ARTICLES

Extinction theorem, dispersion forces, and latent heat

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We show that multiple dipole scattering of zero-point radiation gives rise to the nonadditive contributions to the van der Waals dispersion interaction, and use the Ewald-Oseen extinction theorem to justify the Lifshitz theory of macroscopic (Casimir) effects of intermolecular van der Waals forces in the limit of continuous media. We derive the interaction energy between an atom and a dielectric medium of identical atoms and obtain, using standard "cavity-QED" methods, results identical to those of the source theory of Schwinger, DeRaad, and Milton [Ann. Phys. (N.Y.) **115**, 1 (1978)]. Following Schwinger, DeRaad, and Milton, we apply the results to estimate the latent heat of liquid helium. We argue that the macroscopic theory does not unambiguously justify the conclusion that the dispersion interaction makes a significant contribution to the latent heat and surface tension. Simpler and well-established microscopic models, without the divergences incurred in the macroscopic theory, are invoked to support this conclusion.

I. INTRODUCTION

In this paper we will show a relationship between the optical extinction theorem of Ewald and Oseen [1] and the theory of van der Waals intermolecular dispersion forces. This relationship elucidates various aspects of the dispersion forces, especially their nonadditivity and the limitations of the Lifshitz theory of their macroscopic manifestations.

Latent heat, the energy required to vaporize a unit mass of material without a change of temperature, is a consequence of intermolecular attractive forces. As an application of the theory presented in this paper, we consider the part of the latent heat of vaporization due to molecular dispersion forces. We consider the example of liquid helium, which previously was treated macroscopically through the expedient of a cutoff in transverse photon momenta [2].

A brief history of the subject seems appropriate. It may be said to have begun with van der Waals's modification of the ideal-gas law to account for attractive intermolecular forces. An interaction potential of the form $V(r) = -Ar^{-1}e^{-Br}$, where A and B are constants, was proposed by van der Waals. Much later Keesom obtained the potential $V(r) = -p_1^2 p_2^2/3kTr^6$ for two polar molecules with permanent dipole moments p_1 and p_2. This force was obtained as a consequence of molecular rotations, the force being attractive because attractive orientations are statistically favored over repulsive ones. Debye and others recognized that more general attractive forces must come into play, simply because gases of nonpolar molecules also have nonvanishing van der Waals constants. Moreover, a temperature-independent potential was sought. Debye noted that many molecules have

a permanent quadrupole moment, which can induce a dipole moment in a second molecule, and the resulting dipole-quadrupole force is temperature-independent. Such an "induction force" occurs also if the first molecule has a permanent dipole moment. However, neither case is sufficiently general to account for the van der Waals equation of state.

London [3] employed fourth-order quantum-mechanical perturbation theory to derive the interaction potential $V(r) = -3\hbar\omega_0\alpha^2/4r^6$ between two identical atoms with some dominant transition frequency ω_0, with α the static polarizability; $\hbar\omega_0$ is usually taken to be the ionization potential. London's result showed that there is a universal force of attraction between two atoms or molecules even if neither has a permanent moment. It is only necessary that each particle have a nonvanishing polarizability, i.e., that a dipole moment can be *induced*. Moreover London's result, unlike Keesom's, is temperature independent. London's calculation was regarded as a major triumph of quantum theory.

Since it involves the polarizability, which in turn is related to the refractive index and dispersion, London's force is often called a "dispersion force." Dispersion forces, together with the orientation and induction forces of Keesom and Debye, are now regarded as the three principal types of van der Waals forces.

The dispersion force is usually weak compared with ionic or covalent bonding forces, but there are many substances, including liquid helium and many organic crystals, where it can reasonably be assumed to be the dominant contribution to the latent heat of vaporization of sublimation; it is also believed to account for the thickness of liquid helium films [4]. The principal theoretical difficulty is that the dispersion forces are not pairwise ad-

ditive. This difficulty goes back a long way in a related context, namely, the problem of calculating the van der Waals forces between macroscopic dielectric layers. Lifshitz [5] circumvented a many-body approach to such systems by taking a macroscopic approach. His results can be obtained from several different physical perspectives [6], but its main feature for the present discussion is that the field mediating the interaction between any two molecules propagates through the medium formed by *all the other* molecules. This medium affects the field through its dielectric constant, and thus accounts in a macroscopic way for the nonadditivity of the dispersion force. Although questions have occasionally been raised concerning the validity of the Lifshitz theory [2], we shall show that the results of the theory are perfectly valid *for virtual-photon wavelengths large compared with interatomic separations*. The zero-temperature results have been found to be in good agreement with experimental results obtained with liquid helium films [7] and the results of this theory have been usefully applied, for instance, in the theory of biomembranes [8].

The macroscopic approach of Lifshitz, albeit in the framework of Schwinger's source theory rather than conventional QED, has been applied by Schwinger, DeRaad, and Milton [2] in a calculation of the latent heat and surface tension of liquid helium. The result was considered to be consistent with experiment, but only if a physically motivated choice was made of a photon transverse-momentum cutoff required to avoid a divergence. As discussed in Sec. VI, the macroscopic theory is not required to support the conclusion that dispersion forces play a substantial role in latent heat and surface tension.

We begin in the following section with a description of our approach and the principal equations. In Sec. III we establish the connection with the Ewald-Oseen extinction theorem and the macroscopic approach to dispersion forces, and in Sec. IV we show how N-body contributions to the dispersion interaction may be identified in a perturbative solution to the general scattering problem. In Secs. V and VI we estimate the latent heat of liquid helium by macroscopic and microscopic approaches, respectively. Section V derives results obtained by Schwinger's source theory [2] using standard "cavity QED." Our conclusions are given in Sec. VII.

