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Many-body optics
V. Virtual-mode theory, and phenomenological binding energies in the complex-dielectric-constant approximation

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Abstract. We show that the one-component virtual-mode theory of the previous paper, which is a well-defined translationally invariant many-body optical theory of the molecular fluid, can be extended without difficulty to the two-component fluid. We infer that the theory of both 'virtual' and 'real' electromagnetic modes developed previously is applicable to fluids with any number of components.

The dielectric constants $\epsilon_{l,t}(k, \omega)$ of the virtual-mode theory are independent of k at wavelengths long compared with intermolecular correlation lengths. We define a complex dielectric constant $\epsilon(\omega)$ equal to these and to the square of the transverse refractive index in the long-wavelength low-energy limit. The dielectric constant $\epsilon(\omega)$ depends on cluster integrals of all orders: in the strongest form of $\epsilon(\omega)$ (valid in the complex-dielectric-constant approximation—c.d.c.a.) these integrals depend on ω, and $\mathrm{Im}\{\epsilon(\omega)\}$ describes the extinction of the electromagnetic modes by external scattering. We show that the virtual-mode theory in the c.d.c.a. is equivalent as a response function theory to the translationally invariant long-wavelength (virtual) photon theory of Dzyaloshinskii and others: we derive Dzyaloshinskii's macroscopic integral equation from the microscopic integral equation considered in the three previous papers, I, III and IV of this series.

We also consider the weak c.d.c.a. which entirely omits the radiation field from the intermolecular interactions of the cluster integrals. We show that the prescription of Dzyaloshinskii and others for calculating the free energy of a macroscopic translationally invariant dielectric is equivalent in the weak c.d.c.a. to the change in free energy on coupling the oscillators of the free radiation field to the oscillators of a dielectric coupled by Coulomb interactions alone. We suggest that this appealing result is nevertheless incompatible with the quantal theory which yields the fundamental integral equation of this series of papers. The two theories coincide when but apparently only when both the local and Lorentz fields are neglected in the theory. We infer that the prescription of Dzyaloshinskii for the free energy of a real fluid may neglect important contributions from thermal fluctuations; we can conclude that the low-frequency dispersion relation does not determine the intermolecular binding energy of a molecular fluid to better than a continuum approximation of the type reported in part II of this series of papers.

Finally we summarize the results of the three papers III, IV and V of the series.

1. Introduction

In the two previous papers (Bullough 1970 a,b—to be referred to as III and IV respectively) we developed the theory of the total electromagnetic response function for a molecular fluid: we obtained transverse and longitudinal (k, ω)-dependent dielectric constants but showed that these were sufficient to describe only a part of that total response. This part we called the virtual response (longitudinal or transverse) and we showed that it could be considered to be the whole of the translationally

invariant response. Likewise we showed that a theory which ignored all but the virtual response to an imposed current distribution was a translationally invariant theory with natural normal modes: this theory we called the 'virtual-mode theory'. In this paper V we examine some consequences of this virtual-mode theory.

We first extend (in §2) the theory to a two-component system: this is perfectly straightforward and the result allows us to regain the two-component dispersion relations derived in the first paper of this series (Bullough 1968 a—to be referred to as I).

In §3 we next examine the virtual-mode theory in the complex dielectric constant approximation (c.d.c.a.). This is a physically important case since it is a natural long-wavelength low-energy theory valid whenever $k \ll l^{-1}$ and $k_0 \ll l^{-1}$ where l is an intermolecular correlation length. A molecular fluid has a natural k-independent frequency-dependent dielectric constant, which we denote by $\epsilon(\omega)$ in this case. We find we can derive the translationally invariant form of the semi-phenomenological integral equation of Dzyaloshinskii *et al.* (1961) from the virtual-mode theory in the c.d.c.a. This integral equation depends on $\epsilon(\omega)$.

The integral equation of Dzyaloshinskii *et al.* is an adjunct to the exposition of a many-body theory of van der Waals forces which, like the earlier work of Lifshitz (1956), recognizes that the individual molecular wave functions are severely distorted in a condensed dielectric. The macroscopic dielectric constant is used as a place for concealing this complication. The work of §3 shows that this is a legitimate point of view as far as the response functions are concerned. Dzyaloshinskii *et al.* explicitly focus attention on long-wavelength photon contributions which we must recognize as virtual photon contributions and a comparison with the c.d.c.a. is appropriate.

It does not necessarily follow from this that long-wavelength virtual photon contributions to the free energy can be described by the dielectric constant alone. Indeed we have already reported (Bullough 1969—to be referred to as II) a theory of van der Waals forces which fits naturally into the many-body optical theory and which will be presented in detail later in this series: this theory shows that $\epsilon(\omega)$, or the refractive index $m_t(\omega)$, is sufficient to determine the bulk binding of a molecular fluid in the 'continuum approximation' there described (providing the energies of the free molecules are also available); but it implicitly suggests that $\epsilon(\omega)$ or $m_t(\omega)$ are insufficient for this purpose if any sort of intermolecular correlation, as for example in the c.d.c.a., is included. Dzyaloshinskii *et al.* 'decorrelate' their theory by summing one selected set of diagrams to all orders arguably in a way which neglects inter-molecular correlation;† they also introduce their coupled photon propagator in a semi-phenomenological way. This paper V is a natural place to examine the signifi-cance of such assumptions for an arbitrary dielectric by making particular use of the virtual-mode theory in the c.d.c.a.; and this is the problem treated in §4.

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† The structure of this decorrelation is very comparable with the decorrelation of the quantal theory we invoke to reach the classical integral equation of I. In Bullough *et al.* (1968) we call this the polarization diagram approximation (p.d.a.) for reasons which will appear later (see the argument reported for the classical integral equation, equation (7), there). Because we appeal to the (quasi-static) Born–Oppenheimer type of approximation, we need an additional de-correlation of intermolecular interactions. As far as the integral equations go this corresponds to appealing to the 'continuum' integral equation I (2.2) rather than I (2.1) which admits 2-particle correlation explicitly and ν-particle correlation for all ν in most general form. Within the structure of the Dzyaloshinskii free-energy theory this continuum integral equation seems to be most consistent with the results of that theory although the question of the role of the Lorentz field still arises. See §4.

In the following §5 we summarize the three papers III, IV and V as a whole: they have together constituted a connected and necessarily rather mathematical analysis of the fundamental integral equation first presented and solved for acceptable mode dispersion relations in I.

2. The total virtual response for a two-component system

We here derive the proper generalization of the expression IV, (2.11) for the dielectric constants $\epsilon_{l,t}(\boldsymbol{k}, \omega)$ when the system is a two-component molecular fluid. The extension of III, (3.3) to a two-component system is the pair of equations

$$\{\alpha(\omega)\}^{-1}\boldsymbol{P}_a(\boldsymbol{k}, \omega) = \{\beta(\omega)\}^{-1}\boldsymbol{P}_b(\boldsymbol{k}, \omega)$$

$$= \boldsymbol{E}(\boldsymbol{k}, \omega) + (k_0^2\boldsymbol{U} - \boldsymbol{kk})4\pi.\{n_a\boldsymbol{P}_a(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_b(\boldsymbol{k}, \omega)\}(k^2 - k_0^2)^{-1}$$

$$+ \tfrac{4}{3}\pi\{n_a\boldsymbol{P}_a(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_b(\boldsymbol{k}, \omega)\} + (k_0^2\boldsymbol{U} - \boldsymbol{kk}) . \int \frac{I(\boldsymbol{k}, -\boldsymbol{k}'; \omega)}{k'^2 - k_0^2}$$

$$\times \{n_a\boldsymbol{P}_a(\boldsymbol{k}', \omega) + n_b\boldsymbol{P}_b(\boldsymbol{k}', \omega)\}\, d\boldsymbol{k}'. \tag{2.1}$$

From this it follows that instead of IV (2.5) for the virtual transverse response we have the pair of equations

$$4\pi n_a\{4\pi n_a\alpha(\omega)\}^{-1}\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega) = 4\pi n_b\{4\pi n_b\beta(\omega)\}^{-1}\boldsymbol{P}_{tb}(\boldsymbol{k}, \omega)$$

$$= \boldsymbol{E}_{t1}(\boldsymbol{k}, \omega) + (k_0^2\boldsymbol{U} - \boldsymbol{kk}) . 4\pi\{n_a\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_{tb}(\boldsymbol{k}, \omega)\}$$

$$\times (k^2 - k_0^2)^{-1} + \tfrac{4}{3}\pi\{n_a\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega)\}. \tag{2.2}$$

The calculation of the virtual response of a two-component system thus reduces to no more than the solution of a pair of simultaneous equations, whilst it is also clear that the arguments for the real response of the two-component system are likewise little changed.

We are not interested in the dipole responses of the individual components but only in the response in the total transverse dipole moment density

$$n_a\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_{tb}(\boldsymbol{k}, \omega).$$

By including the intermolecular correlation series for the two components (see I §4, equations (4.26), (4.27)) we easily find by solving (2.2) for $\boldsymbol{P}_{ta}$ and $\boldsymbol{P}_{tb}$ that

$$4\pi\{n_a\boldsymbol{P}_{ta}(\boldsymbol{k}, \omega) + n_b\boldsymbol{P}_{tb}(\boldsymbol{k}, \omega)\} = \frac{(k^2 - k_0^2)\{\epsilon_t(\boldsymbol{k}, \omega) - 1\}}{\{k^2 - \epsilon_t(\boldsymbol{k}, \omega)k_0^2\}} \boldsymbol{E}_{t1}(\boldsymbol{k}, \omega) \tag{2.3}$$

in which

$$\epsilon_t(\boldsymbol{k}, \omega) - 1 = \frac{4\pi[n_a\alpha(\omega) + n_b\beta(\omega) + n_a n_b\alpha(\omega)\beta(\omega)\{J_{taa}(\boldsymbol{k}, \omega)}{1 - 4\pi/3\{n_a\alpha(\omega) + n_b\beta(\omega)\} - n_a\alpha(\omega)J_{taa}(\boldsymbol{k}, \omega) - n_b\beta(\omega)J_{tbb}(\boldsymbol{k}, \omega)} \cdots$$

$$\text{(cont.)} \cdots \frac{+ J_{tbb}(\boldsymbol{k}, \omega) - J_{tab}(\boldsymbol{k}, \omega) - J_{tba}(\boldsymbol{k}, \omega)\}]}{+ n_a n_b\alpha(\omega)\beta(\omega)\det\|J_{t\alpha\beta}(\boldsymbol{k}, \omega)\|} \tag{2.4}$$

in which $\|J_{t\alpha\beta}(\boldsymbol{k}, \omega)\|$ is the 2×2 matrix with elements $J_{taa}(\boldsymbol{k}, \omega)$, $J_{tab}(\boldsymbol{k}, \omega)$, etc. The formal structure thus exactly reproduces the refractive index theory of the two-component system of I (4.24c) and it follows from (2.3) that

$$\epsilon_t(m_t k_0\hat{\boldsymbol{k}}; \omega) = m_t^2(\omega).$$

Thus the transverse dispersion relations of I (4.24c) are again the surfaces of singularity of the response function and the transverse modes whose vectors satisfy this dispersion relation can again be interpreted as normal modes within the virtual mode theory, as in IV §2.

