

Many-body optics II. Dielectric constant formulation of the binding energy of a molecular fluid

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1969 J. Phys. A: Gen. Phys. 2 477

(<http://iopscience.iop.org/0022-3689/2/5/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 19:38

Please note that [terms and conditions apply](#).

Many-body optics

II. Dielectric constant formulation of the binding energy of a molecular fluid

R. K. BULLOUGH

Department of Mathematics, University of Manchester Institute of Science and Technology

MS. received 30th December 1968, in final form 20th May 1969

Abstract. We indicate how the microscopic optical scattering theory already reported elsewhere can be developed into a theory of the binding energy of a molecular fluid. We first report (\mathbf{k}, ω) dependent dielectric constants for the molecular fluid: these determine the linear response in all processes which depend on virtual optical processes alone. We then briefly describe bulk contributions to the stopping power, to the emission of Čerenkov radiation and to the collective molecular binding in terms of these dielectric constants. We take full account of the radiation field at every order in the ensemble averaged polarization diagram approximation and we extend the theory of the non-relativistic Lamb shift. We show that, in the continuum approximation which neglects thermal fluctuations, the molecular binding energy is completely determined by the frequency spectrum of the transverse complex refractive index. We make a numerical estimate of the importance of strictly transverse contributions to the binding energy in this approximation.

We defer consideration of the problems posed in part I of this series to the following paper III. We develop the theory of the longitudinal dielectric constant in full detail there.

1. Introduction

We have already reported elsewhere in brief (Bullough *et al.* 1968, Bullough and Hynne 1968, to be referred to as A, B, respectively) an optical scattering theory for a molecular fluid which, within the polarization diagram approximation there defined, takes account of intermolecular correlation to all orders. We have already presented as the previous paper in this journal (Bullough 1968, to be referred to as I) the first of a series of papers in which that optical scattering theory will later be developed in greater detail. There the scattering theory will emerge from a unified theory of the optical properties of the molecular fluid, which is not restricted to scattering properties alone and which provides a comprehensive view of the microscopic interactions which may be said to occur inside the fluid. It is therefore capable in principle of determining from fundamentals all of the macroscopic properties of a molecular fluid, and in practice it certainly yields all of those macroscopic properties which depend on long-range electromagnetic interactions.

A theory of this kind is naturally a complicated one and its adequate development relies first of all on an exhaustive treatment of the integral equation which underlies it. This was the immediate programme embarked on in I and which was to be continued in the next two papers of this series. However, we have found it convenient to depart a little from the programme of publication there envisaged: we shall take up and complete the analysis of the fundamental integral equation of the theory in the three papers which will constitute parts III, IV and V of this series, rather than in the parts II and III originally intended. We shall also use this second paper II to report now a number of connected physical results of the theory simply as results. These are mainly in the theory of binding energy, and this paper II therefore constitutes a very much more precise statement of the introductory remarks on these which appeared in the final § 4 of I.

This compact statement of these results, their interrelations and their connection with the scattering theory (A, B) reported will greatly help the presentation of the work which follows later. In particular, the results on binding energy presented here are especially relevant to the forthcoming paper V of this series: there we shall investigate the semi-phenomenological binding energy theory of Dzyaloshinskii *et al.* (1961) in the complex

dielectric constant approximation we first introduce below. We shall be able to draw on the result (22*b*) reported below to contrast the results of the semi-phenomenological theory with those of the strictly non-phenomenological strictly microscopic theory reported here. The microscopic theory of binding energy will be presented in detail rather later in this series.

The whole microscopic theory is ultimately a quantal theory, even though the fundamental integral equation presented for study in I was a classical one, for this integral equation can be derived from the quantum theory. Indeed, the scattering theory already reported (A, B) starts from the interaction Hamiltonian density in dipole approximation in Heisenberg representation and in second quantization

$$H_{\text{int}}(\mathbf{x}, t) = -e \sum_i \delta(\mathbf{x} - \mathbf{x}_i) \mathbf{r}_i(t) \cdot \mathbf{e}(\mathbf{x}, t) \quad (1)$$

in which $\mathbf{e}(\mathbf{x}, t)$ is a field operator and the $\mathbf{e}r_i(t)$ are electric dipole operators. It goes on to show that the most general form of the integral equation studied in I can be derived in the polarization diagram approximation, and hence that it is possible to derive the macroscopic complex refractive index of the molecular fluid from the microscopic interaction (1). Then this refractive index can actually be used to derive to a good approximation the phenomenological result for the total optical scattering cross section in the precise form obtained by Einstein (1910).

Our purpose here is to indicate in brief how we are able to use the same theoretical structure to extract expressions for the binding energy and free energy of a molecular fluid. In particular, we wish to indicate the essential steps of an argument, which shows how it comes about that the microscopic intermolecular scattering processes can lead to an essentially collective process of binding for the bulk of the fluid. To this end we first report (\mathbf{k}, ω)-dependent dielectric constants for the molecular fluid and contrast these with the dispersion relations already partly derived in detail in I. Then we use these dielectric constants both to express and to estimate the contribution of the interaction (1) to the binding energy of the fluid. In this way we greatly facilitate the presentation of the details of a complicated and far-reaching theoretical structure when we come to develop this later.