II. COHESIVE ENERGY DUE TO DISPERSION FORCES

We begin as in Ref. [6] with the fact that the expectation value of the potential energy of an induced dipole **p** in an electric field **E** is

$$\langle E \rangle = -\tfrac{1}{2}\langle \mathbf{p} \cdot \mathbf{E}(\mathbf{R}, t) \rangle , \qquad (1)$$

where the dipole is treated as a point particle at **R** (electric dipole approximation). The quantized electric field has the form

$$\mathbf{E}(\mathbf{r}, t) = i \sum_{\beta} (2\pi\hbar\omega_\beta)^{1/2} a_\beta(0) \, \mathbf{A}_\beta(\mathbf{r}) e^{-i\omega_\beta t} + \mathrm{H.c.} , \qquad (2)$$

where $a_\beta(0)e^{-i\omega_\beta t}$ is the source-free, Heisenberg-picture

photon-annihilation operator for mode β of the field, with associated (c-number) mode function $\mathbf{A}_\beta(\mathbf{r})$. The dipole moment induced by **E** is

$$\mathbf{p}(t) = i \sum_{\beta} (2\pi\hbar\omega_\beta)^{1/2} \alpha(\omega_\beta) a_\beta(0) \, \mathbf{A}_\beta(\mathbf{r}) e^{-i\omega_\beta t} + \mathrm{H.c.} , \qquad (3)$$

where, for frequencies ω_β away from any absorption resonances, the polarizability $\alpha(\omega_\beta)$ may be assumed to be real. Equations (1)–(3), together with the vacuum-field expectation values $\langle a_\beta(0)a_{\beta'}(0)\rangle = \langle a_\beta^\dagger(0)a_{\beta'}(0)\rangle = 0$ and $\langle a_\beta(0)a_{\beta'}^\dagger(0)\rangle = \delta_{\beta\beta'}$, imply

$$\langle E \rangle = -\tfrac{1}{2} \sum_{\beta} (2\pi\hbar\omega_\beta)\alpha(\omega_\beta) |\, \mathbf{A}_\beta(\mathbf{R})|^2 . \qquad (4)$$

Note that we are assuming for simplicity here an isotropic polarizability, i.e., $\alpha_{ij} = \alpha\delta_{ij}$, as is the case for atoms but, of course, not necessarily for molecules.

In Ref. [6] it was shown that van der Waals dispersion forces and their macroscopic (Casimir) manifestations can be obtained from either source fields or source-free fields, depending on how field annihilation and creation operators are ordered. Here we are taking the source-free (vacuum-field) approach, corresponding to a symmetric ordering of annihilation and creation operators [9]; this ordering is already implicit in Eq. (1), since **E** is the (symmetric) sum of annihilation and creation parts. However, whichever approach we adopt, we must use the appropriate mode functions $\mathbf{A}_\beta(\mathbf{r})$ for the field. For a collection of atoms, this means that the $|\mathbf{A}_\beta(\mathbf{R})|^2$ appearing in Eq. (4) for the energy of an atom at **R** *must account for the presence of all the other atoms*. That is, the quantization of the field as in Eq. (2) must be performed subject to the presence of all the atoms [6].

As emphasized in Ref. [6], the mode functions $\mathbf{A}_\beta(\mathbf{r})$ in the presence of polarizable matter are determined by purely *classical* electromagnetic considerations. Let $\mathbf{A}_\beta^{(0)}(\mathbf{r})$ be a mode function corresponding to frequency ω_β in the absence of any particles:

$$\mathbf{A}_\beta^{(0)}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_\beta \cdot \mathbf{r}} \mathbf{e}_\beta \qquad (5)$$

or

$$\mathbf{A}_\beta^{(0)}(\mathbf{r}) \rightarrow \mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{r}) = \frac{1}{\sqrt{V}} \mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k} \cdot \mathbf{r}} , \qquad (6)$$

where V is a quantization volume and $\mathbf{e}_{\mathbf{k}\lambda}, \lambda = 1, 2$, is a polarization unit vector. The form $e^{i\mathbf{k}\cdot\mathbf{r}}$ is this case is dictated by the requirement that the energy (4) for an atom in an otherwise perfect vacuum must be independent of the position **R** of the atom. The equation (4) then yields the nonrelativistic expression for the Lamb shift [6].

To determine the modification of the mode functions (6) due to the presence of identical atoms at the positions $\mathbf{R}_j$, we use the superposition principle for electromagnetic fields, which in this case states that the total field $\mathbf{A}_{\mathbf{k}\lambda}(\mathbf{r})$ at **r** corresponding to the mode $(\mathbf{k}, \lambda)$ is the unperturbed field $\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{r})$ plus the fields produced by all the atoms. The field from each atom is a dipole field associat-

ed with the dipole moment induced by the total field $A_{k\lambda}(R_j)$ at the atom. This dipole moment is $\alpha(\omega_k)A_{k\lambda}(R_j)\times e^{-i\omega_k t}$. Thus

$$A_{k\lambda}(r)=A_{k\lambda}^{(0)}(r)+\sum_j \alpha(\omega_k)\nabla\times\nabla\times\frac{A_{k\lambda}(R_j)e^{ik|r-R_j|}}{|r-R_j|},$$