Likewise the total longitudinal virtual response satisfies

$$4\pi\{n_a P_{la}(k, \omega) + n_b P_{lb}(k, \omega)\} = \{1 - 1/\epsilon_l(k, \omega)\} E_l(k, \omega) \tag{2.5}$$

instead of III (3.15a) and

$$\epsilon_l(k, \omega) - 1 = \frac{4\pi[n_a\alpha(\omega) + n_b\beta(\omega) + n_a n_b\alpha(\omega)\beta(\omega)\{J_{laa}(k, \omega)}{1 - \tfrac{4}{3}\pi\{n_a\alpha(\omega) + n_b\beta(\omega)\} - n_a\alpha(\omega)J_{laa}(k, \omega) - n_b\beta(\omega)J_{lbb}(k, \omega)} \cdots$$

$$\text{(cont.)} \cdots \frac{+ J_{lbb}(k, \omega) - J_{lab}(k, \omega) - J_{lba}(k, \omega)\}]}{+ n_a n_b\alpha(\omega)\beta(\omega) \det\|J_{l\alpha\beta}(k, \omega)\|}. \tag{2.6}$$

Then the zeros of $\epsilon_l(k, \omega)$ are the longitudinal dispersion relations of I (4.25c).

It is now clear that the whole virtual-mode theory generalizes to an arbitrary number of components without changing the pseudo-macroscopic forms (2.3) for the transverse virtual response and (2.5) for the longitudinal virtual response. It is then rather clear that the total response functions like IV (2.22) (virtual plus real response) which depend on $\epsilon_{l,t}(k, \omega)$ and $m_t^2(\omega)$ and on the surface Σ will be unchanged providing we always concern ourselves systematically with the total dipole density response. It is only the expressions like (2.4) and (2.6) for the $\epsilon_{l,t}(k, \omega)$ and the dispersion relations themselves which change to accommodate the different correlations in the different systems. It is then clear that the *whole* theory of III and IV will generalize and that we have found from the microscopic theory a formal theory which is wholly macroscopic in this sense.

With this certainty behind us we can return to the virtual-mode theory of the one-component system: this theory is translationally invariant in the sense of IV §2 and macroscopic in the sense of the remarks above. It is not a physical theory in the very fact that it is translationally invariant as we discussed in IV §§2 and 4; but it is not a physical theory also in that it depends on the $\epsilon_{l,t}(k, \omega)$ rather than on the refractive index $m_t(\omega)$ or the physical frequency-dependent dielectric constant $\epsilon(\omega)$. We now show how far the virtual-mode theory is determined by the dispersion of the refractive index alone. We exploit the short-range character of the local order in a molecular fluid under normal conditions far from any critical point. The approximation which results is the complex dielectric constant approximation (the c.d.c.a.). We introduced it briefly in II and have referred to it in III and IV. It is obviously an important physical approximation.

3. The total virtual response and its long-wavelength limit

We here exhibit the total virtual response, transverse plus longitudinal, and investigate the case when k and k_0 are much less than reciprocal cluster correlation lengths $l^{-1}(\equiv 2\pi l^{-1})$. We find that the dielectric constants are then essentially independent of k; and the most general approximation in which this is so is the c.d.c.a. The c.d.c.a. is a natural and important physical approximation in the description of external scattering processes (Bullough *et al.* 1968 and Bullough and Hynne 1968); but its relation as a long-wavelength theory to the work of Dzyaloshinskii *et al.*† was the important question raised in §1. It is this problem we consider here.

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† The theory is also presented in Abrikosov *et al.* (1965). We refer to this book as AGD in the following.

The total virtual response of a one-component molecular fluid excited by fields $E_t(\boldsymbol{k}, \omega)$ and $E_l(\boldsymbol{k}, \omega)$ is given by III (3.8) and IV (2.8) as

$$4\pi n\{\boldsymbol{P}_t(\boldsymbol{k}, \omega) + \boldsymbol{P}_l(\boldsymbol{k}, \omega)\} = \{1 - 1/\epsilon_l(\boldsymbol{k}, \omega)\}\boldsymbol{E}_l(\boldsymbol{k}, \omega) + \left\{\frac{(k^2 - k_0{}^2)(\epsilon_t(\boldsymbol{k}, \omega) - 1)}{k^2 - \epsilon_t(\boldsymbol{k}, \omega)k_0{}^2}\right\}\boldsymbol{E}_t(\boldsymbol{k}, \omega).$$

(3.1)

In terms of the total applied field this is compactly

$$4\pi n\boldsymbol{P}(\boldsymbol{k}, \omega) = \left[\left\{1 - \frac{1}{\epsilon_l(\boldsymbol{k}, \omega)}\right\}\hat{\boldsymbol{k}}\hat{\boldsymbol{k}} + \left[\frac{(k^2 - k_0{}^2)\{\epsilon_t(\boldsymbol{k}, \omega) - 1\}}{k^2 - \epsilon_t(\boldsymbol{k}, \omega)k_0{}^2}\right](\boldsymbol{U} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\right].\boldsymbol{E}(\boldsymbol{k}, \omega).$$

(3.2)

We also recall the equation, IV (2.11) (or II (2) as first reported) for the $\epsilon_{l,t}(\boldsymbol{k}, \omega)$: this was

$$\epsilon_{l,t}(\boldsymbol{k}, \omega) - 1 = \frac{4\pi n\alpha(\omega)}{1 - \frac{4}{3}\pi n\alpha(\omega) - n\alpha(\omega)J_{l,t}(\boldsymbol{k}, \omega)}.$$

(3.3)

In this the $J_{l,t}(\boldsymbol{k}, \omega)$ are defined in simplest form in III (2.6) but, as briefly reported already in II §2, constitute most generally a multiple scattering cluster expansion developed to all orders: first terms of the series are defined by II (4a,b) with II (3a,b), but the structure of the series will be developed explicitly and in detail only later in this sequence of papers. The two equations (3.2) and (3.3) summarize the total virtual response of a molecular fluid to an external field $\boldsymbol{E}(\boldsymbol{k}, \omega)$: we are confined to the virtual-mode theory of IV and if the external field is a free field (light) the total virtual response is zero; the real mode response of IV must be included to admit the response to light.

We now consider the long-wavelength approximation where $k^{-1} \gg l$. In this case $J_{t,l}(\boldsymbol{k}, \omega) \simeq J_{t,l}(0, \omega)$ and from the definitions of these quantities (III (2.6), II (3) with II (4) or I (4.19) with I (4.17) and I (4.18)) we find that

$$J_t(0, \omega) = J_l(0, \omega)$$

so that from (3.3)

$$\epsilon_t(\boldsymbol{0}, \omega) = \epsilon_l(\boldsymbol{0}, \omega) = \epsilon(\boldsymbol{0}, \omega) \quad \text{(say)}.$$

(3.4)

This result conforms with the usual long-wavelength limit of standard many-body theory (e.g. Pines 1963—p. 200 for the isotropic solid or Ambegaokar and Kohn 1960). However, (3.4) remains approximately valid whenever $k^{-1} \gg \lambda \equiv l/2\pi$ and l is a molecular cluster dimension: we thus have an explicit criterion for the validity of the long-wavelength approximation. It is not valid for any k close to a phase transition where l is very large, and it is not valid at optical wavelengths for systems of macromolecules, for example.

We shall now define the frequency-dependent dielectric constant $\epsilon(\omega)$ to be $\epsilon(\boldsymbol{0}, \omega)$ when *in addition* $k_0{}^{-1} = \omega^{-1}c \gg l$: this has the important property that

$$\epsilon(\boldsymbol{0}, \omega) \equiv \epsilon(\omega) = m_t{}^2(\omega)$$

(3.5)

in the same approximation: otherwise the only relationship between $m_t{}^2(\omega)$ and $\epsilon_t(\boldsymbol{k}, \omega)$ is

$$\epsilon_t(m_t k_0\hat{\boldsymbol{k}}, \omega) = m_t{}^2(\omega)$$

for all directions $\hat{\boldsymbol{k}}$ and there is no comparable relation between $m_t{}^2(\omega)$ and $\epsilon_l(\boldsymbol{k}, \omega)$.

The result (3.5) is the principal reason for defining $\epsilon_{l,t}(\boldsymbol{k}, \omega)$ in such a way that they satisfy (3.3). A consequence of the result is that long-wavelength low-energy virtual photon contributions can be described entirely in terms of the refractive index. This is the basis of previous phenomenological calculations of things like electron stopping power, for which the longitudinal response and $\epsilon_l(\boldsymbol{k}, \omega)$ is really needed, and of energy loss by Čerenkov radiation, for which $\epsilon_t(\boldsymbol{k}, \omega)$ is really needed. We noted this in II.

An important feature of this dielectric constant approximation is that at lowest order in $k_0 l$ it corresponds to replacing the tensor $\boldsymbol{F}$ of III (2.3) everywhere in $J_{l,t}(0, \omega)$ by the longitudinal time-like photon propagator

$$\boldsymbol{T}(\boldsymbol{x}, \boldsymbol{x}') \equiv \nabla \nabla r^{-1} \tag{3.6}$$

which is independent of ω (see I (2.8b)): thus this approximation eliminates all contributions of the radiation field to the cluster integrals which make up the $J_{l,t}(0, \omega)$. The quantities $J_{l,t}$ still depend on ω, however, because they depend on powers of $\alpha(\omega)$. If the $\alpha(\omega)$ are real this approximation makes $\epsilon(\omega)$ purely real and the relations (3.4) and (3.5) certainly hold. It is then possible to introduce a formal *complex* dielectric constant by the substitution $\omega \rightarrow (\omega + i\delta)$ with $\delta > 0$ the usual positive infinitesimal. (See below III (2.2) and the discussion surrounding I (2.3) and (2.5)). This substitution maintains the choice of outgoing boundary conditions as causal boundary conditions and shows us how to negotiate the passage around any singularity of the theory. We shall call this approximation 'the *weak* complex dielectric constant approximation' (weak c.d.c.a.) for we introduce a stronger result, the c.d.c.a. proper, in a moment. The weak c.d.c.a. is fundamental to our analysis of the free-energy of a molecular fluid in the following §4: we now look at it more closely therefore.

