{\gamma\mu} \tfrac{1}{2} v_{0\gamma\mu} - \beta v' \\ -\beta \min_{\{\mu\}} \phi)\,, \tag{18}$$

where[11]

$$\phi \equiv \phi(\{\boldsymbol{\mu}\}, \{\mathbf{r}\}, \{\Omega\}, E_0) \\ \equiv \textstyle\sum_\gamma (-\mu_x{}^\gamma E_0 + \tfrac{1}{2} \sum_a \mu_a{}^{\gamma 2}/ \\ \alpha_a + \tfrac{1}{2} \sum_\nu \mu_i{}^\gamma \mu_j{}^\nu D_{ij}{}^{\gamma\nu})\,, \tag{19}$$

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[11] We will use the lower case Latin subscripts a through h to denote the space components of a vector or matrix referred to the principal axes (1,2,3) of the polarizability ellipsoid fixed in the molecule. Latin subscripts from i onward will be used to denote space components referred to the orthogonal principal axes (x,y,z) of the ellipsoidal sample fixed in the laboratory.

is the function which is minimized by our choice of the $\mu_a{}^\gamma$ and

$$\exp[-\beta v'(\{\mathbf{r}\},\{\Omega\})]\equiv\int d\{\nu_a\}$$

$$\times\exp[-\tfrac{1}{2}\beta\textstyle\sum_\gamma(\nu_a{}^{\gamma 2}/\alpha_a+\sum_\mu \nu_i{}^\gamma D_{ij}{}^{\gamma\mu}\nu_j{}^\mu)]. \quad (20)$$

The symbol $\{\boldsymbol{\mu}\}$ represents the set of all values of the $\mu_a{}^\gamma$. The intermolecular potential v' defined by (20) cannot depend on the electric field E_0 (or the $\{\boldsymbol{\mu}\}$ would not minimize ϕ) and represents, of course, the long range van der Waal's potential due to induced dipole-induced dipole interactions. This potential has been analyzed in the literature[10] and we need not discuss it further here.

It is too difficult to find an exact explicit expression for $[\min_{\{\mu\}}\phi]$, but if we insert wrong values for the $\{\boldsymbol{\mu}\}$ into ϕ, we at least obtain an estimate for the field dependent part $\mathfrak{F}_E$ of $\mathfrak{F}$ that is too high. We therefore have the useful inequality that for any $\{\boldsymbol{\mu}\}$ whatever

$$\mathfrak{F}_E\leq F \quad (21)$$

where

$$e^{-\beta F}=\int\int d\{\mathbf{r}\}d\{\Omega\}w(\{\mathbf{r}\},\{\Omega\})e^{-\beta\phi} \quad (22a)$$

and

$$w\equiv\frac{\exp(-\beta\sum_{\gamma\mu}\frac{1}{2}v_{0\gamma\mu}-\beta v')}{\int d\{\mathbf{r}\}d\{\Omega\}\exp(-\beta\sum_{\gamma\mu}\frac{1}{2}v_{0\gamma\mu}-\beta v')}. \quad (22b)$$

With this inequality we may proceed with a variational calculation of the desired field-dependent part $\mathfrak{F}_E$ of the free energy.

IV. THE EFFECTIVE FIELD APPROXIMATION

We will use a local field approximation in which we use the approximate values

$$\mu_a{}^\gamma=\alpha_a R_{xa}{}^\gamma E', \quad (23a)$$

or equivalently[11]

$$\mu_j{}^\gamma=R_{ja}{}^\gamma\alpha_a R_{xa}{}^\gamma E', \quad (23b)$$

in ϕ as if each molecular moment saw only an effective x-directed local field of magnitude E'. We will then adjust E' to minimize the resulting upper bound F for the free energy (calculated to fourth order in E'). The F thus obtained is a function of the shape of the ellipsoidal sample, but the dielectric constant derived from it via (9) is not. (Otherwise one could vary the shape parameters to improve further the accuracy of the estimate for the dielectric constant.)

Using (23) in (19) gives

$$e^{-\beta F}=\langle\langle e^{-\beta(\mu_2-\mu_1)}\rangle\rangle \quad (24)$$

where

$$u_1\equiv\textstyle\sum_\gamma \mathbf{G}\cdot\boldsymbol{\alpha}^\gamma\cdot\mathbf{E}', \quad (25a)$$

$$\mathbf{G}\equiv\mathbf{E}_0-\tfrac{1}{2}\mathbf{E}', \quad (25b)$$

and

$$u_2\equiv\tfrac{1}{2}\textstyle\sum_{\gamma,\nu}\mathbf{E}'\cdot\boldsymbol{\alpha}^\gamma\cdot\mathbf{D}^{\gamma\nu}\cdot\boldsymbol{\alpha}^\nu\cdot\mathbf{E}'. \quad (26)$$

