

Retarded Dispersion Energy between Macroscopic Bodies

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(Received 2 April 1970)

We calculate the change in self-energy of the electromagnetic radiation field in the presence of two dielectric bodies A and B . Starting from Maxwell's equations, the perturbed radiation field is expanded in terms of plane waves. The perturbed frequencies are obtained by applying quantum-mechanical perturbation theory. The sum over the perturbed minus the unperturbed frequencies, giving the retarded dispersion energy between the two bodies, is evaluated explicitly for the case of two spheres A and B . It is shown to assume a finite value at zero separation d of the spheres, so that no assumptions regarding an appropriate minimum separation are necessary. The total dispersion energy between bodies A and B , which includes also the energy gain of the material modes, is found via a complex integral transform. The total dispersion energy at small and medium separations is in agreement with previous results, i. e., we obtain a d^{-1} relationship at separations smaller than the radii of the spheres, and a d^{-6} relationship at separations larger than the radii of the spheres. In the retarded case, i. e., at separations d large compared with the characteristic wavelengths in the absorption spectra of the dielectrics, the dispersion energy is found to obey a d^{-2} law at separations d smaller than the radii of the spheres and the Casimir-Polder d^{-7} law at separations d larger than the radii.

I. INTRODUCTION

The dispersion energy between two molecules A and B is due to a correlated motion of their electrons. Calculations of the dispersion energy between the two molecules must account not only for these quantum-mechanical electron correlations, but also for their quantum-electrodynamical coupling to the external radiation field. The energy gain due to the electron correlations is proportional to the inverse sixth power of the separation d between the molecules. The coupling of the electron correlations to the radiation field removes the latter from the position of the molecules so that the d^{-6} dependence of the dispersion energy is reduced to a d^{-7} dependence at separations d larger than the characteristic molecular wavelengths.

The dispersion energy between two macroscopic bodies A and B was first treated by de Boer¹ and Hamaker,² who calculated the dispersion energy between two spheres by summing that between any two molecules. These additive pair terms do not account for the screening of the interaction fields by the remaining molecules, so that the calculations on the dispersion energy are correct only at separations d smaller than the Debye radii of the dielectrics involved. Lifshitz³ conducted a macroscopic investigation on the dispersion energy between two dielectric half-spaces. In his treatment, quantum mechanics is replaced by a random field term in the induction equation. He finds the perturbed radiation field by solving the relevant Maxwell equations and calculating the force of attraction between the half-spaces from the Maxwell stress tensor. A some-

what simpler approach, based on reaction field methods, has been adopted by Linder⁴ and by McLachlan⁵ for the investigation of the dispersion energy between macroscopic bodies. The only quantum-mechanical element left in their treatment is the fluctuation dissipation theorem, which relates the intensity of the dielectric fluctuation fields to their dissipative effect.

A third method of minimizing the quantum-mechanical effort is to calculate the dispersion energy between macroscopic bodies from the energy change of their electromagnetic normal modes. This method is generally applied in connection with the dipole model of dispersion. Its application to molecules is included in London's basic papers⁶ on dispersion forces. Bade⁷ investigated the higher-order interaction terms between identical molecules. Renne and Nijboer⁸ succeeded in summing this perturbation expansion exactly for the case of one molecule opposing a half-space consisting of the same kind of molecules. An extension to include arbitrary spatial distributions of arbitrary molecules was proposed by Langbein.⁹⁻¹¹ Since only macroscopic screened dipole fields enter the final energy expression, it is now possible to treat the dispersion energy between bodies of different geometry explicitly.

Compared with the fluctuation field methods, the dipole model has the disadvantage of not including retardation effects. The electric field of a harmonic dipole oscillator does not satisfy the vector Helmholtz equation, i. e., a harmonic dipole oscillation has only a finite lifetime and interacts only incompletely with the neighboring harmonic dipole

oscillators. An exact treatment of this retardation requires an expansion of the dipole fields in terms of eigenfunctions of the vector Helmholtz equation. This suggests avoiding the dipole model altogether and starting directly from eigenfunctions of the Helmholtz equation.

The inverse method of calculating the dispersion energy between macroscopic bodies only from the energy change of the external radiation field was introduced by Casimir,¹² who applied it to the case of ideal conductors in vacuum. It was later extended to the nonretarded dispersion energy between dielectric half-spaces by van Kampen, Nijboer, and Schram.¹³

In the present paper we expand the radiation interaction between two macroscopic bodies *A* and *B* in terms of plane waves, which represent a complete set of eigenfunctions of the Helmholtz equation. We calculate the dispersion energy from the change in self-energy of the total electromagnetic radiation field. The eigenfrequencies of this radiation field we determine by means of perturbation theory. Owing to the use of plane waves, we can simply write down the perturbation expansion of the eigenfrequencies of the delocalized vacuum modes, which arise by a one-to-one correspondence from the vacuum modes in the absence of the dielectrics. The localized material modes of *A* and *B*, on the other hand, arise from proper linear combinations of degenerate plane waves, so that before setting up their perturbation expansion, one needs a diagonalization with respect to the perturbing dielectrics *A* and *B*.

We discuss in detail the effect of the delocalized vacuum modes. By calculating the perturbed eigenfrequencies and adding up the resultant energy changes, we obtain the dispersion energy. The expression thus derived we evaluate for the case of two attracting spheres. This vacuum contribution to the dispersion energy turns out to be finite at zero separations and to vary as $c_0 - c_1 d + (c_2 - c_3 \ln d) d^2$ at small separations d of the spheres. At separations d larger than the characteristic wavelengths of the dielectrics, we obtain a d^{-2} relationship for the dispersion energy at separations d smaller than the radii and a d^{-7} relationship for the dispersion energy at separations d larger than the radii of the spheres. By shifting the contour of the frequency integration to the imaginary axis, we find that the total dispersion energy between the two spheres *A* and *B* at small separations d is given by the extended nonretarded Hamaker formula² which we derived previously¹⁰ by means of the dipole model, and by an extended retarded Casimir-Polder formula¹⁴ at large separations d . These results still depend on the contour integrals around the poles of the reciprocal dielectric constants

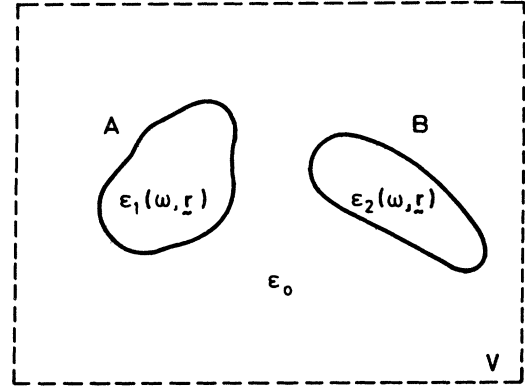


FIG. 1. Dielectrics *A* and *B*.

cancelling with the material-mode contributions to the dispersion energy, as is the case in the Casimir-Polder¹⁴ and in the Lifshitz³ calculations.

A more detailed treatment of the material-mode contributions to the dispersion energy will be given in a later paper.

II. PERTURBATION THEORY

Let us consider a large volume *V*, in which two macroscopic dielectric bodies *A* and *B* of arbitrary shape are embedded (Fig. 1). Bodies *A* and *B* may be inhomogeneous with dielectric constants $\epsilon_1(\omega, \vec{r})$ and $\epsilon_2(\omega, \vec{r})$ but at present nonmetallic, so that Maxwell's equations reduce to

$$(1/\gamma) \dot{\vec{B}} + \text{curl} \vec{E} = 0, \quad -(1/\gamma) \dot{\vec{D}} + \text{curl} \vec{H} = 0, \quad (1)$$

$$\text{div} \vec{B} = 0, \quad \text{div} \vec{D} = 0, \quad (2)$$

where $\gamma^2 = \epsilon_0 \mu_0 c^2$. In order to solve Eqs. (1) and (2) with regard to the eigenfrequencies of the external radiation field, we seek the harmonic solutions

$$\vec{B} = \vec{B}_\omega e^{i\omega t}, \quad \vec{D} = \vec{D}_\omega e^{i\omega t}, \quad (3)$$

thus obtaining the modified Helmholtz equation

$$(\omega^2/c^2 - \text{curl curl } \epsilon_0/\epsilon) \vec{D}_\omega = 0. \quad (4)$$

By assuming that the total volume *V* is large compared with the volume of the dielectrics *A* and *B*, we can consider these dielectrics to be small perturbations for the eigenfunctions of (4) in absence of *A* and *B*. A complete set of such unperturbed eigenfunctions are the transverse plane waves, which suggests a relation of the form

$$\vec{D}_\omega = \sum_{\vec{q}} \vec{a}(\vec{q}) |\vec{q}\rangle, \quad (5)$$

where

$$|\vec{q}\rangle = V^{-1/2} \exp(i\vec{q} \cdot \vec{r}) \quad \text{and} \quad (\vec{q} \cdot \vec{a}) = 0, \quad (6)$$

in agreement with (2).