(7)

where we have used the fact that the electric field produced by a dipole moment $p(t)$ at R_j is [10]

$$E(r,t)=\nabla\times\nabla\times\frac{p(t-|r-R_j|/c)}{|r-R_j|}.$$

(8)

The field at the atom R_i is given by

$$A_{k\lambda}(R_i)=A_{k\lambda}^{(0)}(R_i)+\sum_{j\neq i}\alpha(\omega_k)\nabla_i\times\nabla_i\times\frac{A_{k\lambda}(R_j)e^{ikR_{ij}}}{R_{ij}},$$

(9)

where $R_{ij}\equiv|R_i-R_j|$, and the solution of this (multiple-scattering) equation then yields the potential energy

$$\langle E_i\rangle=-\tfrac{1}{2}\sum_\beta (2\pi\hbar\omega_\beta)\alpha(\omega_\beta)|A_\beta(R_i)|^2$$

(10)

for an atom at R_i.

III. EXTINCTION THEOREM
AND THE MACROSCOPIC APPROACH
TO DISPERSION FORCES

Formally, assuming the polarizability $\alpha(\omega)$ is known exactly, the main problem in the calculation of dispersion forces is the solution of the self-consistent scattering equation (9). One approach to the solution of this equation is to assume a continuous uniform distribution of N atoms per unit volume. In this macroscopic approach (9) is replaced by the integro-differential equation

$$A_{k\lambda}'(R)=A_{k\lambda}^{(0)}(R)+N\alpha(\omega_k)$$

$$\times\int d^3R'\nabla\times\nabla\times\frac{A_{k\lambda}'(R')e^{ik|R-R'|}}{|R-R'|}.$$

(11)

Here it is to be understood that a small volume about R must be excluded from the integration, owing to the restriction $j\neq i$ in (9). As it stands, Eq. (11) is also satisfied by the mode functions at points R *outside* the region occupied by the atoms, being a general statement of the superposition principle. For such points $|R-R'|$ cannot vanish and consequently there is no restriction on the integration in (11).

The Ewald-Oseen extinction theorem [1,11] for isotropic or crystalline media states that the integral in (11) has two parts, one of which satisfies the wave equation in vac-

uum and exactly cancels ("extinguishes") the incident field $A_{k\lambda}^{(0)}$. The other part satisfies the wave equation with propagation velocity $c/n(\omega_k)$, where $n(\omega_k)$ is the refractive index and is related to the polarizability through the relation

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

(12)

for isotropic media. In the proof of the theorem [11] it is shown that $A_{k\lambda}'=A_{k\lambda}+4\pi P/3=[n^2(\omega_k)+2]A_{k\lambda}/3$, so that (11) may be written as

$$\tfrac{1}{3}[\epsilon(\omega_k)+2]A_{k\lambda}(r)$$

$$=A_{k\lambda}^{(0)}(r)+\frac{1}{4\pi}[\epsilon(\omega_k)-1]$$

$$\times\int d^3R'\nabla\times\nabla\times\frac{A_{k\lambda}(R')e^{ik|R-R'|}}{|R-R'|},$$

(13)

or equivalently

$$\nabla\times\nabla\times A_{k\lambda}+\frac{\omega^2}{c^2}\epsilon(\omega)A_{k\lambda}=0.$$

(14)

The fact that the continuum limit of Eq. (9) leads via the extinction theorem to the wave equation (14) plus appropriate (macroscopic) boundary conditions is of course well known [1,11], but does not appear to have been previously stated in the context of van der Waals forces. In our opinion this is somewhat unfortunate, for the extinction theorem provides a foundation for the macroscopic theory of van der Waals forces due originally to Lifshitz. In the present version of the theory, the macroscopic approach to van der Waals forces reduces to (i) the solution of the *classical* Maxwell boundary-value problem (14), and (ii) the evaluation of the energy (10). An example of this procedure is given in Sec. V.

IV. ADDITIVE AND NONADDITIVE
DISPERSION ENERGIES

In the lowest order of approximation $A_{k\lambda}(R_i)\cong A_{k\lambda}^{(0)}(R_i)$ in (9) and then, as already noted, Eq. (10) gives the nonrelativistic Lamb shift [6]. In the next order of approximation,

$$A_{k\lambda}^{(1)}(R_i)\simeq A_{k\lambda}^{(0)}(R_i)$$

$$+\sum_{j\neq i}\alpha(\omega_k)\nabla_i\times\nabla_i\times\frac{A_{k\lambda}^{(0)}(R_j)e^{ikR_{ij}}}{R_{ij}}$$

(15)

and the R_i-dependent part of (10) is

$$\langle E_i^{(2)} \rangle = -\tfrac{1}{2} \sum_{\mathbf{k},\lambda} (2\pi\hbar\omega_k)\alpha(\omega_k)| \mathbf{A}_{\mathbf{k}\lambda}^{(1)}(\mathbf{R}_i)|^2$$

$$\cong -\mathrm{Re} \sum_{\mathbf{k},\lambda} (2\pi\hbar\omega_k)\alpha^2(\omega_k) \sum_{j\,(\neq i)} [\,\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_i)]^* \cdot \nabla_i \times \nabla_i \times \frac{\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_j)e^{ikR_{ij}}}{R_{ij}}$$

$$= -\frac{2\pi\hbar}{V} \sum_{j\neq i} \mathrm{Re} \sum_{\mathbf{k},\lambda} k^3\omega_k\alpha^2(\omega_k)e^{-i\mathbf{k}\cdot\mathbf{R}_{ij}}e^{ikR_{ij}}$$

$$\times \left[[1-(\mathbf{e}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{ij})^2]\frac{1}{kR_{ij}} + [3(\mathbf{e}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{ij})^2-1]\left[\frac{1}{(kR_{ij})^3} - \frac{i}{(kR_{ij})^2}\right] \right] \tag{16}$$

to second order in $\alpha(\omega_k)$. Here $\mathbf{r}_{ij}$ is the unit vector pointing from atom i to atom j ($\mathbf{r}_{ij}=\mathbf{R}_{ij}/R_{ij}$).