2. The dielectric constants

This calculation is certainly non-trivial when proper account is taken, as has been done, of the optical extinction theorem (for this cf. especially I, and Rosenfeld 1965, Mazur 1958). Even so, we find we can define longitudinal and transverse dielectric constants $\epsilon_{l,t}(\mathbf{k}, \omega)$ for the molecular fluid by

$$\epsilon_{l,t}(\mathbf{k}, \omega) - 1 = 4\pi n \sigma(\omega) \{1 - \frac{4}{3}\pi n \alpha(\omega) - n \alpha(\omega) J_{l,t}(\mathbf{k}, \omega)\}^{-1}. \quad (2)$$

In these expressions $\alpha(\omega)$ is the free-particle (isotropic) polarizability of I; and n is the average number density. As reported (A, B), we obtain an integral equation for the coupled photon polarization propagator $\mathbf{\Pi}(\mathbf{x}, \mathbf{x}'; t-t')$ corresponding to a fixed molecular configuration, and then derive the classical scattering equation of A, equation (7) (and implicitly that of I) by an ensemble average. We thus adopt the same approximations for the quantal theory as reported previously, namely the polarization diagram approximation (broadly equivalent to the random phase approximation (r.p.a.)) and a Born-Oppenheimer type† approximation. Thereafter we work to all orders in intermolecular correlation and include all retardation effects.

The quantities $J_{l,t}(\mathbf{k}, \omega)$ describe this intermolecular correlation. They take the exact‡ forms already quoted for arbitrary \mathbf{k} in I in the theory of dispersion. As there,

$$J_l(\mathbf{k}, \omega) = \hat{\mathbf{k}} \cdot \mathbf{J}(\mathbf{k}, \omega) \cdot \hat{\mathbf{k}}; \quad J_t(\mathbf{k}, \omega) = \mathbf{u}(\hat{\mathbf{k}}) \cdot \mathbf{J}(\mathbf{k}, \omega) \cdot \mathbf{u}(\hat{\mathbf{k}}) \quad (3a)$$

† Quasi-static approximation (see I).

‡ However, we now include radiation reaction, and integrals are convergent part integrals in the sense of A where necessary: this modifies the quantities \mathbf{J}_1 and \mathbf{J}_3 and above, but not \mathbf{J}_2 as these quantities appear in equation (3*b*). The 'surface term' problem of A arises again, but we ignore this until later in this series.

(where $\hat{\mathbf{k}}$ and $\mathbf{u}(\hat{\mathbf{k}})$ are unit vectors along and orthogonal to \mathbf{k} respectively). Then (cf. especially I, (4.17) and (4.18)†)

$$n\alpha(\omega)\mathbf{J}(\mathbf{k}, \omega) = \sum_{r=1}^{\infty} \{n\alpha(\omega)\}^r \mathbf{J}_r(\mathbf{k}, \omega) \tag{3b}$$

whilst the tensors $\mathbf{J}_r(\mathbf{k}, \omega)$ are of second rank and are of cluster integral type:

$$\mathbf{J}_1(\mathbf{k}, \omega) = \int \{n^{-1}\delta(\mathbf{r}) + g_2(\mathbf{r}) - 1\} \mathbf{F}(\mathbf{r}, \omega) \exp(i\mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} \tag{4a}$$

$$\begin{aligned} \mathbf{J}_2(\mathbf{k}, \omega) = & \int \int \{n^{-1}\delta(\mathbf{r} + \mathbf{r}')g_2(r) + g_3(\mathbf{r}, \mathbf{r}') - g_2(r)g_2(r')\} \\ & \times \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \quad \text{etc.} \end{aligned} \tag{4b}$$

In these expressions the g_ν are ν -body correlation functions; \mathbf{F} is the free-field dipole photon propagator of I, (2.8),

$$\begin{aligned} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) & \equiv \mathbf{F}(\mathbf{r}, \omega) \\ & \equiv (\nabla\nabla + k_0^2 \mathbf{U}) \exp(i\mathbf{k}_0 \mathbf{r}) r^{-1}; \quad k_0 = \omega c^{-1}, \quad r = |\mathbf{x} - \mathbf{x}'|. \end{aligned} \tag{5}$$

The form of the intermolecular correlation now means that the dielectric constants have the following properties:

$$\epsilon_i(\mathbf{0}, \omega) = \epsilon_i(\mathbf{0}, \omega), \quad \epsilon_t(m_t k_0 \hat{\mathbf{k}}, \omega) = m_t^2(\omega). \tag{6}$$

In this $m_t^2(\omega)$ is a root of $\epsilon_t(\mathbf{k}, \omega) = k^2 k_0^{-2} \equiv m_t^2(\omega)$: it is evident that $m_t^2(\omega)$ is exactly the complex refractive index already both reported (A, B) and derived in more detail (I). Moreover, the roots of $\epsilon_i(\mathbf{k}, \omega) = 0$ are the longitudinal dispersion relations of the detailed theory (I). Next, we must look at the complex dielectric constant approximation: this assumes that both $k \ll t^{-1}$ and $k_0 \ll t^{-1}$, where $2\pi t$ is an intermolecular correlation range, so that in the complex dielectric constant approximation (cf. A, B) we can set $k = 0$ in the $\epsilon_{i,t}(\mathbf{k}, \omega)$ and

$$\epsilon_i(\mathbf{0}, \omega) = \epsilon_t(\mathbf{0}, \omega) = m_t^2(\omega) = \epsilon(\omega) \quad (\text{say}). \tag{7}$$

