Some problems in the theory of van der Waals forces

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Several problems in the theory of van der Waals forces are reviewed: the interaction of atoms, molecules, and small particles of condensed matter at large distances; the van der Waals interaction of atoms with the surface of condensed matter; and the interaction between macroscopic condensed objects of various shapes. These questions have attracted considerable interest in the literature in recent years. Numerous results on these questions are given. All topics are discussed from a common standpoint to the extent possible, on the basis of the understanding of the fluctuational origin of van der Waals forces. Analysis of the physics content of the theoretical results on van der Waals forces is emphasized.

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1. INTRODUCTION

The electromagnetic interaction in a system of many particles (which obviously reduces to the Coulomb interaction when retardation is ignored) takes the form of exchange, multipole, fluctuational, and certain other interaction forces. Among these forces we can distinguish some which fall off in a power-law fashion at large distances. Such forces are frequently called "long-range" forces to distinguish them from the "short-range" forces which fall off rapidly (exponentially in most cases) with increasing distance. The distance dependence of short-range forces can rarely be described as universal to any extent; it is determined by the particular structure of the electron shells of the atoms. In contrast, long-range forces are distinguished by their universal behavior at large distances. While the average charge density and also the average dipole-moment density vanish in a medium at equilibrium, the basic long-range forces are generally forces of fluctuational origin, which are frequently called "van der Waals" or "molecular" forces.

In a description of the van der Waals interaction between objects, the particular features of the atoms and molecules and those of macroscopic objects can be taken into account fully by using their permittivities or polarizabilities. The success of the dielectric formalism in the theory of van der Waals forces can be credited to the universal dependence of these forces on the distance between the objects. Those results of the theory of van der Waals forces which are written exclusively in terms of the permittivities or polarizabilities of the objects are frequently called "macroscopic" results and sometimes referred to collectively as the macroscopic approach in the theory of van der Waals forces or the "macroscopic theory of van der Waals forces."

Indeed, macroscopic distances (i.e., scale lengths large in comparison with atomic dimensions, $a \sim 10^{-8}$ cm)always figure in a study of the van der Waals interaction. One of these scale lengths is the distance between the objects, R, and another is the scale wavelength of the absorption spectrum, λ_0 (typical values are $\lambda_0 \sim 10^{-5}$–10^{-6} cm). A dielectric description of the van der Waals interaction is made possible to a large extent not only by the conditions $R, \lambda_0 \gg a$ but also—and to a greater extent—by the nature of the microscopic fluctuation mechanism which gives rise to van der Waals forces between objects: The van der Waals forces arise directly from the fluctuating charge and current densities of the atoms or macroscopic objects and their interaction through the long-wavelength fluctuating electromagnetic field. The fluctuation nature of van der Waals forces for macroscopic objects is largely the same as for individual atoms and molecules. The macroscopic and microscopic aspects of the theory of van der Waals forces are therefore intimately related.

In reviewing several questions in the theory of van der Waals forces here we will be primarily concerned with this interaction. We will take it into account in reviewing the macroscopic and microscopic aspects of the problem.[1]

A fluctuating electromagnetic interaction may be either classical or quantum-mechanical. At temperatures $T \ll \hbar/\tau$ the fluctuations are known to be of a quantum nature (see, for example, § 110 in Ref. 3). For van der Waals forces the

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[1]Back in 1975 we published a paper in this journal[1] on the theory of van der Waals forces between macroscopic objects. We have recently revised that paper to make it a chapter of a book,[2] adding and refining it to reflect new research. Some of these additions will also appear in the present review, but of course we will not be reproducing the contents of Refs. 1 and 2 here.

scale time τ is usually associated with either a scale value $\omega_0^{-1} = \lambda_0/2\pi c$ for the absorption spectra or a parameter of the inhomogeneity in the system, R/c.

For two ground-state atoms the fluctuations are of course purely quantum in nature. If the propagation time of the interaction, R/c, is considerably shorter than the scale periods of the motion of the electrons in the atoms, $2\pi/\omega_0$, the interaction between atoms can be treated as electrostatic (this condition can be written in the form $R \ll \lambda_0$, where $\lambda_0 = 2\pi c/\omega_0$). London[4,5] offered a satisfactory explanation for the long-range forces acting between nonpolar atoms and molecules back in the infancy of quantum mechanics.

The predominant contribution to the attractive force between atoms in the ground state can be calculated in second-order perturbation theory for the electrostatic interaction between two dipoles. The energy of the interaction (of the attraction) turns out to be proportional to R^{-6} (see, for example, § 89 in Ref. 6). It can be shown that the energy of the interaction between the atoms stems from the appearance of a correlation $\langle d_{1,i} d_{2,j} \rangle$ between fluctuations of the dipole moments of the atoms, $\mathbf{d}_1$ and $\mathbf{d}_2$.

If $R \gtrsim \lambda_0$, and the retardation of the interaction is important, the problem must be treated quantum-mechanically, as was first done by Casimir and Polder.[7] In the limit $R \gg \lambda_0$ the retardation causes the interaction energy to be proportional to R^{-7} (see, for example, § 85 in Ref. 8). The fluctuating vacuum electromagnetic field plays an important role in this limiting case. Values of the fluctuating vacuum electric field at different spatial points are known to be correlated, so that we have $\langle E_i^{(0)}(\mathbf{r}_1) E_j^{(0)}(\mathbf{r}_2) \rangle \neq 0$ but $\langle E_i^{(0)}(\mathbf{r}_1) \rangle = \langle E_j^{(0)}(\mathbf{r}_2) \rangle = 0$. Consequently, if we place atoms at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ the vacuum field will induce in these atoms some fluctuating dipole moments which will in turn be correlated with each other. The interaction of interest is the average retarded interaction between atomic dipoles induced by the fluctuating vacuum field (see Section 2 for more details).

Fluctuational interactions are of a classical nature at sufficiently high temperatures, e.g., in a gas of polar atoms and molecules. If the orientations of the constant dipole moments of the atoms are equiprobable, the dipole moment of the atom averaged over direction will be zero. A calculation of the correlations between the orientations of the dipole moments of different atoms, however, with a Boltzmann distribution in orientations leads in the first nonvanishing approximation to a fluctuating interaction with an energy which falls off in proportion to R^{-6} as the distance between the atoms is increased. Forces of this type were studied a very long time ago by Reinganum[9] and Keesom.[10]

Also a long time ago, London[5b] pointed out that in addition to the problem of the van der Waals interaction between two atoms or molecules there is the interesting problem of the van der Waals interaction of an atom with a macroscopic object. This formulation of the question is important for analyzing physical adsorption of atoms on solid surfaces. However, in the analysis of this question by London and also in some early papers on the van der Waals forces between two macroscopic objects,[11,12] the interaction

was found as simply the sum of the interactions between the individual atoms, but this approach is justified only for low-density gases. For objects of condensed matter, on the other hand, collective effects must be taken into account in an analysis of van der Waals forces.

In certain particular cases it was found possible to circumvent these difficulties even before the development of a general theory of equilibrium fluctuations. For example, in the problem of the van der Waals interaction of an atom or molecule with a metal surface the problem can be solved in the simplest case by the method of images.[13-15] For large distances, at which retardation effects become important, it was found possible to solve the problem by taking into account the change in the energy of the zero-point oscillations of the electromagnetic field.[16] On the other hand, it was only after the development of the fluctuation-dissipation theorem[17] and the analysis of its application to the electromagnetic field[18] that Lifshitz[19] was able to derive some substantially more general results. In Ref. 19 Lifshitz found a general solution for the problem of the van der Waals interaction between two thick plates separated by an empty gap (see also Ref. 20). He shows how one could work from the fluctuational electromagnetic origin of the van der Waals forces to construct a common description, including collective effects, of the van der Waals forces between macroscopic objects with arbitrary permittivities. After quantum-field methods in many-body theory were developed, Lifshitz's approach was generalized by Dzyaloshinskiĭ and Pitaevskiĭ,[21] who derived some general expressions, with a broad range of applicability, for the contribution of van der Waals forces to the thermodynamic characteristics of inhomogeneous condensed media. Questions regarding the van der Waals parts of, for example, the stress tensor and the chemical potential of the condensed media were analyzed quite thoroughly.

On the other hand, the direct effect of van der Waals forces on the thermodynamic potentials (the free energy, in particular) of inhomogeneous media has still not been finally resolved. Only comparatively recently has some light been cast on the general case of absorbing media[22,23] (the problem simplifies in the case of transparent media[24,25]). This question is discussed in most detail in Refs. 1 and 2. An analysis of the van der Waals part of the energy or free energy of a condensed medium benefits from the similarities between this problem and the problem of the energy of thermal radiation in transparent media and that of the energy of fluctuations in electric circuits.

This review of course does not constitute a complete discussion of the problem of van der Waals forces. Much has been published in monographs and other reviews.[1,2,26-49] In going through the literature we saw the need for a comprehensive discussion and theoretical description of the fluctuation mechanism which gives rise to van der Waals forces. To some extent, there was a similar void for the problem of two atoms at large distances. In this other case we are of course not talking about deriving new results but about a method for deriving the results which would clarify both the physical side of the problem and the applicability of the results in describing, for example, the van der Waals interac-

tion between small particles of condensed matter (separated by distances large in comparison with their own dimensions).

Section 2 deals with the van der Waals interaction between atoms, molecules, and small particles of condensed matter. Section 3 deals for the most part with the interaction of atoms with solid surfaces. Section 4 discusses the van der Waals interaction between macroscopic objects of various shapes. We conclude by citing several questions and problems which we were not able to discuss in more detail.

2. LONG-RANGE INTERACTION OF ATOMS, MOLECULES, AND SMALL PARTICLES OF CONDENSED MATTER

a) An expression for the energy of the van der Waals interaction between two atoms is usually derived in second-order quantum-mechanical perturbation theory (§ 89 in Ref. 6), but we wish to begin this discussion of the van der Waals interaction between atoms in a slightly different way. As a result, the interaction energy will be expressed in terms of the polarizabilities of the atoms, but the most important point is that the applicability of the resulting expression to not only atoms but also small particles of condensed matter will become clear. More precisely, we consider from the outset two neutral "systems" (atoms, molecules, or small particles of condensed matter) separated by a distance R substantially larger than the dimensions of the systems, $a_{1,2}$. We then know quite well that in a first approximation we need to consider the dipole-dipole electrical interaction between the systems with the corresponding energy

$$U = \frac{d_1 d_2 - 3 (d_1 n)(d_2 n)}{R^3}, \tag{2.1}$$

where $d_1(r_1, t)$ and $d_2(r_2, t)$ are the dipole moments of systems 1 and 2, respectively, which are at points r_1 and r_2 at time t. We also introduce $R = r_2 - r_1$ and $n = R/R$. As we have stated, we are assuming $R \gg a_{1,2}$, but we also need the condition $R \ll \lambda_0$, where λ_0 is some scale radiation wavelength, so that we can ignore retardation effects (see the Introduction and the discussion below). If the dipole moments are zero or anomalously small, we would of course have to take into account some higher-order multipoles (quadrupoles, etc.), but we will not go into that possibility here.

The interaction U of course takes different forms in the distinct cases in which both systems have some average dipole moment, only one of the systems has, or neither has ("average" here is generally to be understood as the result of quantum-mechanical and statistical averagings). For the moment we are interested in the latter case, which holds, for example, for two S-state atoms and for neutral small particles of condensed matter which lack an average dipole moment.[2] Under these conditions the dipole moments d_1 and d_2, with zero averages, contribute to the interaction only through fluctuations. In the case of small particles of condensed matter at sufficiently high temperatures we could speak of the appearance as a result of thermal motion of

fluctuating charges and corresponding dipole moments. For an atom in a definite energy state with a given parity the wave function is not an eigenfunction of the dipole moment $d = eZr_0 - e\Sigma_i r_i$ (r_i is the coordinate of the ith electron in the atom, and r_0 is the coordinate of the nucleus), so that we could say that this dipole moment and the electric field E which it produces fluctuate. For the general case we assume that a fluctuational dipole moment $d_1^{sp}(r_1, t)$ has spontaneously arisen in system 1 and has produced a field $E_1(r, t)$. This field causes in the other system, 2, an induced dipole moment $d_2^{ind}(r_2, t) = \hat{\alpha}_2 E_1(r_2, t')$; here $\hat{\alpha}_2$ is the polarizability of system 2, which is an integral operator when the frequency (or temporal) dispersion is taken into account. For simplicity we are assuming here that the polarizability of the system is isotropic, so that the dipole moment d^{ind} is directed along the field which causes it, E. The field $E_1(r_2, t)$ is the field produced by the dipole moment of the first system, $d_1^{sp}(r_1, t)$, at the position of the second system:

$$E_1(r_2, t) = \frac{3n (d_1^{sp}(r_1, t) n) - d_1^{sp}(r_1, t)}{R^3}. \tag{2.2}$$

Similarly, a dipole moment $d_2^{sp}(r_2, t)$ which appears spontaneously in the second system induces in the first a dipole moment $d_1^{ind}(r_1, t) = \hat{\alpha}_1 E_2(r_1, t')$. If retardation is ignored, it is the average interaction of the fluctuational dipole in one system with the dipole which it induces in the other which is completely responsible for the dipole-dipole van der Waals forces between these two systems in the case $R \ll \lambda_0$. This mechanism for the onset of the van der Waals interaction in the case of two atoms without retardation has been under discussion for a very long time.[5c,50] After the general fluctuation-dissipation relations were developed,[17] it became possible to carry out the corresponding analysis for the general case of two arbitrary systems.[30,51]

We can go through these extremely simple calculations here. The energy of this interaction can be written immediately:

$$U(R) = -\frac{1}{2} \langle \hat{\alpha}_2 E_1^2(r_2, t) \rangle - \frac{1}{2} \langle \hat{\alpha}_1 E_2^2(r_1, t) \rangle$$

$$= -\frac{3}{R^6} (\hat{\alpha}_2 \langle d_{1, z}^{sp^2} \rangle + \hat{\alpha}_1 \langle d_{2, z}^{sp^2} \rangle). \tag{2.3}$$

Here the angle brackets denote a statistical average, which includes a quantum-mechanical average. In writing this expression we have assumed that both of the "systems" (atoms, etc.) are spherically symmetric, so that the condition $\langle (dn)^2 \rangle = \langle d_x^2 \rangle = \langle d_y^2 \rangle = \langle d_z^2 \rangle$ holds. A factor of 1/2 not seen in (2.1) appears in (2.3) because of the well-known fact that the energy of an "elastic" dipole is $-dE/2$. If absorption (or damping) is taken into account, expression (2.3) would require further justification, which is possible in general only for equilibrium systems.[21,1,2,26,52]

Converting to the spectral densities of the fluctuations in (2.3), we find

$$U(R) = -\frac{3}{R^6} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} (\alpha_2(\omega) \langle d_{1, z}^2 \rangle_\omega + \alpha_1(\omega) \langle d_{2, z}^2 \rangle_\omega), \tag{2.4}$$

where

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[2] Generally speaking, the electrostatic interaction between quadrupoles can also contribute substantially to the long-range interaction. A ground-state atom may also have an average quadrupole moment under certain conditions (because of a strong external magnetic field, for example[326,327]).

$$\langle d_{1,\,2z}^{sp^*}\rangle = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} d\omega\,\langle d_{1,\,2z}^{2}\rangle_{\omega}.\tag{2.5}$$

We recall that since a real field $\mathbf{E}$ means that the induced moment $\mathbf{d} = \hat{\alpha}\mathbf{E}$ must also be real we have

$$\alpha\,(\omega)\,=\,\alpha^{*}\,(-\omega^{*}),\tag{2.6}$$

where, by definition, $\mathbf{d}(\omega) = \alpha(\omega)\mathbf{E}_{0}e^{-i\omega t}$. Assuming that the frequency ω is real, and writing $\alpha(\omega) = \mathrm{Re}\,\alpha\,(\omega) + i\,\mathrm{Im}\,\alpha(\omega){\equiv}\alpha'(\omega) + i\alpha''(\omega)$, we find

$$\alpha'\,(\omega)\,=\,\alpha'\,(-\omega),\quad \alpha''\,(\omega)\,=\,-\alpha''\,(-\omega).\tag{2.7}$$

We now assume that both systems are at equilibrium with a heat reservoir, and we use the fluctuation-dissipation theorem. According to this theorem, the spectral density of the square of the equilibrium fluctuations of the dipole moment of an isolated atom or particle is related to the imaginary part of the corresponding polarizability by (see, for example, § 124 in Ref. 3)

$$\langle d_{z}^{2}\rangle_{\omega} = \hbar\,\mathrm{cth}\,\frac{\hbar\omega}{2T}\,\mathrm{Im}\,\alpha\,(\omega).\tag{2.8}$$

In the case of atoms the characteristic frequency ω_{0} in the absorption spectrum usually falls in the ultraviolet region, and at room temperature we have $\hbar\omega_{0}{\gg}T$. We therefore set $T = 0$ in (2.8); i.e., we assume that the atoms or macroscopic particles are in the ground state. From (2.8) we then find

$$\langle d_{z}^{2}\rangle_{\omega} = \hbar\,\frac{\omega}{|\,\omega\,|}\,\mathrm{Im}\,\alpha\,(\omega).\tag{2.9}$$

Substituting (2.9) into (2.4), and using (2.7), we find

$$U\,(R) = -\frac{3\hbar}{\pi R^{6}}\,\mathrm{Im}\int\limits_{0}^{\infty} d\omega\,\alpha_{1}\,(\omega)\,\alpha_{2}\,(\omega).\tag{2.10}$$

Since the polarizability $\alpha(\omega)$ is a linear-response function (a generalized permittivity), it has no singularities in the upper half-plane of the complex frequency ω. We also know from the theory of analytic functions that the integral of an analytic function does not depend on the particular integration path (if this path lies in the region in which this function is regular), only on the initial and final points of the path. We can therefore displace the integration contour (which initially coincides with the positive real frequency semiaxis) in expression (2.10) into the upper half-plane and thereby change this integration to one along the upper imaginary frequency semiaxis. This transformation substantially simplifies the integrand, since the polarizabilities $\alpha_{1,2}\,(\omega)$ are known to have a comparatively simple behavior on the upper imaginary frequency semiaxis: Their imaginary part is zero, and as the frequency is varied from zero to infinity along this semiaxis these polarizabilities fall off monotonically, taking on once each real value between $\alpha_{1,2}(0)$ and zero (§ 123 in Ref. 3).