Now as usual $\sum_{\mathbf{k},\lambda}\to(V/8\pi^3)\int dk\, k^2\sum_\lambda\int d\Omega_{\mathbf{k}}$, and the sum over polarizations and the integration over solid angles about $\mathbf{k}$ are easily performed using the identity $\sum_\lambda(\mathbf{e}_{\mathbf{k}\lambda}\cdot\mathbf{r}_{ij})^2=1-(\mathbf{k}\cdot\mathbf{r}_{ij})^2/k^2$. We obtain

$$\langle E_i^{(2)} \rangle = -\frac{\hbar}{\pi c^6} \sum_{j\,(\neq i)} \int_0^\infty d\omega\, \omega^6\alpha^2(\omega)G(\omega R_{ij}/c) , \tag{17}$$

$$G(x) \equiv \frac{\sin 2x}{x^2} + \frac{2\cos 2x}{x^3} - \frac{5\sin 2x}{x^4} - \frac{6\cos 2x}{x^5} + \frac{3\sin 2x}{x^6} . \tag{18}$$

For small R_{ij} the dominant contribution to $\langle E_i^{(2)} \rangle$ comes from the last term in (18) [6]:

$$\langle E_i^{(2)} \rangle \cong -\frac{\hbar}{\pi c^6} \sum_{j\neq i} \frac{3c^6}{R_{ij}^6} \int_0^\infty d\omega\, \alpha^2(\omega)\sin\frac{2\omega R_{ij}}{c} = -\sum_{j\neq i} \frac{3\hbar}{\pi R_{ij}^6} \int_0^\infty du\, \alpha^2(iu)e^{-2uR_{ij}/c}$$

$$= -\sum_{j\neq i} \frac{3\hbar}{\pi R_{ij}^6} \left[\frac{2}{3\hbar}\right]^2 \sum_m \sum_p \omega_{mg}\omega_{pg}|\mathbf{d}_{mg}|^2|\mathbf{d}_{pg}|^2$$

$$\times \int_0^\infty \frac{du\, e^{-2uR_{ij}/c}}{(u^2+\omega_{mg}^2)(u^2+\omega_{pg}^2)} , \tag{19}$$

where we have used the expression

$$\alpha(\omega) = \frac{2}{3\hbar} \sum_m \frac{\omega_{mg}|\mathbf{d}_{mg}|^2}{\omega_{mg}^2 - \omega^2} \tag{20}$$

for the polarizability of an atom in the ground state $|g\rangle$, where ω_{mg} and $\mathbf{d}_{mg}$ are the $m\to g$ (angular) transition frequency and the electric-dipole moment, respectively. If $R_{ij}\to 0$, or more precisely if $R_{ij}\ll c/\omega_{mg}$ for all transitions $m\leftrightarrow g$, we may replace $e^{-2uR_{ij}/c}$ by 1 in (19), and this gives the R_{ij}^{-6} form of the van der Waals interaction derived by London. If we assume furthermore that one particular transition is dominant, then

$$\langle E_i^{(2)} \rangle \cong -\sum_{j\neq i} \frac{3\hbar}{\pi R_{ij}^6} \left[\frac{2}{3\hbar}\right]^2 \omega_0^2|\mathbf{d}|^4\int_0^\infty \frac{du}{(u^2+\omega_0^2)^2}$$

$$= -\sum_{j\neq i} \frac{3\hbar\omega_0\alpha^2}{4R_{ij}^6} , \tag{21}$$

where ω_0 and $\mathbf{d}$ correspond to the dominant transition and $\alpha=(2/3\hbar)|\mathbf{d}|^2/\omega_0$ is the static ($\omega=0$) polarizability in the two-level approximation. This is the London result cited in the Introduction.

For large separations ($R_{ij}\gg 137a_0$, where a_0 is the Bohr radius) we can approximate (17) by

$$\langle E_i^{(2)} \rangle \cong -\frac{\hbar}{\pi c^2} \sum_{j\neq i} \alpha^2\int_0^\infty d\omega\, \omega^6 G\left[\frac{\omega R_{ij}}{c}\right]$$

$$= -\sum_{j\neq i} \frac{23\hbar c\alpha^2}{4\pi R_{ij}^7} , \tag{22}$$

which is the well-known long-range form of the dispersion interaction obtained by Casimir and Polder [12].

These results, based on the single-scattering approximation (15), give $\langle E_i^2 \rangle$ as a sum of *pairwise* ("additive") interactions.