The replacement of $\boldsymbol{F}$ by $\boldsymbol{T}$ of (3.6) means that the dielectric constant in the weak c.d.c.a. is given by

$$\epsilon(\omega) - 1 = \frac{4\pi n \alpha(\omega)}{1 - \frac{4}{3}\pi n \alpha(\omega) - n\alpha(\omega) J(\omega)} \tag{3.7}$$

where (cf. I (2.3), (2.4) and (2.5))

$$\alpha(\omega) = e^2 m_e^{-1} \sum_s f_s \{\omega_s^2 - (\omega + i\delta)^2\}^{-1}, \qquad \delta > 0 \tag{3.8}$$

and $n\alpha(\omega) J(\omega)$ is a power series in $n\alpha(\omega)$ with coefficients which are diagonal components of the tensors

$$\boldsymbol{J}_1(\omega) \equiv \int \boldsymbol{T}(\boldsymbol{x}, \boldsymbol{x}')\{g(r) - 1\} \, \mathrm{d}\boldsymbol{x}' \tag{3.9a}$$

$$\boldsymbol{J}_2(\omega) \equiv \int \int \boldsymbol{T}(\boldsymbol{x}, \boldsymbol{x}').\boldsymbol{T}(\boldsymbol{x}', \boldsymbol{x}'')\{g(\boldsymbol{x}, \boldsymbol{x}', \boldsymbol{x}'') - g(\boldsymbol{x}, \boldsymbol{x}')g(\boldsymbol{x}', \boldsymbol{x}'')$$

$$+ n^{-1}\delta(\boldsymbol{x} - \boldsymbol{x}'')g(\boldsymbol{x}, \boldsymbol{x}')\} \tag{3.9b}$$

etc.†

Because $\alpha(\omega)$ is invariant under $\omega \rightarrow -\omega$, $i \rightarrow -i$, $\epsilon(\omega)$ is also. Further because $\alpha(\omega)$ is real and satisfies $\alpha(\omega) = \alpha(-\omega)$ on the imaginary ω axis, $\epsilon(\omega)$ also does so

† cf. I (4.4) and I (4.18), and II (4a) and II (4b).

there. Thus in the weak c.d.c.a.

$$\epsilon(i\eta) = \epsilon(-i\eta) \qquad \text{for all } real \ \eta. \tag{3.10}$$

This result is essential to the argument of the following §4. It does not hold if the ω-dependence of the tensors **F** is included.

There is a less artificial procedure for introducing a complex dielectric constant $\epsilon(\omega)$. This is a natural physically based approximation in the microscopic theory, which retains outgoing boundary conditions, does not affect (3.4) and (3.5), and makes $\epsilon(\omega)$ complex. We observe from III (2.3) (or more immediately from I (2.8a)) that

$$\mathbf{F}(\mathbf{r}, \omega) \sim \{\nabla\nabla r^{-1} + r^{-3}\mathrm{O}(k_0{}^2 r^2)\} + ik_0{}^3\{\tfrac{2}{3}\mathbf{U} + \mathrm{O}(k_0{}^2 r^2)\}.$$

The approximation we use is therefore to replace $\mathbf{F}(\mathbf{r}, \omega)$ by

$$\mathbf{F}(\mathbf{r}, \omega) \simeq \nabla\nabla r^{-1} + \tfrac{2}{3}ik_0{}^3\mathbf{U} \tag{3.11}$$

at every place in $J_{\mathrm{t},l}(0, \omega)$: equations (3.4) and (3.5) still hold. It is *this* approximation we call the complex dielectric constant approximation proper (the c.d.c.a.). It appears to be the essential approximation in relating the microscopic optical scattering theory to phenomenological scattering theory (Bullough *et al.* 1968 and Bullough and Hynne 1968): it contains within it but is less drastic than both the weak c.d.c.a.† and our interpretation of the long-wavelength virtual photon approximation for the free energy of Dzyaloshinskii *et al.* (1961); so it is most plainly an important physical approximation of the microscopic theory.

Because the ω-dependent term in (3.11) is odd in ω the relation (3.10) valid in the weak c.d.c.a. does not hold in the c.d.c.a. itself. This is associated with the fact that the c.d.c.a. retains most of the external optical scattering whilst the weak c.d.c.a. does not. Thus the c.d.c.a. will describe external scattering processes in the response functions; but the weak c.d.c.a. should be a nearer approach to a normal-mode theory and be important in a binding energy theory: this argument is consistent with that of the following §4 although it is in fact possible to use **F** itself in the dielectric constants $\epsilon_{l,t}(\mathbf{k}, \omega)$ and compute from these a binding energy as we showed in II. In this §3 we now develop the response theory based on the approximation (3.11) of the c.d.c.a. itself.

In the c.d.c.a. (3.2) is

$$4\pi n\mathbf{P}(\mathbf{k}, \omega) = \{\epsilon(\omega) - 1\}\left\{\frac{\hat{k}\hat{k}}{\epsilon(\omega)} + \left(\frac{k^2 - k_0{}^2}{k^2 - \epsilon(\omega)k_0{}^2}\right)(\mathbf{U} -)\hat{k}\hat{k}\right\} . \mathbf{E}(\mathbf{k}, \omega) \tag{3.12}$$

with (3.5) valid. An interesting identity which is useful in later work‡ is

$$\frac{(\mathbf{U} -)\hat{k}\hat{k}k_0{}^2}{k^2 - \epsilon_{\mathrm{t}}(\mathbf{k}, \omega)k_0{}^2} = \frac{1}{\epsilon_{\mathrm{t}}(\mathbf{k}, \omega)}\left\{\frac{\epsilon_{\mathrm{t}}(\mathbf{k}, \omega)k_0{}^2\mathbf{U} - \mathbf{k}\mathbf{k}}{k^2 - \epsilon_{\mathrm{t}}(\mathbf{k}, \omega)k_0{}^2} + \hat{k}\hat{k}\right\} \tag{3.13a}$$

$$\sim \frac{1}{\epsilon(\omega)}\left\{\frac{\epsilon(\omega)k_0{}^2\mathbf{U} - \mathbf{k}\mathbf{k}}{k^2 - \epsilon(\omega)k_0{}^2} + \hat{k}\hat{k}\right\}. \tag{3.13b}$$

By using the approximate form (3.13b) of the identity (3.13a) the response relation

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† Although the weak c.d.c.a. is a more drastic, i.e. stronger approximation than the c.d.c.a. itself, it is a weaker result: hence the nomenclature.

‡ See already the screened binding energy results II (12) and II (14) which depend on (3.13b).

(3.12) can be put in the form

$$4\pi n P(k, \omega) = \{\epsilon(\omega) - 1\} \left[\frac{\hat{k}\hat{k}}{\epsilon(\omega)} \frac{k^2}{k_0^2} + \frac{(k^2 - k_0^2)}{k_0^2 \epsilon(\omega)} \frac{\{\epsilon(\omega)k_0^2 \mathbf{U} - kk\}}{\{k^2 - \epsilon(\omega)k_0^2\}} \right] . E(k, \omega). \qquad (3.14)$$

Since we are considering the virtual response we can ignore all contributions from the surface of V. In this case the following Fourier transforms hold:

$$\frac{-4\pi \hat{k}\hat{k}}{\epsilon(\omega)} \leftrightarrow \frac{1}{\epsilon(\omega)} \nabla\nabla \left(\frac{1}{r} \right) \qquad (3.15a)$$

$$\frac{4\pi}{\epsilon(\omega)} \left\{ \frac{\epsilon(\omega)k_0^2 \mathbf{U} - kk}{k^2 - \epsilon(\omega)k_0^2} \right\} \leftrightarrow \widetilde{\mathbf{F}}(r, \omega) \equiv \frac{1}{m_t^2(\omega)} \{\nabla\nabla + m_t^2(\omega)k_0^2 \mathbf{U}\}\{\exp(im_t(\omega)k_0 r)/r\} \qquad (3.15b)$$

$$\frac{\epsilon(\omega) - 1}{4\pi} \leftrightarrow \frac{\epsilon(\omega) - 1}{4\pi} \delta(r). \qquad (3.15c)$$

For (3.15b) we use (3.5): we then recognize a screened dipole photon propagator $\widetilde{\mathbf{F}}(r, \omega)$ which we have used in the theory of scattering from molecular fluids already and derived by other means (Bullough 1965, 1967). Implicitly we cut off both k and k_0 at radius l^{-1}: then for example the $\delta(r)$ have widths of the order of l corresponding to a resolving power of about l. Otherwise the response (3.15c) is a strictly *local* response.

From (3.15) the response relation (3.14) is

$$4\pi n P(x, \omega) = \frac{\epsilon(\omega) - 1}{4\pi k_0^2} \int_{\text{all space}} -(\nabla^2 + k_0^2)\widetilde{\mathbf{F}}(x, x'; \omega) . E(x', \omega) \, \mathrm{d}x'$$

$$- \left\{ \frac{\epsilon(\omega) - 1}{k_0^2 \epsilon(\omega)} \right\} \nabla\nabla . E(x, \omega). \qquad (3.16)$$

Since, when (3.5) holds,

$$-(\nabla^2 + k_0^2)\widetilde{\mathbf{F}}(x, x'; \omega) = k_0^2\{\epsilon(\omega) - 1\}\widetilde{\mathbf{F}} + 4\pi\epsilon^{-1}(\nabla\nabla + \epsilon k_0^2 \mathbf{U})\delta(x - x') \qquad (3.17)$$

we can reduce (3.16) to the very striking form†

$$n P(x, \omega) = \left\{ \frac{\epsilon(\omega) - 1}{4\pi} \right\} \left[E(x, \omega) + \int_{\text{all space}} \widetilde{\mathbf{F}}(x, x'; \omega) . \left\{ \frac{\epsilon(\omega) - 1}{4\pi} \right\} E(x', \omega) \, \mathrm{d}x' \right].$$

$$(3.18)$$

This is not an integral equation but it is nonetheless worth comparing it with the fundamental integral equation III (2.1) from which we started in the case when $g(r) \equiv 1$. (This is the integral equation of I (2.2).) By (3.3) correlation functions of all orders are now concealed in $\epsilon(\omega)$ and thus also in $\widetilde{\mathbf{F}}$.

A fundamental assumption of the argument is that all the relevant integrals exist; of course this is already implicitly assumed for the Fourier transforms (3.15a,b). However, tensor integrals of this type may exist only in the generalized function

† All integrals in the translationally invariant virtual-mode theory are over all space and we do not indicate this explicitly after (3.18).

sense of IV (4.8). In the present context we therefore write, for example,

$$\int \tilde{\mathbf{F}}(x, x'; \omega) \exp\{-i\mathbf{k} \cdot (x' - x)\} \, dx' = \int_{-v} \tilde{\mathbf{F}}(x, x'; \omega) \exp\{-i\mathbf{k} \cdot (x' - x)\} \, dx'$$

$$+ \int_v \tilde{\mathbf{F}}(x, x'; \omega) \exp\{-i\mathbf{k} \cdot (x' - x)\} \, dx'.$$

(3.19)

The first term on the right-hand side is

$$\frac{4\pi}{m_t^2} \frac{m_t^2 k_0^2 \mathbf{U} - \mathbf{k}\mathbf{k}}{k^2 - m_t^2 k_0^2} + \frac{4\pi}{3m_t^2} \mathbf{U}$$

(3.20)

when v is a small sphere about x. We interpret the second integral as in IV (4.8) by

$$\int_v \tilde{\mathbf{F}}(x, x'; \omega) \exp\{-i\mathbf{k} \cdot (x' - x)\} \, dx' = m_t^{-2} \int_v \nabla\nabla |x - x'| \, dx'$$

$$= -\frac{4\pi}{3m_t^2} \mathbf{U}$$

(3.21)

in the limit when the radius v tends to zero.