The substitution of (5) for \vec{D}_ω in (4), and the use of the Fourier transform

$$(\epsilon_0/\epsilon) |\vec{q}\rangle = \sum_{\vec{q}'} |\vec{q}'\rangle \langle \vec{q}' | \epsilon_0/\epsilon | \vec{q} \rangle$$

before application of the curl operators, yield

$$(\omega^2/c^2)\vec{a}(\vec{q}) + \sum_{\vec{q}'} \langle \vec{q} | \epsilon_0/\epsilon | \vec{q}' \rangle [\vec{q} \times [\vec{q}' \times \vec{a}(\vec{q}')]] = 0. \quad (7)$$

Equations (5) and (7) are valid for both the vacuum and the material modes in V . The vacuum modes in the presence of the dielectrics A and B arise by a one-to-one correspondence with the vacuum modes $|\vec{k}\rangle$ in the absence of A and B , i.e., they can be obtained by the assumption

$$\vec{a}(\vec{q}) \ll \vec{a}(\vec{k}) \text{ for } \vec{q} \neq \vec{k}. \quad (8)$$

The material modes of the dielectrics A and B , on the other hand, are associated with the removal of the vacuum modes from A and B . They arise from properly diagonalized linear combinations of plane waves, which for instance in the case of spheres A and B are given by the spherical Bessel functions.¹⁵

Assuming (8), we restrict ourselves in the following to the investigation of the vacuum modes. A second-order perturbation treatment of (7) by means of the inequality (8) yields

$$\begin{aligned} & \left(\frac{\omega^2}{c^2} - k^2 \left\langle \vec{k} \left| \frac{\epsilon_0}{\epsilon} \right| \vec{k} \right\rangle \right) \vec{a}(\vec{k}) \\ & - \sum_{\vec{q} \neq \vec{k}} \frac{\langle \vec{q} | \epsilon_0/\epsilon | \vec{k} \rangle \langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle}{(\omega^2/c^2) - q^2 \langle \vec{q} | \epsilon_0/\epsilon | \vec{q} \rangle} \\ & \times [\vec{k} \times [\vec{k} \times [\vec{q} \times [\vec{q} \times \vec{a}(\vec{k})]]]] = 0. \end{aligned} \quad (9)$$

Since it is a vector equation, (9) is equivalent to a second-order secular determinant, hence

$$\begin{aligned} \frac{\omega^2}{c^2} &= k^2 \left(\left\langle \vec{0} \left| \frac{\epsilon_0}{\epsilon} \right| \vec{0} \right\rangle + \sum_{\vec{q} \neq \vec{k}} \frac{\langle \vec{q} | \epsilon_0/\epsilon | \vec{k} \rangle \langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle}{(\omega^2/c^2) - q^2 \langle \vec{0} | \epsilon_0/\epsilon | \vec{0} \rangle} \right) \\ & \times [q^2 - \frac{1}{2}(q_1^2 + q_2^2)] \pm \Delta, \end{aligned} \quad (10)$$

where q_1, q_2 denote the components of \vec{q} normal to \vec{k} , and Δ is given by

$$\begin{aligned} \Delta^2 &= \left(\sum_{\vec{q} \neq \vec{k}} \frac{\langle \vec{q} | \epsilon_0/\epsilon | \vec{k} \rangle \langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle}{(\omega^2/c^2) - q^2 \langle \vec{0} | \epsilon_0/\epsilon | \vec{0} \rangle} \frac{1}{2}(q_1^2 - q_2^2) \right)^2 \\ & + \left(\sum_{\vec{q} \neq \vec{k}} \frac{\langle \vec{q} | \epsilon_0/\epsilon | \vec{k} \rangle \langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle}{(\omega^2/c^2) - q^2 \langle \vec{0} | \epsilon_0/\epsilon | \vec{0} \rangle} q_1 q_2 \right)^2. \end{aligned} \quad (11)$$

2Δ is the splitting between the two transverse modes corresponding to the same wave vector \vec{k} .

III. DISPERSION ENERGY

The dispersion energy ΔE_{AB} between bodies A and B is given by that portion of the total radiation energy, which depends on the relative positions of A and B . The summation over the radiation

field must include both the vacuum and the materials modes and both polarization directions for a given wave vector \vec{k} . This entails that out of the three terms on the right-hand side of (10), only the second contributes to the dispersion energy ΔE_{AB} . The first term does not depend on the relative position of A and B ; the splitting $\pm \Delta$ vanishes by summing over the polarization directions.

Since the dielectric constants $\epsilon_1(\omega, \vec{r})$, $\epsilon_2(\omega, \vec{r})$ are, in general, complex, the perturbed radiation frequencies ω are also complex. The presence of bodies A and B causes the perturbed modes to decrease exponentially in time according to the general relationship $\text{Im} \{ \epsilon_0/\epsilon_i; (\omega, \vec{r}) \} < 0$ for arbitrary ω . This exponential decrease is a consequence of the classical treatment of the perturbed modes by means of the macroscopic Maxwell equations. Its quantum-mechanical analog is the destruction of single photons by absorption in the dielectrics, that is, by absorption by the material modes of A and B . However, if the two bodies A and B are assumed to be in thermal equilibrium with the radiation field, the material modes of A and B must emit as many photons to the vacuum modes as the latter emit to the material modes.

The total sum over the imaginary parts of the perturbed frequencies must vanish in the case of thermal equilibrium. Thus for the vacuum contribution to the dispersion energy, we have

$$\Delta E_{AB} = \text{Re} \left(\sum_{\vec{k}, \text{pol}} \frac{1}{2} \hbar (\omega - ck) \coth \frac{\hbar \omega}{2kT} \right) + \text{const}, \quad (12)$$

where by const we indicate terms independent of the relative position of A and B .

Substituting (10) for ω , we obtain

$$\begin{aligned} \Delta E_{AB} &= \frac{1}{2} \hbar \text{Re} \sum_{\vec{k}} ck \coth \frac{\hbar \omega}{2kT} \\ & \times \sum_{\vec{q} \neq \vec{k}} \frac{\langle \vec{q} | \epsilon_0/\epsilon | \vec{k} \rangle \langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle}{(\omega^2/c^2) - q^2} \\ & \times \frac{k^2 q^2 + (\vec{k} \vec{q})^2}{2k^2} + \text{const}. \end{aligned} \quad (13)$$

The sums over \vec{k} and \vec{q} in (12) include all plane waves, which satisfy periodic boundary conditions at the surface of V , i.e., the number of terms in these sums is proportional to V . The matrix elements $\langle \vec{k} | \epsilon_0/\epsilon | \vec{q} \rangle$, on the other hand, are inversely proportional to V due to the orthogonality of $|\vec{k}\rangle$ and $|\vec{q}\rangle$ for $\vec{k} \neq \vec{q}$ and $\epsilon_0/\epsilon = 1$ in the exterior. We obtain, according to (6),

$$\begin{aligned} \left\langle \vec{k} \left| \frac{\epsilon_0}{\epsilon} \right| \vec{q} \right\rangle &= -\frac{1}{V} \left\{ \int_A + \int_B \right\} d\vec{r} \left(1 - \frac{\epsilon_0}{\epsilon} \right) \\ & \times \exp [-i(\vec{k} - \vec{q}, \vec{r})]. \end{aligned} \quad (14)$$

Equation (14) allows a continuous transition to infinite volumes V in (13), if simultaneously the sums over \vec{k} and \vec{q} are transformed into integrals. This transition means that the perturbation of the individual plane waves $|\vec{k}\rangle$, $|\vec{q}\rangle$ by the presence of bodies A and B becomes infinitely small, while the number of waves increases in such a manner that the total energy change remains finite.

Hence,

$$\Delta E_{AB} = \frac{\frac{1}{2}\hbar c}{(2\pi)^6} \operatorname{Re} \int d\vec{k} k \coth \frac{\hbar\omega}{2kT} \times \int d\vec{q} \frac{k^2 q^2 + (\vec{k} \cdot \vec{q})^2}{2k^2(k^2 - q^2)} \quad (15)$$

$$\times [F_A(\vec{k} - \vec{q})F_B(\vec{q} - \vec{k}) + F_A(\vec{q} - \vec{k})F_B(\vec{k} - \vec{q})],$$

where $F_A(\vec{k})$, $F_B(\vec{k})$ are the dielectric form factors

$$F_{A,B}(\vec{k}) = \int_{A,B} d\vec{r} (1 - \epsilon_0/\epsilon) e^{i\vec{k} \cdot \vec{r}}. \quad (16)$$

Equation (15) is valid for arbitrary composition and geometry of the two bodies A and B . It represents only the vacuum contribution to the dispersion energy, and is obtained by applying second-order perturbation theory, i. e., higher-order terms in $F_A(\vec{k})$, $F_B(\vec{k})$ are omitted.