We therefore find from (2.10) that the energy of the van der Waals dipole-dipole interaction of two atoms or particles in the ground state is

$$U\,(R) = -\frac{3\hbar}{\pi R^{6}}\int\limits_{0}^{\infty} d\omega\,\alpha_{1}\,(i\omega)\,\alpha_{2}\,(i\omega)\equiv-\frac{C_{6}}{R^{6}}.\tag{2.11}$$

Expression (2.11) was first found by Casimir and Polder[7] in the problem of the van der Waals interaction between atoms without retardation. Again we wish to point out that relations (2.2), (2.3), and (2.9), which underlie this derivation of expression (2.11), contain nothing which would specifically imply atoms. These relations apply equally well to any two small, isotropic, condensed-matter particles under the conditions

$$T \ll \hbar\omega_{0}\ll\frac{\hbar c}{R}\ll\frac{\hbar c}{a_{1,\,2}}\,;\tag{2.12}$$

here $\omega_{0} = 2\pi c/\lambda_{0}$, so that the condition $\omega_{0}{\ll}c/R$ is equivalent to the inequality $R{\ll}\lambda_{0}$, under which we can ignore retardation. The condition $R{\gg}a_{1,2}$ not only allows us to restrict the discussion to the dipole-dipole contribution to the van der Waals interaction but also allows us to use certain other approximations. In particular, there is the circumstance that expression (2.9) is strictly valid only for isolated particles.

In this derivation we also see the purely correlational origin of the van der Waals interaction between objects.[3] Actually, in this approximation the average dipole moments of the particles or atoms have not yet arisen, and the charge distribution in them remains spherically symmetric on the average. All that has appeared is a correlation between the spherically symmetric fluctuations of the dipole moments of the atoms, and it is this correlation which gives rise to the dipole-dipole van der Waals forces.

b) It is convenient and useful at this point to recall the relationship between our approach here and the more common approach in studies of atoms. We appeal to an expression for the polarizability of a ground-state atom from the theory of atomic dispersion (see, for example, § 59 in Ref. 8):

$$\alpha\,(\omega)\,=\,\sum_{n}\frac{e^{2}f_{0n}}{m\,[(\omega_{n0}^{2}-\omega^{2})-i\omega\delta]}\,,\quad \delta\rightarrow+0.\tag{2.13}$$

Here f_{0n} is the so-called oscillator strength of the transition from the state zero to the state n, given by

$$f_{0n} = \frac{2m}{\hbar^{2}}\,(E_{n}-E_{0})\left|\sum_{i}(z_{i})_{0n}\right|^{2} = \frac{2m}{\hbar}\,\omega_{n0}\left|\sum_{i}(z_{i})_{0n}\right|^{2},$$

$$\tag{2.14}$$

where $(z_{i})_{0n}$ is the matrix element of the coordinate z_{i} of the ith electron (of charge e and mass m) in the atom. Substituting (2.13) into (2.11), and carrying out the elementary integration, we find

$$U\,(R) = -\frac{3\hbar}{2R^{6}}\sum_{n,\,n'}\frac{e^{4}f_{0n}^{(1)}\,f_{0n'}^{(2)}}{m^{2}\,(\omega_{0n'}^{(2)}+\omega_{0n}^{(1)})\,\omega_{0n}^{(1)}\,\omega_{0n'}^{(2)}}$$

$$= -\frac{6e^{4}}{R^{6}}\sum_{n,\,n'}\frac{\left|\sum_{i}(z_{i}^{(1)})_{0n}\right|^{2}\left|\sum_{k}(z_{k}^{(2)})_{0n'}\right|^{2}}{E_{n}^{(1)}+E_{n'}^{(2)}-E_{0}^{(1)}-E_{0}^{(2)}}\equiv-\frac{C_{6}}{R^{6}},$$

$$\tag{2.15}$$

where the subscripts 1 and 2 specify atoms 1 and 2, respectively.

Expression (2.15) is exactly the same as the result[4,5a] derived in second-order quantum-mechanical perturbation

[3]In contrast with a study of objects of condensed matter of macroscopic size, in studies of atoms and molecules the term "van der Waals interaction" is sometimes understood to represent all long-range interactions, including in particular those which are not of a fluctuational origin. In the present review we are considering only the interaction of fluctuational origin, and this is what we are calling the "van der Waals interaction."

theory for the dipole interaction of two ground-state atoms separated by a large distance (see also § 89 in Ref. 6).

We assume that only one transition is important in each of the atoms and that the corresponding frequencies are $\omega_1 \to \omega_{n0}^{(1)}$ and $\omega_2 \to \omega_{n'0}^{(2)}$. From (2.15) we then find the London interpolation formula:

$$U(R) = -\frac{3\hbar e^4 f_1 f_2}{2 m_1 m_2 R^6 \omega_1 \omega_2 (\omega_1 + \omega_2)} = -\frac{3\hbar \omega_1 \omega_2}{2(\omega_1 + \omega_2)} \frac{\alpha_1(0)\,\alpha_2(0)}{R^6},$$

(2.16)

where we have introduced the two masses m_1 and m_2 (in place of m), and in obtaining the final expression we have used $e^2 f_{1,2} = \alpha_{1,2}(0) m_{1,2} \omega_{1,2}^2$, which follows from (2.13). London called the van der Waals interaction between ground-state atoms "dispersive" since it is expressed in terms of the polarizabilities $\alpha_{1,2}$, which also figure in dispersion theory.

At $T = 0$ the electromagnetic fluctuations (and, in particular, the fluctuations of the dipole moments of the atoms or particles) are quantum fluctuations, so that the van der Waals interaction between the "systems" at $T = 0$ is of a purely quantum-mechanical nature. This nature is explicitly reflected in expressions (2.11) and (2.16), which are proportional to Planck's constant $\hbar$. The quantum nature of the van der Waals forces at $T = 0$ becomes particularly clear if, following London,[50b,c] we note that if we ignore retardation and damping the energy of the van der Waals interaction between atoms is the change (due to the dipole-dipole interaction) in the zero-point-oscillation energy of the electric field produced by the zero-point vibrations of the dipole moments of the atoms.

To pursue this point we consider two 3-dimensional undamped oscillators which are coupled with each other by a dipole interaction. The equations of motion of these oscillators are

$$\left.\begin{array}{l} \ddot{\mathbf{r}}_1 + \omega_1^2 \mathbf{r}_1 = \dfrac{e^2 f_1}{m_1} \dfrac{3\mathbf{n}\,(\mathbf{r}_2 \mathbf{n}) - \mathbf{r}_2}{R^3}, \\[2mm] \ddot{\mathbf{r}}_2 + \omega_2^2 \mathbf{r}_2 = \dfrac{e^2 f_2}{m_2} \dfrac{3\mathbf{n}\,(\mathbf{r}_1 \mathbf{n}) - \mathbf{r}_1}{R^3}, \end{array}\right\}$$

(2.17)

where the unit vector $\mathbf{n}$ runs along the line connecting the oscillators, R is the distance between them, and f_1 and f_2 are the oscillator strengths of the first and second vibrations. In this system the natural frequencies $\omega_z^{\pm}$ of the normal vibration modes polarized along $\mathbf{n}$ (along the z axis) differ from the frequencies $\omega_{x,y}^{\pm}$ of the normal modes polarized perpendicular to $\mathbf{n}$. It is not difficult to see that the interaction potential, taken as the change in the energy of the zero-point vibrations of the oscillators,

$$U(R) = \frac{\hbar}{2}(\omega_x^+ + \omega_y^+ + \omega_x^- + \omega_y^- + \omega_z^+ + \omega_z^- - 3\omega_1 - 3\omega_2),$$

(2.18)

is exactly equal to the potential of the van der Waals interaction, (2.16), in the first nonvanishing approximation at large distances. This coincidence is by no means simply fortuitous. We will return to this question in Section 4.

The theory of the van der Waals forces between atoms and molecules went through its growing pains a long time

ago (see Refs. 4, 5, 50, 53, and 54; see also Refs. 29–34, 36, 37, and 55 and the literature cited there). The present thrust of theoretical research in this field is toward concrete quantitative studies of the interaction of atoms and molecules—over the spectrum of complexity ranging from the hydrogen atom and inert gas atoms to biopolymers. The calculation methods used in this research are analyzed, and the specific results available are reviewed, in Refs. 34, 56, 57, 63, and 64, among other places (see also the monographs in Refs. 29–33 and the papers in Refs. 58–62). In particular, these papers derive and discuss many approximate expressions for $U(R)$ or, equivalently, for the coefficient C_6 in (2.11). As the electronic structure of the atom or molecule becomes more complex, the accuracy of the calculations of C_6 naturally falls off substantially. Occupying a special place in this regard is the case of two hydrogen atoms, for which the coefficient C_6^{H-H} was calculated extremely accurately a long time ago[65]:

$$C_6^{H-H} = 6.49903 \text{ a.u.} = 6.2205 \cdot 10^{-60} \text{ erg·cm}^6.$$

Recommended semiempirical values of the coefficient C_6^{A-B} have been tabulated for various pairs of atoms and molecules.[66–68] Table I shows the values recommended by Dalgarno[67] for inert gas atoms.

c) If we ignore the effect of the temperature and use expression (2.8) instead of (2.9), then it is a simple matter to derive the following expression for the free energy of the van der Waals interaction of two remote "systems":

$$F(R) = -\frac{6T}{R^6} \sum_{n=0}^{\infty}{}' \alpha_1(i\omega_n)\,\alpha_2(i\omega_n), \quad \omega_n = \frac{2\pi T}{\hbar} n, \quad (2.19)$$

where the prime on the summation sign means that the term with $n = 0$ is to be assigned a weight of $1/2$.

At room temperature ($T \approx 300$ K), the typical range of frequencies in the sum over frequencies in (2.19) is $\omega_T \approx 2.5 \cdot 10^{14}$ s^{-1}. On the other hand, the typical frequency for the electron polarizability of an atom,

$$\alpha_e = \frac{f e^2}{m(\omega_e^2 - \omega^2)},$$

lies in the ultraviolet part of the spectrum, so we can use the rough approximation $\omega_e \approx 2 \cdot 10^{16}$ s^{-1}. Since $\omega_T \ll \omega_e$, in analyzing the electron contribution to the interaction we can very accurately replace the sum over frequencies ω_n in (2.19) by an integration; this is equivalent to taking the low-temperature limit, which is described by (2.11).

In certain polar liquids an important component of the effective polarizability stems from the rotation of a molecule

TABLE I. Values of the coefficient C_6^{A-B} for hydrogen atoms and inert gas atoms (in atomic units[67]).

B \ A	H	He	Ne	Ar	Kr	Xe
H	6,50	2,83	5,6	20	29	42
He		1,47	3,0	9,6	13	19
Ne			6,3	20	27	38
Ar				65	91	130
Kr					130	190
Xe						270

and the associated rotation of its dipole moment. The average dipole moment of a molecule in such a liquid has a part which is constant in magnitude and vanishes only after a statistical average is taken over all possible orientations of the dipole axis. For the orientational fluctuations of the dipole moments of molecules in (slightly nonideal) liquids the typical frequencies $\omega_{rot} \approx 10^{12}$ s^{-1} fall in the microwave region. The corresponding component of the polarizability is

$$\alpha_d = \frac{d^2}{3T\,[1-(i\omega/\omega_{rot})]}.$$

Since $\omega_{rot} \ll \omega_T$, this contribution is important in (2.19) only in the $n = 0$ term. An analysis of only the $n = 0$ term corresponds to taking the high-temperature limit of expression (2.19), where the electromagnetic fluctuations and the corresponding van der Waals interaction are classical (not quantum-mechanical). Substituting the polarizability

$$\alpha_{1,2}(0) = \alpha_{e_{1,2}}(0) + \alpha_{d_{1,2}}(0),$$

into the $n = 0$ term in (2.19), we find

$$F_{n=0} = -\frac{3T}{R^6}\,\alpha_1(0)\,\alpha_2(0)$$

$$= -\frac{d_1^2 d_2^2}{3TR^6} - \frac{\alpha_{e1}(0)\,d_2^2 + \alpha_{e2}(0)\,d_1^2}{R^6} - \frac{3T\alpha_{e1}(0)\,\alpha_{e2}(0)}{R^6}.$$

$$(2.20)$$

The first term on the right side of (2.20) describes the classical orientational interaction[9,10] which we mentioned in the Introduction. The second term on the right side of (2.20) corresponds to the Debye-Falkenhagen induction interaction.[69,70] As for the third term we note that it may be regarded as the classical (again, not quantum-mechanical) limit of the dispersion interaction. It can be shown that this limit is reached only under the inequality $\omega_T \gg c/R$ [which does not hold under the conditions assumed here, (2.12)], i.e., only at distances $R \gg (\hbar c/T) \sim 7 \cdot 10^{-4}$ cm. At such large distances the van der Waals interaction is usually very weak. If we can ignore the temperature dependence of the polarizability of the "systems," then the last term in (2.20) arises from a purely entropic contribution to the free energy. Specifically, in this case we have

$$E = -T^2 \frac{\partial}{\partial T}\left(\frac{F(R,T)}{T}\right)_R = 0,$$

$$S(R,T) = -\left(\frac{\partial F(R,T)}{\partial T}\right)_R = \frac{3\alpha_{e1}(0)\,\alpha_{e2}(0)}{R^6}. \quad (2.21)$$

Since we are dealing with another limit—the low-temperature limit—for the dispersion interaction under the conditions assumed here [see (2.12)], we should ignore the last term in (2.20). The free energy of the van der Waals interaction is then described by the sum of (2.11) and (2.20). The dispersion interaction (2.11) usually dominates the total energy of the van der Waals interaction. According to estimates given in Ref. 40, for example, the dispersion component amounts to 99% of the total energy of the van der Waals interaction for carbon monoxide [the contribution in (2.20) is included in this total energy], and the corresponding figure for HCl is 86%. There are exceptions to this rule, the most important of which is water. In H_2O the contribution of dispersion interaction (2.11) is only 24% of the total van der

Waals interaction, while the contribution of orientational interactions is about 69%. We find a similar situation in certain aqueous solutions of macromolecules and in several other substances of interest for applications in biological and biophysical problems. In solutions of macromolecules (in protein solutions, for example), an important role may be played by "proton fluctuations" with typical frequencies in the microwave region. These fluctuations, which are classical in nature, also give rise to a corresponding (van der Waals) interaction between macromolecules. This interaction has been studied by Kirkwood and Shumaker.[71]

d) Up to this point we have been discussing the van der Waals forces acting between two spherically symmetric systems. If the systems are not spherically symmetric, the van der Waals forces will depend on the relative orientation of the interaction systems. A moment of the forces acting on the systems will naturally arise. An anisotropy of van der Waals forces can be seen, for example, in the interaction between linear diatomic molecules (Fig. 1)[72] (see also Refs. 31, 32, 61, 73, and 74). An expression for the interaction energy of axially symmetric molecules of this type (under the condition $a_{1,2} \ll R \ll \lambda_0$) can be derived by an approach completely analogous to that leading to expression (2.11) above. It is simply necessary to make some obvious changes in Eqs. (2.3) and (2.9) to allow for an anisotropy of the polarizabilities of the molecules. As a result we find the expression

$$U(R,\,\theta_1,\,\theta_2,\,\varphi)$$

$$= -\frac{\hbar}{2\pi R^6}\,[(A - B_1 - B_2 + C)$$

$$\times\,(\sin\theta_1 \sin\theta_2 \cos\varphi - 2\cos\theta_1 \cos\theta_2)^2 + 3\,(B_1 - C)\cos^2\theta_1$$

$$+\,3\,(B_2 - C)\cos^2\theta_2 + B_1 + B_2 + 4C]; \quad (2.22)$$

here R is the distance between the centers of the molecules, the angles $\theta_{1,2}$ are the angles between the axis of each molecule and the line connecting the centers of the molecules, and φ is the angle between the projection of each of the axes of the molecules onto the plane perpendicular to the line connecting the centers of the molecules. The coefficients A, B_1, B_2, and C are defined by

$$A = \int_0^\infty d\omega\, \alpha_{||}^{(1)}(i\omega)\,\alpha_{||}^{(2)}(i\omega), \quad B_1 = \int_0^\infty d\omega\, \alpha_{||}^{(1)}(i\omega)\,\alpha_{\perp}^{(2)}(i\omega),$$

$$C = \int_0^\infty d\omega\, \alpha_{\perp}^{(1)}(i\omega)\,\alpha_{\perp}^{(2)}(i\omega), \quad B_2 = \int_0^\infty d\omega\, \alpha_{||}^{(2)}(i\omega)\,\alpha_{\perp}^{(1)}(i\omega).$$

$$(2.23)$$

The quantities $\alpha_{||}^{(1)}(\omega)$ and $\alpha_{\perp}^{(1)}(\omega)$ are respectively the longitudinal (along the axis of the molecule) and transverse compo-
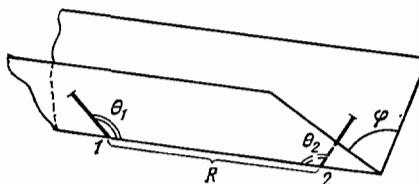

FIG. 1.

nents of the polarizability of the first molecule; a corresponding notation is used for the second molecule.