The rather beautiful result (3.18) has an obvious and immediate physical significance which tells us a great deal about the nature of the virtual response in the c.d.c.a. The strictly local macroscopic response function (3.15c) which can be most significantly exhibited in the form

$$\frac{\epsilon(\omega) - 1}{4\pi} \mathbf{U}\delta(x - x') \equiv \tilde{\mathbf{\Pi}}_0(x, x'; \omega) \qquad \text{(say)}$$

(3.22)

determines the response in density of dipole moment at the point x due to a field $E(x', \omega)$ at all points x' by the integral relation

$$nP_0(x, \omega) = \int \tilde{\mathbf{\Pi}}_0(x, x'; \omega) \cdot E(x', \omega) \, dx'.$$

(3.23)

However, in addition the dipoles $P_0(x', \omega)$ at all points x' radiate via the macroscopic screened dipole photon propagator $\tilde{\mathbf{F}}$ and enhance the field at x which stimulates the response function (3.22) there. The response function (3.22) is strictly local and translationally invariant; but the second, radiating term in (3.18) is *not* local even though it is still translationally invariant. Of course the consequences of the breakdown of translational invariance all lie in the real response which is omitted in the virtual-mode theory: the real response is certainly not local and nor is it translationally invariant.

The form (3.22) is directly comparable with the translationally invariant polarization propagator of Dzyaloshinskii *et al.* (compare e.g. AGD—pp. 259–60, equations (29.3) and (29.5)). We can identify $\tilde{\mathbf{\Pi}}_0(x, x'; \omega)$ as the local and translationally invariant part of the time Fourier transform of the retarded commutator polarization propagator of the coupled many-body system†

$$i\hbar^{-1} \langle\langle c|[r(x, t), r(x', t')]\theta(t - t')|c\rangle\rangle_{\text{av}}$$

(3.24)

† Compare equation (2.5) of I for the *free* molecule propagators; and see II, Bullough *et al.* (1968), and Obada and Bullough (1969) for other helpful comparisons.

in which $\theta(t)$ is the unit step function, $r(x, t)$ is the dipole density operator for the coupled system of fluid and field in Heisenberg representation, the states $|c\rangle$ are conveniently† states of the coupled system and $\langle \ldots \rangle_{\mathrm{av}}$ is an ensemble average which is a trace over these states $|c\rangle$. This function coincides‡ with the thermal Green function of Dzyaloshinskii *et al.* at the set of points $i\omega_\nu = 2\pi\nu i k_{\mathrm{B}} T \hbar^{-1}$ on the imaginary axis in the ω plane: ν is an integer (AGD, e.g. equations (28.11) and (28.12) and §17) and k_{B} is Boltzmann's constant. The identification (3.24) also establishes a link with the microscopic theory as reported in II and elsewhere. We now show that (3.18) is identical with Dzyaloshinskii's integral equation and thus establish the equivalence of the c.d.c.a. to the long-wavelength (virtual) photon approximation of these authors.

Equation (3.18) can be written in the form

$$nP(x, \omega) = \int \mathbf{\Pi}(x, x'; \omega) . E(x', \omega) \, dx'. \tag{3.25}$$

If (3.18) is true for arbitrary E then it is equivalent to the translationally invariant expression

$$\mathbf{\Pi}(x, x'; \omega) = \tilde{\mathbf{\Pi}}_0(x, x'; \omega) + \int \int \tilde{\mathbf{\Pi}}_0(x, x''; \omega) . \tilde{\mathbf{F}}(x'', x'''; \omega) . \tilde{\mathbf{\Pi}}_0(x''', x'; \omega) \, dx'' \, dx'''. \tag{3.26}$$

The Fourier transform of (3.25) is the Fourier transform of (3.18) which is (3.12). By manipulating this Fourier transform the following identity can be established:

$$\int \mathbf{\Pi}(x, x''; \omega) . \mathbf{F}(x'', x'; \omega) \, dx'' = \int \mathbf{F}(x, x''; \omega) . \mathbf{\Pi}(x'', x') \, dx''$$

$$= \int \tilde{\mathbf{F}}(x, x''; \omega) . \tilde{\mathbf{\Pi}}_0(x'', x'; \omega) \, dx''. \tag{3.27}$$

This result is obviously of interest in the interpretation of the non-local response in (3.18). If we contract (3.26) with the tensor $\mathbf{F}(x, x'; \omega)$ (the *free*-field propagator) and integrate so that we can use (3.27) and if we then formally 'cancel' a factor $\tilde{\mathbf{\Pi}}_0$ we get

$$\tilde{\mathbf{F}}(x, x'; \omega) = \mathbf{F}(x, x'; \omega) + \int \int \mathbf{F}(x, x''; \omega) . \tilde{\mathbf{\Pi}}_0(x'', x'''; \omega) . \tilde{\mathbf{F}}(x''', x'; \omega) \, dx'' \, dx'''. \tag{3.28}$$

With (3.22) and the identification of the thermal and time-dependent Green functions‡ (3.28) is exactly the translationally invariant form of the integral equation§ of Dzyaloshinskii *et al.* (AGD—p. 259 equation (29.2)‖). It may easily be checked as an *identity* by Fourier transformation using (3.22) and (3.15*b*).

Equations (3.28) and (3.22) establish the equivalence of the virtual-mode theory in the c.d.c.a. with the translationally invariant form of the long-wavelength virtual photon approximation of Dzyaloshinskii *et al.* This is the main point of the arguments

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† The trace is independent of the representation: the precise form (3.24) is not.

‡ The thermal Green function $\mathscr{G}_{\mathrm{T}}(\omega_\nu)$ is identical with the retarded commutator Green function $\mathscr{G}(i|\omega_\nu|)$.

§ Equation (3.28) is an integral equation for $\tilde{\mathbf{F}}$ when $\tilde{\mathbf{\Pi}}_0$ is determined: in the c.d.c.a. $\tilde{\mathbf{\Pi}}_0$ can be evaluated from (3.3) with (3.11) and $\tilde{\mathbf{F}}$ is then completely determined by (3.15*b*).

‖ Dzyaloshinskii *et al.* (and AGD) work in the gauge in which $\phi = 0$.

of this section although we are concerned also to examine the physical content of the virtual-mode theory and to introduce both the c.d.c.a. and the still more approximate 'weak c.d.c.a.' In assessing this connection (3.28) between the work of Dzyaloshinskii *et al.* and the microscopic theory we should again remember the point noted in §1: the Dzyaloshinskii theory starts from an operator form of the Maxwell phenomenological equations (AGD—p. 251): the microscopic theory of our papers I–IV starts from the microscopic integral equation III (2.1). Although this integral equation is a classical one it will be derived by microscopic arguments from the quantal theory later in this series (see II). It is nowhere phenomenological.

We shall now investigate the free energy according to the virtual-mode theory in the *weak* c.d.c.a. adopting the prescription for the free energy given by Dzyaloshinskii *et al.* (AGD—p. 262): there are difficulties in doing this within the c.d.c.a. itself. Equation (3.28) valid in the c.d.c.a. is also necessarily valid in the weak c.d.c.a. and it still conceals microscopic thermal fluctuations to all orders since, by (3.7), (3.22) does. Although (3.28) is then a correct macroscopic description of the dipole response of a molecular fluid within the virtual-mode theory in the weak c.d.c.a., and although this theory coincides with the Maxwell phenomenological theory as our paper III has shown, we shall find that the Dzyaloshinskii semi-phenomenological prescription for finding the free energy coincides with the microscopic theory reported in II only if both theories neglect the important contributions of the microscopic thermal fluctuations to the free energy of the fluid.†

4. Semi-phenomenological free energy theory

We take the expression of Abrikosov *et al.* (AGD—p. 262, equation (30.1)) for the free energy F of the molecular fluid. In our notation (and choice of electromagnetic gauge) this free energy is the sum of a short range part F_0 and an infinite series of 'closed-loop' expressions like this one at order two:

$$-\tfrac{1}{2}k_B T \operatorname{Tr}\left\{\tfrac{1}{2}\sum_{\nu=-\infty}^{\infty}\int\int\int\int \tilde{\mathbf{\Pi}}_0(x,x';\mathrm{i}|\omega_\nu|)\,.\,\mathbf{F}(x',x'';\mathrm{i}|\omega_\nu|)\,.\,\tilde{\mathbf{\Pi}}_0(x'',x''';\mathrm{i}|\omega_\nu|)\right.$$

$$\left.\,.\,\mathbf{F}(x''',x;\mathrm{i}|\omega_\nu|)\,\mathrm{d}x'''\,\mathrm{d}x''\,\mathrm{d}x'\,\mathrm{d}x\right\}. \quad (4.1)$$

Each successive term introduces an extra $\tilde{\mathbf{\Pi}}_0$. $\mathbf{F}$ in the integrated loop and replaces the factor $+\tfrac{1}{2}$ by $1/\zeta$ where ζ is the number of such terms in the loop.

In the translationally invariant case the terms of the series simplify considerably. For example in (4.1) we can integrate out the δ-functions in the now local response $\tilde{\mathbf{\Pi}}_0$ and then we can Fourier transform on x–x' etc. to get

$$-\tfrac{1}{2}k_B T V \operatorname{Tr}\left\{\tfrac{1}{2}\sum_{\nu=-\infty}^{\infty}\{\epsilon(\mathrm{i}|\omega_\nu|)-1\}^2\frac{1}{(2\pi)^3}\int\left(\frac{-k_\nu^2\mathbf{U}-\mathbf{kk}}{k^2+k_\nu^2}\right)^2\mathrm{d}k\right\}. \quad (4.2)$$

We write $k_\nu \equiv \omega_\nu c^{-1}$, and recall that $\omega_\nu \equiv 2\pi\nu k_B T\hbar^{-1}$. The factor of volume V appears in the translationally invariant case because in this case only relative coordinates appear in the integrals like (4.1). Then there is always one 'spare' integration. Expressions like (4.2) will give the correct contributions to the free energy per

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† The semi-phenomenological theory has the advantage over the virtual-mode theory that it is not restricted to translationally invariant systems: we believe that the microscopic theory need not be restricted to these either—as long as we include the complicated surface-dependent real response.

unit volume after dividing by V and setting $V \to \infty$. This is why the binding free energy can actually be very insensitive to surface effects even though the arguments of III and IV show that the response theory certainly is not.