In the next order of approximation we replace (15) by

$$\mathbf{A}_{\mathbf{k}\lambda}^{(2)}(\mathbf{R}_i) \cong \mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_i) + \sum_{j\neq i} \alpha(\omega_k)\nabla_i \times \nabla_i \times \frac{\mathbf{A}_{\mathbf{k}\lambda}^{(1)}(\mathbf{R}_j)e^{ikR_{ij}}}{R_{ij}}$$

$$= \mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_i) + \sum_{j\neq i} \alpha(\omega_k)\nabla_i \times \nabla_i \times \frac{\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_j)e^{ikR_{ij}}}{R_{ij}}$$

$$+ \sum_{j\neq i}\sum_{p\neq j} \alpha^2(\omega_k)\nabla_i \times \nabla_i \times \left[\frac{e^{ikR_{ij}}}{R_{ij}}\nabla_j \times \nabla_j \times \frac{\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_p)e^{ikR_{jp}}}{R_{jp}}\right] \tag{23}$$

and obtain a correction to $\langle E_i \rangle$ that is of third order in the polarizability. This correction is associated with nonadditive three-body contributions to $\langle E_i \rangle$. Although the calculation of the detailed form of the nonadditive contributions is somewhat complicated, we can understand their general form from (23). The $\nabla_i \times \nabla_i$ and $\nabla_j \times \nabla_j$ terms give rise to (near-field) terms varying as R_{ij}^{-3} and R_{jp}^{-3}, respectively. Cross products of the form $[\mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_i)]^* \cdot \mathbf{A}_{\mathbf{k}\lambda}^{(0)}(\mathbf{R}_p) \propto e^{-i\mathbf{k}\cdot\mathbf{R}_{ip}}$ give rise similarly to terms varying as R_{ip}^{-3} after the integration over all solid angles about $\mathbf{k}$ is carried out as required by (10). Then we obtain a three-body (nonretarded) contribution to $\langle E_i \rangle$ of the form

$$\langle E_{ijp}^{(3)} \rangle \propto \frac{\alpha^3}{R_{ij}^3 R_{jp}^3 R_{ip}^3} , \tag{24}$$

associated with the three-atom triplet i,j,p. Detailed forms of such nonadditive nonpairwise interaction energies have been derived from standard perturbation theory by Axilrod and Teller [13] an more recently by Power and Thirunamachandran [14] using the iteration procedure above in the interaction picture. These authors note that $\langle E_{ijp}^{(3)} \rangle$ may be attractive or repulsive, depending on the geometrical arrangement of the atoms.

The three-body interaction is roughly a factor α/R^3 smaller than the usual (two-body) van der Waals interaction, where R is a characteristic interatomic spacing. This point will play an important role in Sec. VI.

V. LATENT HEAT: MACROSCOPIC THEORY

We will consider first the case of an atom at a distance $z > 0$ from a half space filled with identical atoms. The half space $(z \leq 0)$ will be treated macroscopically according to the wave equation (14) plus the boundary conditions at the interface $z = 0$ between vacuum and the half space with dielectric constant $\epsilon(\omega)$.

For an atom at $z > 0$ we require, according to (10), the mode functions in the vacuum to the right of the dielectric half space. Consider a plane-wave electric field

$$\mathbf{A}_{\mathbf{k}\lambda1}^{(I)}(\mathbf{r}) \equiv \frac{1}{\sqrt{2}V}\mathbf{e}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{25}$$

incident on the interface from the right. Such an incident field leads to a reflected field

$$\mathbf{A}_{\mathbf{k}\lambda1}^{(R)}(\mathbf{r}) \equiv \frac{1}{\sqrt{2}V}\mathbf{e}_{\mathbf{k}\lambda}\frac{k_3 - k_3'}{k_3 + k_3'}e^{i\mathbf{k}^{(R)}\cdot\mathbf{r}} , \tag{26}$$

where

$$\mathbf{k} = (k_1, k_2, k_3) , \tag{27}$$

$$\mathbf{k}^{(R)} = (k_1, k_2, -k_3) , \tag{28}$$

$$k_3 = \left[\frac{\omega^2}{c^2} - k_1^2 - k_2^2\right]^{1/2} , \tag{29}$$

$$k_3' = \left[\epsilon(\omega)\frac{\omega^2}{c^2} - k_1^2 - k_2^2\right]^{1/2} . \tag{30}$$

These fields correspond to transverse electric (TE) modes. We also have transverse magnetic (TM) modes with incident and reflected electric fields

$$\mathbf{A}_{\mathbf{k}\lambda2}^{(I)}(\mathbf{r}) = \frac{1}{\sqrt{2}V}(\mathbf{e}_{\mathbf{k}\lambda} \times \mathbf{k}/k)e^{i\mathbf{k}\cdot\mathbf{r}} , \tag{31}$$

$$\mathbf{A}_{\mathbf{k}\lambda2}^{(R)}(\mathbf{r}) = \frac{1}{\sqrt{2}V}(\mathbf{e}_{\mathbf{k}\lambda} \times \mathbf{k}^{(R)}/k)$$
$$\times \left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 - k_3'}\right]e^{i\mathbf{k}^{(R)}\cdot\mathbf{r}} . \tag{32}$$