IV. SPHERES

In the following, we restrict ourselves to the attraction between two spheres A and B , see Fig. 2. We denote the centers of the spheres by \vec{O} and \vec{Z} and their radii by R_1 and R_2 . The composition of the spheres we assume spherical, so that the dielectric constants depend on the relative radii r_1 , r_2 only. Then, for the form factors $F_A(\vec{k})$, $F_B(\vec{k})$ we obtain

$$F_A(\vec{k}) = 4\pi \int_A d\vec{r} r_1^2 \left(1 - \frac{\epsilon_0}{\epsilon_1(\omega, r_1)}\right) \frac{\sin kr_1}{kr_1}, \quad (17)$$

$$F_B(\vec{k}) = \exp(i\vec{k} \cdot \vec{z}) 4\pi \int_B d\vec{r} r_2^2 \left(1 - \frac{\epsilon_0}{\epsilon_2(\omega, r_2)}\right) \frac{\sin kr_2}{kr_2}. \quad (18)$$

Substitution of (17) and (18) in (15) yields

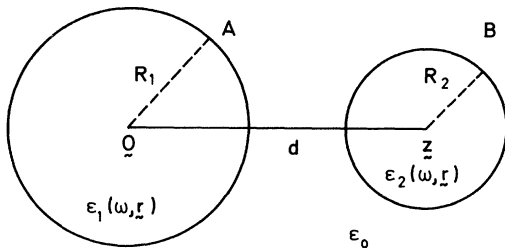


FIG. 2. Attracting spheres.

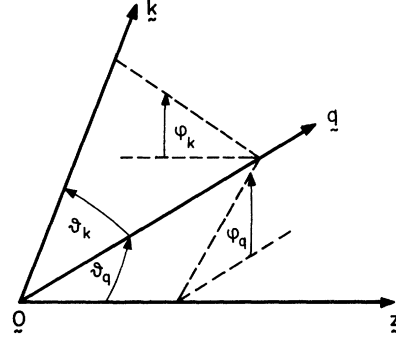


FIG. 3. Polar coordinates.

$$\Delta E_{AB} = \operatorname{Re} \frac{2\hbar c}{(2\pi)^4} \int d\vec{k} k \coth \frac{\hbar\omega}{2kT} \int d\vec{q} \cos \vec{q} \cdot \vec{z} \times \int_A dr_1 r_1^2 \left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \frac{\sin qr_1}{qr_1} \int_B dr_2 r_2^2 \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \times \frac{\sin qr_2}{qr_2} \frac{k^2 |\vec{k} - \vec{q}|^2 + (\vec{k}, \vec{k} - \vec{q})^2}{k^2(k^2 - |\vec{k} - \vec{q}|^2)}. \quad (19)$$

For an evaluation of the \vec{k} and \vec{q} integrals in (19), we introduce polar coordinates with respect to the axis \vec{z} for \vec{q} and with respect to the axis \vec{q} for \vec{k} (see Fig. 3). Noting that the θ_q , φ_q integrals relate only to $\cos \vec{q} \cdot \vec{z}$, whereas the θ_k , φ_k integrals relate only to the last quotient, we use

$$\int_{-1}^{+1} d \cos \theta_k \frac{k^2 |\vec{k} - \vec{q}|^2 + (\vec{k}, \vec{k} - \vec{q})^2}{k^2(k^2 - |\vec{k} - \vec{q}|^2)} = \left(\frac{k}{q} - \frac{q}{2k} + \frac{q^3}{8k^3}\right) \times \ln \left| \frac{2k - q}{2k + q} \right| - 4 + \frac{q^2}{2k^2} \quad (20)$$

and find

$$\Delta E_{AB} = \frac{\hbar c}{\pi^2} \operatorname{Re} \int_0^\infty dk \coth \frac{\hbar\omega}{2kT} \int_A dr_1 r_1 \left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \times \int_B dr_2 r_2 \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \phi(k, z), \quad (21)$$

where

$$\phi(k, z) = \int_0^\infty \frac{dq}{q^2} \sin qz \sin qr_1 \sin qr_2 \times \left((k^4 - \frac{1}{2}k^2q^2 + \frac{1}{8}q^4) \ln \left| \frac{2k - q}{2k + q} \right| - 4k^3q + \frac{1}{2}kq^3 \right). \quad (22)$$

By partial integration we can obtain for $\phi(k, z)$ the simpler equation

$$\phi(k, z) = -\pi \int_0^{2k} (dq/q^2) \cos qz \sin qr_1 \sin qr_2 \times (k^4 - \frac{1}{2}k^2q^2 + \frac{1}{8}q^4). \quad (23)$$

In the special case of homogeneous spheres A and B , we also evaluate the r_1 and r_2 integrals in (21), yielding

$$\Delta E_{AB} = -\frac{\hbar R_1 R_2}{\pi z} \int_0^\infty d\omega \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \times \coth \frac{\hbar \omega}{2kT} X(k, z), \quad (24)$$

where

$$X(k, z) = \int_0^{2k} dq \cos qz \left[\frac{\sin q r_1}{q r_1} - \cos q r_1 \right] \times \left[\frac{\sin q r_2}{q r_2} - \cos q r_2 \right] \left(\frac{k^4}{q^4} - \frac{1}{2} \frac{k^2}{q^2} + \frac{1}{8} \right). \quad (25)$$

The dispersion energy between two homogeneous spheres turns out to be a frequency integral ($\omega = ck$) over the deviations of the dielectric constants $\epsilon_1(\omega)$, $\epsilon_2(\omega)$ from ϵ_0 .

A sketch of the weight function $X(k, z)$ over k is shown in Fig. 4. The parameter of the different curves is the separation $d = z - R_1 - R_2$ of spheres A and B . By expanding the brackets in (25) as a Taylor series with respect to qR_1 , qR_2 in the region kR_1 , $kR_2 \ll \pi$, and by retaining only the cosine terms in the region kR_1 , $kR_2 \gg \pi$, we obtain the following approximations:

$$X(k, z) \approx \frac{1}{9} R_1^2 R_2^2 \begin{cases} \frac{22}{15} k^5, & \text{for } kR_i, kz \ll \pi \\ k^4 \sin 2kz/z, & \text{for } kR_i \ll \pi, kz \gg \pi \end{cases} \quad (26)$$

$$X(k, z) \approx \frac{1}{4} \begin{cases} \frac{11}{24} k - \frac{1}{4} \pi k^2 (z - R_1 - R_2), \\ \text{for } kR_i \gg \pi, kz \ll \pi \\ \frac{1}{16} \frac{\sin 2k(z - R_1 - R_2)}{z - R_1 - R_2}, \\ \text{for } kR_i, k(z - R_1 - R_2) \gg \pi. \end{cases} \quad (27)$$

The degree of approximation to this asymptotic behavior can be gathered from Fig. 4, which is plotted using the assumption of equal radii, $R_1 = R_2$.

V. ASYMPTOTIC BEHAVIOR

For the evaluation of (24) we note that the dielectric factors $1 - \epsilon_0/\epsilon_i(\omega)$ are in general resonance functions, i.e., $1 - \epsilon_0/\epsilon_i(\omega)$ is positive at $\omega = 0$, has peaks at the characteristic frequencies $\omega = \omega_{ij}$ ($j = 1, \dots, n$) of the dielectrics A and B , and decreases with ω^{-2} at high frequencies $\omega \gg \omega_{ij}$.