It is clear from the example of (4.1) and (4.2) and the prescription of AGD for the total free energy from long-wavelength virtual photons $\Delta F \equiv F - F_0$ that this is now

$$\Delta F = -\tfrac{1}{2}k_{\mathrm{B}}TV \int \frac{\mathrm{d}k}{(2\pi)^3} \left[\sum_{\nu = -\infty}^{\infty} 2 \ln\{1 + (\epsilon(\mathrm{i}|\omega_\nu|) - 1)k_\nu^2(k^2 + k_\nu^2)^{-1}\} \right.$$

$$\left. + \sum_{\nu = -\infty}^{\infty} \ln\{1 + (\epsilon(\mathrm{i}|\omega_\nu|) - 1)\} \right] \tag{4.3a}$$

$$= -\tfrac{1}{2}k_{\mathrm{B}}TV \int \frac{\mathrm{d}k}{(2\pi)^3} \left[\sum_{\nu = -\infty}^{\infty} \ln \det \left\| \mathbf{U} - \frac{\{\epsilon(\mathrm{i}|\omega_\nu|) - 1\}\mathbf{U}}{4\pi} \cdot \frac{(-k_\nu^2\mathbf{U} - kk)4\pi}{(k^2 + k_\nu^2)} \right\| \right]. \tag{4.3b}$$

For this result we most conveniently split the tensor propagators into longitudinal and transverse components and use $(\hat{k}\hat{k})^\varsigma = \hat{k}\hat{k}$ with trace unity whilst $(\mathbf{U} - \hat{k}\hat{k})^\varsigma = (\mathbf{U} - \hat{k}\hat{k})$ has trace two: the tensors $(\mathbf{U} - \hat{k}\hat{k})$ and $\hat{k}\hat{k}$ are of course orthogonal, i.e. $(\mathbf{U} - \hat{k}\hat{k})$ $.\hat{k}\hat{k} = \mathbf{0}$, the zero tensor.

If $\epsilon(\mathrm{i}|\omega_\nu|) - 1$ is defined only at the points $\mathrm{i}|\omega_\nu|$ there may be difficulties in finding the analytic continuation of that set of quantities (AGD—§17). In our case there is no problem. For $\epsilon(\mathrm{i}|\omega_\nu|)$ can be continued as $\epsilon(\omega)$ in the upper half ω plane and, even in the c.d.c.a. itself, $\epsilon(\omega)$ is defined there by (3.3), or by (3.5) and the dispersion relation of III (2.5b) for $m_{\mathrm{t}}^2(\omega)$ taken in the same approximation. Then for the same reasons $\epsilon(\mathrm{i}|\omega_\nu|)$ can be continued in the lower half ω plane as $\epsilon(-\omega)$.

An important point now is that although $\epsilon(\omega)$ and $\epsilon(-\omega)$ do not coincide across the real ω axis in the c.d.c.a. itself, they do coincide in the *weak* c.d.c.a.† This is why we shall now choose to work in the *weak* form of the approximation.

The continuation of the photon propagator $4\pi(-k_\nu^2\mathbf{U} - kk)(k^2 - k_\nu^2)^{-1}$ is defined from all the points $\mathrm{i}\omega_\nu$ by $4\pi(k_0^2\mathbf{U} - kk)(k^2 - k_0^2)^{-1}$ over the whole ω plane. Thus the continuation of the integrand in (4.3b) is defined over the whole ω plane and we can replace (4.3b) by the integral expression

$$\Delta F = -\frac{\hbar V}{4\pi \mathrm{i}} \int \frac{\mathrm{d}k}{(2\pi)^3} \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \{\ln \det\|\mathbf{D}(\omega)\|\} \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \mathrm{d}\omega \tag{4.4a}$$

in which

$$\mathbf{D}(\omega) \equiv \mathbf{U} - \frac{\epsilon(\omega) - 1}{4\pi}\mathbf{U} \cdot \frac{4\pi(k_0^2\mathbf{U} - kk)}{k^2 - k_0^2}; \tag{4.4b}$$

$k_0 = \omega c^{-1}$ as usual, and the contour leaves all poles of $\coth(\hbar\omega/2k_{\mathrm{B}}T)$ on the left.

Notice that we have appealed to the weak form of the c.d.c.a. in order that $\epsilon(\omega)$ can be defined, by (3.7), over the whole of the ω plane. The result (4.4a) is a consequence of the AGD prescription in the weak c.d.c.a. and is apparently equivalent to it only in this or in any still weaker approximation. Indeed there are formidable additional difficulties in applying the c.d.c.a. approximation (3.11) to the tensor $\mathbf{F}(r, \omega)$ at large values of $|\omega|$ for the imaginary term becomes very large there; and

† On the real axis ω is real and is not to be interpreted as $(\omega \pm \mathrm{i}\delta)$ now.

these are not removed, even if they change in character, if we use $\mathbf{F}(r, \omega)$ itself. But as II shows these difficulties are connected with the well-known ultraviolet divergences of quantum electrodynamics. We would not expect a long-wavelength virtual photon theory to be concerned with these since they are associated with distances of the order of the Compton wavelength of the electron ($\sim 2.4 \times 10^{-10}$ cm) and shorter; implicitly they are concealed in the short-range contribution to the free energy F_0. These remarks indicate that the *weak* c.d.c.a. is the proper approximation for comparison with the semi-phenomenological theory of free energy due to Dzyaloshinskii *et al.* and its formulation as the AGD prescription (4.1).

The weak c.d.c.a. has the important property that†

$$\epsilon(\omega) - 1 \sim O(|\omega|^{-2}) \qquad \text{as} \qquad |\omega| \to \infty. \qquad (4.5)$$

From this it follows that

$$\mathbf{D}(\omega) \sim (\mathbf{U} - \hat{k}\hat{k})\{1 + O(|\omega|^{-2})\} + \hat{k}\hat{k}\{1 + O(|\omega|^{-2})\}$$

and

$$\det \mathbf{D}(\omega) \sim 1 + O(|\omega|^{-2}) \qquad \text{as} \qquad |\omega| \to \infty. \qquad (4.6)$$

We can now express (4.4*a*) in the form

$$\Delta F = \frac{\hbar V}{4\pi \mathrm{i}} \int \frac{\mathrm{d}k}{(2\pi)^3} \left[\left(\frac{2k_\mathrm{B}T}{\hbar}\right) \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \ln \sinh \left(\frac{\hbar\omega}{2k_\mathrm{B}T}\right) \left[\left\{\frac{\mathrm{d}}{\mathrm{d}\omega} \det \mathbf{D}(\omega)\right\} \{\det \mathbf{D}(\omega)\}^{-1} \right] \mathrm{d}\omega \right] \qquad (4.7)$$

by using (4.6) and one integration by parts: although the coth and sinh functions are not bounded on the imaginary ω axis, (4.6) permits a shift of the contour into the right half ω plane. The same property also means that the inner square bracket in (4.7) is $O(|\omega|^{-3})$ as $|\omega| \to \infty$ whilst $\ln \sinh (\hbar\omega/2k_\mathrm{B}T) \sim O(|\omega|)$. This now means that the contour in (4.7) can be replaced by a simple closed contour in the right half ω plane which embraces all the singularities of the inner square bracket there. The cuts from the $\ln \sinh (\hbar\omega/2k_\mathrm{B}T)$ function can be connected outside this contour.

Before explicitly evaluating this integral in the ω plane in (4.7) it will be helpful for a later comparison with the details of the comparable argument in the microscopic theory already reported in II to display (4.7) in a second slightly different form. An important property of the $\epsilon_{l,\mathrm{t}}(k, \omega)$ is that they are invariant under $\omega \to -\omega$, $\mathrm{i} \to -\mathrm{i}$. This important property will be discussed in detail later but it is intuitively an obvious consequence of the choice of outgoing boundary conditions on the free field Green function $\mathbf{F}$ in the fundamental integral equation III (2.1). Because of this property which must then apply also to $\epsilon(\omega)$ in the c.d.c.a. or in any weaker form of this approximation it follows that on the real ω axis $\mathbf{D}(-\omega) = \mathbf{D}^*(\omega)$ where * denotes complex conjugate: the singularities of $\mathbf{D}(\omega)$ lie in the lower half ω plane and those of the function $\mathbf{D}^*(\omega)$ which is the analytic continuation of $\mathbf{D}^*(\omega)$ the complex conjugate of $\mathbf{D}(\omega)$ on the real ω axis lie in the upper half plane, and in the weak c.d.c.a. in particular ω is to be interpreted as $(\omega + \mathrm{i}\delta)$ in $\mathbf{D}(\omega)$. It then follows that (4.7) can be

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† Providing we ignore the continuum of ionization levels in the polarizabilities $\alpha(\omega)$: these introduce cuts below the real ω axis as the singularities of $\alpha(\omega)$, but because the $J_{l,\mathrm{t}}(0, \omega)$ are infinite series in the $\alpha(\omega)$ the singularities would become more complicated. Thus we assume in fact that $\alpha(\omega) \sim O(|\omega|^{-2})$ as $|\omega| \to \infty$: then (4.5) follows.

written in the alternative form

$$\Delta F = \frac{\hbar V}{4\pi i} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[\left(\frac{2k_B T}{\hbar} \right) \int_{0+}^{\infty} \ln \left\{ \sinh \frac{\hbar \omega}{2k_B T} \right\} \left[\left\{ \frac{d}{d\omega} \det \mathbf{D}(\omega) \right\} \{ \det \mathbf{D}(\omega) \}^{-1} \right. \right.$$

$$\left. \left. - \left\{ \frac{d}{d\omega} \det \mathbf{D}^*(\omega) \right\} \{ \det \mathbf{D}^*(\omega) \}^{-1} \right] d\omega. \right] \tag{4.8}$$

This form is plainly more comparable with some of the expressions quoted for ΔF in II than is (4.17). (And see also Bullough and Obada 1969 a,b). We now return to (4.7) and evaluate it.†

The singularities of the inner square bracket in (4.7) occur at both the zeros and the singularities of det $\mathbf{D}$. To determine these we examine the solution of the integral equation (3.29) for the screened photon propagator $\tilde{\mathbf{F}}$. By Fourier transformation on $\mathbf{x} - \mathbf{x}'$ we find (in obvious notation for the Fourier transform)

$$\tilde{\mathbf{F}}(\mathbf{k}, \omega) = \mathbf{F}(\mathbf{k}, \omega) \cdot \left\{ \mathbf{U} - \left(\frac{\epsilon(\omega) - 1}{4\pi} \right) \mathbf{F}(\mathbf{k}, \omega) \right\}^{-1}$$

$$= 4\pi \left(\frac{k_0^2 \mathbf{U} - \mathbf{k}\mathbf{k}}{k^2 - k_0^2} \right) \cdot \{ \mathbf{D}(\omega) \}^{-1}. \tag{4.9}$$

From this it follows that the zeros of det $\mathbf{D}$ occur at the poles of det $\| \tilde{\mathbf{F}}(\mathbf{k}, \omega) \|$ and at the zeros of det $\| \mathbf{F}(\mathbf{k}, \omega) \| = \det \| 4\pi (k_0^2 \mathbf{U} - \mathbf{k}\mathbf{k})(k^2 - k_0^2)^{-1} \|$ whilst the singularities of $\mathbf{D}$ are poles at the poles of det $\| \mathbf{F}(\mathbf{k}, \omega) \|$ and the zeros of det $\| \tilde{\mathbf{F}}(\mathbf{k}, \omega) \|$.