The factors of $1/\sqrt{2}$ are introduced for normalization [15]. The addition of (25) and (26) gives a TE mode, and addition of (31) and (32) gives a TM mode:

$$\mathbf{A}_{\mathbf{k}\lambda1}(\mathbf{r}) \equiv \frac{1}{\sqrt{2}V}\mathbf{e}_{\mathbf{k}\lambda}e^{i\mathbf{k}_\perp\cdot\mathbf{r}}\left[e^{ik_3z} + \left[\frac{k_3 - k_3'}{k_3 + k_3'}\right]e^{-ik_3z}\right] , \tag{33}$$

$$\mathbf{A}_{\mathbf{k}\lambda2}(\mathbf{r}) \equiv \frac{1}{\sqrt{2}V}e^{i\mathbf{k}_\perp\cdot\mathbf{r}}\left[(\mathbf{e}_{\mathbf{k}\lambda} \times \mathbf{k}/k)e^{ik_3z}\right.$$
$$+ (\mathbf{e}_{\mathbf{k}\lambda} \times \mathbf{k}^{(R)}/k)$$
$$\left.\times \left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 + k_3'}\right]e^{-ik_3z}\right] , \tag{34}$$

where $\mathbf{k}_\perp = (k_1, k_2)$. Thus

$$|\mathbf{A}_{\mathbf{k}\lambda1}(\mathbf{R}_i)|^2 = \frac{1}{2V}\left[1 + \left[\frac{k_3 - k_3'}{k_3 + k_3'}\right]^2\right.$$
$$\left. + 2\left[\frac{k_3 - k_3'}{k_3 + k_3'}\right]\cos2k_3z\right] \tag{35}$$

and

$$|\mathbf{A}_{\mathbf{k}\lambda2}(\mathbf{R}_i)|^2 = \frac{1}{V}\left[\frac{c^2}{\omega^2}\left[2k_\perp^2 - \frac{\omega^2}{c^2}\right]\left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 + k_3'}\right]\right]$$
$$\times \cos2k_3z$$
$$+ \frac{1}{2V}\left[1 + \left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 + k_3'}\right]^2\right] , \tag{36}$$

where z is the distance of the atom from the dielectric. The z-dependent part of (10) is therefore [16]

$$\langle E(z) \rangle = -\frac{1}{V}\sum_{\mathbf{k},\lambda}(2\pi\hbar\omega_k)\alpha(\omega_k)\left[\frac{k_3 - k_3'}{k_3 + k_3'} + \frac{c^2}{\omega_k^2}\left[2k_\perp^2 - \frac{\omega_k^2}{c^2}\right]\left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 + k_3'}\right]\right]\cos2k_3z$$

$$\rightarrow -\frac{1}{V}\frac{V}{8\pi^3}\sum_\lambda \int dk_3 \int d^2k_\perp(2\pi\hbar\omega)\alpha(\omega)\left[\frac{k_3 - k_3'}{k_3 + k_3'} + \frac{c^2}{\omega^2}\left[2k_\perp^2 - \frac{\omega^2}{c^2}\right]\left[\frac{\epsilon(\omega)k_3 - k_3'}{\epsilon(\omega)k_3 + k_3'}\right]\right]\cos2k_3z \tag{37}$$

in the mode continuum limit. The change of integration path as in (19) allows us to write $\langle E(z) \rangle$ as

$$\langle E(z) \rangle = -\frac{\hbar c}{2\pi} \int_0^\infty d\xi \int_0^\infty dk\, k \frac{1}{\kappa} \alpha(i\xi c) \left[-\xi^2 \frac{\kappa - \kappa_1}{\kappa + \kappa_1} + (2k^2 + \xi^2) \frac{\epsilon(i\xi c)\kappa - \kappa_1}{\epsilon(i\xi c)\kappa + \kappa_1} \right] e^{-2\kappa z} , \tag{38}$$

which is identical to the result of Schwinger, DeRaad, and Milton [2]. Here [17]

$$\kappa \equiv (\xi^2 + k^2)^{1/2} \tag{39}$$

and

$$\kappa_1 \equiv [\epsilon(i\xi)\xi^2 + k^2]^{1/2} . \tag{40}$$

Note that the limiting case of a perfect conductor may be obtained by taking $\epsilon \to \infty$:

$$\langle E(z) \rangle \to -\frac{\hbar c}{2\pi} \int_0^\infty d\xi \int_0^\infty dk\, k \frac{\alpha(i\xi c)}{(\xi^2 + k^2)^{1/2}} [\xi^2 + 2k^2 + \xi^2] e^{-2(\xi^2 + k^2)^{1/2} z}$$

$$= -\frac{\hbar c}{8\pi z^4} \int_0^\infty du\, \alpha \left[\frac{iuc}{2z} \right] (1 + u + \tfrac{1}{2} u^2) e^{-u} . \tag{41}$$

For large distances of the atom from the conductor we can replace $\alpha(iuc/2z)$ by $\alpha(0) = \alpha$ and obtain the well-known Casimir-Polder interaction [12]

$$\langle E(z) \rangle = -\frac{3\alpha\hbar c}{8\pi z^4} . \tag{42}$$

For $\epsilon(i\xi c) = 1 + 4\pi N\alpha(i\xi c) \cong 1$, (41) reduces to [2]

$$\langle E(z) \rangle \cong -\frac{\hbar c}{8\pi^2 N} \int_0^\infty d\xi [\epsilon(i\xi c) - 1]^2$$

$$\times \int_0^\infty dk\, k \frac{1}{\kappa^3} [k^4 + k^2\xi^2$$

$$+ \tfrac{1}{2}\xi^4] e^{-2\kappa z} . \tag{43}$$

For small z the leading contribution to (43) is

$$\langle E(z) \rangle \cong -\frac{\hbar N}{2z^3} \int_0^\infty du\, \alpha^2(iu) \equiv -\frac{N}{z^3} \left[\frac{\pi}{6} \right] C , \tag{44}$$

where, according to (19), the short-range interaction between two atoms a distance R apart is $-C/R^6$. The result (44) can be derived by integrating over pairwise interactions between the atom outside the dielectric and all the atoms comprising the dielectric:

$$\langle E(z) \rangle = -NC \int_z^\infty dz' \int_0^\infty dr(2\pi r) \frac{1}{[(r^2 + z'^2)^{1/2}]^6}$$

$$= -\frac{\pi}{6} NC \frac{1}{z^3} . \tag{45}$$

Schwinger, DeRaad, and Milton [2] have applied the result (43) in a calculation of the latent heat of liquid helium. Here we briefly summarize their result. If the latent heat q is due primarily to the dispersion force between atoms, then

$$q = -E(0)N/\rho$$

$$= \frac{\hbar c}{8\pi^2 \rho} \int_0^\infty d\xi [\epsilon(i\xi c) - 1]^2$$

$$\times \int_0^\infty dk\, k \frac{1}{\kappa^3} [k^4 + k^2\xi^2 + \tfrac{1}{2}\xi^4] , \tag{46}$$

where $E(0)$ is the $z \to 0$ limit of (43), i.e., the limit in which the atom is at the surface of the dielectric, and N and ρ are, respectively, the number and mass densities. For liquid He Schwinger, DeRaad, and Milton use the approximation [7]

$$\epsilon(\omega) \cong 1 + \frac{0.05}{1 - \omega^2/\omega_0^2} \tag{47}$$

with $\omega_0 = 3.5 \times 10^{16}$ sec^{-1}. The divergence of (46) is avoided by cutting off the upper limit of integration over the transverse photon momentum k at $k_c = \omega_c/c$ to obtain [2]

$$q \cong \frac{k_c^3}{96\pi\rho} (0.05)^2 \hbar\omega_0 . \tag{48}$$

Schwinger, DeRaad, and Milton take $\omega_c = 10^{18}$ sec^{-1}, corresponding to $k_c = 3.3 \times 10^7$ cm^{-1}; this corresponds to $k_c = 1/a$, where $a = 3$ Å is roughly the interatomic spacing in liquid helium. Then, using $\rho = 0.15$ g/cm^3 for liquid He, Schwinger, DeRaad, and Milton obtain [2]

$$q = 7 \text{ J/g} , \tag{49}$$

which they refer to as the "Casimir contribution to the latent heat." The experimental value [18] they compare this to is about twice as large:

$$q_{\text{exp}} = 15 \text{ J/g} . \tag{50}$$

The same cutoff k_c gives a predicted surface tension of liquid helium that is about three times larger than the experimental value. Schwinger, DeRaad, and Milton write, "We can fairly conclude that the Casimir effect, a manifestation of van der Waals forces, is responsible for a significant part of these phenomena" [2].

The divergence of the calculated latent heat and surface tension in the theory of Schwinger, DeRaad, and Milton is due to the macroscopic nature of the theory, which does not account for the finite distances between atoms. (Note that the value of the latent heat obtained in this approach is very sensitive to the numerical value of

the transverse-momentum cutoff k_c.) That is, the theory treats the dielectric medium as a perfect continuum. Obviously the divergence of the macroscopic theory for $z \to 0$ can be anticipated from the fact that for $\epsilon \cong 1$, the interaction of the atom with the dielectric is simply an integral over all the pairwise interactions with the atoms comprising the dielectric [Eqs. (44) and (45)]. Since these interactions diverge as the distance between the atoms approaches 0 [19], a continuum theory cannot give a finite latent heat or surface tension.

VI. SIMPLE MICROSCOPIC THEORY

Slater and Kirkwood [20] obtained the following expression for the energy of interaction between two He atoms separated by R (Å):

$$E^{(2)}(R) = \left[7.7 e^{-4.58R} - \frac{0.015}{R^6} \right] \times 10^{-10} \text{ erg .} \quad (51)$$

The first (repulsive) term is actually a fit to a more complicated repulsion term resulting from wave-function overlap at short distances. The second, dispersion interaction term is about 30% larger than the London approximation $-3\hbar\omega_0\alpha^2/4R^6$, with $\alpha \cong 2.0 \times 10^{-24}$ cm^3 the static polarizability for He [21]. For $R \cong 3.16$ Å, however, corresponding to the peak of the pair distribution function for liquid He^4 at $T = 0$ K [22], the London approximation differs from (51) by less than 10%.

X-ray scattering data indicate that each atom in liquid He^4 at $T = 0$ K has six nearest neighbors at separations $R = 3.16$ Å [22]. In the approximation of retaining only nearest-neighbor interactions, each atom therefore participates in six pairs of interactions. Since there are $\frac{1}{2}(6.023 \times 10^{23})$ pairs of atoms in a mole, the total cohesive energy per mole is expected to be

$$6(\tfrac{1}{2})(6.023 \times 10^{23})E^{(2)}(3.16 \text{ Å})$$

$$= 2.0 \times 10^9 \text{ erg/mol} = 50 \text{ J/g} \quad (52)$$

on the basis of this simple model. This is more than three times the experimental value of 15 J/g. However, London [23] noted that each atom in liquid He can be regarded as vibrating in the "cage" formed by its nearest neighbors, and made the semiempirical estimate of 30 J/g for the zero-point energy of this vibration. Following London, we subtract this effectively repulsive energy from (52) to obtain

$$q = 20 \text{ J/g ,} \quad (53)$$

in fair agreement with the observed value.