These properties, together with properties (26) and (27) of $X(k, z)$, guarantee the convergence of the dispersion energy (24) for arbitrary radii R_1 and R_2 and arbitrary distances z , and also for arbitrary temperatures T . Omitting the temperature dependence of ΔE_{AB} , we distinguish the following types of convergence of (24):

(a) The dielectric term $\operatorname{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ decreases more rapidly than the structure term $X(k, z)$. This is the case if $k(z \pm R_1 \pm R_2) \ll \pi$ for all values k up to the characteristic wave numbers $k = k_{ij} = \omega_{ij}/c$ of the dielectrics, that is, if the radii R_1 and R_2 and the distance z are small compared with the characteristic wavelengths λ_{ij} of the absorption spectra. Substituting for $\operatorname{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ its limit at high frequencies, we ob-

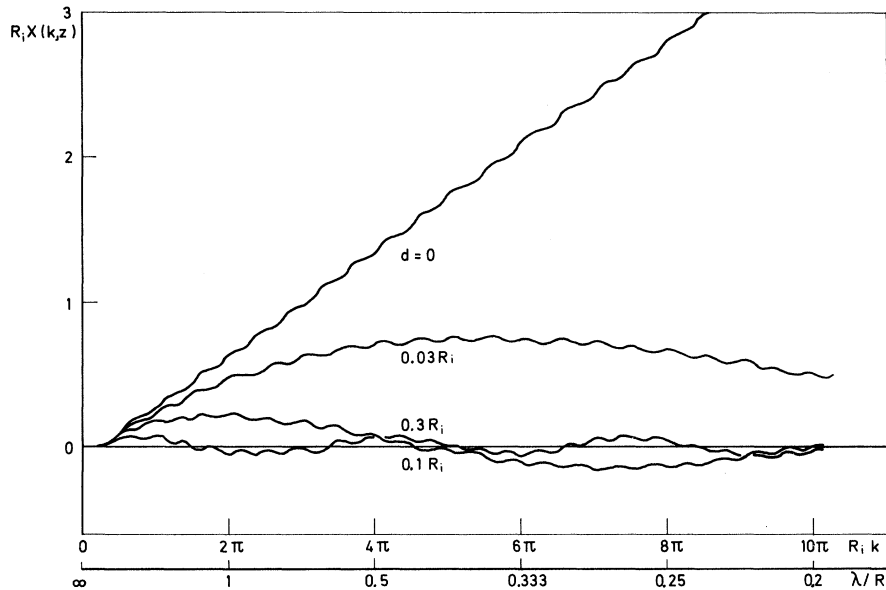


FIG. 4. Weight function $X(k, z)$.

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$$\Delta E_{AB} = -\frac{\hbar c R_1 R_2}{\pi z} \lim_{k \rightarrow \infty} \left[k^4 \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right] \\ \times \int_0^\infty \frac{dk}{k^4} X(k, z), \quad (28)$$

$$\int_0^\infty \frac{dk}{k^4} X(k, z) = -\frac{7}{24} \left\{ \frac{1}{6} (z^2 + 3R_1^2 + 3R_2^2) \right. \\ \left. + \frac{1}{R_1 R_2} \left[\left[\left(\frac{(z - r_1 - r_2)^2}{24} - \frac{1}{6} (r_1^2 - r_1 r_2 + r_2^2) \right) \right. \right. \right. \right. \\ \left. \left. \left. \times (z + r_1 + r_2)^2 \ln(z + r_1 + r_2) \right] \right]_{-R_1}^{R_1} \right]_{-R_2}^{R_2} \right\} \quad (29)$$

At separations small compared with the radii, $z - R_1 - R_2 \ll R_1, R_2$, ΔE_{AB} takes the general form

$$\Delta E_{AB} \propto \frac{R_1 R_2}{z} \{ c_0 - c_1 (z - R_1 - R_2) \\ + [c_2 - c_3 \ln(z - R_1 - R_2)] (z - R_1 - R_2)^2 \}. \quad (30)$$

The dispersion energy ΔE_{AB} and its spatial derivative, the dispersion force, are finite at the separation $d = z - R_1 - R_2 = 0$, whereas the second derivative has a logarithmic pole. For the dispersion force F_{AB} at $z - R_1 - R_2 = 0$, we obtain

$$F_{AB} = -\frac{d}{dz} \Delta E_{AB} \propto \frac{c_0}{(R_1 + R_2)^2} + \frac{c_1}{R_1 + R_2} = \left(\frac{R_1 R_2}{R_1 + R_2} \right)^2 \\ (d \ll R_1, R_2 \ll \lambda_{ij}). \quad (31)$$

For radii R_1 and R_2 small compared with the separation d , we obtain from (28) and (29)

$$\Delta E_{AB} \propto -\frac{R_1^3 R_2^3}{z^3} \lim_{k \rightarrow \infty} \left[k^4 \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right]. \quad (32)$$

The dispersion energy between spheres with very small radii, $R_1, R_2 \ll z \ll \lambda_{ij}$, is proportional to the volume of the spheres and inversely proportional to the third power of the separation $d \approx z$.

(b) The structure term $X(k, z)$ decreases more rapidly than the dielectric term $\operatorname{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$, which requires that $k(z \pm R_1 \pm R_2) \gg \pi$ for the characteristic wave numbers $k = k_{ij} = \omega_{ij}/c$ of the dielectrics. We expect a retarded interaction. Substituting for $\operatorname{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ its limit at low frequencies, we obtain

$$\Delta E_{AB} = -\frac{\hbar c R_1 R_2}{\pi z} \lim_{k \rightarrow 0} \left[\operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right] \\ \times \int_0^\infty dk X(k, z), \quad (33)$$

$$\int_0^\infty dk X(k, z) = \frac{1}{R_1 R_2} \left[\left[\frac{r_1 r_2}{(z - r_1 r_2)^2} - \frac{r_1 + r_2}{z - r_1 - r_2} \right. \right. \\ \left. \left. - \ln(z - r_1 - r_2) \right]_{-R_1}^{+R_1} \right]_{-R_2}^{+R_2}. \quad (34)$$

At separations small compared with the radii, $z - R_1 - R_2 \ll R_1, R_2$, we keep only the first term in (34) and find

$$\Delta E_{AB} = -\frac{23}{15} \frac{\hbar c}{2^7 \pi} \lim_{k \rightarrow 0} \left[\operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right] \\ \times \frac{R_1 R_2}{z(z - R_1 - R_2)^2}. \quad (35)$$

The retarded dispersion energy ΔE_{AB} between two rather close spheres is proportional to the inverse square of their separation d . This is one power in $1/d$ more than we obtained for the nonretarded case in Ref. 10. Moreover, the frequency integral over the dielectric term $\operatorname{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ is replaced by its limit at low frequencies.

At separations large compared with the radii, $z - R_1 - R_2 \gg R_1, R_2$, we obtain from (33) and (34)

$$\Delta E_{AB} = -\frac{23}{36} \frac{\hbar c}{\pi} \lim_{k \rightarrow 0} \left[\operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right] \frac{R_1^3 R_2^3}{z^7}. \quad (36)$$

The retarded dispersion energy is proportional to the volume of the spheres and obeys a z^{-7} law. This again is one power in $1/d$ more than obtained for the nonretarded case in Refs. 10 and 11.

We will learn in Sec. VII that the oscillations (27) of $X(k, z)$ and the explicit shape of $\operatorname{Re}(1 - \epsilon_0/\epsilon_1) \times (1 - \epsilon_0/\epsilon_2)$ may cause oscillations of ΔE_{AB} with the separation d , which at medium separations predominate over the d^{-7} relationship.

(c) A third important situation occurs if the radii R_1 and R_2 are large, but the separation d is small compared with the characteristic wavelengths of the dielectrics. From $k(z - R_1 - R_2) \ll \pi$ and

$$k(z + R_1 - R_2), k(z - R_1 + R_2), k(z + R_1 + R_2) \gg \pi,$$

we deduce that, of the products of circular functions in $X(k, z)$, only those yielding circular functions in $q(z - R_1 - R_2)$ must be retained. Using (27) we obtain

$$\Delta E_{AB} = -\frac{\hbar c R_1 R_2}{\pi z} \left[\frac{11}{96} \int_0^\infty dk k \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right. \\ \left. - \frac{1}{16} \pi (z - R_1 - R_2) \int_0^\infty dk k^2 \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) \right. \\ \left. + (z - R_1 - R_2)^2 [c_2 - c_3 \ln(z - R_1 - R_2)] \right]. \quad (37)$$

Since from the general relation $\epsilon^*(\omega) = \epsilon(-\omega^*)$ we can prove

$$\begin{aligned} \int_0^\infty dk k^n \operatorname{Re} \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right) &= 0 \quad \text{for } n = 0, 2 \\ &= - \int_0^\infty dk k \left(1 - \frac{\epsilon_0}{\epsilon_1} \right) \left(1 - \frac{\epsilon_0}{\epsilon_2} \right)_{ik} \quad \text{for } n = 1, \end{aligned} \quad (38)$$

we find the first term in the braces of (37) to be negative and the second term to vanish. We obtain a positive dispersion energy ΔE_{AB} , i.e., a repulsion of bodies A and B rather than an attraction. The removal of the vacuum modes from the inter-space between A and B causes an increase of the total radiation energy.