When we analyze the interaction of only two atoms we lose sight of a very important property of van der Waals forces: their many-particle nature. Many-particle forces arise because the interaction energies in a system of many particles are not additive. Generally speaking, this nonadditivity arises because the superposition principle pertains to the amplitudes of the electromagnetic field, while the interaction energy depends on quadratic combinations of these amplitudes. A nonadditivity in interaction energy can be seen even in classical electrostatics. For example, if a spherically symmetric small object (or atom) of polarizability α is in the field of a constant electric dipole, the interaction energy will be $-(1/2)\alpha(0)E^2$, where $\mathbf{E}$ is the field of the dipole at the position of the atom. We now place another, identical, dipole at the same distance from the particle but on the opposite side. The field at the position of the particle and thus the energy of the interaction of the particle with the two dipoles then vanish. In this case the three-body term in the energy of the interaction of the particle with the dipoles is exactly equal to the sum of the energies of the binary interactions of the particle with each separate dipole, taken with the opposite sign. As for the nonadditive part of the energy in the case of the van der Waals interaction, we note that it is frequently small in comparison with the sum of the corresponding energies of the binary interactions. There are several problems in which many-body van der Waals interactions are important and in some cases even give rise to qualitatively new effects. An example of the latter case is the effect of a substrate on the van der Waals interaction of nearby atoms. Many-body forces should in general also be taken into consideration in a study of the van der Waals interaction between thick plates. We turn now to the very simplest system in which the nonadditivity of the van der Waals interaction is manifested (albeit weakly): a system of three ground-state atoms (Fig. 2).

The energy of the van der Waals interaction in this system can be written in the form

$$U = U_{12} + U_{23} + U_{31} + U_{123}. \tag{2.24}$$

We already have an expression—(2.11)—for the binary interaction potential $U_{ij}(i, j = 1, 2, 3; i \neq j)$ in the case of isotropic atoms or particles of condensed matter. In general, however, the energy of the interaction among three atoms, (2.24), is not additive since in addition to the sum of binary interactions there is a three-body term U_{123}. This term vanishes when any of the three atoms goes off to infinity. It was first found by Axilrod and Teller[75] and Muto[76] in a study of dipole dispersion interactions of atoms in third-order per-
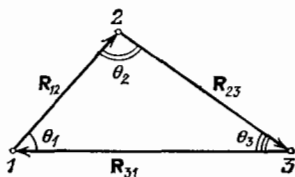
turbation theory [see expression (2.31) below]. As we have already seen, the binary van der Waals forces arise from an interaction of a spontaneously fluctuating (virtual) dipole moment in one atom with its "image" in another atom. To find the three-body interaction we must also note that a spontaneous fluctuating dipole moment in, for example, the first atom, $\mathbf{d}_1^{sp}(\mathbf{r}_1,t)$, gives rise to not only a dipole moment in the second atom, $\mathbf{d}_2^{ind}(\mathbf{r}_2,t') = \hat{\alpha}_2\mathbf{E}_1(\mathbf{r}_2,t)$—through the direct dipole interaction of the two atoms [see (2.3) and (2.2)]—but also another contribution to the dipole moment of the second atom, given by

$$\mathbf{d}_{32}^{ind}(\mathbf{r}_2, t') = \hat{\alpha}_2\hat{T}(\mathbf{R}_{23})\hat{\alpha}_3\mathbf{E}_1(\mathbf{r}_3, t), \tag{2.25}$$

where

$$T_{ij}(\mathbf{R}) = \frac{3n_in_j - \delta_{ij}}{R^3}, \qquad \mathbf{n} = \frac{\mathbf{R}}{R}. \tag{2.26}$$

As can be seen from (2.25), this three-body contribution means that we are first considering the dipole moment induced in the third atom by the first, $\mathbf{d}_3^{ind}(\mathbf{r}_3,t') = \alpha_3\mathbf{E}_1(\mathbf{r}_3,t)$; only after we have done this do we take into account the fact that this dipole moment $\mathbf{d}_3^{ind}(\mathbf{r}_3,t)$ in turn induces a dipole moment $\mathbf{d}_{32}^{ind}(\mathbf{r}_2,t)$ in the second atom. It is the interaction of the dipole moment $\mathbf{d}_1^{sp}(\mathbf{r}_1,t)$ with its "secondary image" $\mathbf{d}_{32}^{ind}(\mathbf{r}_2,t)$ which contributes to the three-body interaction. In an analogous way we need to consider the interaction of the dipoles $\mathbf{d}_2^{sp}(\mathbf{r}_2,t)$ and $\mathbf{d}_3^{sp}(\mathbf{r}_2,t)$ with their secondary images, and once we have done so we have exhausted the three-body contribution to the energy of the van der Waals interaction.

Since there is an error in the derivation of the expression for the three-body term U_{123} in the literature,[30] and since this derivation is based on the arguments we are presenting here, we will go through the detailed derivation of the expression for the energy of the three-body interaction. As before, our derivation will apply equally well to any small, spherically symmetric particles of condensed matter—not only atoms—at large distances.

It is not absolutely correct to use expression (2.3) for the energy of the dipole interaction of three atoms. We write the interaction energy in the dipole approximation in the following form:

$$U(R) = \delta\left[-\frac{1}{2}\langle\mathbf{d}_1(\mathbf{r}_1, t)\mathbf{E}(\mathbf{r}_1, t)\rangle\right], \tag{2.27}$$

where $\mathbf{d}_1(\mathbf{r}_1,t)$ is the total fluctuational dipole moment of the first atom (which incorporates both the spontaneous fluctuational terms and those induced by other atoms). The field $\mathbf{E}(\mathbf{r}_1,t)$ is created by the total fluctuational dipole moments of the second and third atoms. The variation sign δ in (2.27) means that we are to subtract from the expression in square brackets the values found for this expression by letting the distances between the atoms go to infinity. In this manner we eliminate the self-energy, which has no bearing on the interaction between atoms.

With an accuracy appropriate for this discussion we can write the following expressions for $\mathbf{d}_1(\mathbf{r}_1,t)$ and $\mathbf{E}(\mathbf{r}_1,t)$ (which are consistent with the comments above):

FIG. 2.

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$$\mathbf{d_1\,(r_1,\ }t) = \mathbf{d_1^{sp}} + \hat{\alpha}_1 \hat{T}\,(\mathbf{R}_{12})\mathbf{d_2^{sp}} + \hat{\alpha}_1 \hat{T}\,(\mathbf{R}_{31})\,\mathbf{d_3^{sp}}$$

$$+ \hat{\alpha}_1 \hat{T}\,(\mathbf{R}_{12})\,\hat{\alpha}_2 \hat{T}\,(\mathbf{R}_{23})\,\mathbf{d_3^{sp}}$$

$$+ \hat{\alpha}_1 \hat{T}\,(\mathbf{R}_{31})\,\hat{\alpha}_3 \hat{T}\,(\mathbf{R}_{23})\,\mathbf{d_2^{sp}} + \ldots, \qquad (2.28)$$

$$\mathbf{E\,(r_1,\ }t) = \hat{T}\,(\mathbf{R}_{12})\,\mathbf{d_2^{sp}} + \hat{T}\,(\mathbf{R}_{31})\,\hat{\alpha}_3 \hat{T}\,(\mathbf{R}_{23})\,\mathbf{d_2^{sp}} + \hat{T}\,(\mathbf{R}_{31})\,\mathbf{d_3^{sp}}$$

$$+ \hat{T}\,(\mathbf{R}_{12})\,\hat{\alpha}_2 \hat{T}\,(\mathbf{R}_{23})\,\mathbf{d_3^{sp}} + \hat{T}\,(\mathbf{R}_{12})\,\hat{\alpha}_2 \hat{T}\,(\mathbf{R}_{12})\,\mathbf{d_1^{sp}}$$

$$+ \hat{T}\,(\mathbf{R}_{31})\,\hat{\alpha}_3 \hat{T}\,(\mathbf{R}_{31})\,\mathbf{d_1^{sp}}$$

$$+ \hat{T}\,(\mathbf{R}_{12})\,\hat{\alpha}_2 \hat{T}\,(\mathbf{R}_{23})\,\hat{\alpha}_3 \hat{T}\,(\mathbf{R}_{31})\,\mathbf{d_1^{sp}}$$

$$+ \hat{T}\,(\mathbf{R}_{31})\,\hat{\alpha}_3 \hat{T}\,(\mathbf{R}_{23})\,\hat{\alpha}_2 \hat{T}\,(\mathbf{R}_{12})\,\mathbf{d_1^{sp}} + \ldots, \qquad (2.29)$$

where $T\,(\mathbf{R})$ is the matrix whose elements are shown in (2.26). Substituting (2.28) and (2.29) into (2.27), and using the fluctuation-dissipation relation (2.9), we find (2.24), where

$$U_{123} = -\frac{\hbar}{4\pi}\,\mathrm{Sp}\,[\hat{T}\,(\mathbf{R}_{12})\,\hat{T}\,(\mathbf{R}_{23})\,\hat{T}\,(\mathbf{R}_{31})]$$

$$\times \int\limits_{-\infty}^{+\infty} \frac{\omega\,d\omega}{|\,\omega\,|}\,\{2\alpha_2^*\,(\omega)\,\alpha_3^*\,(\omega)\,\mathrm{Im}\,\alpha_1\,(\omega)$$

$$+ \alpha_1\,(\omega)\,[\alpha_2\,(\omega) + \alpha_2^*\,(\omega)]\,\mathrm{Im}\,\alpha_3\,(\omega)$$

$$+ \alpha_1\,(\omega)\,[\alpha_3\,(\omega) + \alpha_3^*\,(\omega)]\,\mathrm{Im}\,\alpha_2\,(\omega)\}. \qquad (2.30)$$

Substituting in (2.26) for $T_{ij}\,(\mathbf{R})$, and using (2.7), we find, after some straightforward calculations,

$$U_{123} = \frac{C_{123}}{R_{12}^3 R_{23}^3 R_{31}^3}\,(3\cos\theta_1 \cos\theta_2 \cos\theta_3 + 1), \qquad (2.31)$$

$$C_{123} = \frac{3\hbar}{\pi}\,\mathrm{Im}\int\limits_0^\infty d\omega\,\alpha_1\,(\omega)\,\alpha_2\,(\omega)\,\alpha_3\,(\omega)$$

$$= \frac{3\hbar}{\pi}\int\limits_0^\infty d\omega\,\alpha_1\,(i\omega)\,\alpha_2\,(i\omega)\,\alpha_3\,(i\omega). \qquad (2.32)$$

The procedure for deriving the expression in (2.32) is completely analogous to that for going from (2.10) to (2.11). The complex-conjugate values of the polarizabilities appear in (2.30) because for stationary fluctuations we have (see, for example, § 122 in Ref. 3)

$$\langle d_\omega E_{\omega'}\rangle = 2\pi\,\langle dE\rangle_\omega\,\delta\,(\omega + \omega'), \qquad (2.33)$$

and the polarizabilities furthermore satisfy (2.6). It is this last point which was ignored in Ref. 30, where an expression similar to (2.30) was derived for the three-body contribution to the interaction energy, but the operation of complex conjugation did not appear in that expression even once. The result was the derivation of an incorrect expression for the coefficient C_{123} in Ref. 30 with absorption [i.e., with $\mathrm{Im}\,\alpha(\omega)\neq 0$]. The correct expression, (2.32), was first derived by a different (quantum-electrodynamic) method by Aub and Zienau[77] for atoms (see also Refs. 31 and 78).

The three-body component of the interaction energy may take on both positive and negative values. This point should not be surprising since to analyze this component of the energy is equivalent to using third-order perturbation

theory (not second-order, as for binary interactions). It follows from (2.31) that we have $U_{123} > 0$ if all the angles $\theta_{1,2,3}$ are less than 117°. If, for example, three atoms form an equilateral triangle, then the three-body term is repulsive and thus reduces the attraction between the atoms due to their binary interaction. If, on the other hand, one of the angles $\theta_{1,2,3}$ is greater than 126°, then we have $U_{123} < 0$, and this term intensifies the attraction. This is the case, in particular, when the atoms lie on a common straight line.

In a system of three atoms separated by large distances the three-body term amounts to only a small fraction of the binary interaction (usually, no more than a few percent[79]). In principle, the role of three-body forces (and of higher-order, many-body forces) might become more important in a system of many atoms, since the number of different trios of atoms is significantly larger than the number of different pairs, as is clear from combinatorics. Nevertheless, in most cases the three-body van der Waals forces continue to play a minor role even in systems of many particles. This is a consequence of the very anisotropic nature of the three-body interaction. As a result, if there is any symmetry in the arrangement of the atoms the different three-body terms will cancel out to a significant degree. This effect can be seen, for example, in a numerical study of the contribution of van der Waals forces to the binding energy of crystals.[80] The reader is referred to Refs. 31, 42, 56, and 80–84, for example, for discussions of the role played by three-body terms in some other cases.

A discussion of many-body forces in a system of many atoms generally cannot be restricted to three-body interactions alone. In a system of four atoms, a four-body interaction will of course arise. In general, the van der Waals forces are of an n-body nature. We might naturally ask how we could find the total contribution of all the many-body forces to the energy of the van der Waals interaction of atoms. In the sections which follow we will return to this and some related questions, but at this point we simply note that if we examine the energy shift of the zero-point vibrations of three oscillators coupled with each other by dipole forces [cf. Eqs. (2.17) for two oscillators] we see that this shift also contains a three-body term. For a system of n oscillators, on the other hand, the energy shift of the zero-point vibrations due to the fluctuational dipole interaction of these oscillators contains all the n-body terms corresponding to van der Waals forces. An analysis of van der Waals forces on the basis of the energy of zero-point vibrations for an oscillator model (also called the Drude-Lorentz model) is widely used for qualitative discussions of many problems (see, for example, Refs. 5b and 83–93).

e) We now consider the van der Waals interaction between atoms (or small particles of condensed matter) at distances large enough $(R \gtrsim \lambda_0)$ that retardation effects are important. As before we assume that the atom is in its ground state. The spontaneously fluctuating (virtual) dipole moment of such an atom creates a dipole field (2.2) in the near zone. No real radiation (i.e., no average energy flux) from the atom can arise in the wave zone, since the atom is in its ground state. To describe fluctuational phenomena at dis-

tances $R \gtrsim \lambda_0$ and, in particular, in the wave zone we need to allow for the fact that in the quantum-electrodynamics vacuum there is a fluctuational electromagnetic field (virtual photons). The virtual excitation of an atom is of course related to the absorption of a virtual photon and to a corresponding influx of electromagnetic energy to the atom. In the case of radiation, on the other hand, there is a cancellation of the original electromagnetic energy flux, whose average value remains equal to zero. Because of virtual processes of this type, the atom leads to a change in the polarization of the electromagnetic vacuum (a change from that in the case in which there is no atom). This change naturally depends on the distance from the atom, and at sufficiently large distances it is a small perturbation. The van der Waals interaction at distances $R \gtrsim \lambda_0$ is due directly to this change in the polarization of the vacuum. Consequently, calculations on the van der Waals interaction between atoms at $R \gtrsim \lambda_0$ should be carried out in quantum electrodynamics. The corresponding expression for the interaction energy [see expression (2.40) below] is now well known (see, for example, § 85 in Ref. 8). This expression is derived in fourth-order perturbation theory. It was found first by Casimir and Polder,[7] and since then it has been analyzed by a variety of methods and discussed many times (see, for example, Refs. 16, 31, 58, 94–98, and 100). Here, as before (in the case $R \ll \lambda_0$), we are interested in the concrete fluctuational mechanism which gives rise to the van der Waals interaction. Under the condition $R \gtrsim \lambda_0$ this interaction is, as before, due to correlations between the fluctuating dipole moments of the atoms, but here we find a completely new reason for the appearance of these correlations. We will demonstrate this point and derive a general expression for the energy of the van der Waals interaction of two spherically symmetric atoms or small particles of condensed matter (for an arbitrary relation between R and λ_0) by working, as before, from expression (2.27) for the average energy of the interaction of a polarizable dipole with an electric field.