These results make the complex dielectric constant approximation an important physical approximation.‡

Because of the optical extinction theorem the total dipole response

$$\mathbf{P}(\mathbf{k}, \omega) = \mathbf{P}_i(\mathbf{k}, \omega) + \mathbf{P}_t(\mathbf{k}, \omega)$$

to a field probe $\mathbf{E}(\mathbf{k}, \omega)$ satisfies the pair of relations

$$\mathbf{P}_i(\mathbf{k}, \omega) = \left\{ 1 - \frac{1}{\epsilon_i(\mathbf{k}, \omega)} \right\} \left[1 - \{m_t^2(\omega) - 1\} \frac{k_0^2}{k^2 - k_0^2} \hat{S}_i(\Sigma; \mathbf{k}, \omega) \right] \mathbf{E}_i(\mathbf{k}, \omega) \tag{8a}$$

$$\mathbf{P}_t(\mathbf{k}, \omega) = \frac{\epsilon_t(\mathbf{k}, \omega) - 1}{k^2 - \epsilon_t(\mathbf{k}, \omega)k_0^2} [(k^2 - k_0^2) - \{m_t^2(\omega) - 1\}k_0^2 \hat{S}_t(\Sigma; \mathbf{k}, \omega)] \mathbf{E}_t(\mathbf{k}, \omega). \tag{8b}$$

The $\hat{S}_{i,t}$ symbolize complicated operators depending on \mathbf{k}, ω and the surface Σ of the whole fluid system. The important point is that both the longitudinal and the transverse response functions break into two parts: one part depends on the $\epsilon_{i,t}(\mathbf{k}, \omega)$ alone, and we call it the virtual response; the other part depends on these, on $m_t^2(\omega)$ and on Σ , and we call it the real response. In the total transverse response the virtual response dominates in the non-relativistic region $k \gg k_0$; the real response dominates in the relativistic region $k \simeq k_0$;

† See second footnote on p. 478.

‡ In the most general form of the complex dielectric constant approximation we replace \mathbf{F} of (5) by $\nabla\nabla r^{-1} + \frac{1}{2}ik_0^3 \mathbf{U}$ (see A, B and paper V to follow in this series).

and on the free-field energy shell $k = k_0$ there is a finite real response, but the virtual response is exactly zero. Thus when \mathbf{E} is light only the real response is excited. In this case the theory now coincides exactly with the refractive index theory of both the report (A, B) and the detailed theory.

These particular results will all be developed in detail in parts III and IV of this series of papers. We now demonstrate here how the virtual response dominates the external scattering of light in the non-relativistic region, and something of how that changes in the approach to the relativistic region.

3. Application to electron stopping power and Čerenkov radiation

The complete theory depends on the total response—longitudinal plus transverse, virtual and real. We shall here quote the contributions of the virtual responses only: evidently the real responses explicitly describe the influence of the boundary Σ of the system on the cross section and, for example, the transverse real response is concerned with the description of the conversion of the excited internal transverse modes into externally observable Čerenkov radiation. We find from the virtual response that the energy dissipated per unit length by a fast electron travelling at velocity $v \equiv \beta c$ is†

$$\frac{dW}{dz} = \frac{2e^2}{\pi v^2} \int_0^\infty \frac{dk}{k} \int_0^{vk} \omega d\omega \operatorname{Im} \left[\left\{ 1 - \frac{1}{\epsilon_l(\mathbf{k}, \omega)} \right\} - \frac{(k^2 \beta^2 - k_0^2) k_0^2}{k^2 - k_0^2} \frac{\epsilon_t(\mathbf{k}, \omega) - 1}{k^2 - \epsilon_t(\mathbf{k}, \omega) k_0^2} \right]. \quad (9)$$

In the complex dielectric constant approximation (7) holds and (9) is expressible in the exact forms given by Fano (1956). The theory here thus justifies and generalizes Fano's argument based on an intuitive microscopic oscillator model. However, even in the complex dielectric constant approximation our expressions for $\epsilon(\omega)$ are to be obtained from (2) and are complex because they contain, as fluctuations, microscopic multiple-scattering processes to all orders: more generally, the $\epsilon_{l,t}(\mathbf{k}, \omega)$ are k -dependent, whilst the addition of the real response in principle extends the theory to include the important surface effects. We note also that in the complex dielectric constant approximation (9) depends only on $\operatorname{Im}\{\epsilon(\omega)\}$ and $|\epsilon(\omega)|$, which are $\operatorname{Im}\{m_l^2(\omega)\}$ and $|m_l^2(\omega)|$. But within the complex dielectric constant approximation $\operatorname{Im}\{m_l^2(\omega)\}$ is expressible as the Einstein *optical* scattering cross section (A, B). Thus for $k \ll \lambda^{-1}$ (so that $vk \ll c\lambda^{-1}$) (9) is expressible in terms of the Einstein (1910) scattering cross section. Evidently it is the complex dielectric constant approximation which justifies all previous work on Čerenkov radiation given in terms of the refractive index.

The most significant feature of (9) in the present context is the contribution of the transverse virtual processes which control the emission of Čerenkov radiation. For we can now show how this is related to the contribution of transverse virtual photons to the intermolecular binding energy.