Expression (37) matches the general form (30) for small separations d , so that we finally obtain

$$\begin{aligned} \Delta E_{AB} &\propto [c_0 - c_1 d + (c_2 - c_3 \ln d) d^2] R_1 R_2 / z, \quad d \ll \lambda_{ij}, R_i \\ &\propto R_1 R_2 / z d^2, \quad \lambda_{ij} \ll d \ll R_i \\ &\propto R_1^3 R_2^3 / z^3, \quad R_i \ll \lambda_{ij} \ll d \\ &\propto R_1^3 R_2^3 / z^7, \quad \lambda_{ij}, R_i \ll d. \end{aligned} \quad (39)$$

VI. COMPLEX INTEGRATION

We stated in Sec. III that ΔE_{AB} according to (15) represents only the vacuum-mode contribution to the dispersion energy. However, an exact theory on the dispersion energy must include the material-mode contributions.

The material modes of a dielectric are linked to the zeros of its dielectric constant ϵ . Close to these zeros large electric fields \vec{E} require only a small electric displacement \vec{D} , so that the electric modes inside the dielectric have only small amplitudes in the exterior.¹⁵ Correspondingly, we find that the perturbation expansion (9) for $(\omega/c)^2$ in the presence of A and B diverges in the vicinity of $\epsilon_i = 0$. There exist additional branches for $(\omega/c)^2$ which can be obtained by a perturbation treatment of (7), if zero-order functions diagonalized with respect to A or with respect to B are used.

Although we defer an exact treatment of the material modes to a later paper, we may obtain a strong hint regarding their influence from this correlation to the poles of $1/\epsilon_i(\omega)$: A shift of the contour of integration in ΔE_{AB} according to (24) from the real to the imaginary frequency axis requires an exclusion of the poles of $1/\epsilon_i(\omega)$. We suggest that the contour integrals around these poles yield the contribution of the material modes to the dispersion energy. Arguments in favor of this suggestion, besides the general correlation of both quantities, are the fact that it proves true in

the investigations of Casimir and Polder and of Lifshitz and that the results based on this suggestion agree with our previous results for the non-retarded case. Casimir and Polder¹⁴ exclude the poles of the molecular susceptibility by their path of integration and add the material modes afterwards. Lifshitz³ includes the material modes from the beginning, so that the resultant integrand has no poles in the ω region in question. The cancellation in the case of Dirac electrons in a common external potential, which interact with photons, was discussed in detail by Power and Zienau.¹⁶

Let us first transform the weight function $X(k, z)$ according to (25). We express $\cos qz$ as exponentials, introduce complex variables $\pm iq$ instead of q , and shift the contour of integration from the dashed line to the solid lines in Fig. 5. Γ is an arbitrary point on the real positive q axis. Hence,

$$\begin{aligned} X(k, z) &= -\frac{1}{2}i \left(\int_{-2ik}^{\Gamma} + \int_{\Gamma}^{2ik} \right) dq e^{-qz} \\ &\times \left[\cosh q R_1 - \frac{\sinh q R_1}{q R_1} \right] \\ &\times \left[\cosh q R_2 - \frac{\sinh q R_2}{q R_2} \right] \left(\frac{k^4}{q^4} - \frac{1}{2} \frac{k^2}{q^2} + \frac{1}{8} \right). \end{aligned} \quad (40)$$

For the complex integration of (24) we represent $\operatorname{Re} (1 - \epsilon_0/\epsilon_1) (1 - \epsilon_0/\epsilon_2)$ on the real k axis by

$$\begin{aligned} &\frac{1}{2} [(1 - \epsilon_0/\epsilon_1) (1 - \epsilon_0/\epsilon_2)]_k \\ &+ \frac{1}{2} [(1 - \epsilon_0/\epsilon_1) (1 - \epsilon_0/\epsilon_2)]_{-k}, \end{aligned}$$

according to the general relation $\epsilon^*(\omega) = \epsilon(-\omega^*)$. Inserting (40) in ΔE_{AB} according to (24), we shift the contour of integration from the dashed line to the upper and lower solid lines in Fig. 6 in the terms containing the q integrals from $-2ik$ to Γ

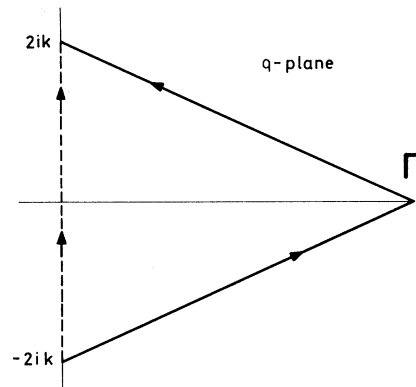
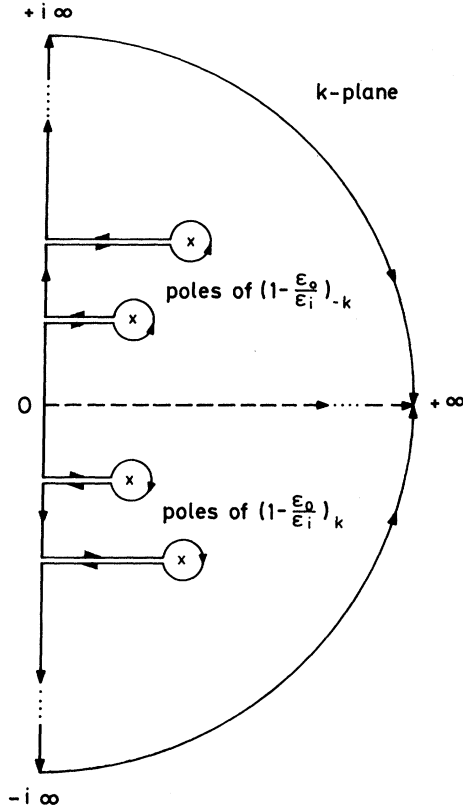


FIG. 5. Contour of $X(k, z)$ integration.

FIG. 6. Contour of ΔE_{AB} integration.

and from Γ to $2ik$, respectively. The k integrals over the quarter-circles vanish if we put $\Gamma = \infty$. The contours of the q integrals can then be chosen such that $|q| \geq |k|$ everywhere, entailing that the last parenthesis in (40) stays finite and the real parts of the total exponents $-q(z \pm R_1 \pm R_2)$ are negative. In the k integrals over the straight lines in Fig. 6 we introduce complex variables $\pm ik$ instead of k , yielding

$$\begin{aligned} \Delta_1 E_{AB} = & -\frac{\hbar c R_1 R_2}{2\pi z} \int_0^\infty dk \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right)_{ik} \right. \\ & + \left. \left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right)_{-ik} \right] \\ & \times \int_{2ik}^\infty dq e^{-qz} \left[\cosh q R_1 - \frac{\sinh q R_1}{q R_1} \right] \\ & \times \left[\cosh q R_2 - \frac{\sinh q R_2}{q R_2} \right] \left(\frac{k^4}{q^4} - \frac{1}{2} \frac{k^2}{q^2} + \frac{1}{8} \right). \end{aligned} \quad (41)$$

In order to evaluate the k integrals around the poles of $[(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)]_{\pm ik}$, we use the fact that the zeros of $\epsilon(-\omega)$ are complex conjugates of

those of $\epsilon(\omega)$: The poles shown in the first quadrant in Fig. 6 are complex conjugates of those shown in the fourth quadrant and yield complex-conjugate contributions to the dispersion energy. We obtain

$$\begin{aligned} \Delta_2 E_{AB} = & \frac{\hbar c R_1 R_2}{z} \operatorname{Re} \sum_{k=k_{ij}} \operatorname{Re} \tilde{s} \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \right] \\ & \times \int_{2ik}^\infty dq e^{-qz} \left[\cosh q R_1 - \frac{\sinh q R_1}{q R_1} \right] \\ & \times \left[\cosh q R_2 - \frac{\sinh q R_2}{q R_2} \right] \left(\frac{k^4}{q^4} - \frac{1}{2} \frac{k^2}{q^2} + \frac{1}{8} \right) \end{aligned} \quad (42)$$

with the sum over k covering all poles k_{ij} of $1/\epsilon_1(\omega)$, $1/\epsilon_2(\omega)$.

We consider $\Delta_2 E_{AB}$ to equal the negative of the material-mode contribution to the dispersion energy, so that both terms cancel after adding the latter. We are then left with $\Delta_1 E_{AB}$.

From (42) we find that the material-mode contribution to ΔE_{AB} decreases with $\exp[-2(z - R_1 - R_2) \times |\operatorname{Im} k_{ij}|]$ with increasing separation and increasing absorption. This is in agreement with an exponential decrease of the material modes in the exterior. However, the material-mode contribution diverges for zero separations, leaving us with a likewise diverging total dispersion energy $\Delta_1 E_{AB}$.