We have introduced the usual shorthand notation for multiplication among the 3×3 space matrices $\boldsymbol{\alpha}^\gamma\equiv R_{ia}{}^\gamma\alpha_a R_{ja}{}^\gamma$, $\mathbf{D}^{\gamma\nu}\equiv D_{ij}{}^{\gamma\nu}$, and the 3-vectors $\mathbf{E}_0=\hat{x}E_0$ and $\mathbf{E}'=\hat{x}E'$. The double average brackets $\langle\langle\ \ \rangle\rangle$ in (24) symbolize the integrations over $\{\mathbf{r}\}$ and $\{\Omega\}$ weighted by $w(\{\mathbf{r}\})$ which is normalized so that $\langle\langle 1\rangle\rangle=1$. We will often use only the single average bracket when either the angle or position average is required alone; which average is intended will be clear from the context. In either case, $\langle 1\rangle=1$.

We expect (as we will find) that the best local field E' will be of the order of E_0. Therefore (24) implies that, to fourth order in E_0, F is given by

$$F=U_2-U_1-\tfrac{1}{2}\beta[U_{22}-2U_{12}+U_{11}] \quad (27)$$

where

$$U_i\equiv\langle\langle u_i\rangle\rangle \quad (28a)$$

and

$$U_{ij}\equiv\langle\langle u_iu_j\rangle\rangle-\langle\langle u_i\rangle\rangle\langle\langle u_j\rangle\rangle:\quad i,\ j=1,\ 2. \quad (28b)$$

The integrals in U_1 and U_{11} are easily performed to give

$$U_1=N\alpha GE' \quad (29)$$

and

$$U_{11}=NG^2E'^2\alpha^2\Delta \quad (30)$$

where the dimensionless anisotropy parameter Δ is defined by

$$\Delta\equiv 2[(\alpha_1-\alpha_2)^2+(\alpha_2-\alpha_3)^2+(\alpha_1-\alpha_3)^2]/(45\alpha^2) \quad (31)$$

and $\alpha\equiv(\alpha_1+\alpha_2+\alpha_3)/3$ is the usual linear molecular polarizability.

To perform the integrals in U_2 and U_{12} we require the positional average of $D_{xx}{}^{\gamma\mu}$. We assume the weight function w does not depend on $\{\Omega\}$. Then, if the dimensionless two-particle correlation function $p(r)$ defined by

$$p(r_{12})\equiv V^2\int d\mathbf{r}_3\cdots d\mathbf{r}_N w(\{\mathbf{r}\}) \quad (32)$$

approaches a constant value when $r_{12}\equiv|\mathbf{r}_1-\mathbf{r}_2|$ is still small compared with the size of the liquid sample under consideration, the required positional average gives (neglecting terms of order N^{-1} smaller)

$$\langle\textstyle\sum_{\gamma,\mu}D_{xx}{}^{\gamma\mu}\rangle=N\rho l \quad (33)$$

where

$$l\equiv L-4\pi/3, \quad (34)$$

independently of the form of $p(r)$.[10] ρ is the number density of molecules N/V; L is the depolarizing factor along that principal axis of the ellipsoidal sample which is parallel to the external field. Therefore

$$U_2=\tfrac{1}{2}N\alpha^2E'^2\rho l \quad (35)$$

and

$$U_{12}=N\alpha^3GE'^3\rho l\Delta. \quad (36)$$

To perform the integrals required in U_{22}, the exact form of the two-, three-, and four-particle correlation functions is required. For purposes of calculation, we have assumed that $p(r)$ is a simple step function which, properly normalized, is

$$\begin{aligned} p(r) &= 0, & r<d \\ &= (1-\tau/V)^{-1}, & r>d \end{aligned} \tag{37a}$$

where

$$\tau \equiv 4\pi d^3/3. \tag{37b}$$

We have used the usual "Kirkwood superposition approximation" for the three- and four-particle correlation functions, expressing them in terms of $p(r)$. The details of the calculation of U_{22} with these approximations is given in the Appendix; the result is

$$\begin{aligned} U_{22}/(NE'^4\rho^2\alpha^4) = (l^2+2\pi^2/3)\Delta+2\pi^2/3 \\ +\pi^2(32+136\Delta+167\Delta^2)/(45\rho\tau) \\ +0.961\rho\tau(1+K_4/4), \end{aligned} \tag{38}$$

where K_4 is a small contribution ($\sim 10^{-1}$) from an integral that we have not been able to evaluate exactly and which we may neglect without affecting the probable accuracy of the over-all results.