4. Dielectric constant formulation of the binding energy

We have been able to show that the following is an *exact* formula for the total mean binding energy‡:

$$\begin{aligned} \overline{\Delta E_{\text{tot}}} = & -\frac{\hbar}{2\pi i} \int_0^e \frac{de'}{e'} \int_0^\infty d\omega \coth \left(\frac{\hbar\omega}{2k_B T} \right) \\ & \times \int_V \int_V \operatorname{Tr} \{ \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \langle \mathbf{\Pi}(\mathbf{x}', \mathbf{x}; \omega) \rangle_{\text{av}} - \text{c.c.} \} d\mathbf{x} d\mathbf{x}'. \quad (10) \end{aligned}$$

In this $\langle \dots \rangle_{\text{av}}$ denotes an ensemble average and $\mathbf{\Pi}$ is the polarization propagator associated with each configuration of the molecules; e is the actual electronic charge and e' is now the coupling constant in H_{int} of (1); T is the temperature and k_B is Boltzmann's constant and we eventually suppose the ensemble average is taken with coupling constant e and not e' (see § 5).

† The $\epsilon_{l,t}(\mathbf{k}, \omega)$ depend on k (and ω) alone and not on $\mathbf{k} = k\hat{\mathbf{k}}$, as (2) shows; k_0 is to be real in (9).

‡ Exact in terms of the chosen interaction H_{int} , and exact also only as a thermodynamic potential. By taking the ensemble average with coupling constant e we appeal to the Born–Oppenheimer approximation and work towards the mean ground-state energy, which is (16).

In the absence of time-dependent intermolecular correlations the more significant excitations are probably the electronic excitations: therefore for simplicity we shall here simply replace the coth in (10) by unity. We then find that the contribution of virtual photons (i.e. the contribution of the total virtual response only) is expressible in terms of the $\epsilon_{i,t}(\mathbf{k}, \omega)$ as

$$\overline{\Delta E}_{\text{tot}} = -\frac{\hbar V}{\pi} \int_0^e \frac{de'}{e'} \int_0^\infty d\omega \int \frac{d\mathbf{k}}{(2\pi)^3} \text{Im} \left[-\left\{ 1 - \frac{1}{\epsilon_{i,t}(\mathbf{k}, \omega)} \right\} + \frac{2\{\epsilon_{i,t}(\mathbf{k}, \omega) - 1\}k_0^2}{k^2 - \epsilon_{i,t}(\mathbf{k}, \omega)k_0^2} \right] \quad (11)$$

in which, as in (10), V is the volume of the fluid system. Up to neglect of one-particle self-energies the contribution of the longitudinal modes is formally identical with that in the plasma (Nozières and Pines 1958); but the details are very different since we are concerned with the molecular fluid at normal temperatures. Indeed a complete description of the internal field up to all orders of multiple scattering within the polarization diagram approximation is concealed within $\epsilon_{i,t}(\mathbf{k}, \omega)$ in (2). Comparison of (11) with (9) shows that the connection with electron stopping power is identical with that in the plasma for the longitudinal virtual modes.

The exhibition of the *transverse* contributions in an expression like (11) is an entirely new feature (as far as we are aware†) and is one of the more important results of the theory. Its connection with the emission of Čerenkov radiation is obvious from (9), though perhaps not easy to exploit experimentally. It should be noted that when the velocity of light $c \rightarrow \infty$ (11) is indeed formally identical with the result for the plasma (Nozières and Pines 1958), but it should also be noted that $\text{Im}\{\epsilon_{i,t}\}$ contains transverse parts of the free-field photon propagator \mathbf{F} whether $c < \infty$ or $c \rightarrow \infty$.‡ In consequence in the continuum approximation, which we discuss below in § 7, there are transverse contributions to $\overline{\Delta E}_{\text{tot}}$ even when $c \rightarrow \infty$.

In the complex dielectric constant approximation (11) can be expressed in the form

$$\overline{\Delta E}_{\text{tot}} = -\frac{\hbar V}{\pi} \text{Tr} \int_0^e \frac{de'}{e'} \int_0^{c^2-1} d\omega \int_{|k| \leq c^{-1}} \frac{d\mathbf{k}}{(2\pi)^3} \text{Im} \left[\frac{\{\epsilon(\omega)k_0^2 \mathbf{U} - k\mathbf{k}\} \{\epsilon(\omega) - 1\}}{\epsilon(\omega) \{k^2 - \epsilon(\omega)k_0^2\}} \right] \quad (12a)$$

and this is approximately

$$\overline{\Delta E}_{\text{tot}} \simeq -\frac{\hbar V}{\pi} \text{Tr} \int_0^e \frac{de'}{e'} \int_0^{c^2-1} d\omega \text{Im} \left[\int_{\text{all space}} \tilde{\mathbf{F}}(\mathbf{r}, \omega) \cdot \frac{\mathbf{U} \{\epsilon(\omega) - 1\} \delta(\mathbf{r})}{4\pi} d\mathbf{r} \right] \quad (12b)$$

in which

$$\tilde{\mathbf{F}}(\mathbf{r}, \omega) \equiv \{m_i^2(\omega)\}^{-1} (\nabla \nabla + m_i^2(\omega)k_0^2 \mathbf{U}) \exp \{im_i(\omega)k_0 r\} r^{-1}; \quad m_i^2(\omega) \equiv \epsilon(\omega) \quad (13)$$