We start the discussion of $\Delta_1 E_{AB}$ with the case $R_1, R_2 \ll z$, that is with separations d large compared with the radii R_i . Noting that in the q integral of (41) $\exp(-qz)$ decreases more rapidly than the brackets, we expand the latter as a Taylor series and keep only the first term $[\cosh q R_i - \sinh q R_i / q R_i] \approx \frac{1}{3} (q R_i)^2$. Carrying out the q integration, we find

$$\begin{aligned} \Delta_1 E_{AB} = & -\frac{\hbar c R_1^3 R_2^3}{18\pi z^2} \int_0^\infty dk \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right)_{ik} \right. \\ & + \left. \left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right)_{-ik} \right] \\ & \times k^4 e^{-2kz} \left(1 + \frac{2}{kz} + \frac{5}{(kz)^2} + \frac{6}{(kz)^3} + \frac{3}{(kz)^4} \right). \end{aligned} \quad (43)$$

This expression agrees with that obtained by Casimir and Polder for the dispersion energy between molecules [Eq. (55) in Ref. 14], if we replace the molecular polarizability by that of macroscopic spheres.

If $\exp(-2kz)$ decreases more rapidly than the dielectric terms $[(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)]_{\pm ik}$, we can replace the latter by their value at $k=0$, again yielding (36). At separations large compared with the characteristic wavelengths of the dielectrics, only the z^{-7} contribution of the vacuum modes is

left. In the case of small separations, i.e., if the dielectric terms in (43) decrease more rapidly than $\exp(-2kz)$, we cancel the latter and all terms except the last one in parentheses. This leaves us with a z^{-6} law for the dispersion energy, which is due primarily to the material modes.

More general findings on both the retarded and the nonretarded limit we obtain by the following symmetric method: In the retarded case, we put $k=0$ in the dielectric term in (41), yielding

$$\begin{aligned} \Delta_1 E_{AB} = & -\frac{23}{15} \frac{\hbar c}{2^7 \pi z} \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \right]_0 \\ & \times \left[\left[\frac{r_1 r_2}{(z - r_1 - r_2)^2} - \frac{r_1 + r_2}{z - r_1 - r_2} \right. \right. \\ & \left. \left. - \ln(z - r_1 - r_2) \right]_{-R_1}^{R_1} \right]_{-R_2}^{R_2}, \quad (44) \end{aligned}$$

in accordance with (33) and (34). In the nonretarded case, we put $k=0$ in the q integral in (41), yielding

$$\begin{aligned} \Delta_1 E_{AB} = & -\frac{\hbar c}{2^6 \pi z} \int_{-\infty}^{\infty} dk \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \right]_{ik} \\ & \times \left[\left[\frac{r_1 r_2}{z - r_1 - r_2} + z \ln(z - r_1 - r_2) \right]_{-R_1}^{R_1} \right]_{-R_2}^{R_2}. \quad (45) \end{aligned}$$

This result agrees with that obtained previously by means of the dipole model of dispersion. We obtain the unscreened Hamaker formula, i.e., Eq. (18) in Ref. 10, in accordance with our restriction to a second-order perturbation treatment in Sec. II.

Eq. (45) yields a dispersion energy proportional to $1/d$ at small separations d of the spheres and proportional to $1/d^6$ at large separation d . The effect of retardation is an additional factor $1/d$, in accordance with our statement in Sec. V.

VII. COMPUTED RESULTS

In Figs. 7–13 we exhibit some computed results on the dispersion energy between dielectric spheres exclusive or inclusive of the material modes. For the dielectric terms $1 - \epsilon_0/\epsilon_i$, we assumed the typical resonance behavior

$$1 - \frac{\epsilon_0}{\epsilon_i} = \frac{c_i}{(k - k_i)(k + k_i^*)}, \quad k_i = k_{i1} - k_{i2} \quad (46)$$

so that the dielectric factor $\text{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ takes the form shown in Fig. 7. It is constant and positive at small wave numbers, has a sharp negative peak in the vicinity of the characteristic wave numbers k_{11} and k_{21} , and decreases with k^{-4} at large wave numbers. The area of the negative peak equals that of the positive regions, in agreement with the general relation (38). In order to obtain the vacuum-mode contribution ΔE_{AB} according to

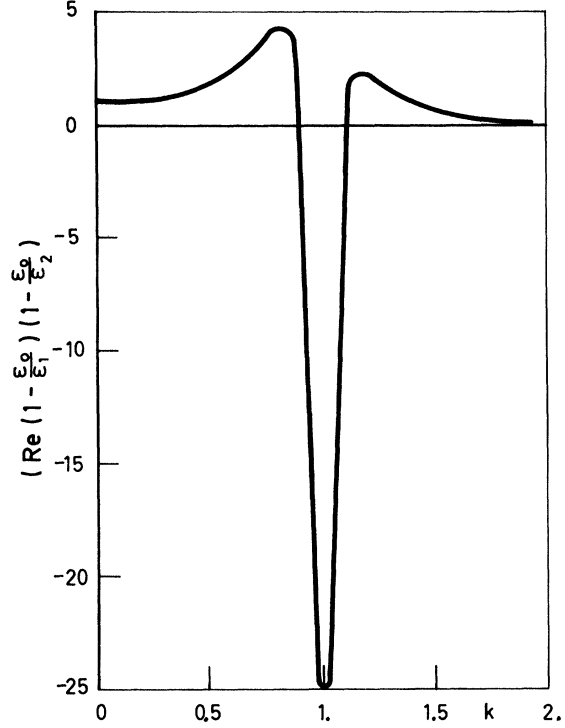
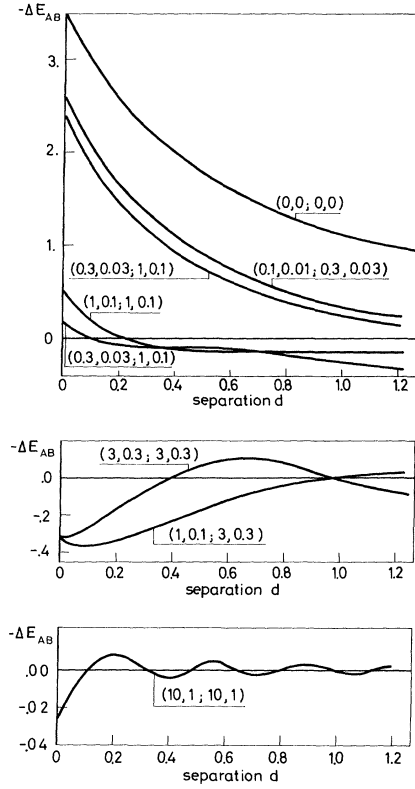


FIG. 7. $\text{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ versus k .

(24), we have to multiply $\text{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ with the weight function $X(k, z)$ as shown in Fig. 4, and to integrate over k . For $R_1=1$, $R_2=1$ and $R_1=0.6$, $R_2=3$, we obtain Fig. 8 and Fig. 9, respectively. The units of R_1 , R_2 , z , d , and of ΔE_{AB} are arbitrary units, with the unit of ΔE_{AB} being inversely proportional to that of the lengths, $[\Delta E_{AB}] = 0.01 c_1 c_2 \hbar c / \pi [R]$. The parameters noted for the different curves are the characteristic wave numbers (k_{11} , k_{12} ; k_{21} , k_{22}), in units $1/[R]$.

For small characteristic wave numbers, we obtain the upper parts of Figs. 8 and 9, i.e., a monotone decrease of ΔE_{AB} with increasing separation d . These plots verify the properties discussed in Sec. V using condition (a), $k(z \pm R_1 \pm R_2) \ll \pi$. ΔE_{AB} assumes a finite value at zero separation d , and decreases with z^{-3} at large separations. While the dispersion energies ΔE_{AB} differ in the two cases $R_1=1$, $R_2=1$ and $R_1=0.6$, $R_2=3$, we find their spatial derivatives, the dispersion forces, to coincide at small separations d , in accordance with (31).

An increase of the parameters (k_{11} , k_{12} ; k_{21} , k_{22}) entails a gradual transition to conditions (c) and (b) of Sec. V. We see from the lower parts of Figs. 8 and 9 that the vacuum-mode dispersion energy ΔE_{AB} becomes positive at small separations d , as inferred from (37) and (38), and oscillates

FIG. 8. Vacuum-mode contribution, $R_1=R_2=1$.

at separations d larger than the characteristic wavelengths. A glance at Figs. 4 and 7 shows that the oscillations of ΔE_{AB} are linked to the position of the peak of $\text{Re}(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)$ relative to the extremes of $\mathbf{X}(k, z)$. The oscillations vary roughly as $\sin 2kd$, and vanish exponentially at large separations, as can be shown by a complex integral transform of (24). For this limit only the retarded z^{-7} relationship is left.