For an arbitrary relation between R and λ_0, there are two circumstances which we ignored in the case $R \ll \lambda_0$ which we must now take into account: the retardation and the interaction with the vacuum fluctuational field. When we take retardation into account, we must replace expression (2.2) for the field dipole. The expression we need for the spectral component of the field with frequency ω is (see, for example, § 72 in Ref. 99)

$$E_i(\omega, \mathbf{r}_1) = -\frac{\omega^2}{\hbar c^2} \mathscr{D}_{il}^{(0)R}(\omega, \mathbf{R}) d_{2l}(\omega, \mathbf{r}_2)$$

$$= \left\{ e^{i(\omega/c)R} \left[\left(\frac{\omega^2}{c^2 R} + \frac{i\omega}{cR^2} - \frac{1}{R^3} \right) (\delta_{il} - n_i n_l) \right.\right.$$

$$\left.\left. + 2\left(\frac{1}{R^3} - \frac{i\omega}{cR^2} \right) n_i n_l \right] \right\} d_{2l}(\omega, \mathbf{r}_2),$$

$$\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{R}, \qquad \mathbf{n} = \frac{\mathbf{R}}{R}. \tag{2.34}$$

The first term in (2.34) is the expression for the retarded Green's function of a free photon in vacuum, $\mathscr{D}_{il}^{(0)R}(\omega, \mathbf{R})$. Furthermore, it follows from the theory of electromagnetic fluctuations that the spectral density of the correlation func-

tion of the vacuum electromagnetic field (without interactions) can be written (see, for example, § § 76, 77 in Ref. 28)

$$\langle E_i^{(0)}(\mathbf{r}_1) E_k^{(0)}(\mathbf{r}_2) \rangle_\omega = -\frac{|\omega|}{\omega} \frac{\omega^2}{c^2} \mathrm{Im}\, \mathscr{D}_{ik}^{(0)R}(\omega, \mathbf{r}_1 - \mathbf{r}_2). \tag{2.35}$$

Expression (2.35) has the meaning of a fluctuation-dissipation relation and is therefore combined with (2.9).

If we ignore retardation, i.e., in the limit $(\omega/c)R \to 0$, the expression in braces (curly brackets) in (2.34) becomes real; as a result, the right side of (2.35) vanishes. In a more general case it follows from (2.35) that there is a spatial correlation between fluctuations of the vacuum electromagnetic field. A correlation between fluctuations of the vacuum field is one reason for the appearance of an interaction between atoms (this is the basic reason for van der Waals forces in the limit $R \gg \lambda_0$). Let us assume that there are atoms at the points $\mathbf{r}_1$ and $\mathbf{r}_2$. The vacuum fluctuational field induces dipole moments $\mathbf{d}^{ind} = \alpha \mathbf{E}^{(0)}$ in these atoms. The average interaction of all the fluctuating dipoles (retardation must of course be taken into account here) will be nonzero because of the correlation of the fluctuations of the vacuum field, $\langle E_i^{(0)}(\mathbf{r}_1) E_k^{(0)}(\mathbf{r}_2) \rangle_\omega$ [see (2.35)]. Working in this manner we can take into account that part of the van der Waals interaction which stems exclusively from the elastic scattering of the vacuum fluctuational field by atoms. Another part of the interaction stems from inelastic virtual processes, i.e., the absorption and emission of virtual photons. This part can be taken into account by an approach analogous to that taken above where we ignored retardation; specifically, we can examine the spontaneous fluctuations of the dipole moments of the atoms and use relation (2.9).

By jointly considering the spontaneous fluctuations of the vacuum electromagnetic field and the atomic dipole moments we can derive a general expression for the energy of the van der Waals interaction. To pursue this point we first write expressions for the spectral components of the total fluctuational dipole moment of the first atom, $\mathbf{d}_1(\mathbf{r}_1, t)$, and for the total fluctuational electric field $\mathbf{E}(\mathbf{r}_1, t)$, which appear in the original expression for the energy, (2.27). With an accuracy sufficient for our purposes the dipole moment can be written

$$d_{1, i}(\mathbf{r}_1, \omega) = d_{1, i}^{sp} + \alpha_1(\omega) E_i^{(0)}(\mathbf{r}_1, \omega)$$

$$+ \alpha_1(\omega)\left(-\frac{\omega^2}{\hbar c^2} \right) \mathscr{D}_{il}^{(0)R}(\omega, \mathbf{r}_1 - \mathbf{r}_2) d_{2, l}^{sp}(\mathbf{r}_2, \omega)$$

$$+ \alpha_1(\omega)\left(-\frac{\omega^2}{\hbar c^2} \right) \mathscr{D}_{il}^{(0)R}(\omega, \mathbf{r}_1 - \mathbf{r}_2)$$

$$\times \alpha_2(\omega) E_l^{(0)}(\mathbf{r}_2, \omega) + \ldots . \tag{2.36}$$

The first term on the right side of (2.36) describes the spontaneous fluctuational contribution to the dipole moment of the first atom. The second term is that part of the dipole moment which is induced by the vacuum fluctuational field at the point $\mathbf{r}_1$. The third term reflects the part of the dipole moment of the first atom which is induced by the field produced by the spontaneous dipole moment in the second atom. Fin-

ally, the last term written in (2.36) reflects the fact that the vacuum fluctuational field induces in the second atom a dipole moment $\alpha_2(\omega)E^{(0)}(r_2,\omega)$, which in turn induces a dipole moment in the first atom.

It is also a simple matter to interpret the expression for the electric field $E(r_1,\omega)$, which can be written

$$E_i(r_1, \omega)$$

$$= E_i^{(0)}(r_1, \omega) + \left(-\frac{\omega^2}{\hbar c^2}\right)\mathscr{D}_{il}^{(0)R}(\omega, r_1 - r_2)d_{2, l}^{sp}(\omega, r_2)$$

$$+ \left(-\frac{\omega^2}{\hbar c^2}\right)\mathscr{D}_{il}^{(0)R}(\omega, r_1 - r_2)\alpha_2(\omega)E_l^{(0)}(\omega, r_2)$$

$$+ \left(-\frac{\omega^2}{\hbar c^2}\right)^2\mathscr{D}_{il}^{(0)R}(\omega, r_1 - r_2)$$

$$\times \alpha_2(\omega)\mathscr{D}_{lk}^{0(R)}(\omega, r_2 - r_1)d_{1, k}^{sp}(r_1, \omega). \qquad (2.37)$$

Substituting (2.36) and (2.37) into (2.27), and using (2.35) and (2.9), we find

$$U(R) = -\frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\left[\hbar\frac{\omega}{|\omega|}\left(\frac{\omega^2}{\hbar c^2}\right)^2\right]$$

$$\times [(\operatorname{Im}\alpha_1(\omega))\mathscr{D}_{il}^{(0)R*}(\omega, R)\alpha_2^*(\omega)\mathscr{D}_{li}^{(0)R*}(\omega, R)$$

$$+ \alpha_1(\omega)\mathscr{D}_{il}^{(0)R*}(\omega, R)\alpha_2^*(\omega)\operatorname{Im}\mathscr{D}_{li}^{(0)R}(\omega, R)$$

$$+ \alpha_1(\omega)\mathscr{D}_{il}^{(0)R}(\omega, R)(\operatorname{Im}\alpha_2(\omega))\mathscr{D}_{li}^{(0)R*}(\omega, R)$$

$$+ \alpha_1(\omega)\mathscr{D}_{il}^{(0)R}(\omega, R)\alpha_2(\omega)\operatorname{Im}\mathscr{D}_{li}^{(0)R}(\omega, R)]. \qquad (2.38)$$

We can now make use of the properties of the real and imaginary parts of the Green's functions and polarizabilities upon the replacement $\omega\rightarrow -\omega$. These properties follow from (2.7) and from the analogous expression for the Green's function (we assume that the frequency ω is real),

$$\mathscr{D}_{il}^{(0)R}(-\omega, R) = \mathscr{D}_{il}^{(0)R*}(\omega, R). \qquad (2.39)$$

Using (2.7), (2.39), and (2.34), we find the following result from (2.38) after some straightforward calculations:

$$U(R) = -\frac{\hbar}{2}\operatorname{Im}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\omega}{|\omega|}\left(\frac{\omega^2}{\hbar c^2}\right)^2$$

$$\times [\alpha_1(\omega)\mathscr{D}_{il}^{(0)R}(\omega, R)\alpha_2(\omega)\mathscr{D}_{li}^{(0)R}(\omega, R)]$$

$$= -\frac{\hbar}{\pi}\int_0^{+\infty}d\omega\,\alpha_1(i\omega)\alpha_2(i\omega)\frac{e^{-2(\omega/c)R}}{R^2}\frac{\omega^4}{c^4}$$

$$\times \left[1 + \frac{2}{\omega R/c} + \frac{5}{(\omega R/c)^2} + \frac{6}{(\omega R/c)^3} + \frac{3}{(\omega R/c)^4}\right]. \qquad (2.40)$$

Expression (2.40) describes the interaction energy of two atoms or condensed-matter particles separated by a large distance for an arbitrary relation between the parameters R and $\lambda_0 = 2\pi c/\omega_0$. In the limit $R\ll\lambda_0$ we should set $(\omega/c)R\rightarrow 0$ in (2.40), and in doing so we find expression (2.11), which we discussed above. In the opposite limit, $R\gg\lambda_0$, the exponential factor in (2.40) means that the integral will be

dominated by frequencies from the spectral interval $\omega\lesssim c/R\ll\omega_0$. We can thus set $\alpha(i\omega)\approx\alpha(0)$, since by assumption there is no dispersion of the polarizability at frequencies $\omega\ll\omega_0$. As a result we find from (2.40) the following simple expression for the interaction energy of the atoms in the limit $R\gg\lambda_0 = 2\pi c/\omega_0$.

$$U(R) = -\frac{23\hbar c}{4\pi R^7}\alpha_1(0)\alpha_2(0). \qquad (2.41)$$

For ground-state helium and hydrogen atoms λ_0 is of the order of 10^{-6} cm, while for certain organic molecules λ_0 is about an order of magnitude larger.

f) If the magnetic susceptibilities of the interacting particles are not too small in comparison with their electric polarizabilities in some important part of the spectrum, then we also need to consider the contribution to the interaction of spontaneous fluctuations of the magnetic dipole moments of these particles. Furthermore, we must recall that the vacuum fluctuating electromagnetic field induces both electric and magnetic dipole moments in the particles. The corresponding calculations are analogous to those given above, so we will proceed immediately to the results. The contribution from the magnetic susceptibilities turns out to be most important in the case $R\gg\lambda_0$, in which the typical frequencies are low, $\omega\ll c/R\ll\omega_0$. Another important point is that under the condition $R\gg\lambda_0$ the particles are outside the near zone with respect to electric and magnetic dipole radiation. Since the electric dipole of, say, the first particle, creates not only an electric field but also a magnetic field outside the near zone, both electric and magnetic dipole moments are induced in the second particle. Analogously, the magnetic dipole moment of the first particle induces in the second not only a magnetic but also an electric dipole moment. Taking into account the correlations which arise between the fluctuations of the electric and magnetic dipole moments of the particles, we find terms in the expression for the interaction energy which are bilinear in the permittivities and susceptibilities of the particles (in addition to quadratic terms). As a result, expression (2.41) is replaced by

$$U(R) = -\frac{\hbar c}{4\pi R^7}[23(\alpha_1(0)\alpha_2(0)$$

$$+ \chi_1(0)\chi_2(0)) - 7(\alpha_1(0)\chi_2(0) + \alpha_2(0)\chi_1(0))], \qquad (2.42)$$

which was found in Ref. 98 by a quantum-field approach. The contribution of magnetic susceptibilities to the dispersion interaction was also discussed in Ref. 58.

In the opposite limit, $R\ll\lambda_0$, terms containing cross products of the permittivities $\alpha(\omega)$ and susceptibilities $\chi(\omega)$ do not appear in the expression for the interaction energy of the particles. The reason is that in the near zone an electric dipole creates only an electric field (the magnetic field is negligibly weak), and a magnetic dipole only a magnetic field (in this case the electric field is very weak). For atoms separated by large distances the magnetic-interaction contribution to the dispersion energy, studied in Ref. 101, is usually small. It is small because the susceptibilities of atoms are small except for very heavy atoms. For particles of condensed matter, on the other hand, the static susceptibility can be quite large, in

which case the magnetic interaction would have to be taken into account. The existence of a magnetic polarizability does not necessarily mean that the object consists of a magnetic material: The polarizability $\chi(\omega)$ might also be due to a shielding of the magnetic field from the object by a skin effect. This circumstance is important for the interaction of two small metal particles.[102]

We see from (2.42) that the cross products of the electric and magnetic polarizabilities enters the interaction energy with a sign opposite that of the other terms. For this reason, if we have $\alpha_1(0) \gg \chi_1(0)$ for one of the particles and $\alpha_2(0) \ll \chi_2(0)$ for the other the van der Waals interaction at distances $R \gg \lambda_0$ is repulsive [if $\chi_2(0) > 0$]:

$$U(R) = \frac{7\hbar c}{4\pi R^7} \alpha_1(0) \chi_2(0) .$$ (2.43)

It is also a straightforward matter to incorporate the magnetic-dipole contribution in an analysis of the van der Waals interaction for anisotropic particles or molecules. If the molecules are not optically active, the calculations would be analogous to those for the isotropic case. For chiral molecules or gyrotropic particles, on the other hand, we would also need to consider the correlation which arises between the spontaneous fluctuations of the electric and magnetic dipole moments, $\mathbf{d}$ and $\boldsymbol{\mu}$:

$$\langle \mu_i d_j \rangle_\omega = -\frac{i\hbar}{2} \frac{\omega}{|\omega|} (\beta_{ij}(\omega) - \beta_{ji}^*(\omega)) .$$ (2.44)

The dipole-magnetic-dipole polarizability tensor $\beta_{ij}(\omega)$ which appears here is expressed in terms of products of matrix elements of the form $\langle 0|d_i|n\rangle \langle n|\mu_j|0\rangle$ and is nonzero only if the molecule lacks an inversion center (when the parity is not an integral of motion). For enantiomorphs (i.e., left- and right-hand-rotating but otherwise identical molecules), the polarizabilities $\beta_{ij}(\omega)$ differ in sign. On the whole, therefore, the van der Waals interaction of two chiral molecules changes slightly if one of them is replaced by its enantiomoph[4] (Refs. 58, 97, 103, and 104). Since an atom generally becomes optically active when the weak interaction of an electron with the nucleus due to neutral currents is taken into account,[105] the atom acquires a nonzero chiral polarizability tensor, which is a measure of the constant of this (parity-breaking) weak interaction. Consequently, a P-odd part appears in the van der Waals interaction between atoms.[106]

To conclude this section we consider the van der Waals interaction of atoms or small bodies in a liquid (up to this point we have been talking about atoms and particles in vacuum). The fluctuational nature of the van der Waals forces can be seen quite clearly when we take into account the screening of the interaction between atoms by the medium. The situation can be seen particularly easily in the case $R \ll \lambda_0$, where it is sufficient to note that the presence of a medium gives rise to a factor ε^{-1} in expression (2.2) for the field of the dipole. Since the dipole-dipole van der Waals interaction is a result of an averaging of expression (2.3),

which is quadratic in the dipole field (2.2), the screening of this interaction by the medium at the frequency ω is proportional to $\varepsilon^{-2}(\omega)$, not $\varepsilon^{-1}(\omega)$.