is a screened photon propagator. Another form of this result, which splits off one-particle self-energies (these cannot really be treated within the complex dielectric constant approximation—see § 6) is

$$\overline{\Delta E}_{\text{tot}} = -\frac{\hbar V}{\pi} \text{Tr} \int_0^e \frac{de'}{e'} \int_0^{c^2-1} d\omega \text{Im} \left[\left\{ \frac{\epsilon(\omega) - 1}{4\pi} \right\}^2 \int_{\text{all space}} \{\mathbf{F}(\mathbf{r}, \omega) \cdot \tilde{\mathbf{F}}(\mathbf{r}, \omega)\} d\mathbf{r} + \frac{\epsilon(\omega) - 1}{4\pi} \frac{1}{3} ik_0^3 \mathbf{U} \right]. \quad (14)$$

Since (7) holds in the complex dielectric constant approximation the expressions (12)–(14) depend only on the real and imaginary parts of the refractive index: thus there is a direct connection with the optical scattering theory (A, B) in the long-wavelength virtual photon theory, which is the complex dielectric constant approximation.

The results (11)–(14) would be very powerful results if the $\epsilon_{i,t}(\mathbf{k}, \omega)$ were known functions of the coupling constant e' : in this case the complex dielectric constant approximation results (12)–(14) in particular express the binding energy in terms of the spectrum of the

† We have already reported (Bullough and Obada 1969) a comparable expression for the isotropic molecular crystal.

‡ In the Lorentz field term (cf. I, § 4, below (4.23)).

frequency-dependent dielectric constant $\epsilon(\omega) \equiv m^2(\omega)$ alone. In practice the $\epsilon_{i,t}(\mathbf{k}, \omega)$ are available as functions of e' only through the polarization diagram approximation results (2). Since the $J_{i,t}(\mathbf{k}, \omega; e')$ are power series in e'^2 , we are obliged to exhibit $\overline{\Delta E}_{\text{tot}}$ as a power series in e^2 . This series is a 'closed loop' expansion consequent on the restriction of the $\epsilon_{i,t}$ to the polarization diagram approximation. It is given in § 5.

There is one important case within the polarization diagram approximation (but no other additional approximation) in which the integration over e' can be carried out to yield a closed form: this is the case of a single molecule of polarizability $\alpha(\omega)$ at the fixed point \mathbf{x}_0 outside V bound to a dielectric region inside V . For this we obtain instead of (10) (and still omitting the coth) the fundamental asymptotic formula

$$\overline{\Delta E}_{\text{tot}} \sim -\frac{\hbar}{4\pi i} \text{Tr} \int_0^\infty \left\{ \alpha(\omega) \int_V \int_{V'} \mathbf{F}(\mathbf{x}_0, \mathbf{x}; \omega) \cdot \langle \mathbf{\Pi}(\mathbf{x}, \mathbf{x}'; \omega) \rangle_{\text{av}} \right. \\ \left. \cdot \mathbf{F}(\mathbf{x}', \mathbf{x}_0; \omega) d\mathbf{x} d\mathbf{x}' - \text{c.c.} \right\} d\omega. \quad (15)$$

This formula is easily developed by iteration of the integral equation for $\mathbf{\Pi}$ already reported (cf. A, equation (3)).

5. The closed-loop expansion for $\overline{\Delta E}_{\text{tot}}$

Substitution of the $\epsilon_{i,t}(\mathbf{k}, \omega)$ from (2) into (11) yields the expansion in terms of ν -body 'potentials' U_ν

$$\overline{\Delta E}_{\text{tot}} = +V \left\{ \frac{1}{2} n^2 \int_V g_2(r) U_2(r) d\mathbf{r} + \frac{1}{6} n^3 \int_V \int_{V'} g_3(\mathbf{r}, \mathbf{r}') U_3(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \right\}. \quad (16)$$

We ignore one-body terms for the moment, and assume both that the g_ν do not depend on the coupling constant e' , and that we can consistently ignore surface effects in inverting from \mathbf{k} space. The first assumption means we compute an ensemble averaged energy. If we admit that the g_ν depend on e' , we obtain a free energy or thermodynamic potential (but only if we can perform the integrations over e')†. The second assumption means that the contribution of the real modes is now implicitly concealed in (16), presumably as a surface contribution closely related to the 'surface terms' of the scattering theory already reported (A, B). This surface contribution has not yet been explored, but it is intuitive that the virtual modes alone determine the bulk binding and the real modes, exhibited in the 'real response' in (8), determine the surface energy.