V. THE BEST EFFECTIVE FIELD; LINEAR AND NONLINEAR INDEX FORMULAS

Having explicit expressions for all the terms in (27) for F, we will adjust the magnitude E' of the effective local field to obtain as low a value as possible for the upper bound F of the electric free energy. Since the terms of order E_0^4 are supposed to be orders of magnitude smaller than those of order E_0^2, it is easily seen that the best E' is that which minimizes the terms of order E_0^2. Any small change of E' from such a value raises these large terms more than it can depress the smaller terms of order E_0^4. That is, we need only minimize (U_2-U_1) with respect to E' and find that

$$E' = E_0/(1+\rho\alpha l) \tag{39}$$

is the best choice for E'. Using (39) in (27) gives immediately the approximate b and c coefficients of (7). Since the inequality (21) holds in the limit of low fields, the estimate for b is a lower bound. Then, from (7)–(12), the following relations result for the linear dielectric constant ϵ and the nonlinear index n_2:

$$\epsilon \geq \frac{1+8\pi\rho\alpha/3}{1-4\pi\rho\alpha/3} \tag{40}$$

and

$$n_2 \approx \frac{\pi\rho\alpha^2\beta}{n(1-4\pi\rho\alpha/3)^4}\left[\Delta+\frac{4\pi^2\rho\alpha^2}{45\tau}(32+136\Delta+167\Delta^2) + \frac{8\pi^2\rho^2\alpha^2(1+\Delta)}{3}+3.843\alpha^2\rho^3\tau\right]. \tag{41}$$

We reiterate that, since the test sample of fluid considered was uniformly irradiated and filled a fixed volume uniformly, the estimate (41) for the nonlinear index does not contain any effects of macroscopic density changes such as would arise after a certain time from electrostriction and heating in a nonuniformly irradiated sample or in a compressible sample uniformly irradiated. The expression (41) contains only the relatively quickly established nonlinearities due to molecular reorientation and redistribution.

TABLE I. Values of n_2, the nonlinear index arising from molecular reorientation and redistribution, calculated from Eq. (41) for various liquids. Values of the threshold power for self-focusing P_c calculated using these values of n_2 in Eq. (7), with $\lambda_c = 6943$ Å. Values of n_{2D}, the nonlinear index of Debye for molecular reorientation alone, and given by the term in (41) lowest order in the density. The optical polarizability data used in calculations was taken from Table 142072 of Ref. (12) whenever possible, and otherwise from Ref. (13) or as noted.

Liquid	$n_2 \times 10^{12}$ esu	$P_c(kW)$ calc. for 6943 Å	$n_{2D} \times 10^{12}$ esu
1-chloronaphthalene[a]	167[b]	1.0	
Lead tetraisopropyl[a]	111	1.5	0
Tin tetra 2-methylbutyl[a]	109	1.5	0
Tin tetrapental[a]	108	1.6	0
CS_2	96	1.7	22
Tin tetrabutyl[a]	89	1.9	0
$SiBr_4$	82	2.0	0
Lead tetraethyl[a]	81	2.1	0
Benzoylchloride	73[b]	2.3[b]	
Nitrobenzene	69	2.4	8.8
Bromobenzene	68[c]	2.5	6.4[c]
Acetophenone	56[d]	3.1[d]	
Chlorbenzene	54	3.1	6.3
Toluene	45	3.8	5.6
$SnCl_4$	44	3.8	0
Benzene	37	4.5	4.4
$Sn(CH_3)_4$	27	6.2	0
CCl_4	24	7.1	0
Chloroform	19	9.0	1.3
Water	11[b]	15[b]	
Acetone	6.7	26	0.6
Acetic acid	5.7[b]	30[b]	
Liquid CH_4	3.0	56	0
Liquid H_2	0.024[e]	7000[e]	0.010

[a] A molecule whose largest dimension is estimated to be larger than $\rho^{-1/3}$; hence, the listed index and power values are less accurate for this than the smaller molecules.

[b] Measured values of Δ not available; n_2 calculated using Δ estimated from the ac Kerr effect data of Ref. (9) and the theory of Ref. (8).

[c] Value of Δ estimated by scaling values in Table 142072 of Ref. (12) to those of Table 142071.

[d] Estimated by assuming molecule is symmetric ($\Delta = 0$).

[e] This value is less accurate than others because the quantum effects that we have ignored are important in liquid H_2.

In order to evaluate (41), a knowledge of the molecular volume $\frac{1}{4}\tau$ is required. This parameter also occurs in the theories of the fluid viscosity, the heat conductivity, and virial coefficients. An examination of data on representative fluids in each of these areas gives values for τ which vary typically by ±10% for a given fluid and which fall within ±15% or $2.5/\rho$. Since data on τ are not available for most of the fluids of interest to us, we have used the value $\rho\tau = 2.5$ throughout our numerical evaluations of n_2. Fortunately, n_2 is not very sensitive to deviations of $\rho\tau$ from 2.5, and we feel that the errors arising from this approximation are less than from other sources.