Another important point is that the presence of a medium also generates another factor causing an interaction between atoms and small objects. In an isotropic medium, even if retardation is ignored, there is a fluctuational spatially correlated electric field $\mathbf{E}^{(\varepsilon)}(\mathbf{r})$. For $\mathbf{r}_1 \neq \mathbf{r}_2$ the spectral density of the spatial correlations for the fluctuations of this field is

$$\langle E_i^{(\varepsilon)}(\mathbf{r}_1) E_k^{(\varepsilon)}(\mathbf{r}_2) \rangle_\omega = \hbar \frac{\omega}{|\omega|} \cdot \frac{3n_i n_k - \delta_{ik}}{R^3} \operatorname{Im} \frac{1}{\varepsilon(\omega)} .$$ (2.45)

If there are atoms or small objects at the points $\mathbf{r}_1$ and $\mathbf{r}_2$, the spontaneous fluctuational field $\mathbf{E}^{(\varepsilon)}$ will induce in them dipole moments

$$\mathbf{d}^{\text{ind}} = \hat{\alpha} \mathbf{E}^{(\varepsilon)} .$$

The average interaction of these dipoles is not zero, by virtue of (2.45), and this interaction can be an important part of the overall dipole-dipole van der Waals interaction. The result, as is easily shown, is that the overall dipole-dipole van der Waals interaction of two particles or atoms in a medium is described by the following expression if we ignore retardation [cf. (2.11)]:

$$U(R) = -\frac{3\hbar}{\pi R^6} \int_0^\infty \frac{\Delta \tilde{\alpha}_1(i\omega) \Delta \tilde{\alpha}_2(i\omega)}{\varepsilon^2(i\omega)} d\omega .$$ (2.46)

A general expression for $\Delta \tilde{\alpha}_{1,2}(\omega)$ will be given a bit later. Here we wish to point out (with reference to the rather simple case of a single-component liquid) that $\Delta \tilde{\alpha}_{1,2}(\omega)$ is essentially the difference between the effective polarizabilities for impurity particles (or the atoms of a dilute solution) in a liquid and for the atoms or molecules of this liquid (or solvent). These effective polarizabilities, which describe a response to an average macroscopic field, may in general be quite different from the polarizabilities of the isolated atoms of a solution and the atoms of a solvent, in particular, because of local-field effects. In the simple case in which only these effects are important, and the Lorenz-Lorentz formula applies, we have

$$\tilde{\alpha}(\omega) = \frac{\varepsilon(\omega) + 2}{3} \alpha(\omega) .$$

Furthermore, differences between effective polarizabilities appear in (2.46) because when the distance between impurity particles changes (when, for example, they are removed to infinity) the positions which they previously occupied do not remain empty but instead become filled with liquid.

When retardation is taken into account, we must replace ω/c by $\omega\sqrt{\varepsilon(\omega)}/c$—equivalently, switch from Maxwell's equations in vacuum to the macroscopic Maxwell's equations in a medium—in addition to making the changes due to the effects which we have already discussed. If absorption is ignored, this replacement corresponds to incorporating a change in the phase velocity of light at the frequency ω in the presence of a medium. As a result, in the limit $R \gg \lambda_0$, for example, expression (2.41) is replaced by

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[4] In gyrotropic particles there is also a correlation between spontaneous fluctuations of the dipole and quadrupole moments. The corresponding contribution to the van der Waals energy also changes sign when one of the particles is replaced by its enantiomorph, and this contribution can in general be greater than the dipole-magnetic-dipole contribution.

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$$U(R) = - \frac{23\hbar c}{4\pi \tilde{\varepsilon}^{5/2}(0) R^7} \Delta \tilde{\alpha}_1(0) \, \Delta \tilde{\alpha}_2(0). \qquad (2.47)$$

The van der Waals interaction of atoms or small objects in a liquid was first analyzed by Pitaevskiĭ.[107] As an initial expression for the energy of the van der Waals interaction he used that for two thick macroscopic plates separated by a liquid-filled gap. He then[107] considered the case in which the gap was filled with a pure solvent, and the "plates" were weak solutions of atoms of a different species with densities N_1 and N_2 in the same solvent. When the expression for the interaction energy of these "plates" is used, it is a simple matter to construct a binary interaction potential of two atoms in a solution. From the results derived in Ref. 107 follows a general definition for the quantities $\Delta \tilde{\alpha}(\omega)$ which figure in (2.46) and (2.47):

$$\Delta \tilde{\alpha}(\omega) = -\frac{1}{4\pi} \left(\frac{\partial \tilde{\varepsilon}(\omega)}{\partial N} \right)_{N=0}. \qquad (2.48)$$

Here $\tilde{\varepsilon}(\omega)$ is the dielectric permittivity of the solution, and N is the concentration of dissolved atoms. Since $\Delta \tilde{\alpha}(\omega)$ is the derivative of a linear-response function, its values on the upper part of the imaginary frequency axis may be either positive or negative. The energy of the van der Waals interaction of atoms in a solution described by (2.46) [or (2.47)] may thus correspond to a repulsion as well as an attraction. The force is repulsive if one of the quantities $\Delta \tilde{\alpha}_{1,2}(i\omega_0)$ [$\Delta \tilde{\alpha}_{1,2}(0)$] is positive and the other negative. The van der Waals interaction between atoms in a liquid is also discussed in Ref. 82.

In examining the long-range forces earlier we assumed that the interacting systems are, on the whole, localized and that in this regard they can be treated quite accurately by a classical approach. We essentially assumed that the conditions for the applicability of the adiabatic approximation were satisfied, so that we could treat the interaction potential $U(\mathbf{r}_1 - \mathbf{r}_2)$ as the interaction energy between systems at points $\mathbf{r}_1$ and $\mathbf{r}_2$. We note in this connection that taking an average over electromagnetic fluctuations may also be convenient in another case, in which we can use the adiabatic approximation for only one of the interacting atoms, while the other system—a light particle—is not localized in any definite place and must be treated quantum-mechanically.[109]

3. VAN DER WAALS INTERACTION OF ATOMS WITH THE SURFACE OF CONDENSED MATTER

a) The interaction of atoms and molecules near the surface of a condensed medium (in particular, a solid) has been the subject of intense experimental and theoretical research (see, for example, the reviews and monographs in Refs. 110–124 and the literature cited there). In this section of the present review we examine the van der Waals interaction of one or two atoms near an interface, ignoring other interactions. As in the preceding section, the results will generally also apply to the interaction of molecules or small objects with a surface.

The van der Waals interaction with a surface is by no means always the dominant one. We know quite well that in an interaction with a surface an atom will often form a chemical bond with it; i.e., the atom will undergo a chemical adsorption. The properties of a chemisorbed atom may be markedly different from those of the isolated atom. For example, in the case of chemical adsorption on a metal the atomic levels (i.e., the levels which convert into the atomic levels as an atom is removed from the surface) are spread out into quasilevels, and the extent to which they are filled depends strongly on the position of the Fermi level in the metal. The binding energy of an atom with a surface in chemical adsorption is usually greater than 0.1 eV. The van der Waals forces play a minor role here, and there is no point in studying them separately. On the other hand, atoms do not always form a chemical bond with a surface. There are cases in which the binding of the atom with the surface occurs primarily as a result of van der Waals forces. This process is called "physical adsorption" and is characteristic of, for example, inert gas atoms on graphite, several alkali halides (LiF, NaF, etc.), and several metals (Ag, Cu, Al, etc.). The interaction energy corresponding to physical adsorption is of the order of 10^{-2}–10^{-3} eV. For heavy inert atoms (Kr, Xe), whose polarizabilities are comparatively large, it is also necessary to take into account the dipole moment induced in these atoms during adsorption in certain cases. This dipole moment is directed perpendicular to the surface. It arises because of a deformation of the electron shells of the originally spherically symmetric atom by its interaction with the substrate.[318–325] For the lighter atoms, with small polarizabilities, the dipole moments induced in the atoms by the surface are small and can usually be ignored. We assume here that the average dipole moment of the atom is zero.

The van der Waals interaction of atoms and molecules with a surface is seen not only in adsorption effects but also in, for example, experiments on the scattering of atoms by a surface at large impact parameters[117,121,125–130] (there are several other situations). The net result is that we need to study the van der Waals interaction of an atom or molecule with a surface.

Let us assume that some impurity atom (or a small object) is in a liquid with a dielectric permittivity $\varepsilon_2(\omega)$, at a distance l from the plane surface of a crystalline solid with a dielectric permittivity $\varepsilon_1(\omega)$ (Fig. 3). We denote the effective polarizability of the atom in the liquid by $\tilde{\alpha}(\omega)$, retaining the notation $\alpha(\omega)$ for the polarizability of the isolated atom in vacuum. In general, the interaction energy of the atom with the surface can be written as
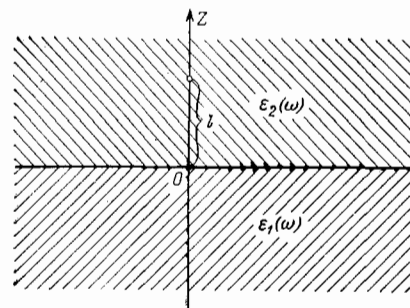

FIG. 3.

$$\widetilde{U}(\mathbf{r}) = U(l) + \sum_{\mathbf{G} \neq 0} U_{\mathbf{G}}(l)\, e^{i\mathbf{G}\boldsymbol{\rho}}, \tag{3.1}$$

where the sum over reciprocal-lattice vectors $\mathbf{G}$ arises because the 2-D periodicity of the crystalline substrate is being taken into account. The 2-D vector $\boldsymbol{\rho}$ describes the position of the atom in the plane parallel to the surface. The sum over 2-D reciprocal-lattice vectors $\mathbf{G}$ in (3.1) corresponds to allowing for the discrete structure of the condensed medium. These terms must be taken into account if the distance from the atom to the surface is of the order of the interatomic distances in the crystal. Here we are considering the opposite case, of large distances l, for which only the first term, $U(l)$, is important in (3.1). We also assume that l is larger than the scale correlation length in the medium. We can then ignore spatial-dispersion effects in analyzing the van der Waals interaction.

The van der Waals dipole-dipole interaction of an atom with a surface arises for essentially the same reasons which lead to the interaction between two atoms (see Section 2). If a fluctuational dipole moment $\mathbf{d}_1^{\mathrm{sp}}$ arises spontaneously in an atom, then we know that a polarization is induced in the medium, and this polarization is of such a nature that the field outside the medium corresponds to the field of an image dipole with a moment

$$\widetilde{\mathbf{d}}^{\mathrm{ind}} = \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)\,(\varepsilon_2(\omega) + \varepsilon_1(\omega))} \{d_{1x}^{\mathrm{sp}},\ d_{1y}^{\mathrm{sp}},\ -d_{1z}^{\mathrm{sp}}\}, \tag{3.2}$$

at the point $\{\boldsymbol{\rho}, -l\}$. For simplicity we assume $l \ll \lambda_0$ and ignore retardation. The energy of the interaction of the dipole with its image, averaged over the fluctuations of the dipole moment of the atom, is then described by

$$U^{(1)}(l) = \frac{1}{2} \langle \mathbf{d}_1^{\mathrm{sp}}\widetilde{\mathbf{d}}^{\mathrm{ind}} - 3\,(\mathbf{n}\mathbf{d}_1^{\mathrm{sp}})\,(\mathbf{n}\widetilde{\mathbf{d}}^{\mathrm{ind}}) \rangle \frac{1}{(2l)^3}$$

$$= \frac{1}{4l^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)\,(\varepsilon_2(\omega) + \varepsilon_1(\omega))} \langle d_{1z}^{\mathrm{sp}\,\mathbf{2}} \rangle_\omega. \tag{3.3}$$

In the case of an atom in a solution (or a small object in a liquid), we would have to replace $\mathbf{d}_1^{\mathrm{sp}}$ in (3.3) by the difference $(\Delta\, \mathbf{d}_1^{\mathrm{sp}})$ between the fluctuational dipole moments at the point $(\boldsymbol{\rho}, l)$ in the case in which the impurity atom (or object) is at this point and in the case of a pure liquid. Taking this circumstance into account in (2.9), which we now use, we should replace the polarizability $\alpha(\omega)$, of the isolated atom, by the quantity $\Delta\widetilde{\alpha}(\omega)$ defined in (2.61). The latter quantity, as mentioned earlier, is the difference between the effective polarizabilities for an atom (or particle) in a dilute solution and for the corresponding small volume element of a pure liquid. Also using (2.7), and writing a corresponding relation for the dielectric permittivity for real frequencies (see, for example, Ref. 131),

$$\varepsilon(\omega) = \varepsilon^*(-\omega),$$
$$\mathrm{Re}\,\varepsilon(\omega) \equiv \varepsilon'(\omega) = \varepsilon'(-\omega), \quad \mathrm{Im}\,\varepsilon(\omega)$$
$$\equiv \varepsilon''(\omega) = -\varepsilon''(-\omega), \tag{3.4}$$

we find from (3.3)

$$U^{(1)}(l) = \frac{\hbar}{4\pi l^3} \int_0^\infty d\omega\, \mathrm{Re} \left\{ \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)\,[\varepsilon_1(\omega) + \varepsilon_2(\omega)]} \right\} \mathrm{Im}\,(\Delta\widetilde{\alpha}(\omega)). \tag{3.5}$$

In analyzing the second part of the van der Waals interaction of an atom with a condensed medium we take into account the spontaneous fluctuations of the dipole-moment densities in the medium. The electric field $\mathbf{E}(\mathbf{r})$ which arises from these fluctuations induces a dipole moment $\mathbf{d}_1^{\mathrm{ind}}$ in the atom. The interaction energy corresponding to this effect is

$$U^{(2)}(l) = \delta \left[-\frac{1}{2} \langle \Delta\hat{\widetilde{\alpha}} E^2(\mathbf{r},\, t) \rangle \right]$$

$$= \delta \left[-\int_{-\infty}^{+\infty} \frac{d\omega}{4\pi} \Delta\widetilde{\alpha}(\omega) \langle E^2(\mathbf{r}) \rangle_\omega \right]. \tag{3.6}$$

Here the variation sign means that we are to subtract from the expression in square brackets the value found for this expression when the impurity atom is removed from the surface to infinity. The quantity $\Delta\widetilde{\alpha}(\omega)$ appears in (3.6), as it did in (3.5), since when the impurity atom (or particle) is removed the resulting vacancy will be filled with liquid, so that the corresponding polarizability will change by the amount $\Delta\widetilde{\alpha}(\omega)$ given in (2.61).

According to the familiar result from the theory of electromagnetic fluctuations, the spectral density of the quadratic correlation function for the electromagnetic field in an inhomogeneous medium at temperatures which are not too high $(T \ll \hbar/\tau)$ satisfies the following relation [see, for example, §§ 76, 77 in Ref. 28; cf. expression (2.45), which refers to vacuum fluctuations]:

$$\langle E_i(\mathbf{r}_1)\, E_k(\mathbf{r}_2) \rangle_\omega = -\frac{|\omega|}{\omega} \frac{\omega^2}{c^2} \mathrm{Im}\, \mathscr{D}_{ik}^{\mathrm{R}}(\omega;\ \mathbf{r}_1,\ \mathbf{r}_2), \tag{3.7}$$

where the retarded Green's function for the electromagnetic field in the medium satisfies the equations

$$\left[\mathrm{rot}_{ik}\, \mathrm{rot}_{hl} - \frac{\omega^2}{c^2}\, \varepsilon(\omega,\ \mathbf{r})\, \delta_{il} \right] \mathscr{D}_{lm}^{\mathrm{R}}(\omega;\ \mathbf{r},\ \mathbf{r}')$$

$$= -4\pi\hbar\delta_{im}\delta(\mathbf{r}' - \mathbf{r}). \tag{3.8}$$

We recall that Maxwell's equations for the field of a neutral point particle with a dipole moment $\mathbf{d}(\mathbf{r}', t)$ at the point $\mathbf{r}'$ can be written as

$$\left[\mathrm{rot}\,\mathrm{rot} - \frac{\omega^2}{c^2}\, \varepsilon(\omega,\ \mathbf{r}) \right] \mathbf{E}(\omega,\ \mathbf{r}) = \frac{\omega^2}{c^2}\, 4\pi\mathbf{d}(\omega)\, \delta(\mathbf{r} - \mathbf{r}'). \tag{3.9}$$

A comparison of (3.8) and (3.9) shows that the Green's function $\mathscr{D}_{lm}^{\mathrm{R}}(\omega, \mathbf{r}, \mathbf{r}')$ with fixed values of the index m and of $\mathbf{r}'$ [which appear in (3.8) as parameters] is the same as the field $\mathbf{E}(\omega, \mathbf{r})$ created by a point dipole $d_l(\omega) = -(c^2/\omega^2)\,\hbar\delta_{lm}$ at the point $\mathbf{r}'$. It follows, in particular, that in the long-wavelength approximation which we are using here the function $\mathscr{D}_{lm}^{\mathrm{R}}(\omega; \mathbf{r}, \mathbf{r}')$ tends toward infinity in the limit $\mathbf{r} \to \mathbf{r}'$ in the same manner as the field of a point dipole as the position of the dipole is approached. In expressions (3.6) and (3.7) for the interaction energy $U^{(2)}(l)$ we see the quantity $\delta\mathscr{D}_{ii}^{\mathrm{R}}(\omega; \mathbf{r}, \mathbf{r}) = \sum_{i=x,y,z} [E_{1,i}(\omega, \mathbf{r}) - E_{2,i}(\omega, \mathbf{r})]$, which is a difference between two fields. The field $\mathbf{E}_1(\omega, \mathbf{r})$ is the field of a dipole at the point $\mathbf{r}' \to \mathbf{r}$ in a homogeneous medium with a dielectric permittivity $\varepsilon_2(\omega)$, separated by a distance l from a plane interface with a second medium of dielectric permit-

tivity $\varepsilon_1(\omega)$. The field $\mathbf{E}_2(\omega, \mathbf{r})$ is the field of the same dipole in the case in which the interface has been removed to infinity. We wish to emphasize that the difference between these fields has no singularity at the point $\mathbf{r}$, and it is easy to show that this field is simply the field of the image dipole (at the point $\{\boldsymbol{\rho}, -l\}$) evaluated at the position of the atom, $\{\boldsymbol{\rho}, l\}$. Taking this circumstance into account, we find from (3.6), (3.7), (3.2) and (2.7), (3.4)

$$U^{(2)}(l) = \frac{1}{4\pi} \int_{-\infty}^{+\infty} d\omega \Delta\widetilde{\alpha}(\omega) \frac{|\omega|}{\omega}$$

$$\times \mathrm{Im}\left[\hbar \frac{4}{(2l)^3} \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)(\varepsilon_2(\omega) + \varepsilon_1(\omega))}\right]$$

$$= \frac{\hbar}{4\pi l^3} \int_{0}^{+\infty} d\omega\, \mathrm{Re}(\Delta\widetilde{\alpha}(\omega))\, \mathrm{Im} \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)(\varepsilon_1(\omega) + \varepsilon_2(\omega))}.$$

$$(3.10)$$

We see from this expression that the energy $U^{(2)}(l)$ is determined by those frequency regions in which $\mathrm{Re}(\Delta\widetilde{\alpha}(\omega))$, $\mathrm{Im}\,\varepsilon_1(\omega)$, and/or $\mathrm{Im}\,\varepsilon_2(\omega)$ are comparatively large. Furthermore, certain spectral regions in which the media are transparent may contribute substantially. In this case we would have

$$\lim_{\mathrm{Im}\,\varepsilon_{1,2}(\omega)\to 0} \mathrm{Im} \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega)(\varepsilon_2(\omega) + \varepsilon_1(\omega))}$$

$$= -\pi[\varepsilon_2(\omega) - \varepsilon_1(\omega)]\, \delta(\varepsilon_2(\omega)[\varepsilon_2(\omega) + \varepsilon_1(\omega)]). \quad (3.11)$$

It follows that if we ignore absorption the frequencies which are important in the integral in (3.10) are those which satisfy one of the equations

$$\varepsilon_2(\omega) = 0, \quad (3.12)$$

$$\varepsilon_1(\omega) + \varepsilon_2(\omega) = 0. \quad (3.13)$$

We recall that Eq. (3.12) is the dispersion relation for longitudinal waves in a homogeneous medium, while (3.13) is the dispersion relation for surface waves at the plane interface between two media without retardation.