Since

$$\det \| \tilde{\mathbf{F}}(\mathbf{k}, \omega) \| = \det \left\| \frac{4\pi}{\epsilon(\omega)} \left\{ \frac{\epsilon(\omega) k_0^2 \mathbf{U} - \mathbf{k}\mathbf{k}}{k^2 - \epsilon(\omega) k_0^2} \right\} \right\|$$

$$= -(4\pi)^3 k_0^4 [\epsilon(\omega) \{ k^2 - \epsilon(\omega) k_0^2 \}^2]^{-1} \tag{4.10a}$$

it has zeros at the poles‡ of $\epsilon(\omega)$ and poles at the roots of

$$k^2 k_0^{-2} = \epsilon(\omega) \quad \text{and} \quad \epsilon(\omega) = 0. \tag{4.10b}$$

Likewise

$$\det \| \mathbf{F}(\mathbf{k}, \omega) \| = -(4\pi)^3 k_0^4 (k^2 - k_0^2)^{-2} \tag{4.11a}$$

with poles at the roots of

$$k = k_0 \tag{4.11b}$$

and no zeros.

† To the author's knowledge an argument comparable with that from (4.7) to (4.14) below was first given in a similar context by McLachlan et al. (1963): this paper constitutes a beautiful exposition of the significance of equivalent oscillators in the intermolecular potential. Mahan (1965) pursues the reverse of our argument and uses the zero-point energies of oscillators equivalent to the free and Coulomb-coupled excitons of a molecular crystal to compute its binding energy. Comparable work has been reported by Nijboer and Renne (1968). Bullough and Obada (1969 a,b) report a fundamental justification of Mahan's work valid in the p.d.a. but also handle the radiation field. Bullough and Thompson (1970) show how to generalize Mahan's argument to include the radiation field by including the Umklapp processes for that field.

‡ Provided $\epsilon(\omega)$ has no other singularities but poles. We have omitted cuts for large $|\omega|$ but since the $J_{l,t}(k, \omega)$ are infinite series in $\alpha(\omega)$ even in the weak c.d.c.a. we cannot expect that this is actually so. We therefore assume that $\epsilon(\omega)$ is well approximated by a function whose singularities are nothing but poles and consider this rather than $\epsilon(\omega)$ itself.

The first equation in (4.10b) is exactly the dispersion relation for transverse normal modes in the weak c.d.c.a.†: the second equation in (4.10b) is just the dispersion relation for longitudinal normal modes in the weak c.d.c.a. We denote the transverse roots by $w_s^{(t)}(k)$ and the longitudinal roots by $w_s^{(l)}(k)$ (even though the latter do not depend on k): we denote the poles of $\epsilon(\omega) - 1$ by ω_s (simply) and these do not depend on k.

If we apply this notation and analysis to (4.7) it now takes the form

$$\Delta F = \tfrac{1}{2}\hbar V \int \frac{\mathrm{d}k}{(2\pi)^3} \left(\frac{2k_B T}{\hbar}\right) \left[2\sum_s \ln \Xi\{w_s^{(t)}(k)\} + \sum_s \ln \Xi\{w_s^{(l)}(k)\} \right.$$
$$\left. - 3\sum_s \ln \Xi(\omega_s) - 2\ln \Xi(ck) \right] \tag{4.12}$$

in which

$$\Xi(x) = 2\sinh(\hbar x/2k_B T).$$

If we observe that

$$\ln \Xi(x) = (\hbar x/2k_B T) + \ln\{1 - \exp(-\hbar x/k_B T)\}$$
$$\equiv (\hbar x/2k_B T) - \ln Z(x) \qquad \text{(say)} \tag{4.13}$$

we have finally that the free energy per unit volume of the molecular fluid is‡

$$V^{-1}\Delta F = \int \frac{\mathrm{d}k}{(2\pi)^3} \left[\tfrac{1}{2}\hbar\{2\sum_s w_s^{(t)}(k) + \sum_s w_s^{(l)}(k) - 3\sum_s \omega_s - 2ck\}\right]$$

$$- \int \frac{\mathrm{d}k}{(2\pi)^3}\left[k_B T \left[2\sum_s \ln Z\{w_s^{(t)}(k)\} + \sum_s \ln Z\{w_s^{(l)}(k)\} - 3\sum_s \ln Z(\omega_s) \right. \right.$$

$$\left. \left. - 2\ln Z(ck)\right]\right]. \tag{4.14}$$

Equation (4.14) is the striking result that the free energy of the molecular fluid is the difference between the free energies of two sets of oscillators. The first set of oscillators is exactly those of the dielectric in the c.d.c.a.: indeed they are just the quantized oscillators we would associate with the normal electromagnetic modes of the virtual-mode theory according to the discussion of that theory in IV §§2 and 4. The second set of oscillators is a combination of the oscillators of the free radiation field and of the *excitations* of the dielectric when it is not coupled to the radiation field.

The conclusion from (4.14) therefore is that in broad terms the prescription (4.1) for the free energy together with the assumption of the weak c.d.c.a. for $\epsilon_t(k, \omega)$ and

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† We show in IV §2 that these are normal-mode dispersion relations in the virtual-mode theory which coincide with the dispersion relations for the real modes in the total response theory.

‡ Since $w_s^{(t)}(k) \sim ck$ for large k it is possible that the transverse contribution is convergent: since $w_s^{(l)}(k)$ and ω_s do not depend on k the integrand is at most O(1) for large k. Since we are concerned with a long-wavelength theory we can ensure convergence by cutting off k at (say) a reciprocal molecular radius.

$\epsilon_l(\mathbf{k}, \omega)$ is equivalent to the free energy change in coupling the material of the dielectric to the radiation field. At first sight this is an attractive conclusion since the assumption of the weak c.d.c.a. precisely means the elimination of the contribution of the radiation field to the dielectric constants. Further we see a reason why we should work in the *weak* c.d.c.a. rather than the c.d.c.a. itself: for that approximation excludes those terms which describe external scattering and these should be excluded from a normal-mode theory.

Unfortunately for this interpretation the singularities of the dielectric constants $\epsilon_{l,t}(\mathbf{k}, \omega)$ have no physical significance in the theory we developed in III and IV; and although we work in the weak c.d.c.a. for which (3.5) holds it is clear that in this virtual-mode theory $\epsilon(\omega)$ must be an approximation to ϵ_t and ϵ_l. Moreover (4.14) does not agree with the results of the microscopic theory so far reported in II. In the case of the molecular fluid we have found as reported that the problem is complicated by the cluster integral series $J_{l,t}(\mathbf{k}, \omega)$ although expressions for the free energy could be obtained without appealing to either the weak c.d.c.a. or the c.d.c.a. itself. We found we could achieve a simple equivalent oscillator result like (4.14) (as equation II (22*b*)) by, and apparently *only by*, neglecting the $J_{l,t}(\mathbf{k}, \omega)$. This is in the continuum approximation of II §7, but then the $\hbar\omega_s$ are now energies of the *free* molecules coupled neither by the radiation field nor the Coulomb interaction.

The case of the molecular crystal is also instructive (Bullough and Obada 1969 a,b). There is no obvious reason why the Dzyaloshinskii prescription should not apply to the molecular crystal† and in the case of the rigid molecular crystal, which exhibits no density fluctuations even at a finite temperature, the result which has been reported is clear cut: we obtain (4.14) precisely but find that the energies $\hbar\omega_s$ are again those of the free molecules. Since the theory couples free molecules and free field the result is exactly the one to expect.‡

Now it is plain that (4.14) reduces to this particular result when but only when

$$m_t{}^2(\omega) - 1(= \epsilon(\omega) - 1) = 4\pi n\alpha(\omega). \qquad (4.15)$$

This result ignores the Lorentz field, the local field $J_{l,t}(0, \omega)$ and all the fluctuations which continue to contribute to the $J_{l,t}(0, \omega)$ (as $J(\omega)$ of (3.7) and (3.9)) even in the weak c.d.c.a. The treatment of the Lorentz field in binding-energy theory is a delicate question we can discuss when we come to develop the details of II later in this series. Except in this, the approximations and the result which (4.14) becomes with (4.15) coincide with the 'continuum approximation of II §7 and its results. The point here then is that the two theories for the molecular fluid agree when but only when both theories neglect the fluctuations described by the $J_{l,t}(\mathbf{k}, \omega)$.

We might note also the paradoxical consequences of the broad interpretation of (4.14) which couples the radiation field to the dielectric coupled by Coulomb interactions in the weak c.d.c.a.: the poor approximation to the dielectric constant which is (4.15) and which omits Coulomb interactions would therefore couple in both Coulomb interactions and the radiation field in (4.14) and, since the Coulomb

† In a long-wavelength prescription we should perhaps expect to ignore all the effects of crystal structure which are on the scale of angstroms: this seems to be precisely the point of (4.15).

‡ It can only be obtained by a thermal decorrelation scheme of the quantal theory analogous to the p.d.a.: decorrelation seems to be essential for an equivalent oscillator result like (4.14). Thus we should not expect it when we include all order intermolecular correlation by the $J_{l,t}(k, \omega)$ or $J(\omega)$.

interactions are numerically the most important part of the bulk binding, this poorer approximation would give the better estimate of the total bulk binding.

Another way of looking at the relation between (4.15) and (3.7) which is instructive is this. We are concerned in (4.14) with the excitations of $\epsilon(\omega)$ which in general are of quasi-particle type. If $\epsilon(\omega)$ in the weak c.d.c.a. expression (3.7) is meromorphic it can be written in the form (4.15) with $\alpha(\omega)$ actually replaced by a quasi-particle polarizability (Bullough 1968 b). Since $J(\omega)$ is an infinite series, $\epsilon(\omega)$ is not in general meromorphic, however, even when only a finite number of discrete energy levels contribute to $\alpha(\omega)$ and cuts from free-particle continuum levels are excluded. Quasi-particle arguments like this typify much of the very beautiful work of the Landau school: even so, and whether the quasi-particle picture is valid or not, we cannot justify the prescription we have used for ΔF in this §4 this way.