The values of n_2 that result from using this approximation and polarizability data appropriate for the wavelength 0.589 μ of the sodium *D*-line are given for 24 liquids in the first column of Table I.[12,13] The threshold powers P_c for self-focusing estimated by using our values for n_2 in (7) are listed in the second column. Also given in the last column for comparison are the values n_{2D} which would be obtained from the low density formula of Debye for the nonlinear index [i.e., the first term on the *RHS* of (41)] which neglects molecular redistribution.[14]

VI. EXAMINATION OF ACCURACY AND DISCUSSION

The inequality (40) is equivalent to the statement that the Clausius-Mossotti function $(\epsilon-1)/[\rho(\epsilon+2)]$ is always larger than $4\pi\alpha/3$ for a classical fluid of molecules of fixed linear polarizability, regardless of the intermolecular forces, provided that the two-particle correlation function depends only on the intermolecular spacing and becomes constant for large spacing. The fact that many fluids have been found which slightly disobey (40) demonstrates that at least one of these assumptions is not entirely valid.[15] However, the observed deviation of the Clausius-Mossotti function from $4\pi\alpha/3$ is rarely more than a few percent in liquid.[15] This suggests that our nonlinear index should be accurate to within 10 to 50%, depending on the molecule. However, in arriving at (41), several added approximations have been made so that this absolute accuracy may not be attained. The result for n_2 is sensitive to the forms of the two-, three-, and four-particle correlation functions. The first of these we have approximated by the step function (37), and even the best parameter τ to use in (37) is uncertain. Probably least certain of all the approximations is the Kirkwood superposition approximation for the three- and four-particle correlation functions. Also, for those "large" molecules listed in Table I whose largest dimensions are probably larger than $\rho^{-1/3}$, extra errors are introduced because such molecules are clearly not representable as hard spheres with ideal polarizable dipoles at their centers. Furthermore, in the listed threshold powers there are the added errors inherent in (7) which, when applied to a given laser beam, could easily err by an order of magnitude. Despite these and other difficulties, we believe there are some significant correlations between our theoretical values of n_2 or P_c and the available experimental results on self-focusing. The reasons for this and some detailed comparisons with experiment are given below.

From recent time-resolved studies of the formation of self-trapped filaments of an unfocused ruby laser beam in CS_2 and nitrobenzene, it was found that the filaments do not persist for more than a few nanoseconds even when the laser pulse is several tens of nanoseconds long.[16] In all of the experimental studies of self-trapping to date, unfocused beams of cross section of the order of 1 mm or larger have been used. Therefore, during the lifetime of a "filament," a sound wave could travel only a small fraction ($<10^{-2}$) of the width of the parent beam. This suggests that macroscopic density changes and the effects (such as electrostriction) which produce them may not have time to affect the index in many, if not all, materials studied to date. Further evidence against density change effects comes from the observed instability in the nonlinear propagation of a circularly polarized beam, an instability which would not exist if density changes alone altered the index.[16] It is true that stimulated Brillouin scattering may accompany or precede self-focusing, but the usual theory suggests that the density changes associated with this are not such as to case an index change at the parent frequency, although they may of course contribute a loss which can effect self-focusing. Therefore, it seems reasonable to expect that a comparison between present data and our theory which omits effects of macroscopic density changes will yield some information on the accuracy of the theory and of the conclusions that it suggests. Such a comparison and suggestions for more definitive experimental checks of molecular redistribution effects are now given.

In the first data on self-trapping of Hauchecorne and Mayer,[2] nitrobenzene was found to self-focus about the same fraction of an incident beam as does 1-chloronaphthalene. This suggests that the threshold powers are about the same in these two materials, as has been verified more recently by Bret *et al.*[9] Therefore, the ratio of the threshold for 1-chloronaphthalene to that of nitrobenzene inferred from Table I is two times too low. However, 1-chloronaphthalene is a "large" molecule (its maximum dimension is greater than $\rho^{-1/3}$) for which our model of a point dipole at the center of a spherical molecule is obviously bad. This suggests that the critical powers listed for the other "large" molecules indicated in Table I may also be too low relative to the other powers listed.

Shen and Shaham[3] found that the threshold powers for self-focusing in nitrobenzene, acetophenone, benzene, and water increased in that order. This is in agreement with the order of Table I.

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[12] Landolt-Börnstein, *Zahlenwerte und Functionen I/3* (Springer-Verlag, Berlin, 1962), p. 509.

[13] *Dictionary of Organic Compounds* (Oxford University Press, New York, 1965).

[14] Y. R. Shen, Phys. Letters **20**, 378 (1966), also uses this formula for n_{2D} to tabulate nonlinear indices. However, his values often differ from ours by a factor ~ 2 because he employs the dc Kerr coefficients, with data on permanent dipole moments and the theory of C. V. Raman and K. S. Krishnan, Phil. Mag. **3**, 724 (1927), to determine Δ, rather than the optical values measured directly by Rayleigh scattering. This latter theory was shown by Raman and Krishnan to be commonly in error by 2 or more.