It follows from (3.10) and (3.11) that the potential $U^{(2)}(l)$ must in general be taken into account even if absorption is ignored, provided that $\mathrm{Re}\,\Delta\widetilde{\alpha}(\omega)$ is not too small at the frequencies which are the roots of Eq. (3.12) or (3.13).

We can find an expression for the van der Waals interaction of an atom with a surface (under the condition $l \ll \lambda_0$) by summing energies (3.5) and (3.10):

$$U(l) = U^{(1)}(l) + U^{(2)}(l) = \frac{\hbar}{4\pi l^3} \int_{0}^{\infty} d\omega\, \mathrm{Im} \frac{[\varepsilon_2(\omega) - \varepsilon_1(\omega)]\,\Delta\widetilde{\alpha}(\omega)}{\varepsilon_2(\omega)[\varepsilon_2(\omega) + \varepsilon_1(\omega)]}$$

$$= \frac{\hbar}{4\pi l^3} \int_{0}^{+\infty} d\omega \frac{\varepsilon_2(i\omega) - \varepsilon_1(i\omega)}{\varepsilon_2(i\omega)[\varepsilon_2(i\omega) + \varepsilon_1(i\omega)]} \Delta\widetilde{\alpha}(i\omega). \quad (3.14)$$

The last expression in (3.14) was derived by a method analogous to that used to derive (2.11). An important point here is that the integrand in the next-to-last expression in (3.14) is analytic and has no singularities in the upper part of the plane of the complex frequency ω. As we have already mentioned, the polarizabilities and dielectric permittivities have the same properties. Furthermore, we should bear in mind that the roots of Eqs. (3.12) and (3.13) lie in the lower half-plane of the complex frequency ω, since all the natural waves must decay in equilibrium media.

In the particular case in which the atom which is interacting with the surface is in vacuum, we must set $\varepsilon_2(\omega) \equiv 1$ in (3.14) and replace $\Delta\widetilde{\alpha}(\omega)$ by the polarizability of the isolated atom, $\alpha(\omega)$. We then find

$$U(l) = -\frac{\hbar}{4\pi l^3} \int_{0}^{\infty} d\omega \frac{\varepsilon(i\omega) - 1}{\varepsilon(i\omega) + 1} \alpha(i\omega) = -\frac{C_3}{l^3}. \quad (3.15)$$

We have omitted the subscript from the dielectric permittivity $\varepsilon_1(\omega)$.

That the energy of the van der Waals interaction of an atom with a surface is proportional to l^{-3} was first pointed out by London,[5b] who analyzed this interaction approximately as a sum of binary van der Waals interactions between an adatom and atoms of the condensed medium. To adopt this approximation is essentially to treat the condensed medium as a low-density gas of atoms with a surface number density of particles N and with a polarizability $\alpha_m(\omega)$ of each atom. We can then substitute

$$\varepsilon(\omega) \approx 1 + 4\pi N \alpha_m(\omega) \quad (3.16)$$

into (3.15) and restrict the analysis to the term which is linear in the density N. The resulting estimate for the coefficient C_3 frequently turns out to be completely at odds with reality for actual condensed media. The reason is the well-known fact that the optical properties of condensed media may differ substantially from those of the corresponding isolated atoms or molecules. This difference is of course not restricted to the optical part of the spectrum but extends over a broader range. Even for the restricted class of substances in which the atoms or molecules retain their individual properties to a large extent relation (3.16) does not hold, in particular, because of local-field effects. In this regard the image method may have important advantages in deriving an expression for the energy of the van der Waals interaction of an atom with a surface, since this method allows one to incorporate collective effects in the condensed medium by a simple macroscopic approach which uses only the dielectric permittivity of the medium.

The image method was first applied to this problem by Lennard-Jones,[13] who took up the particular case in which a substrate creates an ideal image of the fluctuating dipole moment in an adatom. Bardeen[14] later used perturbation theory and the image method to analyze the more general case of a metallic substrate. A related question was studied in Ref. 15. To see the meaning of the results of those papers we substitute into (3.15) a very simple expression for the high-frequency dielectric permittivity of a metal:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}, \quad (3.17)$$

where ω_p is the plasma frequency. We find

$$U(l) = -\frac{\hbar\omega_s^2}{4\pi l^3} \int_{0}^{\infty} d\omega \frac{\alpha(i\omega)}{\omega_s^2 + \omega^2}, \quad (3.18)$$

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where $\omega_s = \omega_p/\sqrt{2}$ is the frequency of a surface plasmon. Substituting expression (2.13) for the polarizability of an atom into (3.18), we then find[132,133]

$$U(l) = -\frac{\hbar}{8l^3} \sum_n \frac{e^2 f_{0n}}{m\omega_{n0}} \frac{\omega_s/\omega_{n0}}{1 + (\omega_s/\omega_{n0})} . \qquad (3.19)$$

If we now restrict the sum (3.19) to a single characteristic transition frequency ω_1 and use expression (2.14) for the oscillator strength, we find from (3.19) the following simple expression which corresponds to the result found by Bardeen[14]:

$$U(l) = -\frac{\hbar\omega_1 \alpha(0)}{8l^3} \frac{\omega_s/\omega_1}{1 + (\omega_s/\omega_1)} = -\frac{e^2 \langle r^2 \rangle}{12l^3} \left[\frac{\omega_s/\omega_1}{1 + (\omega_s/\omega_1)} \right]; \quad (3.20)$$

here $\langle r^2 \rangle$ is the mean square radius of the electron in the atom. Lennard-Jones's result[13] can be obtained formally from (3.20) under the condition $(\omega_s/\omega_1) \gg 1$, when the expression in brackets can be replaced by unity.

General expression (3.15) for the energy of the van der Waals interaction of an atom with the surface of a condensed medium is the same as the expression which follows from Lifshitz's result[19] for the interaction of two thick plates if, in the latter result, we take the limit in which one of the plates is a low-density gas of atoms. Expression (3.15) has been discussed in several places by a variety of methods.[132–138] It follows from (3.15) that the van der Waals interaction of an atom in vacuum with a surface is of the nature of an attraction. If the atom (or molecule) is instead in a liquid bounding the solid surface,[139] the energy of the interaction determined by (3.14) may correspond to either an attraction or a repulsion. According to the general properties of linear-response functions we have $\alpha(i\omega) > 0, \varepsilon(i\omega) > 1$ at $\omega > 0$. The integral which appears in (3.15) therefore always takes on positive values. The sign of the integral over the frequency in (3.14), on the other hand, depends on the relation between the dielectric permittivities of the solvent, $\varepsilon_2(i\omega)$, and of the condensed medium, $\varepsilon_1(i\omega)$; it also depends on the sign of $\Delta\tilde{\alpha}(i\omega)$ in the spectral region most important for the integration.

In this regard there is an analogy with the electrostatic interaction of a charge with a surface. If the charge is in vacuum then it is of course always attracted to its image and thus to the surface. If the charge is instead in a medium with a dielectric permittivity ε_2, which borders another medium with ε_1, then the image force leads to a repulsion if $\varepsilon_2(0) > \varepsilon_1(0)$ or to an attraction if $\varepsilon_2(0) < \varepsilon_1(0)$ (see, for example, § 7 in Ref. 20).

The onset of a repulsion in the van der Waals interaction of an impurity atom in a liquid with a wall can be explained quite simply not only by the image method but also from a microscopic standpoint. As in the case of the interaction of two impurity atoms in a homogeneous liquid, it is convenient to consider the limit of low-density media and to note that in this limit the potential $U(l)$ is the difference between two quantities. The first of these quantities is the energy of the binary van der Waals interactions of the atoms in the case in which the impurity atom lies a distance l from the interface between the two low-density media, and the second quantity is the corresponding energy in the case in which the impurity atom is removed an infinite distance

from the interface (but remains in the same gas). If this energy difference is positive, then energy considerations favor an increase in the distance from the impurity atom to the interface; this situation corresponds to a repulsion. If we assume that only the second medium, in which the impurity atom is immersed, has a low density, then we can use the approximations $\varepsilon_2 \approx 1$ and $\Delta\tilde{\alpha} \approx \alpha - \alpha_m$ in (3.14). In this particular case the repulsion has a particularly simple explanation. Clearly, if the atoms of the low-density gas are attracted more strongly than the impurity atom toward the wall, then the effective interaction of the impurity atom with the surface will be repulsive.

b) We believe that these solutions give a good explanation of the particular fluctuational mechanism which gives rise to the van der Waals forces and also the relationship between the questions of image forces and van der Waals forces (when results from the theory of electromagnetic fluctuations are additionally taken into account). Many other problems of van der Waals interactions could be solved by methods analogous to that described above. In particular, the image method could be used to treat the interaction of an atom with a surface with retardation effects (the analysis would have much in common with the analysis in Section 2 for the case of two atoms under the condition $R \gtrsim \lambda_0$) and to incorporate certain other effects, which we will be discussing below. However, there is hardly any point in pursuing these calculations in this review, and we will simply look at the results.

If $l \gg \lambda_0$, such that retardation effects are important, and the interaction stems from the existence of spatial correlations of the spontaneous fluctuational electromagnetic field in the medium, the potential of the van der Waals interaction of an atom (in vacuum) with a surface becomes[26]

$$U(l) = -\frac{3\hbar c\alpha(0)}{8\pi l^4} \frac{\varepsilon(0)-1}{\varepsilon(0)+1} \varphi_{AD}(\varepsilon(0)); \qquad (3.21)$$

here the monotonically increasing function $\varphi_{AD}(x), x = \varepsilon(0)$, is of the order of unity: $0.77 \leqslant \varphi_{AD}(x) \leqslant 1$ for $x > 1$. The function $\varphi_{AD}(x)$ is given explicitly in Ref. 26 and generalized to the case of the interaction of a molecule in a solution with a wall in Ref. 139. For a metal we would have $\varepsilon(0) \to \infty$ and $\varphi(x) \to_{x \to \infty} 1$, so that expression (3.21) would become the well-known result for the interaction of an atom with the plane surface of an ideal conductor.[7,16]

If the distance from the atom to the surface reaches a value of the order of the scale length (l_{sp}) for spatial dispersion in the medium, then we need to consider the effect of spatial dispersion on the interaction. These questions were discussed in Refs. 138 and 140–144 for the interaction of an atom with a surface. The effect of a surface roughness on the interaction of a surface with an atom was discussed in Refs. 144–146. The effect of an external magnetic field on the van der Waals interaction of an atom with a semiconductor plasma was studied in Ref. 147. Dynamic corrections to the van der Waals interaction of an atom with a surface—corrections which depend on the velocity of the atom—were studied in Refs. 148–151 and 146. To some extent this latter question is related to the problem of the dynamic image of a charge moving near a surface. For atoms adsorbed on the

surface of micropores and microcapillaries in solids or on the surfaces of small particles of condensed matter and filaments (with a radius of the order of 10^{-7}–10^{-5} cm), the dependence of the van der Waals energy on the surface geometry becomes important.[146,148,152–154] For molecules or small objects with anisotropic polarizabilities, the energy of the van der Waals interaction with a surface depends on the orientation of the molecule with respect to the surface.[74,155]

If there are two atoms near a surface, the van der Waals interaction between them will differ from the interaction of these atoms in free space (in the case in which the atoms lie an infinite distance from the surface). The effect of a substrate on the interaction between atoms is of course governed by the many-body nature of the van der Waals forces. This effect was studied theoretically in Refs. 74, 134, 156, 157–160, and 234; some corresponding experimental results are reported and analyzed in Refs. 161–167. General formulas describing the van der Waals interaction of two atoms (or of two small objects) near a plane surface (under the conditions $R, l_{1,2} \ll \lambda_0$) were first derived by McLachlan,[134] who used an image method. The van der Waals energy, which depends on the distance between the atoms, is (Fig. 4)

$$U\,(R,\ l_1,\ l_2) = -\frac{3\hbar}{\pi R^6} \int_0^\infty d\omega\,\alpha_1\,(i\omega)\,\alpha_2\,(i\omega)$$

$$+\frac{\hbar}{2\pi R^3 R'^3}\,(2 + 3\,\cos 2\theta + 3\,\cos 2\varphi)$$

$$\times \int_0^\infty d\omega\,\alpha_1\,(i\omega)\,\alpha_2\,(i\omega)\,\frac{\varepsilon\,(i\omega)-1}{\varepsilon\,(i\omega)+1}$$

$$-\frac{3\hbar}{\omega R'^6} \int_0^\infty d\omega\,\alpha_1\,(i\omega)\,\alpha_2\,(i\omega)\,\left[\frac{\varepsilon\,(i\omega)-1}{\varepsilon\,(i\omega)+1}\right]^2\,;$$

$$(3.22)$$

here

$$\sin\theta = \frac{l_2 - l_1}{R}, \quad \sin\varphi = \frac{l_1 + l_2}{\sqrt{R^2 + 4l_1 l_2}}, \quad R' = \sqrt{R^2 + 4l_1 l_2},$$

$$l_2 > l_1. \qquad (3.23)$$

The simple geometric meaning of R', φ, and θ is clear from Fig. 4. In particular, R' is the distance between the image of the first atom in the condensed medium and the second atom.

The first term in (3.22) corresponds to the ordinary dipole-dipole van der Waals interaction of two atoms in free
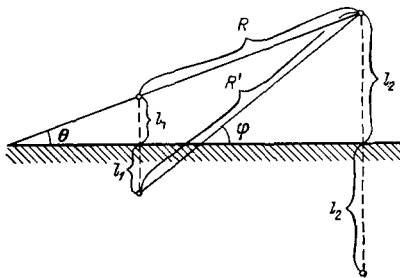
space, (2.11). We denote the sum of the two other terms in (3.22) by U_{12s}. These terms, like the three-body U_{123} in the van der Waals energy (2.24), stem from intermediate (secondary) images. In this case the role of the third body is played by the condensed medium with a plane boundary. Clearly, the image field of the spontaneous dipole moment $\mathbf{d}_1^{sp}$ of one of the atoms will induce an additional dipole moment $\tilde{\mathbf{d}}_2^{ind}$ in the other. The average interaction of the dipoles $\mathbf{d}_1^{sp}$ and $\tilde{\mathbf{d}}_2^{ind}$ contributes to the second term in (3.22). The third term here receives a contribution from the interaction of the dipole $\mathbf{d}_1^{sp}$ with the image field of the induced dipole $\tilde{\mathbf{d}}_2^{ind}$. In addition to these processes we must also take into account the fact that there is a spatially correlated fluctuational electric field near the surface of a condensed medium, even if we ignore retardation. The spectral correlation density $\langle E_i(\mathbf{r}_1)E_j(\mathbf{r}_2)\rangle_\omega$ depends not only on the distance $(\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1)$ between the points $\mathbf{r}_1$ and $\mathbf{r}_2$ under consideration but also, generally speaking, on the distances from these points to the surface: l_1 and l_2. This fluctuational field induces in the atoms at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ some fluctuating dipole moments which are correlated with each other. The average interaction of these dipoles also contributes to the second and third terms in (3.22).