To see this consider the prescription based on terms like (4.1) when, for simplicity, $T = 0$. In this case (4.1) is (AGD—§17 p. 146)

$$- \frac{\hbar}{2\pi} \mathrm{Tr} \int_0^\infty \mathrm{d}\omega \tfrac{1}{2} \int \int \int \int \widetilde{\mathbf{\Pi}}_0(x, x'; i\omega) \,.\, \mathbf{F}(x', x''; i\omega) \,.\, \widetilde{\mathbf{\Pi}}_0(x'', x'''; i\omega)$$
$$. \, \mathbf{F}(x''', x; i\omega) \, \mathrm{d}x''' \, \mathrm{d}x'' \, \mathrm{d}x' \, \mathrm{d}x. \qquad (4.16)$$

At $T = 0$ the expression (4.15) for $\epsilon(\omega) - 1$ will not be changed since the fluctuations have been excluded. With this form for $\epsilon(\omega) - 1$ in the definition (3.22) of $\widetilde{\mathbf{\Pi}}_0$, (4.16) is

$$- \frac{\hbar}{2\pi} \mathrm{Tr} \int_0^\infty \mathrm{d}\omega \int_0^\infty 2 \frac{\mathrm{d}e'}{e'} \mathrm{Tr} \int \int \int \int \widetilde{\mathbf{\Pi}}_0(x, x'; i\omega) \,.\, \mathbf{F}(x', x''; i\omega) \,.\, \widetilde{\mathbf{\Pi}}_0(x'', x'''; i\omega)$$
$$. \, \mathbf{F}(x''', x; i\omega) \, \mathrm{d}x''' \, \mathrm{d}x'' \, \mathrm{d}x' \, \mathrm{d}x. \qquad (4.17)$$

We are treating $\widetilde{\mathbf{\Pi}}_0$ as a function of the coupling constant e' and are using the fact that (4.15) is linear in $(e')^2$. It is now clear that the succession of terms like (4.17) lose their factors ν^{-1} on integration over e' and constitute the iteration of†

$$\Delta E = - \frac{\hbar}{2\pi} \int_0^\infty 2 \frac{\mathrm{d}e'}{e'} \int_0^\infty \mathrm{d}\omega \mathrm{Tr} \int \int \widetilde{\mathbf{\Pi}}_0(x, x'; i\omega) \,.\, \widetilde{\mathbf{F}}(x', x; i\omega) \, \mathrm{d}x' \, \mathrm{d}x \qquad (4.18)$$

since $\widetilde{\mathbf{F}}$ satisfies (3.28). If we turn the contour in the ω plane, include an energy cut-off instead of the short-range contribution F_0, and perform one integration on x (since $\widetilde{\mathbf{\Pi}}$ and $\widetilde{\mathbf{F}}$ depend only on $x - x'$ in virtual-mode theory) we get exactly the equation (12b) of II. Now that equation is *exact* in virtual-mode theory and the c.d.c.a. However, it is clear that we get (4.18) here only because (4.15) is linear in $(e')^2$. Equation (3.7) is a very much more complicated function of $(e')^2$ because the fluctuations $J(\omega)$ depend on $\alpha(\omega)$ and $(e')^2$.

It is worth remarking here that (4.18) has an elegant interpretation. For this we need a generalized function interpretation we have used in the scattering theory (cf. Bullough *et al.* 1968, Bullough and Hynne 1968 and Bullough 1970 c) and will make much use of later in this series of papers. We write

$$\int \delta(x - x') \widetilde{\mathbf{F}}(x', x; i\omega) = \tfrac{2}{3}\omega^3 c^{-3} m_{\mathrm{t}}(i\omega) \mathbf{U} \qquad (4.19)$$

which on investigation proves to be precisely the convergent part of an otherwise divergent integral. The factor $m_{\mathrm{t}}(i\omega)$ is of interest here since it will not appear if the free-field propagator $\mathbf{F}$ is used instead of $\widetilde{\mathbf{F}}$. If $\mathbf{F}$ is used the right-hand side of (4.19) is

† ΔE and ΔF are the same at $T = 0$.

just the radiation reaction (Bullough *et al.* 1968 a,b) at complex frequency $i\omega$. Thus the right-hand side of (4.19) with the factor $m(i\omega)$ is the *screened* radiation reaction. Equation (4.19) in (4.18) enables us to express the binding energy ΔE in terms of $\epsilon(\omega) - 1$ and the screened radiation reaction.† However, whilst this elegant result is exact for virtual-mode theory in the c.d.c.a. it is equivalent to the prescription of this §4 for ΔE only if (4.15) holds.

We must observe also that in II (16) we exhibit a series analogous to the succession of terms like (4.1). The agreement is complete after decorrelation, restoration of the coth function of II (10), *and* appeal to the continuum approximation (4.15). Otherwise the series II (16) depends explicitly on the intermolecular correlation functions; and although these functions are partially an artefact of the Born–Oppenheimer approximation underlying the whole theory, some sort of fluctuation terms should appear.‡

It seems to follow from these several points that the prescription typified by (4.1) for ΔF really should be used with (4.15). If this is so we must conclude that the Dzyaloshinskii prescription is an instructive but rather crude prescription for the free energy which cannot give better than order-of-magnitude estimates. This raises the important question of whether or not the frequency-dependent dielectric constant, or the refractive index, is of itself sufficient to determine the long-range part of the free energy of a molecular fluid.

The answer to this question so far is that the transverse and longitudinal dispersion relations and their generalizations§ for all directions $\hat{k}$ determine the binding energy of the rigid molecular crystal (in the p.d.a.) once the energies of the free molecules are known: this is the result like (4.14) reported in Bullough and Obada (1969 b) valid for arbitrary $\hat{k}$. Then the refractive index does not seem to determine the free energy of the molecular fluid to better than a continuum approximation: this is the result II (22*b*) and again needs the free molecular energies. We noted in II that closed loop diagrams contributing to the binding energy appear explicitly in the expression for the refractive index but cannot be extracted from that quantity. These several points must be discussed in detail later.

The result (4.14) and the conclusions we derive from it are the main results of this paper V. We have also introduced the important complex dielectric constant approximation (c.d.c.a.) in §3 and demonstrated the equivalence of the virtual-mode theory of the response function in the c.d.c.a. to the translationally invariant form of the long-wavelength (virtual) photon approximation of Dzyaloshinskii *et al.* (1961). We were obliged to use the *weak* c.d.c.a. to reach (4.14): this neglects all contributions of the radiation field to the thermal fluctuations but retains the Coulomb interactions. Before this in §2 we showed that the whole virtual-mode theory, and indeed the whole response theory of III and IV, could be extended to a system of more than one component. This now completes our analysis based on the fundamental integral

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† The first-order Lamb shift of II (21) can be expressed in exactly the same way in terms of the free-particle polarizability $\alpha(\omega)$ and the unscreened radiation reaction. The details of the processes screening the radiation reaction are reported by Hynne (1970).

‡ Although equations (4.16)—(4.18) assume $T = 0$, this is a device to eliminate the coth $\hbar\omega/2k_BT$. It should not be taken to eliminate the fluctuations or the intermolecular correlation. If disorder of this type does not obtain, the dielectric constants are those of a crystal and our results for this (Bullough and Obada 1969 a,b) are applicable here.

§ It is not possible to consider merely transverse and longitudinal dispersion relations in the arbitrary crystal and not even in the cubic crystal for all k (Bullough and Obada 1969 a).

equation III (2.1) of the microscopic theory. In the final section of this paper we summarize the main results and conclusions of the three connected papers, III, IV and V.

5. Summary of main results and conclusions

The papers III, IV and V of this series on 'Many-body optics' are devoted in the first place to an exhaustive analysis of the solution of the fundamental integral equation of the many-body optical theory. This integral equation is the classical equation III (2.1) which will be justified by quantal theory later in this series. It was introduced and partially solved for transverse and longitudinal solutions in I: in order to show that these solutions and the associated dispersion relations derived in I were correct we still had to show that these results were compatible with the optical extinction theorem due in the first instance to Ewald (1912).

We do considerably more in the papers III, IV and V than show that all of the results of I are indeed consistent with this extinction theorem. We achieve a number of explicit formulae which describe electromagnetic processes in a molecular fluid in a much more general context that that of the introductory paper I. That paper was concerned only with the interaction of the system with light. Now we have considered the interaction of the system with an arbitrary externally imposed electromagnetic field and we have also considered the balance of the system when there is no external probe. In this summary we attempt a synthesis of the material we have examined so far and the conclusions we have reached: we do not follow the sequence of development adopted in the papers themselves for, because of the complication of the argument, each section of each paper is already summarized at the end of that particular section. This leaves us free to achieve the final synthesis here.

The simplest part of the theory is that part of it which deliberately ignores the optical extinction theorem. This is the 'virtual-mode theory' of IV §2. It is a translationally invariant theory with the usual structure of conventional linear response theory. In particular we can define (k, ω)-dependent transverse (t) and longitudinal (l) dielectric constants for an isotropic molecular fluid of one or more components. For a one-component system these take the form

$$\epsilon_{l,t}(k, \omega) - 1 = \frac{4\pi n \alpha(\omega)}{1 - \frac{4}{3}\pi n \alpha(\omega) - n\alpha(\omega)J_{l,t}(k, \omega)} \tag{5.1}$$

which mimics by intent the form of the dispersion relation I (4.11a) for the transverse refractive index $m_t(\omega)$. The $J_{l,t}$ are complicated expansions in terms of cluster integrals. They may be interpreted as intermolecular multiple scattering processes and are implicitly obtained to all orders: the structure and properties of this series will be discussed later. The result (5.1) and some discussion of the $J_{l,t}$ appears already in II.

In terms of these dielectric constants the longitudinal response function in dipole density is (see III 3.15)

$$\frac{\delta n P_l(k, \omega)}{\delta E_l(k, \omega)} = \left(\frac{1}{4\pi}\right)\left(1 - \frac{1}{\epsilon_l(k, \omega)}\right)\hat{k}\hat{k} \tag{5.2a}$$

and the transverse response is (see IV (2.8))

$$\frac{\delta n P_t(k, \omega)}{\delta E_t(k, \omega)} = \frac{(k^2 - k_0{}^2)(\mathbf{U} - \hat{k}\hat{k})}{k^2 - \epsilon_t(k, \omega)k_0{}^2}\left\{\frac{\epsilon_t(k, \omega) - 1}{4\pi}\right\}. \tag{5.2b}$$

The response functions have the two dispersion relations of I as their surfaces of singularity: in simplest form these surfaces are poles for fixed k but can be more complicated singularities. The form of the response functions does not change as the number of components changes: the formulae for $\epsilon_{l,t}(k, \omega)$ do change (see V—§2). The longitudinal response function takes the form due to Nozières and Pines (1958), for example, but it is new for the molecular fluid: we believe that even the form of (5.2b) for the transverse response is new and it is certainly new for the molecular fluid.