[15] C. M. Knobler, C. P. Abiss, and C. J. Pings, J. Chem. Phys. **40**, 2200 (1964).

[16] D. H. Close, C. R. Guiliano, R. W. Hellwarth, L. D. Hess, F. J. McClung, and W. G. Wagner, IEEE J. Quant. Electron. **QE-2**, No. 9, 553 (1966).

Lallemand and Bloembergen found that the threshold powers of CS_2, nitrobenzene, bromobenzene, and acetone increased in that order, in agreement with Table I. They also failed to observe self-trapping in water and CCl_4. However, from a more detailed examination of Raman scattering near threshold, Bret *et al.* have found evidence for self-trapping in CCl_4 at powers where there was none for acetone, chloroform, and acetic acid.[9] Table I is consistent with the latter possibility.

Other measurements of Bret *et al.* give the threshold powers to produce stimulated Raman scattering in CS_2, nitrobenzene, benzoylchloride, 1-chloronaphthalene, toluene, benzene, and CCl_4 to be in the ratios 1:2:3:3:6:10:300.[9] Since Bret *et al.* present indirect evidence that self-trapping occurs in each of these liquids, we may suppose that this ordering is also that for the self-trapping threshold powers. Again, except for the "large" molecule 1-chloronaphthalene, the ordering is consistent with that in Table I. The connection between these threshold powers covering a power range of 300 and the self-trapping thresholds for beams of a fixed spatial pattern is not clear enough to warrant studying a numerical comparison, especially since the experimental procedure was not given.

From a study of the cell length dependence of stimulated Raman thresholds, Wang has inferred that the trapping threshold powers for nitrobenezene, toluene and benezene are in the ratios 1:2.9:3.4. This may be compared with corresponding ratios 1:1.6:1.9 from Table I. We do not feel that this difference represents a fundamental disagreement, but is probably representative of the experimental and theoretical errors in such ratios.

If even rough comparisons are to be made between the *absolute* values of the threshold powers for self-focusing predicted by (7) and observation, a highly degenerate diffraction limited beam of smooth wavefront must be employed. Otherwise corrections to (7) discussed by Wang[5] must be devised. The only published efforts to study self-focusing with a beam approximating the ideal conditions are those of Garmire *et al.*[6] They found beam constriction to set in at 25±5 kW in nitrobenzene, an order of magnitude higher power than given by our value of n_2 used in (7). With a multimode, multi-lobe beam, Wang inferred from Raman data that the self-focusing in nitrobenzene set in at 19 kW,[5] again a much higher power than in Table I. Such discrepancies could not be said to be surprising in view of the combined absolute errors of (7) and (41). However, there is some evidence that it is premature to assume that this discrepancy is entirely established. First, Chiao and Garmire have reported that very small filaments have been discovered subsequently to be present while the overall constriction of the beam, on which the previous threshold estimate was based, is just beginning.[17] This sub-structure in the beam sets in at an as yet undetermined lower power level than the large scale beam constriction. Secondly, Emmett has observed in nitrobenzene what appear to be self-trapped filaments in the stimulated Raman scattering at 90° from a beam that has been focused onto a perpendicular line.[18] These "filaments" vary in number with the beam power as do the usual parallel filaments. However, single "filament" outputs of between 5 and 10 kW have been observed, in rough agreement with the values of Table I.[18] Evidently, further work is required to establish definitive estimates of thresholds for the self-trapping of highly degenerate diffraction limited beams.

There are two kinds of measurements which have been performed that do not involve n_2 or self-focusing, but which may give information about redistribution effects. First, Mayer and Gires have measured the optical birefringence induced in one beam traversing a material by another strong linearly polarized congruent beam of a different wavelength.[9,19] They describe their results by an optical Kerr constant B_0, which, if the low density theory[8] were correct, would equal $3n_{2D}/(2\lambda_1)$, where λ_1 is the free space wavelength of the birefringent beam.[20] However, when molecular redistribution effects at liquid densities are also considered, a different relation between B_0 and n_2 will result. Unfortunately, our theory of n_2 is not capable of giving the "two beam" property B_0, but it could be extended to do so. After such an extension, a comparison of predicted values of B_0 with those that have been measured would probably make a much more accurate test of theory than comparisons of n_2, because the measurements of B_0 are probably more accurate than those of n_2.[21]

Secondly, Maker *et al.* have measured the change in the state of polarization of a strong, elliptically polarized, beam as a function of beam power and distance

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[17] R. Y. Chiao and E. Garmire, IEEE J. Quant. Electron. **QE-2**, No. 9, 467 (1966).

[18] J. L. Emmett (private communication).