The first-order contribution to $U_2(r)$ in terms of the free-particle polarizabilities $\alpha(\omega)$ is

$$U_2^{(1)}(r) = -\hbar\pi^{-1} \int_0^\infty d\omega \{ \alpha(i\omega) \}^2 (3r^{-4} + 6k_0 r^{-3} + 5k_0^2 r^{-2} + 2k_0^3 r^{-1} + k_0^4) \\ \times \exp(-2k_0 r) r^{-2} \\ \sim -\frac{23}{4\pi} \{ \alpha(0) \}^2 \hbar c r^{-7}, \quad r \rightarrow \infty. \quad (17)$$

This is exactly the Casimir-Polder interaction (Casimir and Polder 1948). The first-order contribution $U_3^{(1)}(\mathbf{r}, \mathbf{r}')$ to $U_3(\mathbf{r}, \mathbf{r}')$ is the Aub-Zienau three-body interaction (Aub and Zienau 1960); first-order contributions to U_ν are the properly retarded ν -body potentials of McLachlan (1963), and at each order retardation modifies the asymptotic behaviour at large particle separations. However, because $g_2(r) = 0$ for $r < a$ (where a is an intermolecular diameter) we can sum all two-body interactions and find that $U_2(r)$ is neither the Casimir-Polder nor the London interaction. It is in fact the two-body potential *exact in the polarization diagram approximation*

$$U_2(r) = \frac{\hbar}{2\pi} \int_0^\infty d\omega \ln \det \| \mathbf{U} - \alpha^2(i\omega) \mathbf{F}(\mathbf{r}, i\omega) \cdot \mathbf{F}(\mathbf{r}, i\omega) \|. \quad (18)$$

† Since H_{int} is the 'long-range part' only, there is a short-range part of the g_ν which does not depend on the e' .

Some comparable results apply to U_ν for $\nu \geq 3$, and these must be explored in the detailed theory. Evidently the inclusion of the coth function of (10) makes all of these potentials temperature-dependent.

6. The one-body terms

At first sight the dipolar form of H_{int} restricts the potentials to their long-range part (and the g_ν look after the short-range part). However, the scattering theory correctly handles radiation reaction (this is one consequence of the identity of the two extinction coefficients τ_s and τ_m reported in the papers A, B), and we can expect that the theory contains a correct formulation of the one-body non-relativistic Lamb shift of the ground state. We find†

$$\overline{\Delta E}^{(1)} = nV \frac{3\hbar}{2\pi} \int_0^R \ln \{1 - \frac{2}{3}\omega^3 c^{-3} \alpha(i\omega)\} d\omega \tag{19}$$

which is undefined as R becomes large. We therefore choose the natural cut-off for a non-relativistic electron theory $R = m_e c^2 \hbar^{-1}$ (in which m_e is the electron mass). For larger R the integrand has branch points on the contour of integration at the roots of

$$1 - \frac{2}{3}\omega^3 c^{-3} \alpha(i\omega) = 0 \tag{20}$$

and thus approximately at $\omega = \frac{3}{2} m_e c^2 (\hbar \alpha_0)^{-1}$. Here $\alpha_0 \equiv e^2 \hbar^{-1} c^{-1}$ is the fine-structure constant. The wavelength corresponding to this singularity is approximately 12×10^{-13} cm —comparable both with the ‘size’ of the electron and more precisely with the wavelengths of the π (or μ) mesons.‡ Our chosen cut-off is at the Compton wavelength of the electron $\lambda_C = 2\pi \hbar (m_e c)^{-1} = 2.4 \times 10^{-10}$ cm, and excludes this.

To first order in α_0 , (19) reduces to

$$\overline{\Delta E}^{(1)} = 2nV e^2 (3\pi \hbar c^3)^{-1} \sum_s |v_{0s}|^2 (E_s - E_0) \ln \left(\frac{m_e c^2}{E_s - E_0} \right). \tag{21}$$

The E_s are free molecule energies and v_{0s} is a matrix element of the velocity of the free molecule’s optical electron. Equation (21) is the celebrated Bethe formula (Bethe 1947). Second-order corrections to this in (19) are about 0.2%, and hence about one order of magnitude bigger than current uncertainty in the relativistic calculations (cf. *Physics Today* 1966). We reach (21) from the first-order term of (19) by ignoring a term quadratic in $R\alpha_0$. This term can be interpreted as the electromagnetic correction to the rest mass of the electron (Feynman and Hibbs 1965) and it vanishes with e , but its connection with gauge invariance may also suggest some correspondence with the relativistic photon mass divergence. The calculation differs from Bethe’s original calculation not least in that this divergence, rather than the electron mass divergence, appears, but we have also been able to extract the linearly divergent non-relativistic kinetic electron mass from the first-order theory.

Equation (19) does not exhaust the ‘self-interactions’ in the theory. However, it does exhaust all one-body terms (i.e. those which contribute to $\lim_{n \rightarrow 0} \overline{\Delta E}_{\text{tot}}/nV$) in dipole approximation.||

It is apparently possible to extend the theory to admit interactions of spin magnetic moments with the radiation field also. For the coupled integral equations for the photon propagators which include all dipole magnetic interactions within the polarization diagram approximation have been reported (Obada and Bullough 1969) for the crystal, and these

† In this form we ignore at least pure imaginary contributions on the big $\frac{1}{2}$ -circle $|\omega| = R$.

‡ $m_\mu = 207m_e$, whilst $3m_e/2\alpha_0 = 205.5m_e!$

§ Second-order corrections to (21) ignore a term cubic in R . Some of the terms retained may not be physically significant.

|| The polarization diagram approximation is exact at first order, but there are additional one-body terms outside the polarization diagram approximation which are not described by (19).

can be applied to the fluid within the Born–Oppenheimer approximation. Both these and the one-body results discussed in this § 6 are some indication of the comprehensiveness of the microscopic theory.

We now look at a second physically important approximate form of the theory—the continuum approximation.