Depending on the positions of the atoms with respect to the surface, the three-particle term U_{12s} in the interaction energy of atoms (or small objects) may be either positive or negative; i.e., it may either reduce or increase the total energy of the van der Waals attraction between the atoms. The quantity U_{12s} is always smaller in modulus than the binary van der Waals interaction (2.11). While the three-body contribution to the van der Waals interaction for three atoms amounts to no more than a few percent of the energy of the binary interaction, the interaction between two atoms near a surface may change substantially in value. In particular, if $R \gg l_1, l_2 (\theta \approx \varphi \approx 0, R' \approx R)$, and the surface should be particularly influential, we find from (3.22)

$$U = -\frac{3\hbar}{\pi R^6} \int_0^\infty d\omega\,\alpha_1\,(i\omega)\,\alpha_2\,(i\omega)\cdot\frac{2\,(\varepsilon^2\,(i\omega)+5)}{3\,(\varepsilon\,(i\omega)+1)^2}. \qquad (3.24)$$

In this case the dependence of the interaction energy on the parameters l_1 and l_2 disappears, and there is an effective renormalization of C_6 in comparison with the customary expression, (2.11). This renormalization reaches a maximum in the limit $\varepsilon \to \infty$, where the renormalization reduces to a multiplication of the vacuum value of C_6 (in the absence of a condensed medium) by 2/3. In practice, on the other hand, the effect may be significant if the dielectric permittivity of the medium takes on large values at frequencies $\omega \lesssim \omega_0$. Schmeits and Lucas[160] analyzed the effect of surface curvature on the van der Waals interaction between atoms moving near it. Delanaye et al.[168] studied the role played by many-body effects in the van der Waals interaction in a monolayer of adsorbed atoms.

4. VAN DER WAALS COMPONENT OF THE FREE ENERGY OF CONDENSED MEDIA. INTERACTION BETWEEN MACROSCOPIC OBJECTS

a) van der Waals forces arise between macroscopic (extended) objects for the same reasons as in the case of atoms

FIG. 4.

and small particles of condensed matter. As is clear from the discussion above, we are essentially dealing with the appearance, at sufficiently large distances, of spatial correlations between the densities of the fluctuating charges and currents in the condensed media. These correlations arise because of the induced charge and current densities or polarization in one object caused by spontaneous fluctuations of these quantities in the other object. In a more general case, we would be dealing not with two different objects but with two well-separated regions in an inhomogeneous condensed medium. Another reason for the appearance of these correlations is the presence in the medium (or in vacuum) of a spontaneous fluctuational electromagnetic field, which induces an additional current and an additional polarization in the objects. We know that the spatial correlations of this field may be manifested over large distances.

In Sections 1 and 2 we considered the case in which the atom or small object could be approximated by a point particle of polarizability $\alpha(\omega)$. In finding the van der Waals energy in this case it is convenient to use an image method along with relations of the type in (2.8) and (3.7), which follow from the fluctuation-dissipation theorem. When we make the transition from the problem of point particles to that of extended macroscopic objects, the image method loses its simplicity and clarity to a large extent, and the formalism based on the image method becomes substantially more complicated, because, for example, of the need to consider multiple images for objects of certain particular shapes. Essentially what we are doing here is solving Maxwell's equations for the electromagnetic field of an elementary point dipole in the system under consideration, i.e., the equations for the Green's function of a photon in a medium [as is clear from (3.8)]. Calculations of this sort could of course also be carried out without appealing to the image method. Nevertheless, in the general case of inhomogeneous condensed media it turns out to be simpler to use a different method to find the energy (and the other thermodynamic potentials) of the van der Waals interaction, without making direct use of Green's functions.

The question of the energy of the van der Waals interaction between objects (in a slightly more general formulation, the question of the van der Waals contribution to the thermodynamic characteristics of inhomogeneous condensed media) can be discussed at a general level, without appealing to any specific problem. It is the general formula found for the energy by this approach [or for the free energy; see (4.10) below) which leads us to this comparatively simple method we have mentioned for finding the van der Waals interaction between macroscopic objects. This question is analyzed in detail in Refs. 1, 2, and 23; we will offer only some brief comments about it here.

We know well that the energy of an electromagnetic field in the presence of charged particles contains the energy representing an interaction between these particles. Similarly, the energy of a fluctuational electromagnetic field in a condensed medium must contain, in addition to the energy of thermal radiation, the energy of that interaction between particles, which is of a fluctuational origin. The van der Waals interaction is of just this kind.

In the limiting case of transparent media, with negligible damping, the energy of the equilibrium fluctuational electromagnetic field is obviously described by the Planck expression taking zero-point vibrations into account:

$$E_{fl} = \sum_{\alpha} \left(\frac{\hbar\omega_{\alpha}}{2} + \frac{\hbar\omega_{\alpha}}{\exp\left(\hbar\omega_{\alpha}/T\right) - 1} \right). \quad (4.1)$$

The corresponding expression for the free energy is

$$F_{fl} = T \sum_{\alpha} \ln \left(2 \operatorname{sh} \frac{\hbar\omega_{\alpha}}{2T} \right), \quad (4.2)$$

where the ω_{α} are the natural frequencies of the electromagnetic field in the system under study. Since frequencies ω_{α} are found in the course of the solution of a boundary-value problem for the macroscopic Maxwell's equations, expression (4.1) clearly determines the energy of the fluctuational field in a transparent medium as a functional of the dielectric permittivity. In inhomogeneous media, the spectrum of natural oscillations of the electromagnetic field also contains frequencies which depend strongly on the properties of the inhomogeneities. In particular, in the two-body system there are natural frequencies which depend on the macroscopic distance between these bodies, l. The dependence of the free energy of the fluctuational electromagnetic field on the distance which follows from (4.2) reflects the presence of forces which are acting on the objects. We thus see that (4.1) and (4.2), which apply to transparent media, contain, in accordance with the discussion above, the energy of the van der Waals interaction as well as the energy of the thermal radiation.[5] As a result, if we ignore absorption the question of the van der Waals forces between objects reduces to one of finding the spectrum of natural waves in the system.

We thus see why the van der Waals interaction can be found by calculating the energy of the zero-point vibrations (if the temperature is not too high and if damping is ignored). This assertion applies in particular to the derivation (mentioned in Section 2) of the dispersive interaction between atoms on the basis of the shift of the zero-point-vibration energy in a system of 3-D oscillators with a dipole interaction. In this example we are essentially dealing with the zero-point oscillations of an electric field which is associated with the zero-point vibrations of the dipole moments of oscillators. Clearly, the fact that the interaction can be described not only qualitatively but also quantitatively by this approach is not simply a fortuitous result; it is a consequence of the general nature of expression (4.1). On the other hand, for a qualitative or illustrative discussion of the dispersive interaction between atoms it is sufficient to consider the case of, for example, 1-D oscillators, as is done in several textbooks (see Kittel[169] and Shpol'skiĭ,[170] § 160). It is of course not mandatory to use an oscillator model to calculate the energy shift of zero-point vibrations. One might also consider arbi-

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[5] Expressions (4.1) and (4.2) can be proved in a simple way if the natural frequencies ω_{α} do not depend on the temperature. A temperature dependence of the frequencies ω_{α} arises when the temperature dependence of the dielectric permittivity is taken into account. It can be shown that in this case expression (4.2) does not change, while expression (4.1) acquires terms with derivatives $\partial\omega_{\alpha}/\partial T$ in accordance with the thermodynamic equality $E = - T^2 \partial(F/T)/\partial T$.

trary point particles with real polarizabilities $\alpha_1(\omega)$ and $\alpha_2(\omega)$. As the distance between these particles is changed, there is also a change in the spectral state density for the electromagnetic field in the system under consideration, and this change causes a shift of the energy of the zero-point vibrations. For a discrete spectrum we would be dealing with a shift of each individual natural frequency of the electromagnetic oscillations. This approach can be used to study the van der Waals interaction with retardation[16,171] and many-body forces[86,88] (see also Ref. 29).

Before we discuss the more general case of absorbing media, we will put expression (4.2) in a different form. For this purpose we introduce the spectral state density for photons in inhomogeneous transparent media,

$$\rho(\omega) = \sum_\alpha \delta(\omega - \omega_\alpha). \tag{4.3}$$

Using (4.3), we can rewrite (4.2) as

$$F_{\text{fl}} = \int_0^{\omega_{\text{lim}}} d\omega \rho(\omega) T \ln\left(2\,\text{sh}\,\frac{\hbar\omega}{2T}\right). \tag{4.4}$$

The limiting frequency ω_{lim} defines the long-wavelength part of the spectrum in integral (4.4); the value of ω_{lim} itself is unimportant for the problems we are considering here.[2] The index α in (4.1)–(4.3) denotes both discrete and continuous (or quasicontinuous) variables. We will single out the continuous variables below and denote them by β, leaving α to stand exclusively for the discrete variables (which specify the various branches of natural waves). In a homogeneous medium the components of the wave vector play the role of the variables β. In inhomogeneous media, the specific choice of variables β depends on the nature of the inhomogeneities. It is also convenient to introduce a state density $\rho(\beta)$ for the variable β; for a homogeneous medium we would have $\rho = V/(2\pi)^3$, where V is the volume of the system. In terms of these variables we can rewrite expression (4.3) as

$$\rho(\omega) = \sum_\alpha \int \rho(\beta)\,d\beta\,\delta(\omega - \omega_\alpha(\beta)). \tag{4.5}$$

We also assume that the roots of the equation

$$D(\beta, \omega) \equiv \prod_\gamma \Delta_\gamma(\beta, \omega) = 0 \tag{4.6}$$

constitute all the natural frequencies $\omega_\alpha(\beta)$ of electromagnetic oscillations in the system. In a transparent medium the frequencies $\omega_\alpha(\beta)$ and the functions $\Delta_\gamma(\beta,\omega)$ are real, and we find from (4.5) and (4.6)

$$\rho(\omega) = \int \rho(\beta)\,d\beta\,\sum_\gamma \left|\frac{\partial\Delta_\gamma(\beta,\omega)}{\partial\omega}\right|\delta(\Delta_\gamma(\beta,\omega)). \tag{4.7}$$

If, on the other hand, we assume that the function $\Delta_\gamma(\beta,\omega)$ has a small positive imaginary part, and we use the familiar representation

$$\lim_{\varepsilon\to+0}\frac{\varepsilon}{\Delta_\gamma^2(\beta,\omega)+\varepsilon^2} = \pi\delta(\Delta_\gamma(\beta,\omega)), \tag{4.8}$$

of the δ-function, we can then write $\rho(\omega)$ as

$$\rho(\omega) = -\frac{1}{\pi}\,\text{Im}\,\frac{\partial}{\partial\omega}\left(\int \rho(\beta)\,d\beta\,\ln D(\beta,\omega)\right), \tag{4.9}$$

where the limit of a transparent medium should be taken only at the end of the calculations, under the assumption $\text{Im}\,\Delta_\gamma(\beta,\omega) \to +0$. Now substituting (4.9) into (4.4), and carrying out some transformations in the plane of the complex frequency ω (these calculations are discussed in detail in Ref. 2), we can put the expression for the free energy of an equilibrium fluctuational electromagnetic field in a transparent medium in the following form:

$$F_{\text{fl}} = T\sum_{n=0}^{\infty}{}' \int \rho(\beta)\,d\beta\,\ln D(\beta, i\omega_n), \qquad \omega_n = \frac{2\pi T}{\hbar}n, \tag{4.10}$$

where the prime on the summation sign means that the term with $n = 0$ is to be assigned a weight of 1/2.

The transition to an analysis of absorbing media is extremely important for the theory of van der Waals forces. At the same time, if there is absorption, and the natural frequencies of the oscillations of the electromagnetic field are complex, then expression (4.1), being complex, clearly does not represent an energy. The question of the van der Waals contribution to the free energy in the case with absorption was studied in Refs. 21–23 and is set forth in detail in Refs. 1 and 2. It turns out that the free energy of an equilibrium long-wavelength electromagnetic field in a medium is, by virtue of its fluctuational origin, a functional of the dielectric permittivity even when absorption is taken into account. Generally speaking, this circumstance is not self-evident. We know, for example, that the energy of a nonequilibrium long-wavelength electromagnetic field in an absorbing medium cannot in general be expressed in terms of the dielectric permittivity alone. On the other hand, in the particular case of a transparent medium there is an expression of this sort for the energy of a nonequilibrium field (see, for example, Refs. 35 and 172). For an equilibrium fluctuational long-wavelength field it turns out that the free energy is described by (4.10) also when there is absorption.[22] In this more general case, of course, expression (4.10) is no longer equivalent to (4.2). On the other hand, result (4.10) can also be written in the form (4.4), (4.9) in the case of absorbing media. The effect, however, would be to complicate the interpretation of the function $\rho(\omega)$, which generally is no longer a spectral state density for photons in the medium.

The function $D(\beta,\omega)$ in (4.10) can be determined unambiguously and quite rigorously in terms of the spectral characteristics of certain auxiliary macroscopic Maxwell's equations.[22,23] This circumstance allows us to see in a general way that the function $\ln D(\beta,\omega)$ is analytic in the upper half-plane of the complex frequency ω, to find the relationship between this function and the retarded Green's function for a photon in the medium, and to study the factorization of the function $D(\beta,\omega)$. These questions are discussed in detail in Refs. 1, 2, and 23; here we simply note that the basic property of the function $D(\beta,\omega)$ in the case with absorption is, as before, the circumstance that Eq. (4.6) has the meaning of a dispersion relation for the (generally complex) natural frequencies of electromagnetic oscillations in the system. As a result, the question of finding the van der Waals part of the free energy reduces to finding a dispersion relation of this type [the func-

tion $D(\beta,\omega)$ is also found] and then using expression (4.10).[6] This method has now been used to solve many problems involving van der Waals interactions between macroscopic objects (see, for example, Refs. 1, 2, and 29 and the literature cited there). Skipping the derivations, we will now examine some of the major results obtained in this research.

b) Among problems involving van der Waals interactions between macroscopic objects, that which has been studied most thoroughly is the interaction between two thick plates separated by a plane gap of width l (Fig. 5). Since the corresponding results have been discussed in detail in the literature[19,26–28] (see also Refs. 1 and 2), we will not reproduce them here.

The contribution of classical orientational fluctuations of the dipole moments of polar molecules to the total van der Waals interaction of polar media separated by plane boundaries was analyzed in Refs. 173 and 174. It was shown that this contribution is important in the case of aqueous media separated by a lipid film, which is a case of importance in biology. The van der Waals interactions in systems of interest to biology are also discussed in Refs. 39–41 and 29.

An important application of the results found concerning the problem of the van der Waals interaction between thick plates is to study the equilibrium thermodynamic properties of liquid films on plane surfaces of condensed media.[26,108,175] The dependence of the chemical potential of a film on its thickness $l \gtrsim a \sim 10^{-8}$ cm is due entirely to the van der Waals forces. It was shown in Ref. 175 that this dependence is described by the same expressions as for the force of the van der Waals interaction between the surface of a film and the substrate. The question of the role played by van der Waals forces in forming the equilibrium thickness of a liquid film was recently revived[269] in connection with experiments on the "wetting transition," i.e., the phase transition to a state of total wetting. The conclusion that van der Waals forces play an important role under these conditions has subsequently been confirmed experimentally.[270]

Manifestations of the van der Waals interactions in anisotropic media are also interesting. The dependence of the van der Waals energy on the relative orientation of aniso-

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[6]Errors are sometimes encountered in the analysis and discussion in the literature of the role played by absorption in the van der Waals interaction. For example, most of the assertions in the monograph of Ref. 30 about the effect of absorption are incorrect, especially the assertions in Subsections 3.2 and 3.6. In particular, it is asserted in Ref. 30 that when absorption is taken into account the free energy is described not by (4.10) but by (in our notation)

$$F_{11}' = \frac{T}{2} \sum_{n=}^{\infty_i} \int \rho(\beta)\, d\beta \ln [D(\beta, i\omega_n)\, D(\beta, -i\omega_n)]$$

$$= \frac{T}{2} \sum_{n=-\infty}^{+\infty} \int \rho(\beta)\, d\beta \ln D(\beta, i\omega_n).$$
(*)

Since the function $D(\beta, i\omega_n)$ is of even parity if absorption is neglected, expression (*) is equivalent to (4.10) for transparent media. For absorbing media, on the other hand, Eqs. (*) and (4.10) are substantially different, as is pointed out in Ref. 30. In this connection we wish to point out again that expression (4.10) can be derived from an analysis of electrical fluctuations in an RCL circuit[22] or also by the more rigorous approach which initially uses a microscopic operator for the electromagnetic interaction.[1,2,23]
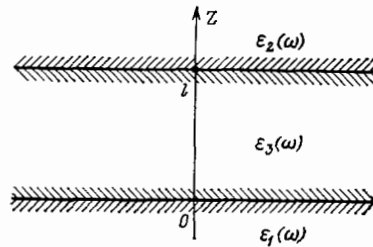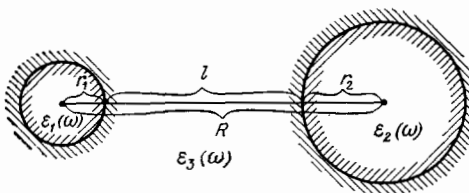

FIG. 5.

tropic objects gives rise to a van der Waals moment of forces which acts on these objects, as we already mentioned back in Section 2 in a discussion of the interaction between linear molecules. An analogous effect occurs in the case of anisotropic thick plates.[176,177] General expressions for the moment of forces with retardation are given in Ref. 177. There is an error in the calculations carried out to derive the moment of forces in Ref. 178. A particular consequence of this error is that the coefficients in the final results are incorrect, and these incorrect coefficients were subsequently reproduced in the review in Ref. 1.