[19] G. Mayer and F. Gires, Compt. Rend. **258**, 2039 (1964).

[20] A comparison of the observations of Mayer and Gires with predictions of the low-density theory of Ref. 8 shows general disagreement. Reference 9 reports that $B_0\times 10^8$ esu is observed to be 42, 29, 9.3, 4.0, 0.5, 1.6, and 0.4 for the liquids CS_2, nitrobenzene, toluene, benzene, CCl_4, choloform, and cyclohexane, respectively (at $\lambda_1=488$ mμ). Using the optical polarizabilities obtained from Rayleigh scattering measurements (Ref. 12) in the low density theory (Ref. 8), one would predict 69, 27, 18, 14, 0, 4.0, and 1.5 for these values.

[21] This extension of theory would also give predictions for the static (dc) Kerr constant B_s for nonpolar molecules which could be compared with a wealth of existing data. These data are in wide disagreement with the predictions of the classical low density theory (Ref. 8). For example, the measured values of $B_s\times 10^8$ esu for CS_2, benzene, CCl_4, liquid N_2, cyclohexane, and liquid H_2, at $\lambda_1=546$ mμ are 35.5, 4.1, 0.84, 0.8, 0.59, and 0.34, respectively [from Landolt-Börnstein, *Zahlenwerte und Funktionen II/8* (Springer-Verlag, Berlin, 1962), Chap. 5, pp. 849–855]. Using the polarizability data of Ref. 12 in the low density theory (Ref. 8), one would predict 60, 12, 0, 0.4, 1.4, and 0.027, respectively, for these values.

along the beam.[22] These measurements have been recently refined by Wang and Racette.[23] Their results were given in terms of a constant B (real in the absence of loss) which would equal $3nn_2/8\pi$ if the low density theory[8] which neglects molecular redistribution were applicable, but will be related to n_2 differently at liquid densities where molecular redistribution is important. Again, when our theory is extended to predict B values, comparison with these experiments will be illuminating.

There is a measurement of n_2 which could be performed, but which does not involve self-focusing and hence might be more accurate. The change in index for a weak, plane polarized, beam congruent with a strong beam of the same polarization but of a different wavelength would equal $n_2\bar{E}^2$, where $\bar{E}^2$ is the mean square amplitude of the strong beam, provided that the two wavelengths are not too widely separated. This change in index could be measured, for example, by putting the strongly irradiated material in one arm of a Mach-Zehnder interferometer, and using the weak beam at a different wavelength as the interferometric source.

Stimulated Brillouin scattering, turbulence, impurities, bubbles, and molecular relaxation processes, all of which tend to prevent the liquid from reaching an equilibrium state in the strong fields, may affect experimental results. Elucidation of these phenomena will doubtless follow a better understanding of the equilibrium state itself, but we will not attempt to analyze them here.

In conclusion, since there are no general relations for liquids among the coefficients n_2, B_0, and B, information concerning the validity of approximations such as the Kirkwood approximation in dealing with molecular redistribution effects can be obtained as yet only from comparing the present theory with experiments which measure n_2. When the theory is extended to treat B_0 and B, additional checks of the approximations will become available. However, with only the relatively crude comparisons between the available results on self-trapping and the theory that we have made above, we are led to conclude that molecular redistribution effects are generally important, and no doubt dominate the nonlinear index of symmetric-molecule liquids. Observations of self-trapping in such symmetric-molecule liquids as $SiBr_4$ and $SnCl_4$ will provide important checks of the theory of the nonlinear index. Further efforts to obtain smooth, diffraction limited, highly degenerate beams would aid in establishing the absolute magnitude of the nonlinear index n_2 in various materials. The measurement of the index change for a weak, linearly polarized, beam congruent within a material to a parallel-polarized strong beam of different wavelength may yield an even more accurate value of n_2 for that material.

APPENDIX

Here we outline the calculation of $U_{22}=\langle\langle u_2^2\rangle\rangle-\langle\langle u_2\rangle\rangle^2$. We will use the form (37) for the probability $V^{-2}p(\mathbf{r}_1-\mathbf{r}_2)d^3r_1d^3r_2$ that if a certain molecule is in d^3r_1, another specified molecule is in d^3r_2. We will use Kirkwood's superposition approximation for $V^{-3}p_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\equiv p_3(123)$ [and for $V^{-4}p_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)\equiv p_4(1234)$] which is the probability (per unit volume for each molecule) for finding specified molecules at $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ (and $\mathbf{r}_4$) simultaneously:

$$p_3(123)\approx p(12)p(23)p(13)\,, \tag{A1}$$

$$p_4(1234)\approx p(12)p(13)p(14)p(23)p(24)p(34)\,. \tag{A2}$$

Here $p(12)$ is an abbreviation for $p(\mathbf{r}_{12})$, and we have ignored terms of order N^{-2} smaller than the leading terms of (A1) and (A2). (Terms of order N must be kept, as the terms in U_{22} which are proportional to N^2 will cancel.)