Similar oscillations of the interaction energy are known from the interaction of two localized perturbations in a free-electron gas. The characteristic wavelength in that case, i.e., the characteristic wavelength of the interaction field, is the Fermi wavelength of the electrons. Grimley¹⁷ reported an interaction energy proportional to $z^{-3} \cos 2kz$. In the present case the characteristic wavelengths are those of the dielectrics A and B . While the origin of the oscillations is the same in two cases – the characteristic wavelengths have to fit the interspace – the z dependences of the amplitude are found to differ owing to the exponential decay of the radiation field of the dielectrics and owing to the different statistics used.

The total dispersion energy between bodies A and B , inclusive of the material-mode contribution is

shown in Figs. 10–13. Figure 10 demonstrates the general behavior of $\Delta_1 E_{AB}$. The solid line of Fig. 10 shows the result computed from (41) with the assumption

$$R_1 = R_2 = 1, \quad (k_{11}, k_{12}; k_{21}, k_{22}) = (1, 0.1; 1, 0.1).$$

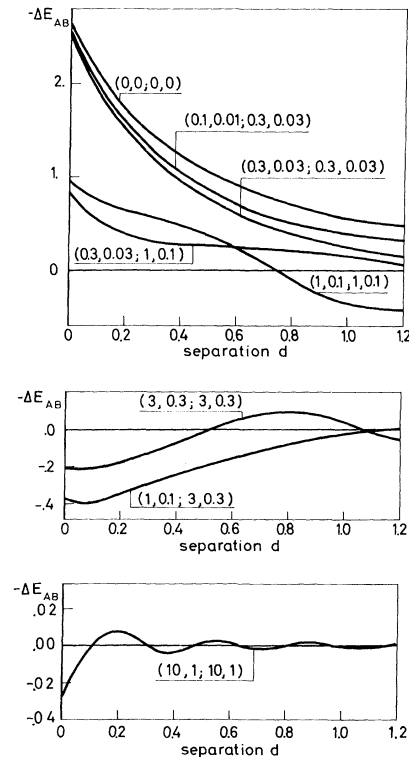
The dash-dotted curve represents the retarded approximation (44), the dash-dotted straight lines are the respective asymptotes, the d^{-2} relationship at small separations and the d^{-7} relationship at large separations. The dashed curve likewise represents the nonretarded approximation (45), the dashed straight lines are its asymptotes, the d^{-1} relationship at small separations and the d^{-6} relationship at large separations. From Fig. 10 we gather a rapid approximation of the exact dispersion energy to the nonretarded and the retarded findings, and a slow approximation to the limiting power laws.

Using (46) we find the dielectric factors in the retarded expression (44) and in the nonretarded expression (45) given by

$$[(1 - \epsilon_0/\epsilon_1)(1 - \epsilon_0/\epsilon_2)]_0 = c_1 c_2 / k_1 k_1^* k_2 k_2^* \quad (47)$$

and

$$\int_{-\infty}^{+\infty} dk \left[\left(1 - \frac{\epsilon_0}{\epsilon_1}\right) \left(1 - \frac{\epsilon_0}{\epsilon_2}\right) \right]_{ik}$$

FIG. 9. Vacuum-mode contribution, $R_1=0.6$, $R_2=3$.

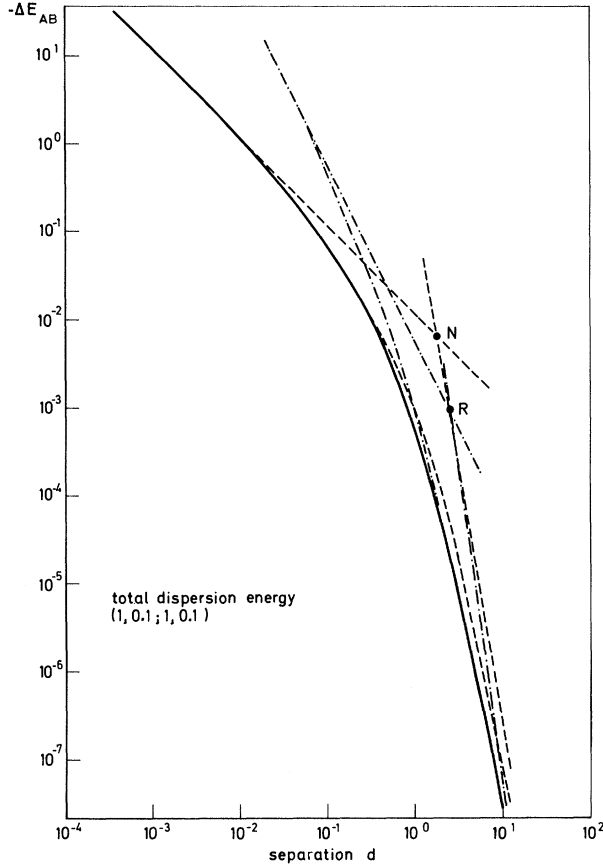


FIG. 10. Comparison of different approximations.

$$= \frac{\pi C_1 C_2 (k_{11} + k_{21})}{k_{11} k_{21} [(k_{11} + k_{21})^2 + (k_{12} - k_{22})^2]} \quad (48)$$

respectively. An increase of the characteristic wave numbers lowers the retarded factor (47) more strongly than the nonretarded factor (48), so that the dash-dotted lines of Fig. 10 are lowered relative to the dashed lines. This entails a transition from the nonretarded case to the retarded case at smaller separations d , in agreement with the general conclusions discussed in Sec. V. An increase of the radii R_1 and R_2 raises the asymptotes for large separations relative to the asymptotes for small separations. This entails a shift of the crossing points R and N in Fig. 10 to the right, and again a transition from the nonretarded case to the retarded case at smaller separations d .

In Fig. 11 we plotted the dispersion energy versus the separation for a fixed radius $R_1 = 1$ and different radii R_2 . The dispersion energy increases rapidly with increasing R_2 if $R_2 < R_1$, and only slowly if $R_2 > R_1$. If $R_2 \rightarrow \infty$, we obtain the dispersion energy between a sphere of radius $R_1 = 1$ and a half-space, which at large separations is proportional to d^{-3}

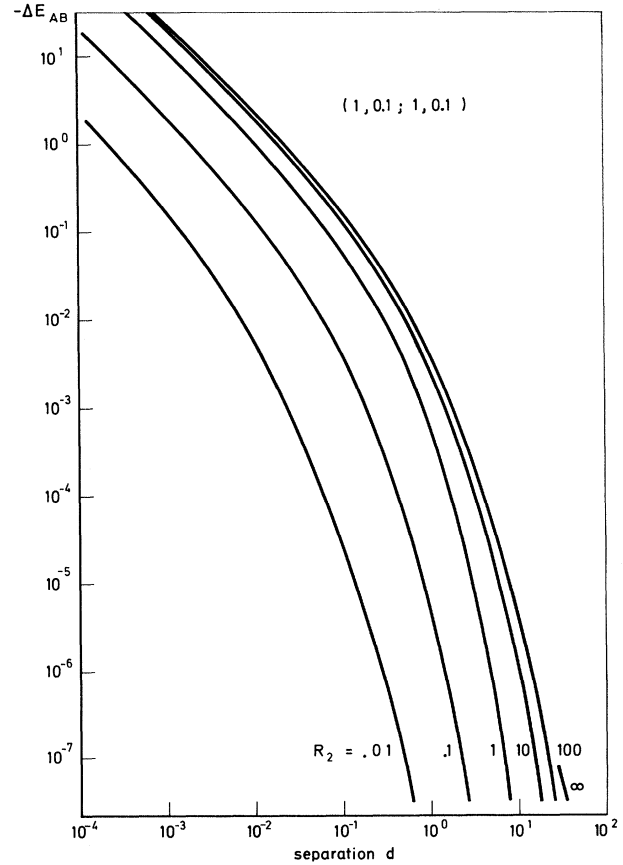
for the nonretarded limit (45) and proportional to d^{-4} for the retarded limit (44).

In Fig. 12 we varied R_1 and R_2 such that $R_1 R_2 / (R_1 + R_2)$ is constant. We note the coincidence of all curves at small separations, and the approximation of a d^{-4} relationship at large separations if $R_2 \gg R_1$.

Figure 13 shows the dependence of the total dispersion energy on the characteristic wave numbers. An increase of $(k_{11}, k_{12}; k_{21}, k_{22})$ causes the dispersion energy to be shifted to lower values and the transition from the nonretarded case to the retarded case to be shifted to smaller separations. The solid lines of Fig. 13 are based on equal characteristic wave numbers $k_1 = k_2$, whereas in calculating the dashed curves we assumed $k_1 = 10k_2$.