There is the interesting question of manifestations of the anisotropic nature of van der Waals interactions in liquid crystals.[179–187] In liquid crystals the short-range forces are comparatively weak, so that the long-range van der Waals forces can in general have significant consequences. It was shown in Refs. 179 and 180 that one reason for the appearance of a spiral structure in cholesteric liquid crystals is the van der Waals dipole-quadrupole interaction between chiral molecules. This question was studied in a more general formulation in Ref. 186, where it was treated as a manifestation of nonlocal (gyrotropic) effects in the van der Waals interaction in liquid crystals. It was shown in Ref. 184 that van der Waals forces contribute substantially to the elastic moduli of a nematic liquid crystal.

The method used for quick plates separated by a plane gap can be used to solve the problem of the van der Waals interaction between objects of other shapes. Both the calculations and the results simplify if, in particular, the smallest distance between the objects is small in comparison with the radii of curvature of the surfaces which are in contact and in comparison with the dimensions of the objects themselves.

For the interaction between two spherical particles of condensed matter of macroscopic size, with radii r_1 and r_2 (Fig. 6), under the conditions

$$l = R - r_1 - r_2 \ll r_{1,2} \tag{4.11}$$

the free energy for the case $R \ll \lambda_0 \ll c\hbar/T$ is given by the fol-

FIG. 6.

lowing expression[188,189] in the zeroth order approximation in the parameters r_1/l and r_2/l:

$$F(l)$$

$$= -\frac{\hbar}{16\pi l}\frac{r_1 r_2}{r_1+r_2}\int_0^\infty d\omega \int_0^\infty x^2\,dx\left[\frac{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}e^x-1\right]^{-1}$$

$$\approx -\frac{\hbar}{16\pi^2 l^2}\cdot\frac{2\pi r_1 r_2 l}{r_1+r_2}\int_0^\infty d\omega\,\frac{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}$$

$$= F_s(l)\,S_{eff}(l);\tag{4.12}$$

here $\varepsilon_j = \varepsilon_j(i\omega), j = 1, 2, 3$. It is not difficult to see that in this case the van der Waals part of the free energy, which depends on the distance between the spheres, is the same as that for the interaction between plane plates with some effective contact area

$$S_{eff}(l) = \frac{2\pi r_1 r_2 l}{r_1+r_2}.\tag{4.13}$$

Significantly, this quantity depends on the distance l.

If the distance between small particles of condensed matter is comparable to the dimensions of the particles, the van der Waals interaction will depend strongly on the shape of the particles. This dependence can be significant in, for example, colloidal solutions and in systems of macromolecules. An analysis of the dependence of the van der Waals interaction between small macroscopic objects on the shape of these objects usually requires extremely complicated and tedious calculations. For a qualitative determination of the functional dependence of the interaction on the shape of the objects and their relative positions it is sometimes assumed that the van der Waals forces are additive.[5b,11,12,190–193] This approach leads to correct estimates if nonlocal effects (spatial dispersion) can be ignored. For a quantitative description of the interaction, on the other hand, one must use the theory outlined above, which correctly incorporates the electromagnetic response of condensed media.

The van der Waals interaction between spherical objects was studied in a case more general than (4.11) in Refs. 12, 29, 30, 188, 189, and 194–196; the corresponding expressions are extremely complicated. Similar expressions describe the interaction between spherical cavities in condensed media.[197–200] The results simplify substantially not only under conditions (4.11) but also for large distances, $l > r_{1,2}$. In the latter case the interaction energy is of course described by the expressions given in Section 2.

The van der Waals interaction between condensed objects of cylindrical shape was studied in Refs. 87, 201–213, 29, and 30. This formulation of the problem arises, for example, in studies of certain biological entities (protein molecules in muscles, the cylindrical mosaic tobacco virus, etc.) and of linear polymers, linked chains in organic macromolecules, and filamentary structures in certain condensed media.

If the smallest distance (R) between two cylindrical rods is much greater than the radii of these rods, r_1 and r_2, then the free energy of the van der Waals interaction between the rods is (Fig. 7)
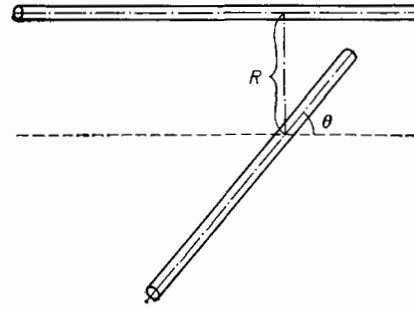

FIG. 7.

$$F(R,\theta) = -\frac{4c(\theta)}{3\sin\theta R^4},\tag{4.14}$$

where

$$c(\theta) = \frac{9s_1 s_2 T}{512\pi}\sum_{n=0}^\infty{}'\left[(18+\cos 2\theta)\frac{(\varepsilon_1^\perp-\varepsilon_3)(\varepsilon_2^\perp-\varepsilon_3)}{(\varepsilon_1^\perp+\varepsilon_3)(\varepsilon_2^\perp+\varepsilon_3)}\right.$$

$$+\frac{1}{2}(6-\cos 2\theta)$$

$$\times\left(\frac{\varepsilon_2^{||}-\varepsilon_3}{\varepsilon_3}\frac{\varepsilon_1^\perp-\varepsilon_3}{\varepsilon_1^\perp+\varepsilon_3}+\frac{\varepsilon_1^{||}-\varepsilon_3}{\varepsilon_3}\frac{\varepsilon_2^\perp-\varepsilon_3}{\varepsilon_2^\perp+\varepsilon_3}\right)$$

$$\left.+\frac{1}{4}\frac{\varepsilon_1^{||}-\varepsilon_3}{\varepsilon_3}\frac{\varepsilon_2^{||}-\varepsilon_3}{\varepsilon_3}(2+\cos 2\theta)\right],\tag{4.15}$$

θ is the angle between the axes of the cylinders, and $s_{1,2}$ are their cross-sectional areas. The dielectric permittivities of the rods are assumed to be anisotropic. The anisotropy axis with the principal value $\varepsilon_{1,2}^{||}(\omega)$ is directed along the axis of the corresponding rod (the indices 1 and 2). The principal values of the dielectric permittivity tensor perpendicular to this axis in each rod are assumed to be identical and equal to $\varepsilon_{1,2}^\perp(\omega)$ for the first and second rods, respectively. It is also assumed in (4.15) that the rods are immersed in an isotropic liquid with $\varepsilon_3(\omega)$. All the dielectric permittivities in (4.15) are taken for imaginary frequencies $i\omega_n = i(2\pi T/\hbar)n$.

For a study of the interaction between long rods it is convenient to introduce the effective rod contact distance $L_{eff}(R,\theta)$. Expressions (4.14) and (4.15) apply if $L_{eff}(R,\theta) < L_{1,2}$, where $L_{1,2}$ are the lengths of the first and second rods. For this reason, expression (4.14) for the free energy of the interaction between the rods diverges in the limit $\theta\to 0$, when the rod axes become parallel to each other. Obviously, at an angle $\theta = 0$ (i.e., for parallel axes)—and only in this case—the rods interact with each other over their entire length. In this case the total free energy of the interaction of rods of infinite length becomes infinite, in accordance with expression (4.14). Under these conditions it is natural to introduce a free energy per unit length. The correct expression for this linear density of the free energy of parallel rods[201–203] can be derived from (4.14) and (4.15) by assuming that for $\theta\neq 0$ the length of rod which is effectively involved in the interaction is

$$L_{eff}(R,\theta) = \frac{4R}{3\sin\theta}.\tag{4.16}$$

From (4.14)–(4.16) we find

$$\frac{F(R,\theta)}{L_{eff}(R,\theta)}\bigg|_{\theta=0} = -\frac{c(\theta=0)}{R^5}.\tag{4.17}$$

Incorporating spatial dispersion generally leads to a change in the functional dependence of the van der Waals energy on the distance between the objects (a change from the dependence found by ignoring spatial dispersion and, in particular, with a simple addition of the binary van der Waals interactions of the atoms making up the objects under study). In the case of thick plates, however, the nonlocal effects usually lead to only small corrections to the basic contribution to the interaction energy. In certain cases one can attempt to single out these corrections on the basis of their qualitative features, e.g., a characteristic dependence on an external magnetic field.[186] If, on the other hand, the gap between the plates is filled with an electrolytic solution, the nonlocal effects will lead, in particular, to a screening of that part of the van der Waals interaction which results from the low-frequency classical fluctuations of the electric field.[214,215] For aqueous electrolytic solutions, the screening effect may be significant at distances $l > 10^{-4}$ cm. In the case of long, thin conducting rods, on the other hand, spatial-dispersion effects may be significant, in particular, at shorter distances and may also lead to qualitatively new results.

London[72] discussed the effect of delocalized conduction electrons on the van der Waals interaction of long molecules many years ago. The concrete problems might involve π electrons in linked organic molecules or quasi-1-D (filamentary) metals and semiconductors if the van der Waals relationship between conducting filaments is important in the latter systems. The problem of the van der Waals interaction of long, thin conducting rods was studied quantitatively in Refs. 32 and 207–213. It was also shown in Ref. 213 that the influence of spatial-dispersion effects on the van der Waals interaction must be taken into account not only for 1-D but also 2-D systems.

We do not have room here to discuss in detail nonlocal effects in the theory of van der Waals forces; furthermore, this problem still requires further study. We simply note that further justification is required for using the existing results of the general theory of van der Waals forces in the case of spatial dispersion. We do know that these results [in particular, expression (4.10)] can be used, for example, to describe plasma-like media in the random phase approximation[1,2] and to study gyrotropic effects in the first nonvanishing approximation.[186] Furthermore, when we use expression (4.10) [and ignore absorption: Eq. (4.2)] we just bear in mind that when spatial dispersion is taken into account the van der Waals interaction may result from not only surface waves but also volume waves. This circumstance has been ignored in several papers, with the consequence that erroneous results have been derived. Barton[43] has published a useful critical review of this question on the basis of the simple example of the hydrodynamic model of plasma half-spaces.

The contribution of van der Waals forces to the binding energies of crystal lattices has been the subject of several studies.[5b,88,83,80,216–288] This problem can be reduced to one of deriving a dispersion relation for collective polarization modes of the crystal. In those cases in which the binding energies of lattices of different structures differ only slightly, van der Waals forces may be important in resolving the question of the stability of the crystalline structures. Crystals of inert gas atoms,[83,216,217,220] the graphite lattice[222] (see also Ref. 213), and metal crystals[218,219,221,223–228] have been studied in this connection. An analysis of the van der Waals interaction of ions in metals must incorporate the screening of the interaction of the ions by conduction electrons. The contribution of van der Waals forces to the binding energy of liquids was studied in Ref. 229. Among some other problems which have been discussed in the literature we can cite the van der Waals contribution to the dependence of surface tension on the radii of curvature of the surfaces[230–232] and to the change in the density near surfaces.[233–235,269]

A comparison of theoretical results on van der Waals forces with experimental data generally requires knowing the dielectric permittivities of the objects and the polarizabilities of the particles as functions of the frequency over an extremely broad frequency range. Once this information is available on specific condensed media and individual atoms or molecules, it is then necessary to evaluate sufficiently accurately the integrals over frequency which appear in the expressions [see, for example expression (4.11)]. One possibility here is to use theoretical model-based expressions for the dielectric permittivities of the condensed media in the calculations. This approach is ordinarily useful, however, only for a qualitative analysis of the dependence of the strength of the van der Waals interaction on the microscopic parameters characterizing the condensed medium. If it is instead necessary to take the specific dielectric properties of the specific substances into account quantitatively, a semiempirical approach is most effective. In this approach, some extremely simple analytic expressions are used to describe the dielectric permittivities as functions of the frequency in each characteristic spectral interval. The numerical coefficients in these analytic expressions are chosen such that these expressions can be used for accurate interpolations of experimental data on the substance. These data of course come from experiments which are totally unrelated to measurements of the van der Waals interaction.

Semiempirical estimates of this type were essentially carried out for quartz in an analysis of the first reliable measurements of the van der Waals interactions between thick plates.[236–238] Detailed semiempirical calculations were later carried out, in particular, for aqueous solutions and lipid films,[173,239] helium films on substrates of fluorite crystals,[240,241] hydrocarbon films on water surfaces,[242] mica and quartz plates,[243] H and He atoms and hydrogen molecules on the surfaces of fluorite crystals, Kr and Xe on the basal plane of graphite,[244] and certain other substances.[245–250,167]

Most of the experiments on the van der Waals interactions between atoms, molecules, and condensed objects[236–238,241,251–263] have yielded results in satisfactory agreement with the theory. There have also been cases of disagreement,[125–128,264,265] and at this point it is difficult to identify unambiguously the reasons for the discrepancies. The point which needs to be considered first is that measurements of van der Waals interactions place extremely stringent requirements on experimental accuracy, in particular, on eliminating such secondary factors as electrostatic effects and surface roughness. In addition, the present level of experimental accuracy places some stringent requirements on

the accuracy of the semiempirical calculations and in the experimental data on the dielectric permittivities of objects over a broad spectral range which are used in these calculations. Measurements of the van der Waals interaction of alkali metal atoms with a gold surface have been discussed in this connection.[125-128] It is mentioned in Ref. 244, for example, that a theoretical (semiempirical) estimate of the interaction of a Cs atom with a Au surface proposed in that paper differs from a similar estimate in Ref. 128. The role played by surface inhomogeneities, dynamic effects, and the effect of surface curvature and of spatial dispersion on the interaction have been discussed in this connection in Refs. 129, 144, and 146. Marvin and Toigo[130] conclude that the most important factor in the experiments of Refs. 125-128 is surface roughness and that this factor must also be taken into account (along with retardation) in analyzing the results. The role played by surface inhomogeneities in the interaction of two thick plates was discussed in Ref. 266. A more general and more detailed study of this question is reported in Refs. 267 and 268.

5. CONCLUDING REMARKS

Over the past two or three decades, and right up to the present day, the van der Waals interaction has been the subject of active theoretical and experimental research. Many results have been derived. Over these years the research on van der Waals forces and related phenomena has essentially become an independent field of research, united by common theoretical concepts and including a variety of applications in physics, physical chemistry, and biophysics. In the general theory of van der Waals forces, several important questions have been developed substantially, and in a sense some have been definitively settled. Many results of the theory of van der Waals forces pertaining to specific problems have found reliable experimental confirmation.

This review has of course excluded many questions of the theory of van der Waals forces and its applications. Some of these questions have not yet been studied adequately. One case is that of van der Waals forces under nonequilibrium conditions. The effect of a deviation from equilibrium on the van der Waals interaction is of interest both from a general physical standpoint and in connection with applications to, for example, biophysical problems. The nonequilibrium nature of electromagnetic fluctuations of course complicates a theoretical description of the van der Waals interaction. Only a few very simple problems have been studied so far. For example, the van der Waals forces acting between atoms or molecules in excited states have been studied in detail (see, for example, Refs. 6, 34, and 271). A qualitatively new aspect which appears here is the possibility of a van der Waals repulsion of two atoms in vacuum, as has been observed experimentally.[272] The interaction between two objects which are in equilibrium states but at different temperatures, so that the system as a whole is not at equilibrium, was studied in Refs. 273 and 274. Under these conditions, there is a radiative heat transfer between the objects due to the absorption of the fluctuational (thermal) electromagnetic field (see Ref. 275 and the literature cited there). Another example

dealing with interactions under nonequilibrium conditions is the case, mentioned above, of the van der Waals interaction between moving objects.[148-151,146]

We also note that the electrodynamic theory which has been derived for van der Waals forces naturally serves as a prototype for a theory of forces of van der Waals type acting between hadrons, which has been derived in quantum chromodynamics (see, for example, Refs. 276-281), and for a theoretical analysis of certain other long-range forces.[282-285] The effect of boundaries on the energy of zero-point vibrations (or, in a more general case, on the polarization of vacuum), which is of importance to the theory of van der Waals forces, is manifested in, and must be taken into account in, not only electrodynamics (see, for example, Refs. 16, 24, 171, and 286-297) but also several problems of quantum field theory and the general theory of relativity.[286,296-317] We will undoubtedly see a growth of research in the field of van der Waals (molecular) forces of an electrodynamic nature and also on analogs of van der Waals forces for nonelectromagnetic interactions.

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