The integrals in $4\langle\langle u_2^2\rangle\rangle$ fall naturally into four groups, which we call I_1, I_2, I_3, and I_4, depending on whether 1-, 2-, 3-, or 4-particle correlations are required:

$$4\langle\langle u_2^2\rangle\rangle=\sum_{i=1}^{4} I_i \tag{A3}$$

where

$$I_1=\sum\nolimits_\mu \langle\langle(\mathbf{E}'\cdot\boldsymbol{\alpha}^\mu\cdot\mathbf{D}^{\mu\mu}\cdot\boldsymbol{\alpha}^\mu\cdot\mathbf{E}')^2\rangle\rangle=0 \tag{A4}$$

$$I_2=2\sum\nolimits_{\mu\nu} \langle\langle(\mathbf{E}'\cdot\boldsymbol{\alpha}^\mu\cdot\mathbf{D}^{\mu\nu}\cdot\boldsymbol{\alpha}^\nu\cdot\mathbf{E}')^2\rangle\rangle \tag{A5}$$

$$I_3=4\sum\nolimits_{\mu\nu\gamma} \langle\langle\mathbf{E}'\cdot\boldsymbol{\alpha}^\mu\cdot\mathbf{D}^{\mu\nu}\cdot\boldsymbol{\alpha}^\nu\cdot\mathbf{E}'\mathbf{E}'\cdot\boldsymbol{\alpha}^\nu\cdot\mathbf{D}^{\nu\gamma}\cdot\boldsymbol{\alpha}^\gamma\cdot\mathbf{E}'\rangle\rangle \tag{A6}$$

and

$$I_4=\sum\nolimits_{\mu\nu\beta\gamma} \langle\langle\mathbf{E}'\cdot\boldsymbol{\alpha}^\mu\cdot\mathbf{D}^{\mu\nu}\cdot\boldsymbol{\alpha}^\nu\cdot\mathbf{E}'\mathbf{E}'\cdot\boldsymbol{\alpha}^\beta\cdot\mathbf{D}^{\beta\gamma}\cdot\boldsymbol{\alpha}^\gamma\cdot\mathbf{E}'\rangle\rangle\,. \tag{A7}$$

Here the summed indices are always unequal in any I_i. The I_1 is zero, of course, because $\mathbf{D}^{\mu\mu}$ is defined to be zero. The angular averages in each of the remaining integrals are easily performed and give

$$\begin{aligned}I_2=2\alpha^4E'^4\sum\nolimits_{\mu\nu}[(1+\Delta/4)^2\langle(D_{xx}^{\mu\nu})^2\rangle\\+(\Delta/2+11\Delta^2/16)\langle\mathrm{Tr}\mathbf{D}^{\mu\nu}\cdot\mathbf{D}^{\mu\nu}\rangle]\end{aligned} \tag{A8}$$

$$I_3=4\alpha^4E'^4(1+\Delta)\sum\nolimits_{\mu\nu\gamma}\langle D_{xx}^{\mu\nu}D_{xx}^{\nu\gamma}\rangle \tag{A9}$$

and

$$I_4=\alpha^4E'^4\sum\nolimits_{\mu\nu\beta\gamma}\langle D_{xx}^{\mu\nu}D_{xx}^{\beta\gamma}\rangle\,. \tag{A10}$$

Here "Tr" denotes the "trace" or sum over diagonal space elements, and the single bracket $\langle\ \ \rangle$ denotes the average over spatial configurations.

Using the form (37) for the two particle distribution function and (20) for $\mathbf{D}^{\mu\nu}$ gives (neglecting terms$\sim N^0$)

$$\begin{aligned}\sum\nolimits_{\mu\nu}\langle(D_{xx}^{\mu\nu})^2\rangle=N^2V^{-1}4\pi\int_0^\pi \sin\psi d\psi\int_d^\infty r^2\,dr\\ \times(1-3\cos^2\psi)^2r^{-6}=N\rho 64\pi^2/(45\tau)\,.\end{aligned} \tag{A11}$$

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[22] P. D. Maker, R. W. Terhune, and C. M. Savage, Phys. Rev. Letters **12**, 507 (1964).

[23] C. C. Wang and G. W. Racette, J. Quant. Electron. **QE-2**, No. 4 53 (1966).