7. The continuum approximation

The thermal fluctuation theory, which overlies the quantal fluctuations responsible for the binding energy, (apparently) means that there are no natural quantal oscillators of the coupled system. But in the continuum approximation we eliminate the cluster integral series $J_{l,t}(\mathbf{k}, \omega)$ in (2), and this situation is changed. This replacement means, first of all, that we can move consistently from (10) to an expression like (11) only by exhibiting the Fourier transform of $\mathbf{F}(\mathbf{r}, \omega)$ as a conditionally convergent integral. With this proviso we can then express the continuum approximation to $\overline{\Delta E}_{\text{tot}}$ as

$$\overline{\Delta E}_{\text{tot}} = -\frac{\hbar V}{2\pi i} \int \frac{d\mathbf{k}}{(2\pi)^3} \int_0^\infty d\omega \ln \left[\frac{\{\epsilon_t(\mathbf{k}, \omega) - 1\}^2 (k^2 - k_0^2)^2 \{\epsilon_l(\mathbf{k}, \omega) - 1\}}{\{k^2 - \epsilon_l(\mathbf{k}, \omega) k_0^2\}^2 \epsilon_l(\mathbf{k}, \omega) \{4\pi n \alpha(\omega)\}^3} \right] \quad (22a)$$

$$= V \int \frac{d\mathbf{k}}{(2\pi)^3} \left[\frac{1}{2} \hbar \left\{ \sum_t 2w_t^{(t)}(\mathbf{k}) + \sum_i w_i^{(i)}(\mathbf{k}) - 3 \sum_s \omega_s - 2ck \right\} \right] \quad (22b)$$

in which the $w_t^{(t)}(\mathbf{k})$ are the roots of $\epsilon_t(\mathbf{k}, \omega) = k^2 k_0^{-2}$ and the $w_i^{(i)}(\mathbf{k})$ are the zeros of $\epsilon_l(\mathbf{k}, \omega)$; the ω_s are the poles of $\alpha(\omega)$ ($\hbar\omega_s = E_s - E_0$ in terms of the free-particle energies) and we have supposed that the $\epsilon_{l,t}(\mathbf{k}, \omega) - 1$ have no zeros. The ‘pure refractive index theory’ of the continuum approximation therefore replaces the free-field and free-particle oscillators by the modes of the coupled system exactly as in the rigid molecular crystal at $T = 0$ (Bullough and Obada 1969). But the result like (22b) for the crystal is exact in the polarization diagram approximation (Bullough and Obada 1969), whilst equations (22) are valid for the fluid only if the $J_{l,t}$ in the $\epsilon_{l,t}$ can be neglected. Equations (22) also ignore the coth in (10): if the coth is included and the $J_{l,t}$ are neglected, there is an approximate thermal decorrelation scheme which replaces (22b) by an expression for the total free energy at temperature T ; this expression is in the form of the sum of the free energies of the several oscillators in (22b) and of additional oscillators, just as it is for the crystal (Bullough and Obada 1969).

The results (22) mean that in the continuum approximation the binding energy is completely determined by the refractive index $m_t(\omega)$, for all the results like (7) for the complex dielectric constant approximation apply in this approximation also. To this extent the microscopic theory supports the fundamental postulate of the phenomenological theory of Lifshitz (1956), but so far we have only been able to obtain the closed-loop expansion of Dzyaloshinskii *et al.* (1961) in terms of $\epsilon(\omega) - 1$ at the expense of neglecting both fluctuations and the Lorentz field term in $\epsilon(\omega)$.†

It is an intriguing fact that the closed-loop expansion in $\alpha(\omega)$, which is (16), is obtained as a part of the result of integrating $[\{m_t^2(\omega) - 1\}/4\pi n \alpha(\omega)]^{-1} - 1$ on e as in § 4. But we have only been able to isolate it and extract it from the (\mathbf{k}, ω) -dependent dielectric constants, and the reason lies in the fact that \mathbf{k} is a free variable in the theory of the virtual modes, but satisfies the dispersion relation $k = m_t(\omega)k_0$ in the theory of the transverse real modes—the only modes which are excited by light.

If we limit the $\alpha(\omega)$ to a single oscillator (i.e. set $\alpha(\omega) = \alpha(0)\omega_1^2(\omega_1^2 - \omega^2)^{-1}$) in the continuum approximation, we can easily estimate long-wavelength virtual photon contributions to $\overline{\Delta E}_{\text{tot}}^\ddagger$ and also the contributions of both $\nu(\geq 3)$ -body terms and the radiation field to this. We find, if we cut off the integral over \mathbf{k} at $k = |\mathbf{k}| \leq k_c \equiv (3\pi)^{1/3} a^{-1}$, that this is

† The problem lies in the integral over coupling constant. This difficulty is noted already in I, § 4; next is an amplification of the second ‘difficulty’ reported there.