The dispersion relations could be taken to be normal-mode dispersion relations within this virtual-mode theory: this is the usual interpretation. But already this may not be a consistent interpretation since the boundary conditions are outgoing and the wave vectors of these 'normal modes' are complex due to external scattering. We do not consider the delicate problem of external scattering in the papers III, IV and V: it will be considered later. The big problem of the virtual-mode theory however is that (5.2b) vanishes when $k = k_0 \equiv \omega c^{-1}$: thus although the virtual-mode theory is a linear response theory it does not include the response to externally imposed light. This problem has not been considered before in linear response theory.

When the probe is light the theory of the integral equation is exactly that developed but not completed in I; and the solution to the difficulty is exactly contained in the optical extinction theorem. We analyse the integral equation, which is the expression of this theorem, when the probe is light and the fluid occupies an infinite slab-like region V of finite width. We find that light couples to the system through the surface: a surface is therefore an essential feature of the region V which accordingly must be finite. We find that the integral equation of the optical extinction theorem is exactly the missing linear response relation: we exhibit it as such in III (2.15) in the particular case when the wave vector direction $\hat{k}$ is along the axis of the slab. It displays all the features of macroscopic Maxwell theory but we assume no surface boundary conditions: again the boundary conditions are outgoing conditions at infinity. The generalization in IV §3 to the case of $\hat{k}$ oblique to the slab axis also confirms the Maxwell theory. This important result shows that all of the optical response, whether there is absorption inside V or external scattering or reflection outside V, is described by a total response function depending only on the frequency ω, the surface geometry, and the transverse refractive index $m_t(\omega)$.

The analysis further shows that the transverse solutions proposed in I are correct solutions of the fundamental integral equation: the transverse dispersion relation which coincides with the singular surfaces of $\epsilon_t(k, \omega)$ in (5.1) is now associated with a linear response theory and not a normal-mode theory. A single mode of light of amplitude E, energy $\hbar\omega$ and wave number $k_0 = \omega c^{-1}$ induces two modes, one forward-going the other backward-going inside V. The linear response which is the extinction theorem fixes the amplitudes of these two modes uniquely. Comparable analysis shows further that the longitudinal dispersion relation is correct, and indeed that with $\hat{k}$ along the axis of V the longitudinal modes are normal modes: this is so because the extinction theorem vanishes in this geometry. When $\hat{k}$ is oblique the extinction theorem does not disappear. Then we find that the longitudinal modes of I can run if, but only if, they are balanced by an external transverse free field (light) outside the system. This seems to mean that the longitudinal modes can be excited by light and constitute the linear response to this. The relationship between the singular case of $\hat{k}$ axial and the case of $\hat{k}$ oblique in V is not clear however: nor is the process of energy transport across the surface in the oblique case.

Whilst this analysis otherwise wholly established the validity of the results of I it poses the awkward problem of making itself compatible with the virtual-mode theory. For any realizable system which responds to an arbitrary electromagnetic field, in particular a molecular fluid excited by an incident charged particle, is certainly finite. The idea of the solution is simple but its expression is complicated. The solution is that, as long as there is no light in the external probe, the surface of the system induces *additional* transverse modes throughout the interior of the whole region V occupied by the fluid: these modes travel at the velocity $c/m_t(\omega)$ in which $m_t(\omega)$ is a root of the transverse dispersion relation at frequency ω. These modes are indistinguishable from the transverse modes induced by light of the same energy: bulk modes of this type induced by the surface in the absence of light have not been reported before however.

The situation may be understood as follows: a mode of the electromagnet probe labelled by (k, ω) induces a dipole response labelled by (k, ω): this induces a free field (light) of frequency ω inside V because of the surface integral of the extinction theorem. Since light cannot run inside the dielectric in V, this induces transverse optical modes of frequency ω inside V: the mechanism is that the transverse optical modes induce a free field inside V because of the surface integral of the extinction theorem: the two free fields inside V exactly balance each other even though they are associated with dipole modes of different wave number; and they can do this because they have the same energy.

We call the modes labelled by (k, ω) 'virtual modes': they do not satisfy a dispersion relation. We call the optical modes they induce 'real modes': they do satisfy a dispersion relation. When V is a slab two transverse modes of wave number $m_t(\omega)k_0$ accompany each virtual mode labelled by (k, ω). The amplitudes of all the induced modes are fixed by the extinction theorem. If the probe contains light we merely add the solutions since the integral equation is linear.

The response functions for the virtual modes are exactly (5.2): these relations contain k, ω and the $\epsilon_{l,t}(k, \omega)$ only. The total dipole response is much more complicated: it takes the form exhibited in IV (2.22) for the transverse response and the form IV (3.6) for the longitudinal response: it was first exhibited in II (2.8 *a,b*). Only the real response depends on the surface geometry: this response also depends on the $\epsilon_{l,t}(k, \omega)$, k, ω *and* $m_t{}^2(\omega)$. It is significant that *transverse* real modes accompany longitudinal virtual modes. These must describe the emission of light from the surface even though the incident longitudinal probe cannot be light. Likewise the additional real response in the total transverse response must describe the emission of light as Čerenkov radiation when the transverse probe is not light. We find that the virtual transverse response dominates the total transverse response in the non-relativistic region; that the real response dominates in the relativistic region; and on the free-field energy shell so that the probe is light the transverse response vanishes whilst the real response is the optical response described already. We thus have a rather beautiful synthesis of the virtual mode and optical response theories.†

From this synthesis we can still isolate the virtual-mode theory: we simply neglect the real responses in the theory. We expect to identify the virtual-mode theory as the unique translationally invariant part of the total response theory, and to find that any normal modes are the modes satisfying dispersion relations in the virtual-mode theory. This identification is confirmed by a search for normal modes within the theory of the total response: we find there are no normal modes in any finite

† Which we believe, and contrary to the remark in I §1, does now provide an 'all-embracing answer' to the question posed by the two different approaches contrasted there.

region like the slab V in the terms of the total response theory: there are formal normal modes in an infinite system only by appeal to a device IV (2.32) which averages out the optical extinction theorem: moreover these exist only at the expense of causality, and although this seems natural for a normal-mode theory, the causal rather than acausal optical Green function will emerge from the quantal basis to the theory which is to be presented later in this series. This is also an objection to the use of acausal Green functions in the normal modes of the virtual-mode theory: thus this translationally invariant theory may still be inconsistent through optical scattering. We conclude that normal modes certainly cannot be constructed without some change in the boundary conditions: this could mean for example, some change in or reinterpretation of the commutation relations of the quantal theory.†

The virtual-mode theory summarized by equations (5.1) and (5.2) is both translationally invariant and surface-independent: this is why it is relatively simple. In the paper V we examine it in two forms of the complex dielectric constant approximation (c.d.c.a.): the c.d.c.a. is valid when $k \ll l^{-1}$, $k_0 \ll l^{-1}$ and l is an intermolecular correlation length. In the c.d.c.a. the $\epsilon_{l,t}(k, \omega)$ are independent of k and coincide with $m_t^2(\omega)$: we define a complex dielectric constant $\epsilon(\omega)$ to represent all three of these quantities in the c.d.c.a. In the c.d.c.a. proper $\epsilon(\omega)$ retains frequency-dependent contributions from the transverse contributions to the intermolecular interactions in the cluster integrals in the $J_{l,t}(k, \omega)$: these two series J_l and J_t are now equal and independent of k but are complex through the transverse contributions: they contain the comprehensive theory of optical scattering which has been reported (Bullough *et al.* 1968 and Bullough and Hynne 1968).

In the paper V we show that the virtual-mode linear response theory coincides with that of the long-wavelength virtual photon theory of Dzyaloshinskii *et al.* (1961) in the c.d.c.a. Then we show that, in the weaker version of the c.d.c.a. which wholly rejects transverse contributions to the $J_{l,t}(k, \omega)$ but retains Coulomb interactions, the Dzyaloshinskii prescription for the free energy of a molecular fluid can be interpreted as the coupling of the radiation field to a dielectric coupled only by intermolecular Coulomb interactions. This is an appealing result with the particular merit that it shows there are natural quantized oscillators in both coupled and uncoupled systems of the virtual-mode theory: the oscillators of the coupled system are exactly those one would obtain by quantizing the normal modes of the virtual-mode theory in the weak c.d.c.a. as is particularly plain from equation V (4.14).

In detail neither the result in this form, nor the prescription for the free energy is the same as results which can be obtained from the microscopic quantal theory and which are reported in II. This theory is wholly consistent with the many-body optical theory as it has been presented in detail so far in this series: the argument takes the free molecules and free field as reference states and includes the Coulomb interactions in the computed free energy shift; but the result is apparently expressible in terms of equivalent oscillators only by working in the 'continuum approximation' described in II. We can achieve the same result from the prescription of Dzyaloshinskii by the work of this paper V only by assuming

$$\epsilon(\omega) - 1 = 4\pi n \alpha(\omega). \tag{5.3}$$

This assumption is a drastic additional restriction of even the weak c.d.c.a. for it ignores all the cluster integrals (in the $J(\omega)$ of (3.7)) which appear in the weak c.d.c.a.; in addition it ignores the Lorentz field contribution. The precise role of this in any

† See the author's lectures at Flagstaff (Bullough 1970 c).

'continuum approximation' like that of II or that of (5.3) above needs rather careful discussion; but it is certainly clear that the two theories thus agree in approximations which neglect all thermal fluctuations and do not seem to do so otherwise.

We can already conclude from the results of the series of papers so far that the frequency-dependent dielectric constant (or the refractive index) is insufficient to describe the free energy density of a molecular fluid to better than a continuum approximation and hence to order of magnitude.

The main conclusion of the three papers III, IV and V is that a consistent description of the interaction of a molecular fluid with an arbitrary electromagnetic field is possible if, but only if, very precise attention is given to the role of the surface of the system in the theory.

The analysis of these three papers leaves outstanding from I only the problem of the effect of the breakdown of translational invariance on the intermolecular correlation functions: we look at this problem later. It is plain that the urgent need now is to find a quantal derivation of the fundamental classical integral equation I (2.1) and III (2.1): this has been reported (Bullough *et al.* 1968, Obada and Bullough 1969) and the presentation of the argument is the task of the next two papers.

Although we have carried intermolecular correlation through the theory in the $J_{l,t}(k, \omega)$ we have not looked closely at the structure of these quantities: in the papers which immediately follow we do this as part of a connected argument which starts with an interaction Hamiltonian with quantized field (namely the equation (1) of II), regains the classical equation and then exhibits the cluster expansion of the $J_{l,t}(k, \omega)$ in detail in the course of reaching the expression (5.1) itself again for the dielectric constants. We can then go on to the delicate problem of external scattering.

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