Similarly,

$$\sum_{\mu\nu} \langle \mathrm{Tr}\mathbf{D}^{\mu\nu}\cdot\mathbf{D}^{\mu\nu}\rangle = N^2V^{-1}12\pi\int_0^\pi \sin\psi d\psi\int_d^\infty r^2\,dr \times(1+3\cos^2\psi)r^{-6} = N\rho 32\pi^2/(3\tau). \quad \text{(A12)}$$

Therefore,

$$I_2 = N\alpha^4E'^4\rho^2 4\pi^2(32+136\Delta+167\Delta^2)/(45\rho\tau). \quad \text{(A13)}$$

To perform the average in (A9) to order N, we write

$$p(r) = (1-h(r))/(1-\tau/V), \quad \text{(A14)}$$

where $h(r)=1$ for $r<d$ and is zero otherwise. Then, with (A1), we obtain to order N

$$\sum_{\mu\nu\gamma} \langle D_{xx}^{\mu\nu}D_{xx}^{\nu\gamma}\rangle = N^3V^2\int d^3r_2d^3r_3\bar{D}_{12}\bar{D}_{23}(1-h_{13}), \quad \text{(A15)}$$

where $\bar{D}_{12}\equiv D_{xx}^{12}(1-h_{12})$, h_{12} denotes $h(\mathbf{r}_2-\mathbf{r}_3)$, etc. The integrals here are easily performed using the theorem that the integral J of D_{xx}^{12} over any volume Q is related to an integral over the surface S bounding Q by

$$J = \int_Q d^3r_2D_{xx}^{12} = -\int_S d^2\mathbf{r}_2\hat{n}\cdot\hat{\imath}\mathbf{r}_{12}\cdot\hat{\imath}r_{12}^{-3}. \quad \text{(A16)}$$

(If S is ellipsoidal and $\mathbf{r}_1$ is inside it, recall that $J=L$. If S is spherical and $\mathbf{r}_1$ is outside it, then $J=QD_{xx}^{13}$ where $\mathbf{r}_3$ is the center of the sphere and Q is the numerical value of the volume bounded by S.) The part of (A15) independent of h_{13} is obviously $N\rho^2l^2$. With the aid of (A16), the part of (A15) involving h_{13} integrates to $N\rho 2\pi^2/3$ whence

$$I_3 = 4N\alpha^4E'^4\rho^2(1+\Delta)(l^2+2\pi^2/3). \quad \text{(A17)}$$

To evaluate I_4 we use (A2) to obtain

$$\begin{aligned}\sum_{\mu\nu\beta\gamma} \langle D_{xx}^{\mu\nu}D_{xx}^{\beta\gamma}\rangle &= N(N-1)(N-2)(N-3)V^{-3}(1-\tau/V)^{-6} \\ &\quad\times\int d^3\mathbf{r}_2d^3\mathbf{r}_3d^3\mathbf{r}_4\bar{D}_{12}\bar{D}_{34}(1-h_{13})(1-h_{14}) \\ &\quad\times(1-h_{23})(1-h_{24}) \\ &= \sum_{i=0}^{4} K_i. \end{aligned} \quad \text{(A18)}$$

The right hand side separates naturally into terms which we call K_i where $i=0, 1, \cdots, 4$ is the number of explicit h factors in the integrand of the term. The K_0 term is integrated trivially and has a part of order N^2 which cancels the N^2 part of $\langle\langle u_2\rangle\rangle^2$, and a part of order N, which combines with $\langle\langle u_2\rangle\rangle^2$ from (41) (corrected by the now important factor $(1-\tau/V)^{-1}$) to give

$$K_0 - 4\langle\langle u_2\rangle\rangle^2 = -4N\rho^2l^2(1-\rho\tau). \quad \text{(A19)}$$

There are four terms in K_1 (there being four possible terms linear in one of the h's) each of which integrates trivially to $-l^2\tau\rho^3$ giving

$$K_1 = -4l^2\rho^3\tau N. \quad \text{(A20)}$$

There are six ways to form integrands quadratic in the h's in (A18), four of which have one space point as an argument of both h's and are equivalent to each other. The remaining two have no space points as arguments of both h factors and are equivalent to each other. Each of the first four terms is seen to be identically zero with the aid of (A16), and the last two can be straightforwardly integrated with (A16) to give

$$K_2 = 0.5066\pi^2\rho^3\tau N. \quad \text{(A21)}$$

Almost the same straightforward integrations are required for each of the four equivalent terms which are cubic in the h's, and one finds that

$$K_3 = -0.11713\pi^2\rho^3\tau N. \quad \text{(A22)}$$

We have not been able to integrate the remaining term K_4 analytically. We estimate that it is an order of magnitude smaller than K_3 because the four h factors combine to limit the volume accessible to the points of integration much more than in K_3. Since K_3 is already a minor contribution to the final result, we feel well within the other limits of our calculation to neglect K_4 in the final result:

$$I_4 - 4\langle\langle u_2\rangle\rangle^2 \approx N\rho^2(-4l^2+3.84\rho\tau). \quad \text{(A23)}$$

Combining all the above terms gives the U_{22} of (38).