VIII. CONCLUSIONS

The reported treatment of the electromagnetic self-energy in the presence of dielectrics provides a general expression for the dispersion energy, which covers (a) the attraction between spheres or half-spaces, (b) arbitrary separations of the inter-

FIG. 11. Total dispersion energy, R_1 fixed, R_2 variable.

action partners, (c) the retarded and the nonretarded limit, and (d) the Casimir-Polder and the Lifshitz formulas.

The effect of the material modes is introduced via the trick of a complex integral transform, which has both positive (+) and negative (-) aspects: (a) the general correlation of the material modes to the zeros of the dielectric constants (+), (b) the agreement of our results with numerous previous findings (+), (c) a possibly different weight of the material modes as compared with the vacuum modes (-), and (d) the use of macroscopic dielectric constants at separations smaller than a few lattice constants. We feel that the positive aspects outweigh the negative ones, except possibly at very small separations d .

Close to the surface of a solid, the use of the bulk dielectric constant is subject to dispute in view of the lattice microstructure and the possible existence of surface states. This affects the dispersion energy between two dielectrics A and B in that a surface dielectric constant has to be used at separations smaller than the electric screening length.¹⁰ However, no reliable information on

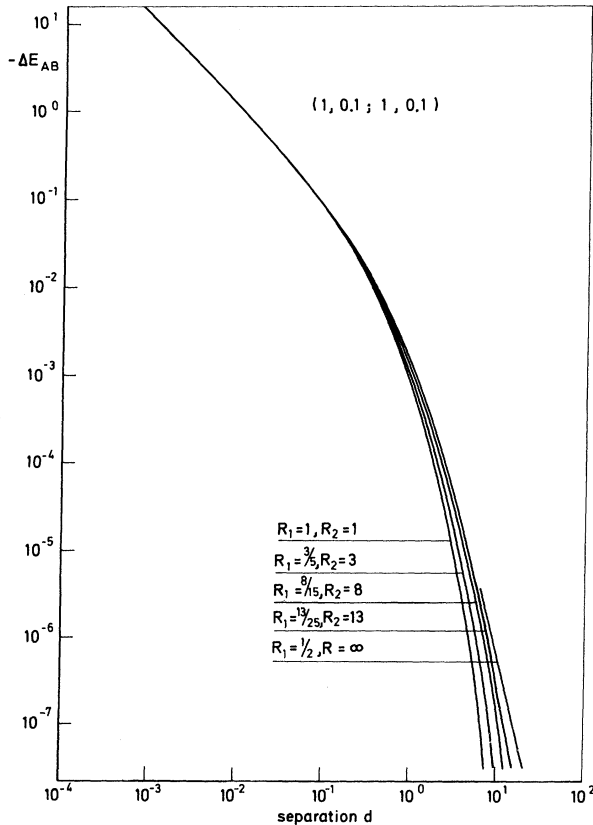


FIG. 12. Total dispersion energy, $R_1 R_2 / (R_1 + R_2)$ fixed, R_1, R_2 variable.

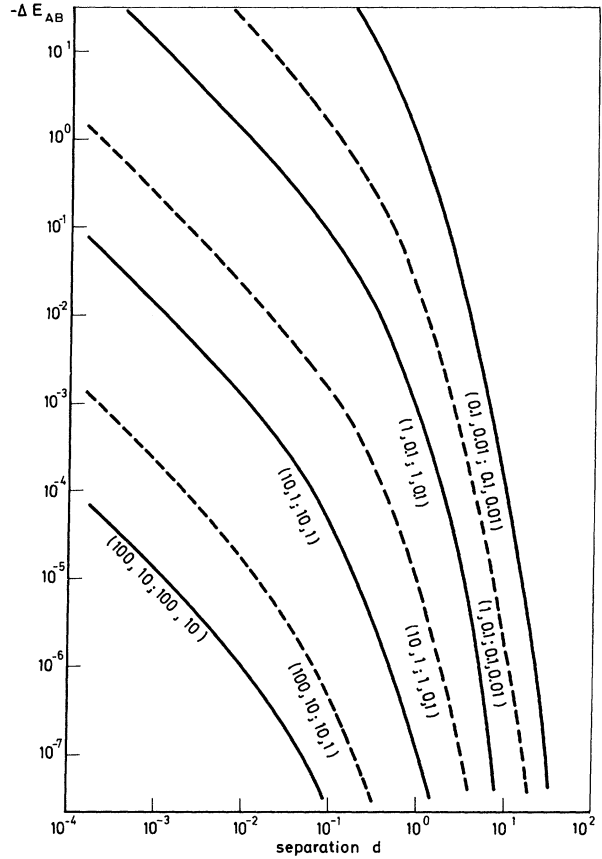


FIG. 13. Total dispersion energy, $(k_{11}, k_{12}; k_{21}, k_{22})$ variable.

this surface dielectric constant has become available so far. An effect of similar importance is the redistribution problem in the case of identical molecules.¹⁸ The resonant interaction between degenerate electron states entails nonadiabatic redistribution terms in their total free energy, which adiabatic susceptibility techniques are unable to account for by definition. However, this redistribution effect enters the dispersion interaction only at very high temperatures, when the system under investigation cannot be assumed to be in its nondegenerate electronic ground state permanently.

In Sec. II, we assumed the dielectrics A and B to be nonmetallic, so that no electric charges and currents enter the Maxwell equations (1) and (2) and the Helmholtz equation (4) for the electric displacement $\vec{D}_\omega = \epsilon \vec{E}_\omega$. In the case of metals we can derive a similar equation with respect to the generalized displacement $\vec{\Delta}_\omega = (\epsilon - i\sigma/\omega) \vec{E}_\omega$, namely,

$$\left(\frac{\omega^2}{c^2} - \text{curl curl} \frac{\epsilon_0}{\epsilon - i\sigma/\omega} \right) \vec{\Delta}_\omega = 0. \quad (49)$$

By expanding $\vec{\Delta}_\omega$ instead of \vec{D}_ω in terms of plane

waves, we can also derive all the above results for metals, with ϵ replaced by the generalized dielectric constant $\epsilon - i\sigma/\omega$. A difficulty to be kept in mind is the increased effectiveness of screening, which increases the importance of higher-order perturbation terms and requires a consideration of the wave-number dependence of the dielectric constant. We expect that the latter effect will largely cancel out, owing to the fact that the weight of an

unperturbed plane wave $|\vec{q}\rangle$ in a perturbed wave $|\vec{k}\rangle$ generally equals that of the unperturbed plane wave $|\vec{k}\rangle$ in the perturbed wave $|\vec{q}\rangle$.

ACKNOWLEDGMENTS

The author wishes to thank H. Büttner and T. B. Grimley for stimulating remarks on the effect of the material modes and on the interaction of perturbations in a free-electron gas.

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Metal-Insulator Transitions: A Simple Theoretical Model

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 (Received 27 April 1970)

A simple theoretical model for metal-insulator transitions is presented. It is based on the existence of both localized (ionic) and band (Bloch) states. It differs from other theories in that it assumes the one-electron states to be essentially unchanged by the transition. The electron-hole interaction is responsible for the anomalous temperature dependence of the number of conduction electrons. The model is studied in detail for several specific band models, in particular, for an *s*-like tight-binding cubic structure. The conditions for the presence of metallic and insulating phases at all temperatures as well as for the existence of first-order and higher-order transitions are given. The possibility of formation of bound-exciton states and the scattering mechanism responsible for the resistivity are also discussed.

I. INTRODUCTION

Transition-metal as well as rare-earth oxides, sulfides, and borides constitute a large group of substances which exhibit an unusually wide variety of electrical and magnetic properties.¹ Among these substances there are (i) excellent conductors, such as TiO, ReO₃, and CrO₃, with resistivities² as low (for ReO₃) as $4 \times 10^{-7} \Omega \text{ cm}$ at 77 °K; (ii) insulators³ such as MnO and CoO with room-temperature resistivities of 10^8 – $10^{15} \Omega \text{ cm}$; and (iii) some substances whose resistivities show an unusually

large variation with temperature. Of this third group, some materials present a first-order transition in the resistivity as a function of temperature; the transition temperature^{1,4} ranges from 119 °K for Fe₃O₄ to 1070 °K for NbO₂ and the change in resistivity at the transition ranges^{5,6} from a factor of about 20 for Ti₆O₁₁ to a factor of 10^8 for V₂O₃ (see Fig. 1). In most cases there is a simultaneous change in crystal structure, as for instance in V₂O₃ which goes from rhombohedral (corundum structure) at high temperatures ($\gtrsim 150$ °K) to monoclinic in the low-temperature phase ($\lesssim 150$ °K).