‡ $\overline{\Delta E}_{\text{tot}}$ is easily expressed as the integral in closed form, which is (22b).

equivalent to estimating the longitudinal two-body contributions as hard-sphere contributions with a closest distance of approach of a . We define the contribution of the radiation field to $\overline{\Delta E}_{\text{tot}}$ as that part of (22a) which vanishes when $c \rightarrow \infty$ there. With this eliminated we find for (22a)

$$\overline{\Delta E}_{\text{tot}} = -\frac{1}{2}\hbar\omega_1 \left(\frac{V}{2\pi a^3}\right) \sum_{r=2}^{\infty} \left\{\frac{\epsilon(0)-1}{\epsilon(0)+2}\right\}^r a_r \{(-2)^r + 2\};$$

$$a_r = \frac{(2r)!}{(r!)^2 2^{2r} (2r-1)}. \tag{23}$$

Then, if, for example, $\epsilon(0) = 2$, the ratio $\Delta E^{(\nu)}/\Delta E^{(2)}$ of ν -body contributions is as follows: $\nu = 3$, -12.5% ; $\nu = 4$, $+5.9\%$; $\nu = 5$, -1.6% ; $\nu = 6$, $+0.7\%$, exactly as for the cubic crystal (Bullough and Obada 1969). The rate of convergence is therefore slow.

The contribution of the radiation field is more complicated: the two-body contributions are ($k_1 = \omega_1 c^{-1}$)

$$\hbar\omega_1 V k_1^3 \{A_1^{(2)}(ak_1)^{-1} + A_2^{(2)} \ln(ak_1) + A_3^{(2)} + O(k_1 a)\} n^2 \{\alpha(0)\}^2 \tag{24}$$

in which the A 's are $O(1)$. The ratio of the leading term in (24) to the two-body contribution to (23) is $-\{2/(3\pi)^{2/3}\} a^2 k_1^2$. With $a = 1 \text{ \AA}$ and $2\pi k_1^{-1} = 10^3 \text{ \AA}$ (12.4 eV) the ratio is approximately equal to -1×10^{-5} , whilst $\Delta E^{(2)} \sim 0.02$ eV per particle; but with $a = 10 \text{ \AA}$ and $2\pi k_1^{-1} = 250 \text{ \AA}$ (49.6 eV) the ratio is approximately equal to -3% , whilst the $\Delta E^{(2)} \sim 0.09$ eV per particle.† The $\nu (\geq 3)$ -body contributions of the radiation field extend each of the A 's in (24) by series in

$$\frac{4}{3}\pi n \alpha(0) = \frac{\epsilon(0)-1}{\epsilon(0)+2}$$

for example

$$A_1^{(2)} \rightarrow A_1^{(2)} \left\{ 1 + \frac{1}{8} \frac{\epsilon(0)-1}{\epsilon(0)+2} + \dots \right\}.$$

Of course, it is easy to extend the whole of the theory reported here to the case of a molecular fluid of several different components, and this has been done. The details of the optical dispersion theory of multi-component systems—the real response to light—have already been presented in I. The corresponding dielectric constant theory will be given in V.

This completes a brief presentation of some of the main results on the binding energy of a molecular fluid which will be obtained in the course of the development of the rigorously argued detailed theory. With this indication of both the route we shall follow and some of the significant physical conclusions we shall reach, we can turn first of all in the papers to come to a derivation of the particularly important expressions (2) and (8). These emerge in the study of the fundamental integral equation of the theory, and this study is the programme for the papers III and IV to follow next.

References

AUB, M. R., and ZIENAU, S., 1960, *Proc. R. Soc. A*, **257**, 464–76.
 BETHE, H. A., 1947, *Phys. Rev.*, **72**, 339–41.
 BULLOUGH, R. K., 1968, *J. Phys. A (Proc. Phys. Soc.)*, [2], **1**, 409–30.
 BULLOUGH, R. K., and HYNNE, F., 1968, *Chem. Phys. Lett.*, **2**, 307–11.

† In this case the Lamb shift computed from (21) for the single oscillator is of the same order of magnitude as (24).

- BULLOUGH, R. K., and OBADA, A.-S. F., 1969, *Chem. Phys. Lett.*, **3**, 177-81.
- BULLOUGH, R. K., OBADA, A.-S. F., THOMPSON, B. V., and HYNNE, F., 1968, *Chem. Phys. Lett.*, **2**, 293-6.
- CASIMIR, H. B. G., and POLDER, D., 1948, *Phys. Rev.*, **73**, 360-72.
- DZYALOSHINSKII, I. YE., LIFSHITZ, E. M., and PITAEVSKII, L. P., 1961, *Adv. Phys.*, **10**, 165-209.
- EINSTEIN, A., 1910, *Ann. Phys. Lpz.*, **33**, 1275-98.
- FANO, U., 1956, *Phys. Rev.*, **103**, 1202-18.
- FEYNMAN, R. P., and HIBBS, A. R., 1965, *Quantum Mechanics and Path Integrals* (New York: McGraw-Hill), p. 254.
- LIFSHITZ, E. M., 1956, *Sov. Phys.-JETP*, **2**, 73-83 (*Zh. Eksp. Teor. Fiz.*, **29**, 94-110 (1955)).
- MCLACHLAN, A. D., 1963, *Molec. Phys.*, **6**, 423-7.
- MAZUR, P., 1958, *Advances in Chemical Physics*, Vol. 1 (New York: Interscience), p. 336.
- NOZIÈRES, P., and PINES, D., 1958, *Nuovo. Cim.*, [10], **9**, 470-90.
- OBADA, A.-S. F., and BULLOUGH, R. K., 1969, *Physica*, **42**, 475-81.
- Physics Today*, 1966, No. 10, p. 87.
- ROSENFELD, L., 1965, *Theory of Electrons* (New York: Dover Publications), chap. VI.