For heavier atoms the zero-point energy contribution to the latent heat is negligible and the simple estimate of the dispersion energy as above can by itself provide a fairly accurate estimate of latent heat. Consider, for instance, the example of solid Ne, where $\alpha = 3.96 \times 10^{-25}$ cm^3 [21], $R = 3.1$ Å [24], and the ionization potential $\hbar\omega_0 = 21.56$ eV. Assuming a close-packed fcc structure with 12 nearest neighbors [25], we estimate

$$q = \tfrac{1}{2}(12)(6.023 \times 10^{23})\frac{3\hbar\omega_0\alpha^2}{4R^6} = 1.7 \text{ kJ/mol} \quad (54)$$

in good agreement with the experimental value of 2.1 kJ/mol for the latent heat of sublimation of solid Ne [26]. Similarly good agreement is obtained for the other inert gas solids. For large molecules such estimates fail, mainly because the molecular radii can be comparable to or larger than intermolecular separations and consequently the London approximation $(-3\hbar\omega_0\alpha^2/4R^6)$ fails.

Simple estimates of this type, due originally to London [23], shed considerable light on the conclusion of Schwinger, DeRaad, and Milton [2] that "the Casimir effect, a manifestation of van der Waals forces, is responsible for a significant part of [latent heat and surface tension]." First, the conclusion about the importance of van der Waals forces is undoubtedly correct, but it should be emphasized that it has in fact been well accepted for many years since the original work of London. Second, the example of liquid He is unfortunately not a good one on which to base the conclusion that specifically macroscopic (Casimir) manifestations of these forces are important, since the repulsive zero-point contribution is not included in the macroscopic theory of Ref. [2] or Sec. V of this paper. Indeed it appears from the estimates above that this contribution by itself is *larger* than the attractive energy calculated by Schwinger, DeRaad, and Milton [27].

Surface tension can also be roughly estimated atomistically after the fashion of London's original work. If we again suppose each atom in liquid He to have six nearest neighbors, then an atom on the surface has one less nearest neighbor than atoms inside, and thus acquires an additional cohesive energy when two surfaces are brought together. With W the work per unit area done against intermolecular forces as the two surfaces are brought together from infinity, the surface tension is defined as $\Sigma = W/2$ [28]. Using the estimate (52), we estimate $W = \frac{1}{6}(3.3 \times 10^{-15} \text{ erg/atom})/(3.16 \text{ Å})^2/\text{atom}$, since (3.16 Å)^2 is the area occupied by each atom in the crude approximation used earlier. Thus $\Sigma \sim 0.28$ erg/cm^2, compared to the experimental value of 0.37 erg/cm^2 for liquid He^4 at $T = 0$ [29].

Finally we emphasize again that Casimir effects, referring specifically to *macroscopic* manifestations of van der Waals forces, cannot without some qualification be said to be responsible for cohesive properties such as latent heat and surface tension. For when simple pairwise London-type microscopic models are accurate, we can reasonably presume that nonadditive contributions to the van der Waals interactions are small, in which case the macroscopic theory, with its requirement of a transverse-momentum cutoff, is unnecessary. For liquid He^4 and solid Ne we have, respectively, $\alpha/R^3 \sim 0.006$ and 0.013. As noted in Sec. IV, this implies that the nonadditive contributions requiring a macroscopic approach are small. We conclude that "Casimir effects" then reduce to ordinary pairwise van der Waals interactions. For substances in which nonadditive effects are large, the Lifshitz-Casimir macroscopic approach may

indeed provide an accurate estimate of cohesive energies, but we are unaware of any calculations along these lines.

VII. SUMMARY

Our main conclusions are as follows.

(i) The Ewald-Oseen extinction theorem shows that all multiple-scattering nonadditive contributions to the van der Waals dispersion interactions are accounted for *in the continuous-medium approximation* by the macroscopic theory associated with the work of Lifshitz [5], Schwinger, DeRaad, and Milton [2], and many others.

(ii) The example of liquid He considered by Schwinger, DeRaad, and Milton does not in our view offer convincing support for their conclusion that the macroscopic "Casimir-type" approach accounts for a significant portion of the latent heat and surface tension. Nonadditive interactions associated with (macroscopic) Casimir effects are small in this application, and a simple London-type model assuming only additive nearest-neighbor interactions leads to a more accurate, cutoff-free prediction. Furthermore the effectively repulsive zero-point contribution, which is not accounted for in the theory of Ref. [2], appears on the basis of London's well-established ideas to be larger than the attractive contribution obtained by Schwinger, DeRaad, and Milton.

Finally another point concerning the Ewald-Oseen ex-

tinction theorem in this context is worth noting. In the original Lifshitz theory, and in all the subsequent work we are aware of, the force between dielectric media is obtained from electromagnetic modes determined by Maxwell equations together with macroscopic boundary conditions. This procedure, as opposed to a completely atomistic treatment of the dielectrics, is justified if the most significant virtual-photon wavelengths determining the interaction are large compared with the spacing of the atoms in the dielectric. In this case the continuum approximation is appropriate and the extinction theorem, as originally obtained by Oseen [1] for continuous media, is applicable. The effect of all the multiple dipole scatterings by the atoms in the dielectrics is then simply to enforce the laws of reflection and refraction, giving the modes of the macroscopic theory. In the case of two dielectric plates, for instance, the significant wavelengths are those on the order of the spacing between the plates, and if this is large compared with interatomic distances, the macroscopic theory can be used with impunity. Obviously the same kind of assumption underlies what is now called "cavity quantum electrodynamics" [30].

ACKNOWLEDGMENT

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